Åbo Akademi University

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Wood Extractives in Conifers

A Study of Stemwood and Knots of Industrially Important Species

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Preface

The work presented in this thesis was carried out at the Laboratory of Wood and Paper Chemistry during the years 2003–2018 under supervision of Professor emeritus Bjarne Holmbom and at the final stage also of Docent Anna Sundberg. The work was part of the activities of Johan Gadolin Process Chemistry Centre (PCC) at Åbo Akademi University.

Some of the sampling and laboratory work was done within the industrial projects Bioactive extractives from important pulpwoods "BioExtra I" (2000–2002) and "BioExtra II" (2002–2004). Another part was done within the EU-project "CERBERUS" QLK5-CT-2002-01027 (2003–2006) and the industrial project "Siberian Larch" (2006–2008).

Financial support was received from the Rector at Åbo Akademi University, Magnus Ehrnrooth foundation, Oscar Öflunds Stiftelse, the Finnish Foundation for Technology Promotion (TES), Victoriastiftelsen and Åbo Akademi University.

Contribution of the author

The author did part of the sampling, and most of the extractions and GC analyses. The author did not do the actual GC-MS analyses, but did contribute to the identification of the peaks in the chromatograms. The author scrutinized all GC chromatograms, treated all data, interpreted the results and wrote the entire thesis.

Abstract

Throughout the years, extractives have been studied with various analytical methods, and it has been found that different tree species contain different types and amounts of extractive compounds. However, many studies have been incomplete and the number of methods used has been almost as vast as the number of publications, making it difficult or even impossible to compare the results of different studies.

This thesis contains data on lipophilic and hydrophilic extractives in heartwood, sapwood and knots of 39 industrially important conifer species: 14 pines (*Pinus*), 7 spruces (*Picea*), 9 firs (*Abies*), 5 larches (*Larix*), 3 hemlocks (*Tsuga*) and Douglas-fir (*Pseudotsuga*). The wood samples were sequentially extracted, and the amount and composition of resin acids, fatty acids, sterols, steryl esters, acylglycerols, juvabiones, lignans, oligolignans, flavonoids and stilbenes were analysed by gas chromatography (GC) and GC-mass spectrometry. The main conclusions were that:

- there are major differences in amount and composition of extractives, not only between genera, but also between species, especially regarding the hydrophilic extractives;
- lignans are present in heartwood and knots of all genera. The knots, however, contain remarkably more, in some cases several hundred times more, lignans than the adjacent heartwood. Some spruce, fir, larch and hemlock species contain especially high concentrations of lignans. Hydroxymatairesinol is the dominating lignan in spruce and hemlock, while secoisolariciresinol dominates in fir and larch;
- considerable amounts of flavonoids are found in all larches, some of the pines and in Douglas-fir;
- stilbenes are present in heartwood and knots of all pines;
- considerable amounts of juvabiones are found in all firs, some pines and in Douglas-fir. The concentrations are significantly higher in knots than in ordinary stemwood; and
- pine heartwood and pine knots in particular contain much more resin acids than the sapwood.

Lipophilic extractives are known to cause problems in pulp and paper mills, mainly in the form of deposits and specks. On the other hand, they can be recovered and utilized as tall oil and sterol-based products. The hydrophilic compounds are not detrimental in pulping and papermaking. They do, however, exhibit strong bioactivity and play a significant role in the protection of trees against insects, bacteria and fungi. Several of these compounds are strong antioxidants, and some are already used as active agents in dietary supplements and cosmetic products. The extraction, purification and utilization of these bioactive polyphenols should be further

studied and developed with special focus on the knots of the most promising conifer species.

This thesis provides a unique collection of data on extractives in conifers, probably the most comprehensive study ever published. The book is not meant to be read from cover to cover, but rather to be used as a reference when information is needed on amount and/or composition of extractives in conifers.

Keywords

Wood, stemwood, heartwood, sapwood, knots, extractives, resin, phenolics, resin acids, fatty acids, sterols, steryl esters, lignans, oligolignans, flavonoids, juvabiones, stilbenes, pine, spruce, fir, larch, Douglas-fir, hemlock, *Pinus, Picea, Abies, Larix, Pseudotsuga, Tsuga.*

Sammanfattning

Under årens lopp har extraktivämnen i stamved undersökts med olika analysmetoder och man har funnit att olika trädarter innehåller olika mängder och typer av extraktivämnen. Tyvärr har analyserna ofta varit ofullständiga och antalet metoder som använts har varit nästan lika många som antalet publikationer, vilket gör det svårt att jämföra resultaten från olika studier.

I den här avhandlingen analyserades extraktivämnen i kärnved, splintved och kviströtter av 39 industriellt viktiga barrträdsarter (14 tallar, 7 granar, 9 ädelgranar, 5 lärkar, 3 hemlockar och douglasgran). Vedproven extraherades sekventiellt och hartssyror, fettsyror, steroler, sterylestrar, acylglyceroler, juvabioner, lignaner, oligolignaner, flavonoider och stilbener identifierades och kvantifierades med gaskromatografi (GC) och GC-masspektrometri. De viktigaste slutsatserna är att:

- Det finns stora variationer i halt och sammansättning av extraktivämnen, både mellan släkten och arter, och speciellt stor är variationen i hydrofila extraktivämnen.
- Det finns lignaner i kärnved och kviströtter hos alla arter. Kviströtterna innehåller dock betydligt mer, i många fall flera hundra gånger mer, lignaner än den närliggande kärnveden. Vissa gran-, ädelgran-, lärk- och hemlockarter innehåller anmärkningsvärt höga lignankoncentrationer. Hydroximatairesinol är den dominerande lignanen i gran och hemlock, medan secoisolariciresinol dominerar i ädelgran och lärk.
- Flavonoidkoncentrationerna är höga i alla lärkar, vissa tallar och i douglasgran.
- Det finns stilbener i kärnved och kviströtter hos alla tallarter.
- Juvabionhalterna är höga i vissa tallar, ädelgranar och douglasgran. Koncentrationerna är mycket högre i kviströtterna än i kärn- och splintveden.
- Kärnved och speciellt kviströtter av tall innehåller mer hartssyror än splintveden.

De lipofila extraktivämnena orsakar problem i pappers- och massabruk, främst i form av avsättningar och fläckar, men de kan även tas till vara och utnyttjas för framställning av tallolje- och sterolbaserade produkter. Kvistroten, dvs. den del av grenen som finns inne i trädstammen, innehåller mycket höga halter lipofila och hydrofila extraktivämnen. De hydrofila extraktivämnena är, till skillnad från de lipofila, inte störande vid massa- eller pappersframställning, men de uppvisar stark bioaktivitet. Deras uppgift i trädet är att skydda stammen mot angrepp av insekter, bakterier och svampar t.ex. då en gren bryts av. Man har kunnat visa att många av

dessa komponenter är starka antioxidanter och vissa har hälsofrämjande effekter, vilket gör att de redan nu används som aktiva ingredienser i kosttillskott och kosmetika. Det är viktigt att undersöka hur man bäst separerar och tillvaratar dessa bioaktiva komponenter, speciellt från kviströtterna som är naturens rikaste polyfenolkälla.

Den här avhandlingen innehåller en unik samling data; det är antagligen den mest omfattande publikationen om icke-flyktiga extraktivämnen i barrträd som någonsin getts ut. Boken är tänkt att fungera som ett uppslagsverk där man kan slå upp halter och sammansättningar. Resultaten är presenterade så att arterna lätt kan jämföras med varandra, vilket underlättar om man vill skapa sig en helhetsbild av området eller om man är intresserad av att jämföra den kemiska sammansättningen i olika alternativa råvaror.

Sökord

Ved, stamved, kärnved, splintved, kviströtter, extraktivämnen, harts, hartssyror, fettsyror, steroler, sterylestrar, lignaner, oligolignaner, flavonoider, juvabioner, stilbener, tall, gran, ädelgran, lärk, douglasgran, hemlock, *Pinus, Picea, Abies, Larix, Pseudotsuga, Tsuga*

Abbreviations

16:0	Fatty acid structures, where the first number denotes the number of carbon atoms and the last number denotes the number of double bonds
1′-DeJuva	1′-Dehydrojuvabione
1′-DeJuvaOH	1′-Dehydrojuvabiol
4′-Dehydrojuva	4’-Dehydrojuvabione
4′-DehydrotodoA	4’-Dehydrotodomatuic acid
4′-DeJuva	4′-Dehydroepijuvabione
4′-DeJuvaOH	4′-Dehydrojuvabiol
4′-DeTodoA	4′-Dehydrotodomatuic acid
a.k.a.	Also known as
Ab	Abietic acid
An	Anticopalic acid
ASE	Accelerated solvent extractor
Avg	Average
Ch17	Cholesteryl heptadecanoate
cLari	Cyclolariciresinol
Com	Communic acid
Coni	α-Conidendrin
ConiA	α-Conidendric acid
CPPA	Canadian Pulp and Paper Association
CTO	Crude tall oil
Cup	Cupressic acid
DCM	Dichloromethane
DeAb	Dehydroabietic acid
DG	Diacylglycerol
DHQ	Dihydroquercetin
DI	Distillate from pitch column
Dihydro-PS	Dihydropinosylvin
Dihydro-PSMME	Dihydropinosylvin monomethyl ether
Dihydro-TodoA	Dihydrotodomatuic acid
DK	Dead knot

DTO	Distilled tall oil
EFSA	European Food Safety Authority
EROD	Ethoxyresorufin-*O*-deethylase
EW	Earlywood
FA	Fatty acid
FDA	Food and Drug Administration
FID	Flame ionization detector
GC	Gas chromatograph(y)
GDB	Growth-differentiation balance
HMR	7-Hydroxymatairesinol
HW	Heartwood
Hydroxy-Lari	9'-Hydroxylariciresinol
Hydroxy-NTG	7′-Hydroxynortrachelogenin
Hydroxy-PSDME	Hydroxypinosylvin dimethyl ether
Hydroxy-PSMME	Hydroxypinosylvin monomethyl ether
Hydroxy-Seco	7-Hydroxysecoisolariciresinol
i.d.	Inner diameter
ICBN	International Code of Botanic Nomenclature
iCup	Isocupressic acid
iLi	7-Isoliovil
Im	Imbricatolic acid
iPi	Isopimaric acid
iso-HMR	*iso*-Hydroxymatairesinol
IUPAC	International Union of Pure and Applied Chemistry
Juva	Juvabione
JuvaOH	Juvabiol
Lam	Lambertianic acid
Lari	Lariciresinol
Lari-Ac	Lariciresinol-9-acetate
Lasio	Lasiocarpenone
LasioOH	Lasiocarpenonol
LDL	Low-density lipoprotein
Levo	Levopimaric acid
Lig A	Lignan A

Lig B	Lignan B
LK	Living knot
LW	Latewood
Max	Maximum
MFO	Mixed-function oxygenase
Min	Minimum
MR	Matairesinol
MS	Mass spectrometry
MTBE	Methyl *tert*-butyl ether
n.a.	not analysed
n.d.	not detected
n.k.	not known
Neo	Neoabietic acid
NTG	Nortrachelogenin
NWFP	Non-wood forest product
o.d.w	Oven-dried wood
oxo-MR	7-Oxomatairesinol
Pal	Palustric acid
PB	Pinobanksin
PB-Ac	Pinobanksin-3-acetate
PC	Pinocembrin
Pi	Pimaric acid
Pino	Pinoresinol
PS	Pinosylvin
PSDME	Pinosylvin dimethyl ether
PSMME	Pinosylvin monomethyl ether
PSt	Pinostrobin
RA	Resin acid
Sa	Sandaracopimaric acid
SB	Strobobanksin
Seco DME	4,4′-Dimethylsecoisolariciresinol
Seco MME	4-Monomethylsecoisolariciresinol
Seco	Secoisolariciresinol
SODD	Soybean oil deodorizer distillate

SW	Sapwood
TG	Triacylglycerol
TMP	Thermomechanical pulp
TMS	Trimethylsilyl
Todo A	7-Todolactol A
Todo B	Todolactol B
Todo C	Todolactol C
Todo D	Todolactol D
TodoA	Todomatuic acid
TOFA	Tall oil fatty acids
TOP	Tall oil pitch
TOR	Tall oil rosin
tr	Traces

Glossary

Balsam is resin containing benzoic acid or cinnamic acid.

Broadleaves are trees with flat leaves and seeds inside fruits. They are also known as hardwoods.

Colophony, see rosin.

Conifers are a taxonomic group comprising more than 600 cone-bearing seed plants. Most of the species have needle- or scale-shaped evergreen leaves. The group is also known as softwoods.

Deciduous trees shed all the leaves at the end of each growing season.

Dermatitis is also called eczema. It is an itching skin inflammation usually characterized by redness, swelling, blister formation and oozing.

EROD activity is a catalytic measurement of cytochrome P4501A induction. It is used as a biomarker in fish to measure chemical exposure e.g. to industrial effluents or contaminated sediments.

Extractives are (i) something that may be extracted. (ii) A substance present in tissue that can be separated by successive treatment with solvents and recovered by evaporation of the solution.

Exudates are formed by the tree through secondary metabolism after microbial or mechanical damage. The excreta are grouped into gum, mucilage, oil, wax, latex and resin.

Forests are areas with a high density of trees.

Gram-positive bacteria possess a thick cell wall containing many layers of peptidoglycan and teichoic acids.

Growing stock is the volume of living trees measured from the stumps to the treetops. The bark is included, but the tree must be over a certain diameter at breast height. It may contain bigger branches, but smaller branches, twigs, foliage, flowers, seeds, stump and roots are excluded.

Gum rosin is oleoresin exuded from living pine trees.

Hardwood is wood from broad-leaved trees (dicot angiosperms).

Industrial roundwood is all commercial roundwood removal except wood fuel. Cf. roundwood.

Introgressive hybridization or **introgression** is the movement of genes from one species to another by repeated backcrossing (interspecific hybridisation with one of its parents). Introgression is a long-term process; it may take many hybrid generations before the backcrossing occurs.

Juvenile is an organism that has not yet reached its adult form, sexual maturity or size. Juveniles sometimes look very different from the adult form.

Mixed-function oxygenase (**MFO)** is group of enzymes in the liver of vertebrates. They are involved in the detoxification of harmful substances.

Monoecious plants have both male and female reproductive organs in the same flower.

Monophyletic is a group that only includes descendants of a common ancestor.

Mucilage is a water-soluble complex of high-molar-mass polysaccharides that occurs in secretory plant structures.

Naval stores is a generic term used for turpentine and rosin products from pine.

Neutral components are non-acidic components such as squalene, diterpenes, aldehydes, sterols, glycerides, steryl esters of fatty acids and pinosylvin dimethyl ether.

Non-wood forest products, NWFPs are goods, other than wood, that are of biological origin and derived from the forest, both plant products and animal products are included.

Oleoresin is a naturally occurring mixture of oil and resin extracted from various plants, such as pine or fir.

Over bark is a measure of volume or diameter of logs before the bark has been removed.

Parenchyma resin constitutes reserve nutrient and cell membrane substances, which occur mainly as fatty acids esters of sterols and triterpenols.

Phenotype is any observable characteristic or trait of an organism, such as its morphology, development, biochemical or physiological properties, or behaviour. Phenotypes result from the expression of an organism's genes as well as the influence of environmental factors and possible interactions between the two.

Phylogenetics describes how organisms (both living and extinct) are related and how they descend from each other.

Phytoalexins are antimicrobial, often antioxidative substances produced by plants in response to infection by fungi or bacteria. They help to defend the plant by inhibiting the growth of invading microbes.

Phytosterol is a plant sterol.

Resin is a thick and sticky hydrocarbon secretion of many plants, particularly coniferous trees. It is a viscous liquid, composed mainly of volatile, fluid terpenes and dissolved, non-volatile resin acids.

Rhinitis is an inflammation of the mucous tissue of the nose. Allergic rhinitis is called hay fever.

Ring shake is a separation of wood fibres along the circumference of an annual ring. The crack is not visible in green wood, only in dried.

Rosin is the solid form of resin. At room temperature rosin is brittle, but it melts at stove-top temperatures. It mainly consists of different resin acids.

Roundwood is wood in its natural state as felled, with or without bark. It may be round, split, roughly squared or in other forms. It can be used for fuel (also for charcoal), sawlogs, veneer, pulp, etc. Cf. Industrial roundwood.

Secondary metabolites are low-molar-mass compounds that lack life-sustaining functions. They contribute to the organism's survival e.g. by maintaining a defence against pathogens and predators.

Softwood is wood from conifers.

Tall oil pitch (TOP) is the non-volatile residue from crude tall oil distillation.

Tall oil rosin (TOR) is rosin distilled from the waste liquor recovered from kraft pulping.

Terpenes are cyclic aliphatic hydrocarbon synthesized from isoprene units. Monoterpenes consist of two, sesquiterpenes of three, diterpenes of four and triterpenes of six isoprene units.

Terpenoids are terpenes substituted with at least one oxygen-containing functional group, e.g. alcohol, aldehyde, ketone or acid.

Tree is a perennial woody plant that has secondary branches supported clear of the ground on a single main stem

Unsaponifiables do not form water soluble aggregates (soaps) with sodium hydroxide in the kraft cook. Hydrocarbons, sterols, fatty alcohols, terpenyl alcohols and waxes are examples of unsaponifiables.

Waxes are fatty acid esters of other alcohols than glycerol.

Wood rosin is oleoresin extracted from aged stumps.

Table of contents

1 Introduction

1.1 Background

What are wood extractives? In a broad definition, wood extractives are all compounds in trees other than the structural, polymeric components, i.e. cellulose, hemicelluloses and lignin. They comprise different classes, such as terpenoid resins, fats and waxes, various polyphenols, sugars and even inorganic salts. Many are part of the life processes of a tree, while others provide protection against microbes and insects.

The oldest extractives discovered are 320 million-year-old pieces of amber, the fossil form of resin (Bray & Anderson 2009). This resin originates from an unknown, extinct, preconifer gymnosperm, which used similar complex biosynthetic mechanisms as seen in conifers today. The first signs of human utilization of extractives are more than 13 000 years old. Neolithic peoples gathered amber from the shores of the Baltic Sea and used it in jewellery, as glue in tools, and it was believed to possess healing and protective powers. Later, amber and pine resin have been used to embalm Egyptian mummies, in sarcophagi, as liquid fire (an early form of napalm), for lighting and in varnishes[1]. (Drew 1989, Hillis 1989, Lucas & Harris 2012, pp. 7–8, Bard 2015, pp. 165 and 271)

The first commercial forest product in the Nordic countries was pine tar. It was used as early as in the Iron Age (Kardell 2003, p. 48) and in the 17th century it became Finland's foremost export product (Figure 1). Tar was used to preserve wooden sailing ships and the production areas were located in Ostrobothnia, as well as in the eastern and central parts of the country. During the years 1758–1762, Ostrobothnia alone produced almost 12 million litres of tar (Villstrand 2001, p. 15). The demand for tar did, however, decline dramatically during the second half of the 19th century when steam ships made of iron and steel replaced wooden sailing ships.

[1] Both Rembrandt and Leonardo da Vinci used amber varnishes as vehicles for their paint (Hillis 1989).

Figure 1 Schooner Axel taking in tar barrels in my home town Kristinestad in 1896 (photo by J. M. Rosengren, Österbottens museums arkiv).

How is the extractives utilization today? Have all products become obsolete and/or replaced by synthetic substances, or are we ignorant everyday users? In fact, extractives are all around us and the market is growing.

Resinous extractives are collected by tapping living pine trees, by extraction of old stumps, or as a by-product of kraft pulping (FAO 1995). The collected rosins are fractionated by distillation and can be used in coatings, paint, varnishes, adhesives, chewing gum, as surfactants, in pulp and paper chemicals, printing inks, road markings, metalworking, as oil and fuel additive and in oilfield chemicals. Turpentine (the volatile fraction) is used as industrial solvent, raw material for adhesives, synthetic vitamins, perfumes and flavourings, while sterols can be included in pharmaceuticals, cosmetics and health-promoting functional foods.

Trees also contain hydrophilic compounds which are utilized. Flavonoids are used in functional foods and beverages, in dietary supplements, cosmetics and pharmaceuticals. Lignans, which are most abundant in the knots, are marketed as health-promoting dietary supplements.

1.2 Objectives

Extractives of a countless number of wood species have been analysed throughout history, so why publish yet another study? The main argument is the lack of homogeneity and the difficulty to compare existing data. Throughout the years, wood has been sampled and pre-treated in many ways. Different solvents, extraction techniques and analytical methods have been applied, and the results have been calculated based on the weight of oven-dry wood, extract-free wood or based on the weight of the extract itself. All this makes it difficult to compare results of different studies.

Another reason is that some results have been presented in small, national journals, where the texts were not written in English. These discoveries have, therefore, often remained inaccessible to the scientific community.

This work gathers data about non-volatile extractives in 39 softwood species in one volume. The book is not meant to be read from cover to cover, but rather to be used as a reference book. Some of the results have been published earlier, but when all data were combined, new trends became visible. This made it possible to correct errors and to reveal previously unnoticed trends. Some chemotaxonomic relationships were also observed. They could help in predicting the extractive composition of species not studied in this thesis.

1.3 Focus and limitations

In this thesis, native, non-volatile extractives have been studied. Volatile extractives were evaporated prior to analysis and all sugars were omitted.

The amount and composition of extractives can vary significantly between trees of the same species. These differences are caused by genetic factors, growth location, climatic factors like cold stress, exposure to wind, snow load, access to water and nutrients and how fast the trees have been growing (Ivanov 1928, Erdtman et al. 1951, Hakkila 1969, Hemingway & Hillis 1971, Fuksman & Komshilov 1979, 1980, 1981, Saranpää & Nyberg 1987a, Fischer & Höll 1992, Bergström et al. 1999, Back & Ekman 2000, p. xii, Fries et al. 2000, Piispanen & Saranpää 2002, Willför et al. 2003a, Ucar 2005, Piispanen et al. 2008). There are also variations both along and across the stem (Erdtman & Rennerfelt 1944, Erdtman et al. 1951, Hancock 1957, Shostakovskii et al. 1969, Hemingway & Hillis 1971, Redmond et al. 1971, Tyukavkina et al. 1972, Ekman 1979b, Saranpää & Nyberg 1987a, Sasaya & Ozawa 1991, Bergström et al. 1999, Piispanen & Saranpää 2002, Piispanen et al. 2008). It would, therefore, have been statistically satisfying to increase the number of samples, but in practice it would have been impossible. The sampling, sample pretreatment, the demand for equipment, chemicals and the time needed for data analysis would have been far too extensive. Furthermore, the longer storage would have increased the risk for alteration and artefact formation. Therefore, it was decided to study 2–3 trees per species. The major part of the chosen species was of significant industrial importance.

For some species it was not possible to cut down the whole trees and as a compromise bore cores were sampled. When bore cores are drilled out, it is difficult not to occasionally hit resin pockets or other areas with abnormal resin content. Sampling of such areas yields extraordinary high lipophilic extractive contents and the results are, thus, not representative for the tree as a whole.

2 Literature review

2.1 Forest utilization

2.1.1 Global forest resources

Twenty-nine percent of the earth's surface is land area, and depending on the climate, i.e. temperature and precipitation, it can be divided into different regions (Figure 2).

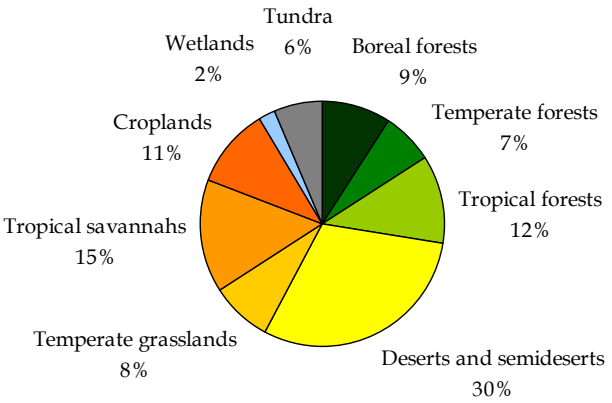


Figure 2 Distribution of the world's land area (Karjalainen et al. 2009, p. 102).

About 28% of the land area is classified as forests. That means that the global forest area amounts to nearly 40 million km^2. The forests are divided into boreal, temperate and tropical forests. The conifers are found mainly in the boreal and temperate forests (Figure 3).

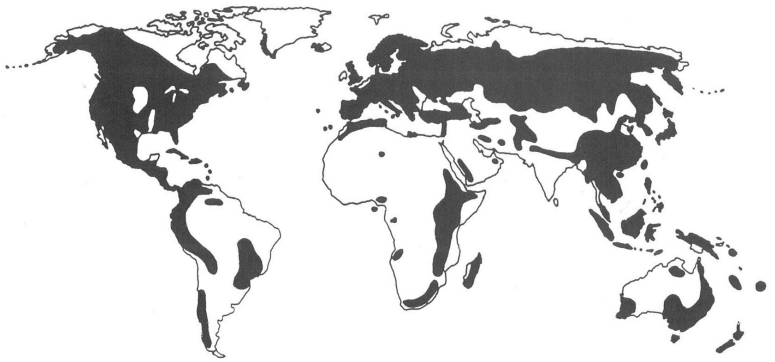


Figure 3 Distribution of conifers (Farjon 1998).

Russia is the forest-richest country in the world; it holds 20% of the total forest area. Other forest-rich countries are Brazil (12%), Canada (8%), the USA (8%) and China (5%) (Karjalainen et al. 2009, p. 104). The global

trend is that the forest area is being reduced. The deforestation is greatest in South America, Africa, South and Southeast Asia. The rest of Asia and Europe, however, show an increase in forest area. In Europe, the cutting has been lower than the annual growth since 1990 (MCPFE et al. 2007).

Thirty percent of the global forest area (Figure 4) is primarily used for production of industrial roundwood, wood fuel and non-wood forest products (NWFPs). An additional 24% is designated for multiple uses, where production of wood or NWFPs often is one of the purposes. Brazil, the USA, Mexico and Papua New Guinea are the only countries where the area designated for production of NWFPs is increasing. In other parts of the world the area for multiple uses is increasing at the expense of the area used for production.

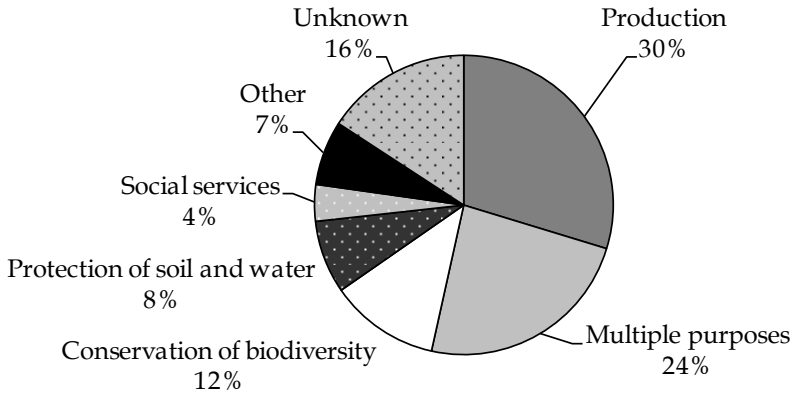


Figure 4 Primary purposes of the global forests (FAO 2010).

The remaining forest area is used for conservation of biological diversity (12%), for protection of soil and water resources, avalanche control, sand dune stabilization, desertification control or coastal protection (8%), for social and cultural functions i.e. recreation, tourism, education or conservation of cultural and spiritual heritage (4%), or for other purposes (23%).

The forests are divided into primary, naturally regenerated and planted forests (Figure 5). The area of both primary and naturally regenerated forests is decreasing, while the planted forest area is increasing.

Thirty-six percent of all forests are primary forests (FAO 2010). They consist of native tree species, lack clearly visible indications of human activities and the ongoing ecological processes are not significantly disturbed. During the last 10 years (2000–2010) the total area of primary forests has decreased by 40 million hectares. For comparison it can be mentioned that the total land area of Finland is 34 million ha.

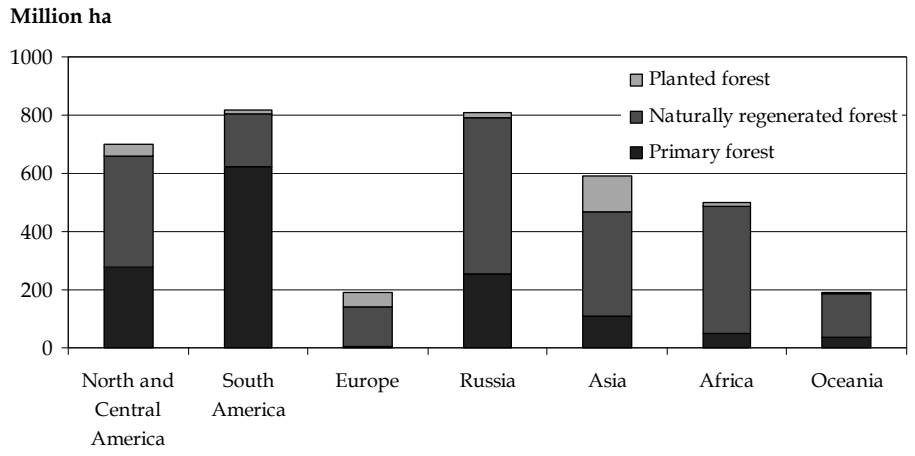


Figure 5 Types of the forests (FAO 2010). Data on Cameroon, the Democratic Republic of Congo and Venezuela are missing.

The major part of the forests, 57%, is so-called naturally regenerated forests. These forests primarily contain native species, but there are clearly visible indications of human activities, such as weeding, fertilizing, thinning and selective logging.

The remaining 7% is planted forests. The planted forests contain one or two species with even age classes and regular spacing between the plants. About 75% of the planted forests consist of native species, the rest of introduced species. More than half of all planted forest is found in China, the USA, Russia, Japan and India. The proportion of planted forest is increased by 5 million hectares per year and most of the increase occurs in Asia, particularly in China. The primary purpose for 76% of all plantations is production (FAO 2010). China, however, has planted trees in large scale for protection against flooding, soil erosion and desertification (Jiang et al. 2003, Jiang & Zhang 2003).

2.1.2 Wood production

It is estimated that 47% of the global forest area consists of wood that can be harvested and used commercially. The limiting factor is usually the lack of infrastructure for wood transport. In 2010, the global wood removal was 3.4 billion m^3 over bark (Figure 6), that was 0.7% of the growing stock. About 45% of the removal was utilized as industrial roundwood and 55% as wood fuel. The true figure is, however, considerably much higher since the illegal harvesting of wood fuel was not accounted for.

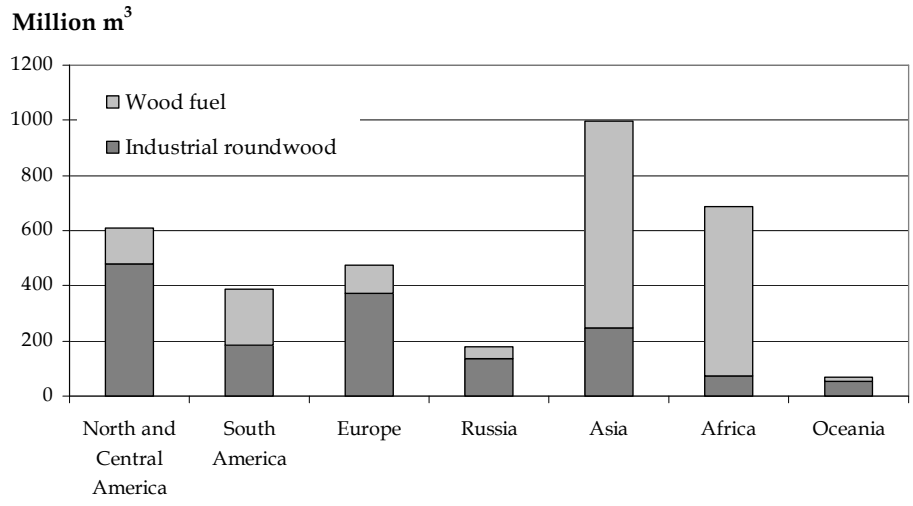


Figure 6 Wood removal per region in 2010 (Flejzor & Higman 2011).

In South and Southeast Asia, Africa, Central America and the Caribbean wood is mostly used for fuel (Figure 6), while it mainly is used for industrial roundwood in North America, Europe, East Asia and Oceania.

The USA was the largest producer of wood with 472 million m^3 per year; 93% was industrial roundwood and 7% fuel. India was the second biggest producer harvesting 329 million m^3/a. However, 93% of that was used for fuel and only 7% for industrial roundwood. Other big producers were China (286 million m^3/a, 67% fuelwood), Brazil (256 million m^3/a, 54% fuelwood), Canada (199 million m^3/a, 99% industrial roundwood) and Russia (186 million m^3/a, 75% industrial roundwood). (FAO 2010)

In the 1990's, when the Soviet Union collapsed, there was a sharp decline in Russian harvesting. Now the removal has increased and is back at its 1990 level. In Malaysia and Indonesia, the wood removal has decreased due to log export restrictions (Flejzor & Higman 2011), and China has imposed a logging ban in 18 provinces along the Yangtze and Yellow River in order to counteract flooding and soil erosion (Jiang & Zhang 2003). The wood removal is, however, increasing in two regions: Africa and South America. In Africa, the growing population needs more fuel and in Brazil the increasing harvesting from plantations contributes to the rising trend (Flejzor & Higman 2011).

2.1.3 Industrial roundwood

The conifers dominate in North and Central America, Europe and Oceania, while broadleaves dominate in South America and Africa. It is estimated that 39% of the global growing stock is coniferous and 61% is broad-leaved. Nevertheless, two thirds of the industrial roundwood is coniferous (Figure 7).

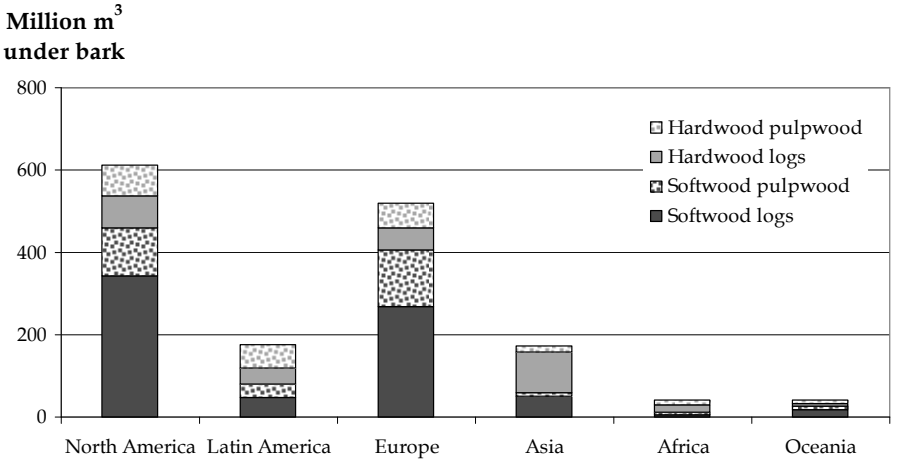


Figure 7 Production of pulpwood and logs per wood type and region in 2005 (Karjalainen et al. 2009, p. 111).

In 2005, North America and Europe were the largest producers of industrial roundwood. Together they accounted for 72% of the production. Globally the dominating end-use was sawlogs (66%), which were utilized as solid roundwood, sawn timber, veneer and panel products. Fully 70% of the produced logs were coniferous. One third of all industrial roundwood was used for pulpwood production; 58% of the raw material came from conifers and 42% from broadleaves. (Karjalainen et al. 2009, p. 111)

It is evident that the conifers dominate as raw material for industrial production, but which are the most important genera and species? FAO has collected data about genera (FAO 2007) and species (Del Lungo et al. 2006) in planted productive forests. As can be seen in Figure 8, the pines dwarf all other genera. The pine species are planted in all regions. Sixty-eight percent of the forests in North America are planted with pines. In South America eucalyptus is dominating, but nevertheless, 46% of the area is planted with pines. In Europe 32% is pine plantations and in Oceania 75% (Carle & Holmgren 2008).

The second most planted genus is *Cunninghamia* R.Br (Figure 8). It is a premiere timber tree in China and despite its English name, China fir, it is a

member of the cypress family. Its wood is strongly fragrant and therefore appreciated for coffins (Eckenwalder 2009, p. 209–210).

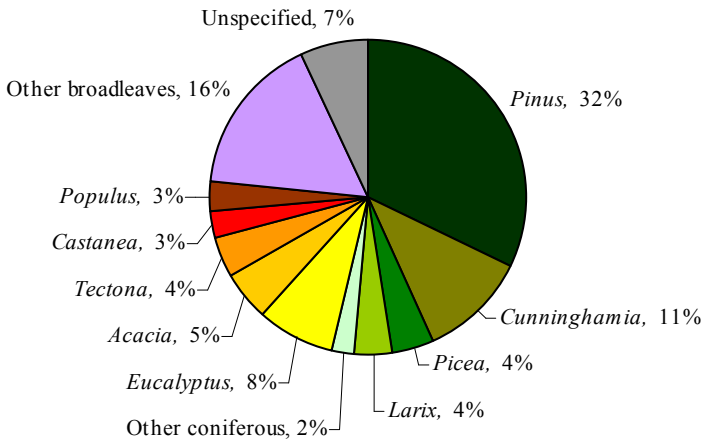


Figure 8 Area coverage of per genus in planted forests used for production in 2005 (FAO 2007, p. 89).

In Table 1, the tree species studied in this thesis are grouped according to their industrial use. According to FAO (Del Lungo et al. 2006) *Pinus taeda* and *P. sylvestris* are the most important species planted for production.

Table 1 The species studied in this work grouped according to their industrial importance (Milyutin & Vishnevetskaia 1995, Del Lungo et al. 2006). The most important species are marked with an asterisk (*).

Large industrial use	Moderate industrial use	Mainly local use
Abies alba	*Abies amabilis*	*Abies concolor*
Abies balsamea	*Abies lasiocarpa*	*Abies pindrow*
Larix gmelinii var. *gmelinii**	*Larix decidua*	*Abies sachalinensis*
Larix kaempferi	*Larix lariciana*	*Abies sibirica*
*Larix sibirica**	*Pinus resinosa*	*Abies veitchii*
*Picea abies**	*Pinus strobus*	*Larix gmelinii* var. *japonica*
Picea glauca	*Tsuga canadensis*	*Larix gmelinii* var. *olgensis*
Picea mariana	*Tsuga heterophylla*	*Picea koraiensis*
Picea sitchensis		*Picea omorika*
Pinus banksiana		*Picea pungens*
Pinus contorta		*Pinus gerardiana*
*Pinus elliottii**		*Pinus sibirica*
Pinus nigra		*Pinus wallichiana*
Pinus pinaster		*Tsuga mertensiana*
*Pinus radiata**		
Pinus roxburghii		
*Pinus sylvestris**		
*Pinus taeda**		
Pseudotsuga menziesii		

2.1.4 Non-wood forest products

NWFPs are goods, other than wood, of biological origin and derived from the forest. The group is very miscellaneous. It includes products such as food, feed, animal skins, medicine, beeswax, fragrances, colorants, dyes, exudates, ornamental plants, etc. Food and exudates are most important categories. (FAO 2010, pp. 104–105)

The NWFPs provide income and employment to millions of people worldwide, especially in developing regions. It is, however, difficult to collect data about the production of NWFPs because a significant share is consumed non-commercially. Nevertheless, it constitutes a substantial contribution to the national product in some countries. In 2005, it was estimated that the value of NWFPs was US$ 18.5 billion (FAO 2010, p. 121). Russia accounted for 29%, China for 27% and South Korea for 11%.

The total value of harvested exudates was 631 million US dollars (FAO 2010, p. 121). Sudan was the world leading producer of exudates (gum arabicum). China was the leading producer of pine resin, tannin extracts and raw lacquers. More information about resin production is found later in this chapter.

2.2 Production and use of rosins and tall oil

Oleoresin products from pine played an important role during the wooden sailing-ship era from the 16th to the mid-19th century. Resinous products, mainly in the form of wood tar, were used to waterproof the hull, to caulk the seams and to preserve the ropes from decay. In fact, the business was so important that the concept of naval stores appeared. The term outlived the wooden sailing-ships and is still used for turpentine and rosin products from pine. (Drew 1989)

The field of application has changed, but the pine oleoresin products continue to be of great commercial importance. In 2008 the total global rosin production was 1.2 million tonnes (Turner 2010) and China was the most productive region, accounting for 46% of the total production (Figure 9). Other large rosin producers were the USA (22%), Brazil (6%), Indonesia (5%), Russia (4%) and the Scandinavian countries (7% together). Japan was the largest importer of naval stores. About 50% of the gum rosin exported from China went to Japan (Iqbal 1994).

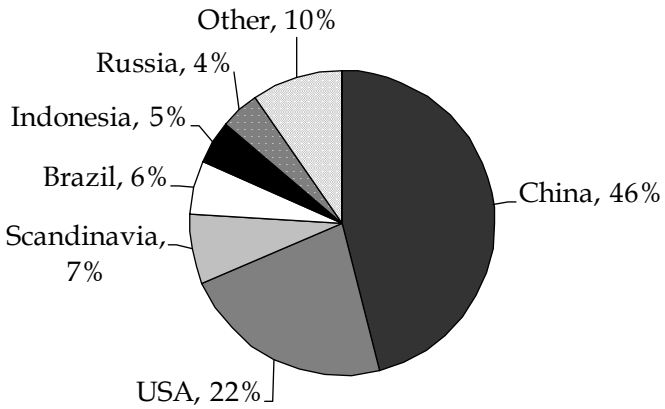


Figure 9 Total global rosin production by region in 2008 (Turner 2010).

The pine rosins have unique tackifying properties, but they are competing with synthetic petroleum resins. The petroleum resins are, however, difficult and expensive to synthesize, so there will be a market for natural rosin as long as the supply of pine rosin is sufficient and the price is stable.

Depending on the source of the rosin, it can be divided into three groups: gum rosin, tall oil rosin (TOR) and wood rosin. Gum rosin is the dominating type, accounting for 64% of the global production (Figure 10). The TOR amounts to 35%, while the wood rosin is accounts for only 1% of the total production.

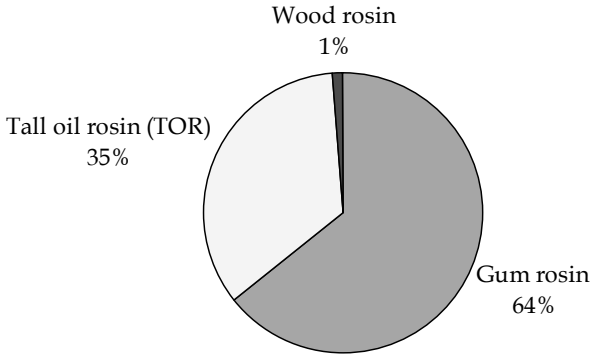


Figure 10 Global rosin production by type in 2008 (Turner 2010).

2.2.1 Gum rosin

Gum rosin (oleoresin) is the exudate tapped from living pine trees. The trees are partially barked, the wood is injured and the resin production is increased with chemical stimulants, e.g. sulfuric acid. The collected crude gum rosin is heated, diluted and filtered to remove bark residues, needles and insects. Thereafter, it is washed with water and steam-distilled to separate the turpentine. (FAO 1995)

Different regions utilize different species for gum rosin production (Table 2). A pine tree grown under favourable conditions normally yields 3–4 kg oleoresin per year, which means that five tons of oleoresin can be collected annually per hectare of forest. The collection of crude gum rosin is, however, very labour intensive. A sedulous worker can tap about 7000 trees per year and the labour costs represent 50–80% of the total production costs. Hence, the gum rosin production is highly dependent on the availability of cheap manpower and low-wage countries like China, Brazil, Indonesia, India, Mexico and Argentina are the most important producers. Portugal has been the only major European gum rosin producer, but the production has declined due to lack of cheap manpower and Portugal has lost its position as a significant producer. (Iqbal 1994, FAO 1995)

Table 2 Most important gum rosin producing pine species in different countries (FAO 1995). Parentheses in the second column indicate minor production. The resin characteristics are rated from poor (-) to very good (+++).

Species	Producing country	Quality	Yield
Pinus elliottii Engelm.*	Brazil, Argentina, South Africa (USA, Kenya)	++	++
Pinus massoniana D.Don	China	+	+
Pinus kesiya Royale ex Gordon	China	+	+/-
Pinus pinaster Aiton*	Portugal	++	+
Pinus merkusii Jungh. & Vriese	Indonesia (Vietnam)	+	+
Pinus roxburghii Sarg.*	India (Pakistan)	+	+
Pinus oocarpa Schiede	Mexico, Honduras	+/-	+/-
Pinus caribaea Morelet	Venezuela (South Africa, Kenya)	+	+++
Pinus sylvestris L.*	Russia	+/-	+/-
Pinus halepensis Miller	Greece		
Pinus radiata D. Don*	(Kenya)	+++	+

*Species studied in this thesis.

China has large pine plantations and access to cheap manpower and is, therefore, the leading gum rosin producer. During the last few years, the forests have though been affected by infestations, drought, heavy rain and snow. Furthermore, eucalyptus plantations have expanded at the expense of pine plantations, the domestic rosin consumption has increased, and there is a shortage of people willing to collect oleoresin. Consequently, the Chinese rosin production has dropped. Brazil, on the other hand, is a growing gum rosin producer. In Brazil, dual-purpose forests are common. There the trees are first used for crude gum tapping and thereafter for wood production. In this way the early returns from oleoresin tapping makes the pine plantations economically more attractive. When tapping is conducted on trees that will be harvested for timber or pulpwood production, a fairly intensive tapping will take place four years prior to felling. This can be compared to plantations intended for rosin production only, where the trees can be tapped for 20 years or even longer (FAO 1995).

2.2.2 Tall oil and tall oil rosin

Tall oil is a by-product from kraft pulping of pine wood. In alkaline black liquor, fatty and resin acids are found as sodium soaps. The soap can be skimmed off and converted to crude tall oil (CTO) by reaction with sulfuric acid. The CTO is then fractionated by distillation (Figure 11) into tall oil pitch (TOP), TOR, distilled tall oil (DTO) and tall oil fatty acids (TOFA) as the main fractions.

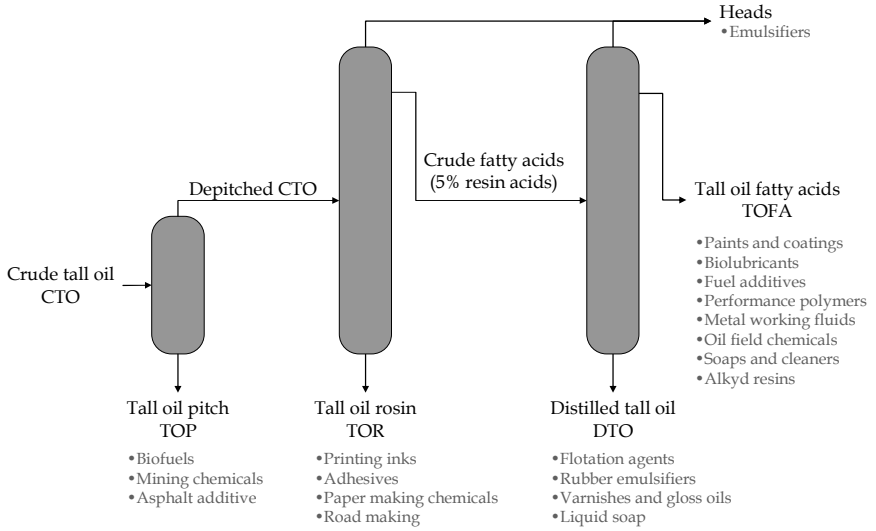


Figure 11 Simplified distillation scheme (McSweeney et al. 1987, p. 6) and applications for the distillation products.

The yield of CTO depends on the wood raw material used, but a typical range is 30–50 kg/t pulp (Alén 2000a, p. 73). *Pinus sylvestris* grown in northern Finland can, however, yield more than 50 kg/t pulp.

Typical yields for CTO from southern USA can be seen in Figure 12. Scandinavian CTO would yield one third TOP, one third TOR, and one third of TOFA and DTO (McSweeney et al. 1987, p. 7).

The tall oil rosin constitutes 35% of the total global rosin production. Lately, however, the production of TOR has decreased as the availability of raw material for distillation has declined. Today, younger trees with less resin acids are harvested, the use of hardwood species, recycled fibres and mechanical pulping processes has increased at the same time as several older kraft pulp mills have been closed.

The USA is the largest TOR producer, followed by Scandinavia, Russia, Japan, China, Brazil and New Zeeland. In the USA, the production is concentrated to the South-eastern states (McSweeney et al. 1987, p. 3). Almost all TOR produced in the USA and Russia is used for domestic consumption.

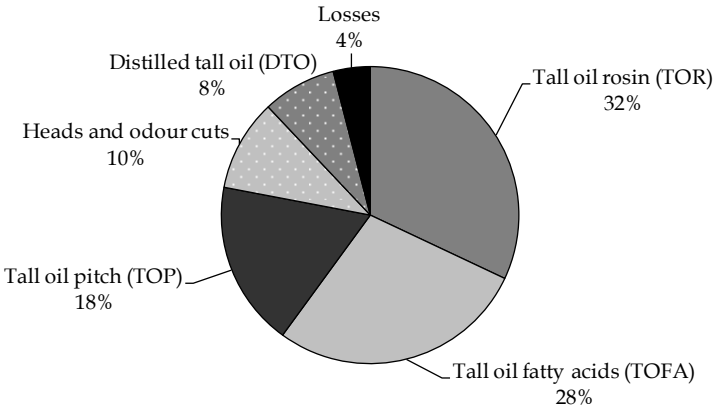


Figure 12 Typical yields from distilling crude tall oil from southern USA (McSweeney et al. 1987, p. 7).

2.2.3 Wood rosin

The third type of rosin is called wood rosin. It is extracted or distilled from the resinous wood of old stumps. It accounts for only 1% of global rosin production. In the USA, stumps of *Pinus palustris* and *P. elliottii* are utilized (Pinova 2017). The USA and Russia produce wood rosin for domestic consumption (Iqbal 1994).

2.2.4 Utilization of rosin products

The rosins are used in many diverse applications. The most important areas are printing ink, adhesives and sealants, paper size, emulsifiers and coatings (Figure 13). As the printing and writing paper consumption is decreasing, the use of ink and size is declining, while the proportions of adhesives, sealants and emulsifiers are increasing.

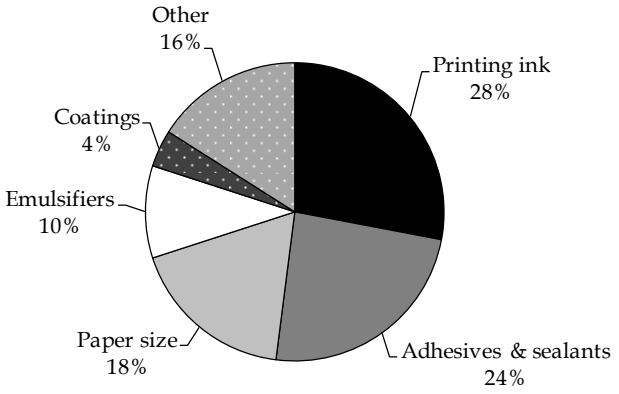


Figure 13 Global rosin consumption per application in 2008 (Turner 2010).

2.3 Utilization of other extractives

The utilization of fatty acids, sterols, juvabiones, stilbenes, lignans and flavonoids is briefly described in chapter 4.4.

2.4 Taxonomy

2.4.1 Linnaean taxonomy and cladistics

The term taxonomy is derived from the Greek words *taxis*, arrangement, and *nomos*, law. The modern taxonomy was founded by Carl von Linné. In his books *Systema Naturae* (1758)[2] and *Species Plantarum* (1753) he introduced the sexual system and the binomial nomenclature. In them, he stipulated rules for naming plants, animals, deceases and minerals by introducing a standard hierarchy consisting of five to seven obligatory ranks: kingdom, division, class, order, family, genus and species[3]. Table 3 presents as an example how Scots pine is ranked in the Linnaean system.

Table 3 Classification of Scots pine according to the Linnaean system.

Rank	Suffix	Example: Scots pine	Rank in Swedish	Example in Swedish
Kingdom	-ae	*Plantae* (plants)	Rike	Växter
Phylum	-phyta	Tracheophyta	Division/Provins	Kärlväxter
Class	-psida	Pinopsida	Klass	Barrväxter
Order	-ales	Pinales	Ordning	Barrträd
Family	-aceae	*Pinaceae* (the pine family)	Familj	Tallväxter
Genus	-	*Pinus* L. (pine)	Släkte	Tallar
Species	-	*Pinus sylvestris* L. (Scots pine)	Art	Pelartall

The binomial system has served as a very important tool for the biologists through the history. Linné's sexual system stated that the plants should be divided into 24 classes according to their reproduction organs. At the time, it provided a totally new, practical approach to plant classification, but the system was artificial and did not take relationships into account, so it soon became outdated.

At present, many researchers have abandoned the fixed, obligatory, ranks of the Linnaean classification and started to follow the cladistic taxa. The term cladistics is derived from the Greek *klados*, branch, and it is often used as a

[2] The binary nomenclature occurs for the first time in the 10th edition of Systema Naturae.

[3] Linné believed that there were not more than a few thousand genera of living things, each with some clearly marked character, and that a good taxonomist could memorize them all, especially if their names were well chosen. In his eagerness to range he classified kidney stone and gallstone as minerals.

synonym to phylogenetics. The systematics was developed by the German entomologist Willi Hennig (1950, 1966) and is an evolutionary system based on genetics. The species are hierarchically divided into groups, clades, based on their ancestors, but only monophyletic taxa are accepted. This means that the group should have only one common ancestor, and all members of the group should be descendants of that ancestor. The hierarchy is presented in a tree-like diagram called cladogram (Figure 14–16 and Appendix B).

When DNA-sequencing techniques were developed in the 1990s they opened a possibility to study relationships in never a beheld way. A lot of data were collected, but mutations and crossbreedings made it difficult to interpret the results. Now, when DNA-sequencing capacity and read length have increased, it has become possible to study genome-scale datasets; phylogenetics is slowly merging into phylogenomics (Parks et al. 2012, Wang 2013).

2.4.2 *Tracheophyta*, the vascular plants

There are approximately 400 000–600 000 plant species on earth (Björkqvist et al. 1983). They are traditionally divided into two groups: vascular and nonvascular plants. The nonvascular plants lack tissues that have been specialized for water and nutrient transport. This group consists of algae and mosses. The vascular plants embrace the vast majority of terrestrial plants. They are divided into three groups according to their reproduction: *Pterophytina* (ferns), *Angiospermae* (flowering plants) and *Gymnospermae*.

2.4.3 *Gymnospermae* or *pinophytina*, the naked seeds

The name Gymnosperm is derived from the Latin word *gymn-* naked and the Greek word *sperma* seed. This means that the seeds are not enclosed by an ovary, a fruit. Instead, they are surrounded by an ovary wall in a cone. The gymnosperms date long back in evolutionary history; they dominated the land area during the Jurassic and Cretaceous periods, but most of the prehistoric species died out. Currently there are about 60–70 surviving genera, with a total of 600–950 species. (Mitchell 1977, Björkqvist et al. 1983)

The gymnosperms form a relatively small and highly distinctive group of plants and their global, cultural and ecological importance is significant. All gymnosperms are woody plants like trees, shrubs or vines, and they are divided into *Cycadophyta* (cycads), *Ginkgophyta* (ginkgos), *Gnetophyta* and *Coniferophyta* (conifers).

2.4.4 *Coniferophyta* or *pinophyta*, the conifers

Coniferophyta, or *pinophyta*, are commonly called conifers or softwoods. Before the appearance of the angiosperms, the conifers dominated the vegetation on earth. The first species date back to the end of the Late Carboniferous epoch 320–286 million years ago, and all extant families can be traced back to the Mesozoic era. Today, the division consists of approximately 630 species (Farjon 1998).

Most of the conifers are evergreens and their leaves are needle- or scale-shaped (Hosie 1979, p. 14). Compared to the wood of angiosperms, the wood of conifers is more primitive, it contains tracheids but no vessel elements, and there is generally less ray parenchyma in coniferous wood.

The discussion about how *coniferophyta* should be subdivided seems endless. There are as many distributions between families and genera as there are authors, and phylogenetics does not seem to simplify the problem. Anyway, one of the possible cladograms is presented in Figure 14.

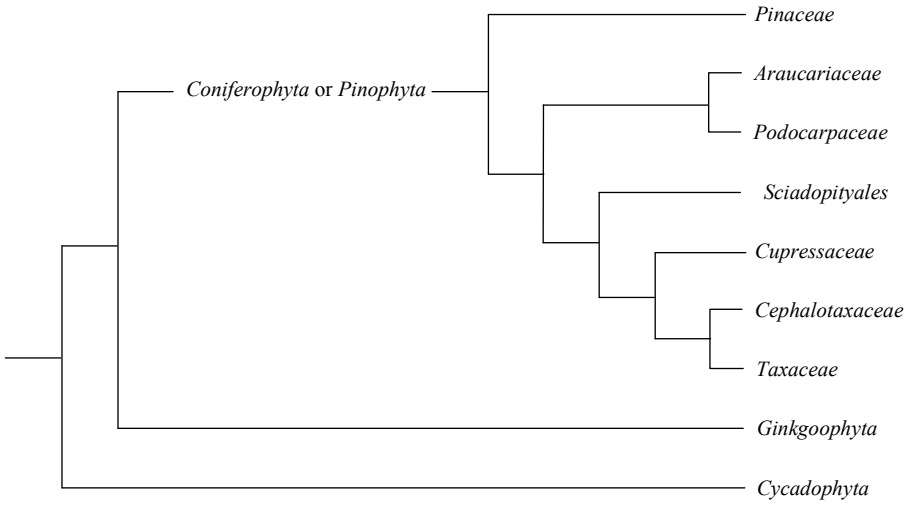


Figure 14 Cladogram of the gymnosperms (based on Farjon 2003, Price 2003, Quinn & Price 2003).

2.4.5 *Pinaceae*, the pine family

Pinaceae is the largest conifer family with 225 species (Farjon 1998). The trees, or in some cases shrubs, are 2–100 m tall. *Larix* and *Pseudolarix* are deciduous, the rest of the genera are evergreen. All are resinous and monoecious. Traditionally, the family has been divided into four subfamilies according to leaf, cone and seed morphology: *Pinoidae*, *Piceoidae*, *Laricioidae* and *Abietoidae* (Figure 15).

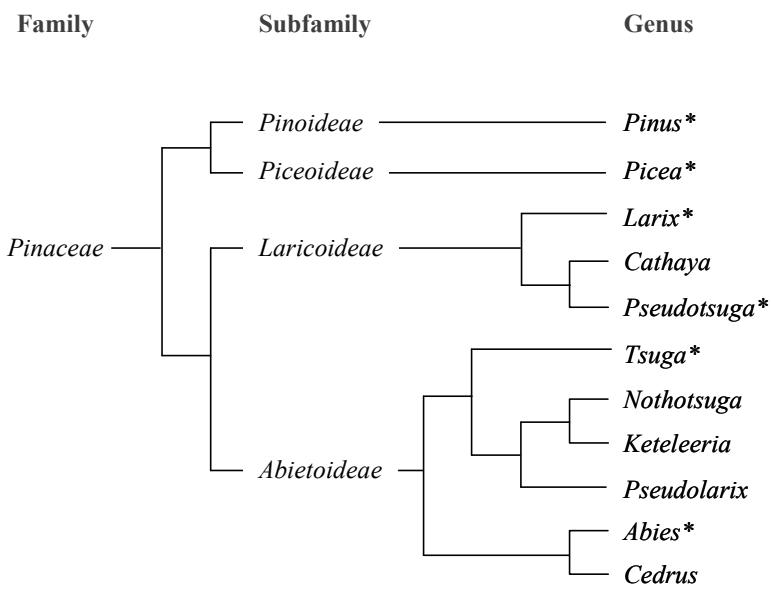


Figure 15 Cladogram of the family Pinaceae (Frankis 1988). Species studied in the present work belong to genera marked with an asterisk (*).

2.4.6 *Pinus*, pine

Pinus, or commonly pine, is the largest and most widespread genus in the family of *Pinaceae* and it includes more than 100 species. The group includes many of the economically most valuable species of trees in the world. They provide a source of wood, pulp, paper, resins, charcoal, food (i.e. seeds) and ornamentals (reviewed by Le Maitre 1998).

Pines are native to all continents and some oceanic islands of the northern hemisphere[4]. They occur mainly in the boreal, temperate, or mountainous tropical regions, but can be found as far south as in Sumatra, Southeast Asia. Many pines are fast growing; they tolerate poor soil and relatively arid conditions, making them popular in reforestation (Gernandt et al. 2005). Pines are extensively planted in the temperate regions of the southern hemisphere as ornamental and timber trees (Critchfield & Little 1966, Mirov 1967, Kral 1993).

The systematics of *Pinus* has a long and extensive history. The first taxonomic publication was made by Linné (1753). The first modern classifications were presented by Shaw (1914, 1924) and Pilger (1926). Duffield (1952) reviewed and compared the two systems and decided to reject Pilger's theory. Critchfield and Little (1966) and Mirov (1967)

[4] Only *Pinus merkusii* Junghun & de Vriese grows natively south of the Equator.

further developed the scheme and divided the groups into sections and subsections.

For many years, morphology was used for identifying and classifying plants. Farjon (1984) tabulated ten characters and states used for mapping pines. However, to classify pines according to their morphological characters is a difficult task; no single character can be used for differentiating them into monophyletic groups. Thus, as the genetic research developed and grew stronger, it also found its way into the plant taxonomy (Strauss & Doerksen 1990, Govindaraju et al. 1992, Moran et al. 1992, Piovesan et al. 1993, Wang & Szmidt 1993, Rosa et al. 1995, Tsumura et al. 1995, Krupkin et al. 1996).

When Price et al. (1998) revised the classification they not only supplemented the list with more recently described pine species, they also took early molecular phylogenetic studies into account. Since then many research teams have studied restriction sites and made sequence comparisons of chloroplast, mitochondrial and nuclear ribosomal DNA to shed light upon the development and classification of *Pinus* (Liston et al. 1999, Wang et al. 1999, López et al. 2002). The most recent update was made by Gernandt et al. (2005). His cladograms can be seen in Appendices B1–3. This classification will be used for comparison further on in this work.

The classification of *Pinus* recognizes two major lines, the subgenera *Pinus* (Diploxylon) and *Strobus* (Haploxylon) (Figure 16). *Strobus* has one fibrovascular bundle in the needle and *Pinus* two. As the composition and monophyletic origin of the genera have been more established, it has turned out that the genetic distance between these two subgenera is large, even larger than between the separate genera *Keteleeria* Carrière and *Abies* Miller (Price et al. 1987). Data also indicate that subgenus *Strobus* is of earlier deviation, and that section *Parraya* is the most primitive one.

The subgenus *Pinus*, also called hard pines, yellow pines or pitch pines, includes about 70 species. The subgenus is divided into two sections: *Trifoliae* and *Pinus*. *Trifoliae* consists of the subsections *Contortae*, *Australes* and *Ponderosae* (Appendix B1), while section *Pinus* is divided into the subsections *Pinus* and *Pinaster* (Appendix B2).

The subgenus *Strobus*, also known as the soft pines, white pines, or five-needle pines, consists of more than 40 species. It is divided into the sections *Quinquefoliae* and *Parraya*. *Quinquefoliae* is then further subdivided into *Gerardianae*, *Krempfianae* and *Strobus*, while section *Parraya* is divided into *Balfourianae*, *Cembroides* and *Nelsoniae* (Appendix B3).

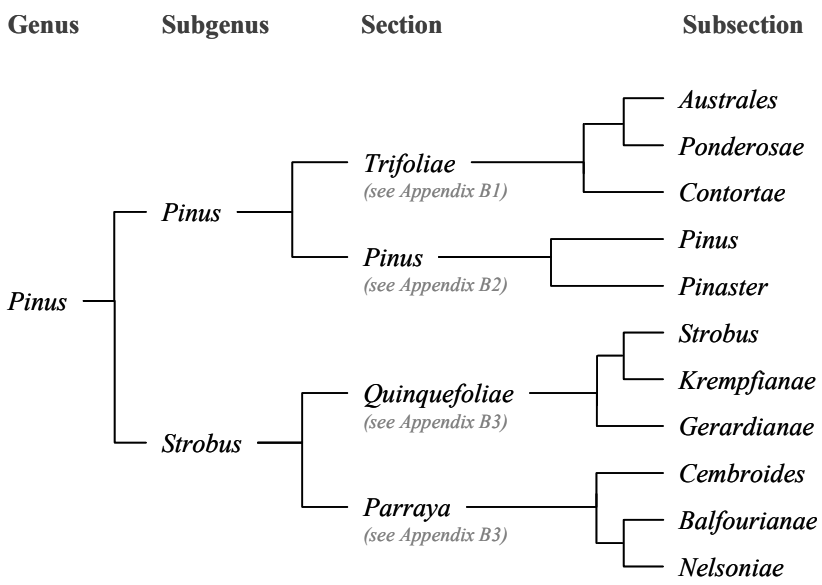


Figure 16 Cladogram of genus Pinus (modified from Gernandt et al. 2005).

Section *Pinus* is predominantly Eurasian and Mediterranean, while sections *Trifoliae* and section *Parraya* are strictly North American. Section *Quinquefoliae* is both Eurasian and North American.

2.4.7 *Picea*, spruce

Picea, or spruce, was first described by Dietrich (1824, p. 794). The name descends either from the Roman word *pix*, pitch (Weber 1987), or from *picis*, the name of a pitchy pine (Taylor 1993). *Picea* grows in the boreal, temperate regions of the northern hemisphere and at high altitude in subtropical regions. It is a very uniform, clearly monophyletic genus without aberrant species. It is most closely related to *Pinus*, but there are some significant differences.

The classification of spruces is problematic. Few of the species have barriers to hybridization, so there has been an extensive gene exchange[5], which seriously complicates the research. Despite numerous attempts, no satisfactory phylogenetic tree has been presented (Wright 1955, Bobrov 1970, Liu 1982, Aldén 1987, Page & Hollands 1987, Rushforth 1987, Schmidt 1989, Farjon 1990, Frankis 1992, Sigurgeirsson & Szmidt 1993). Earlier it was believed that the genus contained fully 50 species. Today,

[5] It is very common that *P. sitchensis*, *P. glauca*, and *P. engelmannii* interbreed, and that *P. mariana* and *P. rubens* cross.

that figure is down to 33, and if the East Asian taxa were properly studied it would probably be reduced even further (Farjon 1990, Sigurgeirsson & Szmidt 1993). A cladogram of genus *Picea* is presented in Appendix B4.

Picea is of great commercial importance. The wood is light, soft, moderately strong, and there is no colour difference between heartwood and sapwood. Therefore, it is indisputably number one in sawn timber, when calculated in produced volume. *P. sitchensis* and *P. abies* are especially important. The fact that spruce wood lacks taste and odour makes it suitable for food containers, but it is also used for construction, interior finishing and plywood, and it is the foremost conifer genera for pulpwood. (Hosie 1979, p. 62)

2.4.8 *Abies*, fir or true fir

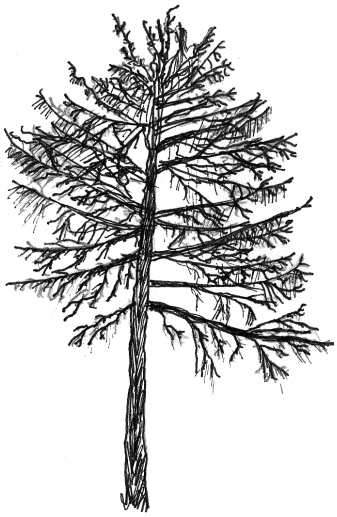
Abies is derived from the Greek *aei*, always, and *bios*, life, here with the meaning evergreen. Originally *Abies* was assigned by Linné to genus *Pinus*, but Miller (1754) promoted it. Later, many different ranks have been proposed: order, family, subfamily, tribe and subtribe, but it has remained a genus. Firs are most closely related to the cedars and should not be mixed with Douglas-fir, that is a *Pseudotsuga*, not an *Abies*.

The genus has been revised several times (Liu 1971, Rushforth 1987, Farjon & Rushforth 1989, Farjon 1990, Hunt 1993a, Fu et al. 1999) and it is estimated that 45–55 species belong to the genus (Appendix B5). Firs do lack barriers for hybridization, so where their ranges overlap, they cross. Examples of closely related species are: *A. balsamea* and *A. fraseri*; *A. bifolia* and *A. lasiocarpa*; and *A. magnifica* and *A. procera*. Except for the two boreal species, *A. balsamea* (in North America) and *A. sibirica* (in Eurasia), the genus is confined to mountainous areas in the subtropical and temperate latitudes of the northern hemisphere.

The wood of *Abies* lack resin ducts, but there are some scattered resin cells and resin blisters in the bark. The wood is generally not considered suitable as timber, but is used for plywood, pulp and as Christmas trees.

2.4.9 *Larix*, larch

Larix was described already by Miller (1754). It belongs to the subfamily *Laricoideae* together with *Cathaya* and *Pseudotsuga* (Frankis 1988, Farjon 1990, Li 1993). It is a small genus containing eleven species. The largest larch forests are found in Russia and Canada, but it also occurs in the USA, China, Korea, Japan, the Himalayas and the Alps.



Earlier, the length of the cone scales (bracts) was used to divide the genus into two sections: *Multiseriales* with long exerted bracts and *Larix* with short bracts (Ostenfeld & Syrach Larsen 1930, Bobrov 1972, LePage & Basinger 1995, Schmidt 1995). Genetic data, however, revealed that a division between the New and Old World is more correct (Gernandt & Liston 1999, Semerikov & Lascoux 1999). The latest results advocate a division into three groups (Semerikov & Lascoux 1999, Wei & Wang 2003, 2004, Gros-Louis et al. 2005):

1. North American species
2. short-bract species from northern Eurasia
3. long-bract species from southern Asia.

It is not easy to rank the larch taxa; they often grow in over-lapping areas, and since they lack barriers against hybridization there are an endless amount of crossings, especially between *L. sibirica* and *L. gmelinii* (Milyutin & Vishnevetskaia 1995). One of the latest proposed cladograms of genus *Larix* is presented in Appendix B6, where the three groups mentioned above are pointed out. It should, though, be noted that *L. sibirica* is separated from the rest of the Eurasian species. *L. sibirica* has short bracts, but it seems to fit better in the group with long bracts. So until the botanists have decided to which group it belongs, they tend to put it separately.

Larch is a deciduous tree, meaning that the needles turn yellow and drop off in the autumn. The wood is hard, heavy and decay-resistant[6] (Parker 2007). It can be used for building boat hulls and masts, week-end cottages or as bonsai trees (mainly *L. kaempferi*). In central Europe, trees from mixed conifer stands are used as pulp wood, but larch seldom mounts more than a few percentage of the pulp raw material.

2.4.10 *Tsuga*, hemlock

Tsuga was originally described by Endlicher (1847, p. 79, 83) as a section of *Pinus*, some years later it was promoted to a genus by Carrière (1855). *Tsuga*'s common name, hemlock, originates from a perceived similarity in the smell of its crushed foliage and that of the totally unrelated herb poison hemlock, *Conium maculatum*[7].

[6] Piles of larch have been used to stabilize the clay under Venice and St Petersburg.
[7] It is said that the Greek philosopher Socrates might have been poisoned with this herb.

Today, there are four species in North America, and four to six in eastern Asia and Himalaya, but no natural stands in Europe (Hosie 1979, p. 74). Pollen found in fossils and peat does, however, indicate that hemlocks did grow in Europe prior to the Pleistocene Ice Age 1.8 million years ago.

The genus is normally divided into two subgenera: *Tsuga* and *Hesperopeuce* (Appendix B6). The latter subgenus contains only one species, *T. mertensiana*, so some botanists treat it as a distinct genus. They call it *Hesperopeuce mertensiana* (Bong.) Rydb. The hemlocks occur in pure or mixed stands. Their wood is slightly harder than the other conifers' and it lacks resin ducts. It is commonly used in the timber and pulp industry, and *Tsuga heterophylla* is especially important in British Columbia. The bark is very rich in tannins, so bark of eastern hemlock, *Tsuga canadensis*, has been a commercially important product for tanning of leather. (Hosie 1979, pp. 74, 78)

2.4.11 *Pseudotsuga*, Douglas-fir

The name *Pseudotsuga* comes from the Greek *pseudo*, false, and *Tsuga*, hemlock (Lipscomb 1993), but it is commonly known as Douglas-fir. It is a very small genus and it was first depicted by Carrière (1867). Before that, the species were thought to belong either to the genus *Abies* or *Pinus*. As many as 22 species and three varieties have been described; however, the vast majority of them were already discriminated by Flous (1937). Today, it is believed that there are two or three species growing in North America and one in Japan. Farjon (1990) claims that there is one additional species in Asia, while Raven and Zheng-Yi (1999, p. 37) found three species. Appendix B6 presents a cladogram of the five most accepted species. DNA restriction fragments (Strauss et al. 1990) and nuclear ribosomal DNA (Gernandt & Liston 1999) have been used to study the relationships among the most widely-accepted species.

Pseudotsuga menziesii is one of the most common trees in western North America. It is estimated that it constitutes 60% of the forest resources and it can be up to 120 m tall in untouched forests. Economically it is a very important timber species and it has become very common, on the edge of invasive, in Europe, southern South America, Chile and New Zealand.

2.4.12 Species

Species is the basic unit for systematic classification, but is not a static system. Constant changes in the local environment cause adjustments through selection and random fixation of mutations.

To be classified as a separate species, the population should have distinct morphological characteristics, and be effectively isolated from other populations. Species are normally separated by sterility barriers that hinder, or at least aggravate, the exchange of genes; in many cases the limitations are only geographical or ecological. So if the isolation is broken, these species do interbreed.

2.4.13 Subspecies, variety and subvariety

There are a number of ranks below the level of species called infraspecific taxa. Their names are ternary and formed so that after the normal genus name (e.g. *Pinus sylvestris*) follows an abbreviation (e.g. var.) and a specific epithet (e.g. *mongolica* Litvinov).

The species can be divided into subspecies (ssp. or subsp.). Geographical or morphological barriers have partly or totally isolated the clumps habitat. This has resulted in minor repeating genetic and morphological differences compared to the original, primary species.

The level below subspecies is variety (v. or var.). Varieties often grow geographically separated. They have a mutation that results in differences in one or a few characteristics. These mutations are inheritable and the varieties do hybridize when they come in contact.

2.4.14 Scientific and common names

Naming and interpreting the names of a species can be confusing. To start with, trees can have several common names. These names can origin, e.g., from a person, the type of soil they grow in, a special feature, a product obtained from the tree, or the geographical location where it grows. Sometimes the species also have one or several “local names”. They generally vary throughout the trees range. The local names generally tend to cause confusion and should therefore be avoided. All species have at least one scientific name. It consists of a generic name, a specific name and an abbreviation recognizing the person who first named the tree. Appendix F contains a list of occurring scientific synonyms for the species studied in this thesis. The synonyms are marked with a cross-reference to the scientific name used in this work.

2.5 Chemotaxonomy

Chemotaxonomy, also called chemosystematics or molecular taxonomy, is an attempt to classify organisms according to their chemical constituents. The plants' molecular characteristics are genetically controlled; mutations that affect the chemical processes also affect the morphological and anatomical structures. Therefore, chemotaxonomy could offer a useful complement to the traditional means of classification, for instance, in groups with morphologic divergences or when only a part of the plant is available for classification.

Abbot (1886) was the first to claim that chemical constituents could be used to understand plant evolution. However, it was not until the 1940s, when the chromatographic techniques spread, that the palmy days of chemotaxonomy dawned. Chromatography provided a simple, fast and cheap way of separating and analysing terpenoids, phenols, alkaloids, carbohydrates, fats, oils and waxes from very small samples[8]. Eager chemists hoped that any taxonomic dilemma could be solved by studying the plant constituents and lots of work was performed. It soon became clear, however, that it was not that simple; not all plant constituents are useful for taxonomic purposes. Common components like cellulose, chlorophyll, sugars, hormones and fatty acids occur in almost all plants, and they are therefore of little or no taxonomic interest. On the other hand, very rare compounds, found only in isolated species, are not either interesting. Instead, one should concentrate on the pattern of substances. It is not so crucial if one individual compound is missing, others may provide the missing link between the related species. (Erdtman 1952, 1956, 1959)

The chemotaxonomists define the relationship between compounds in a little different way; to them similar chemical structure does not always indicate a relationship. Actually, for taxonomic purposes it is much more interesting to know how a molecule is biosynthesized. Chemically identical compounds may be synthesized along different enzymatic pathways, whereas compounds belonging to quite different chemical classes may be formed in a similar way. Normally, compounds formed by relatively simple biosynthetic processes are uninteresting, even though their structure is complex. However, compounds that undergo re-arrangements or other secondary changes (e.g. reduction, oxidation or substitution) are interesting, cf. cinnamic acid and lignans.

Environmental factors like soil conditions, climate and seasonal changes tend to affect all plants. It is, therefore, recommendable to examine several

[8] In this section, amino and nucleic acids are omitted, since they are not within the scope of this work.

plants of the same species, preferably grown under different conditions. The taxonomically important compounds may be found in any part of the plant, but the most important ones occur in phylogenetically old, conservative, little specialized organs. Dead tissue is not affected by environmental factors and, therefore, many scientists have studied heartwood.

The pines comprise an isolated, old and conservative group that has been much studied by botanists and the genus contains some uncertainties regarding the classification, which tease the taxonomists (Erdtman 1963). Mirov (1948, 1953a, 1953b, 1961) studied the diterpene acids (resin acids) and monoterpenes in gum turpentine of 92 pine species and two varieties. He found that the pines produce specific, constant patterns of monoterpenes. Later it was, though, shown that these compounds cannot be used for taxonomic purposes (Smith 1976). Mirov (1938) also suggested that the saturated constituents are evolutionary older than the unsaturated ones.

Lindstedt and Misiorny (1951b, 1952) studied 52 pine species by paper chromatography and found that the pines can be characterized by their specific pattern of heartwood phenolics. The subgenera Diploxylon and Haploxylon can easily be recognized. Of the groups, only S*trobus* and *Gerardianae* (Haploxylon) could be distinguished, not any other. Erdtman (1956) wrote that the ability to produce the stilbene pinosylvin is as old as, or perhaps even older, than genus *Pinus* itself. The ability seems to have been maintained for at least 100 million years.

When comparing Haploxylon and Diploxylon pines, the later have simpler heartwood chemistry. Diploxylon pines contain pinosylvin and flavanones, e.g. pinocembrin and pinobanksin, while the Haploxylon pines contain the same substances as well as dihydropinosylvin and flavones, e.g. chrysin. This indicates that the Haploxylon pines have a redox system, which is absent or inactive in the Diploxylon pines. Since loss mutations are more common than progressive mutations this would lead to the conclusion that Haploxylon pines are more primitive than Diploxylon. Alternatively the separation has taken place already at a much earlier stage. (Erdtman 1956)

What about the other genera? *Larix, Tsuga* and perhaps also *Picea* are rather well chemically characterized, whereas *Abies* is rather poorly studied. For *Picea* it is not possible to distinguish between its two sections, in fact, chemists can not even distinguish between the genera *Picea* and

Tsuga[9] without referring to morphological characteristics (Erdtman 1956). However, there are some overlapping of identical or chemically related constituents indicating phylogenetic relationship between the genera (Erdtman 1952, Nair & Rudloff 1960, Erdtman 1963):

- the lignans conidendrin and 7-hydroxymatairesinol (HMR) are common in *Picea, Tsuga,* a *Larix* and possibly a *Abies* species;
- *Pinus* and *Picea* both contain pinoresinol;
- *Picea, Larix* and some *Pinus* species contain lariciresinol; and
- *Pseudotsuga* and *Larix* both contain taxifolin.

Many scientists got carried away and jumped to conclusions when the chemotaxonomy was introduced (e.g. Baker & Smith 1920). However, with time, the fascination for secondary metabolites petered out and the chemists' interests shifted elsewhere. Gel electrophoresis was the first method to enable amino acid sequencing. Today, the extraction, amplification and sequencing techniques have been developed and nucleotide sequencing of DNA and RNA are the main areas of research. So to conclude: *analysis of extractives can be seen as a complement to classical taxonomy and biochemistry, not as a substitute*.

2.6 Morphology of wood

The basic structure and shape of a tree is determined by genetic factors, but environmental factors like soil, supply of light, water and nutrients at the habitat, as well as climate play a significant role for the growth rate and final shape of the tree. The tree consists of many parts: root, stem, branches, bark and needles (leaves); only stemwood and knots are studied in this work. The root, outer branches, leaves, bark and cones are not utilized for wood products, and will therefore not be subject of any deeper discussion.

2.6.1 Macroscopic structure of softwood

The macroscopic structure of wood is the structure that can be seen with the naked eye (Figure 17). The core, also called pith, is the tissue formed during the saplings first year. It has poor mechanical strength and its colour is often darker than the surrounding wood, xylem.

[9] *Tsuga mertensiana* is much more spruce-like than the other hemlocks. This morphologic resemblance has made many botanists suspect that it is a hybrid of *Tsuga heterophylla* and *Picea sitchensis*. Taylor (1972) studied the phenolic extractives to find evidence for hybridization. He found *T. mertensiana* and *P. sitchensis* to be very similar chemically. However, he is very reluctant to support the theory of hybridization. He prefers to claim that *Picea* and *Tsuga* are closely related and that *Tsuga mertensiana* is the hemlock closest related to the spruces.

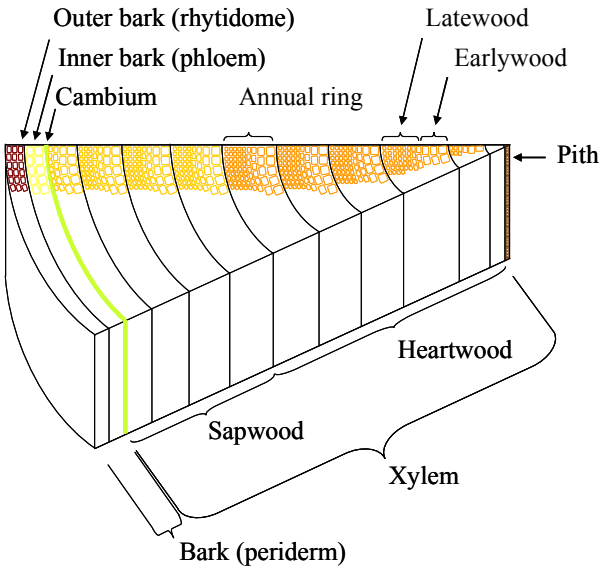


Figure 17 Macrostructure of a softwood stem.

The xylem is divided into sapwood and heartwood. Sapwood is the outer, active part of the stem. It stores reserve nutrients during winter and transports water and minerals from roots to needles. Heartwood is the inner part of the stem which gives rigidity and strength to the tree. It is formed when the capability of water transport decreases and the living parenchyma cells die. During this process, starch and lipids are converted into secondary metabolites, which deposit in cell lumina, cell walls and on pit membranes (Fengel 1970, Kampe & Magel 2013, p. 78). Concurrently the torus of the double-sided ring pits are dislocated towards one side, which hinders the water transport. Lignification and incrustation with condensed phenolic substances further decrease the water conductivity and increase the durability of the heartwood. (Krahmer & Côté 1963)

The moisture content is remarkably lower in heartwood than in sapwood and the heartwood of pine is darker than the sapwood. The discolouration is caused by oxidised stilbenes.

In southern and central Finland, the heartwood formation in pine starts at the age of 30–40 years (Ilvessalo-Pfäffi 1977), while it starts already at the age of 15–20 years in the American southern pines (Koch 1972).

The pith rays (Figure 18) transport nutrients and resin in the radial direction of the stem. The rays are normally one cell row wide and reach out to the bark. Secondary rays do not start from the pith, but inside the xylem. The number of rays their size increases from the core towards the bark.

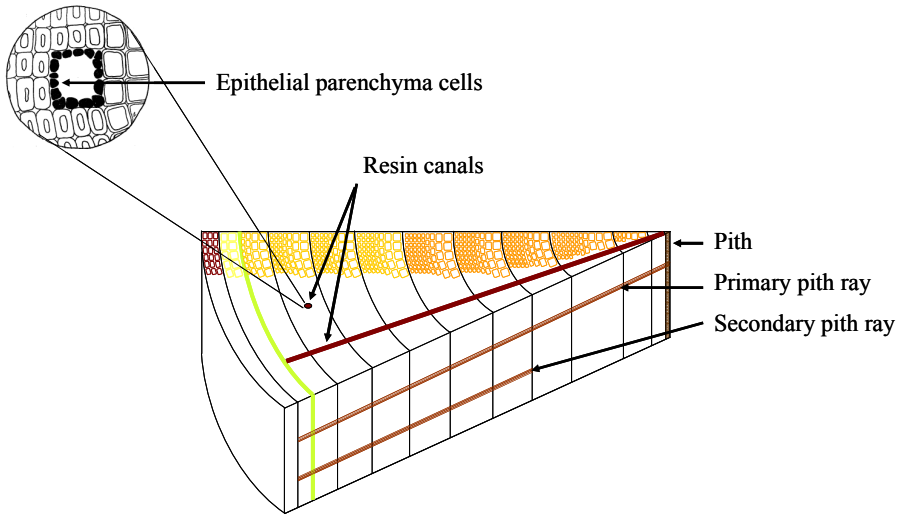


Figure 18 Radial and longitudinal resin canals and pith rays. Primary pith rays star from the core, secondary somewhere in the xylem.

The growth of the tree takes place in a thin layer called cambium situated between the xylem and the bark. Bark, or periderm, is a generic term for all tissues external to the cambium. Sugars and starch are transported through the soft inner bark, bast or phloem, from the leaves downwards along the stem. The outermost layer consists of dead phloem and cork cells, and it is called rhytidome.

In regions with seasonal variations, the growth is fastest in the spring and the cells formed then have thin walls and a large cavity, called lumen, in the middle. These cells, known as earlywood, have many pores and function as pipes, providing fast water transport. As the growing period proceeds, the cell growth slows down and supporting latewood cells are formed. The latewood cells have thicker walls and smaller lumens. Together the earlywood and latewood form an annual ring, also called growth ring or annual increment. The weather and conditions during the growing season affect the thickness and properties of the annual ring.

2.6.2 Microscopic structure of softwood

The wood microstructure comprises the cells and their structures. In conifers, 90–95% of the cells are tracheids or fibres, 5–10% is parenchyma cells, and the rest is pit ray parenchyma cells and epithelial parenchyma cells (Table 4). The cells provide mechanical strength, store reserve nutrients, and transport water, sap and oleoresin through the tree. (Sjöström 1993, p. 6–7, Alén 2000b, p. 18)

Table 4 Cell types in softwood and their properties. LW = latewood, EW = earlywood. Abundance is the vol-% of xylem (Fengel & Wegener 1989).

Cell type	Length mm	Width µm	Abundance %	Orientation	Where	Function
Tracheid	1–5	10–65	90	↕	Stemwood	EW: water transport LW: support
Parenchyma	0.01–0.16	2–50	5–10	↔	Pith ray	Store nutrients
			<5	↔	Pith rays	Water transport
			-	↕	Roots Stemwood[1]	Store nutrients
Epithelial parenchyma			<1	↔ ↕	Resin canals	Secretion of oleoresin

[1]Only in stemwood of *Tsuga*, *Pseudotsuga* and *Abies*.

The tracheids are 1–5 mm long, coarse, parallel tubes with strong walls. The latewood tracheids have thicker and stronger walls, compared to the earlywood tracheids, and they provide mechanical strength. The earlywood tracheids are wider, 20–65 µm, compared to 10–20 µm in the latewood, they have thinner walls, 1.5 µm compared to 5 µm in latewood, and they also have more and larger pores, 200 compared to 10–50 in the latewood (Vihavainen 1970). The purpose of the earlywood tracheids in the sapwood is to conduct water and minerals from the roots to different parts of the tree. The water moves between the cells through small overlapping pores, so-called bordered pits.

The radial water transport takes place in a single row of pit ray tracheids situated on top of and under the pit rays (Figure 19). These tracheids differ remarkably from normal tracheids. In fact, they resemble more of parenchyma cells. The total volume of this cell type is very small.

There are three different types of parenchyma cells: longitudinal parenchyma cells, pit ray parenchyma cells and epithelial cells. They are much smaller than the tracheids, only 10–160 µm long and 2–50 µm wide. The parenchyma cells are connected with simple pits, where the torus and margo are substituted by a thick membrane (Figure 19). Longitudinal parenchyma cells are found in stemwood of *Tsuga*, *Pseudotsuga* and *Abies* (Kettunen 2001), as well as in the roots of Norway spruce.

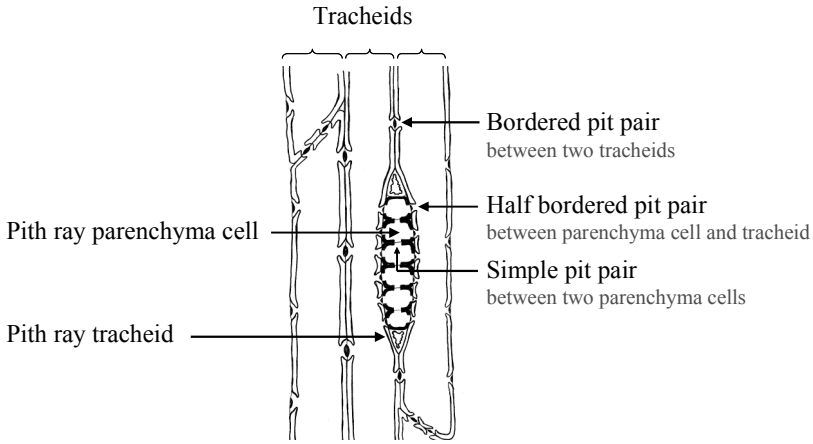


Figure 19 Tangential cut showing the parenchyma cells storing nutrients and the ray tracheids providing radial water transport. Three different pore types are seen in the picture.

The radial parenchyma cells, called pit ray parenchyma, store reserve nutrients (parenchyma resin) during winter when the sap is frozen and hardly moves in the tree. The sap needs to be accessible in the spring when the growth period starts, before the new roots and needles (larch) have begun to function. The active, living parenchyma cells are found in the sapwood. They function only 20–30 years; thereafter they are lignified, die and are transformed into heartwood.

The epithelial cells excrete oleoresin. In *Picea*, *Larix* and *Pseudotsuga* they are found as an one-cell-thick layer surrounding the walls of the resin canals (Figure 18), in *Pinus* the layer is two cells thick (Kettunen 2001). The resin canals are a connected system of pipes that transports resin in both longitudinal and radial directions in the stem. The system is pressurized, 50 kPa in pine, to favour transport to damaged areas. Five genera in the *Pinaceae* family have resin canals: *Picea*, *Pinus*, *Larix*, *Pseudotsuga* and *Keteleeria*. Other softwood species, like *Abies*, *Tsuga*, *Cedrus* and *Pseudolarix* have only traumatic resin canals. They occur as a response to damage, when the tree needs additional protection. The firs also have resin pockets under the bark.

2.6.3 Reaction wood, compression wood

Reaction wood in the stem is formed when the trees normal, straight position is disrupted e.g. if the ground is instable or leaning, or if snow or wind keeps bending the tree. It also occurs in branches and knots (Ilvessalo-Pfäffi 1977). Its function in the stem is to prevent further inclination and to restore the normal posture. In branches, the reaction wood is constantly growing, and it keeps the branch in horizontal position. The type of reaction wood in hardwood species is tension wood, while softwood species contain

compression wood[10]. The compression wood is heavier, harder and 20–30% denser than normal wood (Kärkkäinen 1985). It contains 20–25% less cellulose, 30–40% more lignin, the degree of crystallization is lower, and the fibres are shorter and stiffer. These properties make the compression wood difficult to pulp, and the pulp yield and tensile strength decrease. The high lignin content makes the wood dark and miscolours plywood. When timber containing compression wood is dried, it becomes cracked and distorted.

2.6.4 Branches and knots

The branches carry the leaves or needles responsible for photosynthesis and transport fluids back and forth to the rest of the tree. The branches normally start growing from the pith, so a part of the branch is hidden inside the stem. This part is called knotwood, or shorter: knot.

The macroscopic structure of the branches is the same as that of the stem, but the cross-section is less circular, especially the part of the branch closest to the stem. There the annual rings are narrower and they contain a lot of compression wood (see chapter 2.6.3). The fibre direction of the branches and knots is at right angles to the stem and the stem fibres closest to the knot are contorted because they have to circle the knot.

The branch fibres differ from the stemwood cells both in size and proportion. The tracheids are half as long, they do, however, become a bit longer as the branch grows thicker (Ilvessalo-Pfäffi 1977).

The tree is also prepared to lose its branches. The life time of the branches is limited; sooner or later they will break, naturally or due to thinning. Since the fibre direction of the branch is perpendicular to the stem, microbes and fungi have an excellent chance to attack the tree through the wound of a broken branch. To protect themselves, the pine branches and knots contain much more oleoresin canals and thus more resin than the stem. These resin canals are connected to the network in the stem and when a branch is dying, the resin accumulates, the density increases and the colour turns darker. The wound after a cut or broken branch is normally completely sealed by resin within 3–4 weeks. As the stem grows, it will gradually grow over the stump, and eventually embed it completely (Figure 20). Bark residues and oxidized resin become ingrown together with the stump and when the stem is utilized as pulp wood everything ends up in the

[10] In the old days, people used skis of different length; a short ski for pushing on the right foot, and a long ski for gliding on the left foot. The longer, left ski was normally made of pure compression wood, because the high lignin content made it very tough. It was called “lyly” in Finnish after the raw material (Parviainen 2002).

pulp. Therefore, the dead knots are especially detrimental for the pulp and paper production.

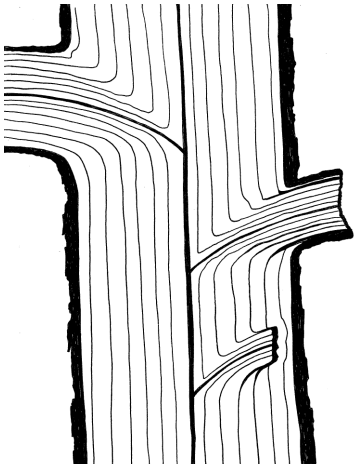


Figure 20 Living knot to the left and dead knots to the right. The lower dead knot is totally embedded in the stem.

Already in the 1930's knots were reported to contain high amounts of extractives (Hägglund & Larsson 1937, Wegelius 1939). Thirty years later, Boutelje (1966) determined the distribution of total extractives in stemwood, branches and knots of spruce. No one did, however, analyse the individual components. The first analytical studies of extractives in knots were made on *Pinus radiata* (Hillis & Inoue 1968) and *Araucaria angustifolia* (Anderegg & Rowe 1974). *Araucaria angustifolia* was reported to contain over 20% (w/w) lignans, but that information passed almost unnoticed. Around those years Ekman (1979b) studied the distribution of lignans in Norway spruce. He found that the heartwood of branches contained 4–6% lignans and the roots 2–3%. He did, however, not analyse any knots. It was not until 1998 that Norway spruce knots were analysed at Åbo Akademi University. The extract immediately attracted attention because it contained remarkably 10% of lignans. This was the beginning of an extensive knot research. First the conifers growing in the Finnish forests, *Picea abies* and *Pinus sylvestris* were studied (Willför et al. 2003a, 2003b). Then, the research was expanded to conifers growing in other regions (Willför et al. 2004a, 2004b, Pietarinen et al. 2006a, Holmbom et al. 2007, Willför et al. 2007), as well as several deciduous species (Pietarinen et al. 2004, 2005a, 2005b, 2006b, Neacsu et al. 2007).

Today, we know that knots contain remarkably high lignan concentrations, but we do not yet know why. The lignans might be involved in the lignification of compression wood or in the natural ability of the tree to self-prune (Kebbi-Benkeder et al. 2015). The lignans are also known to be strong antioxidants and radical scavengers. This could protect the tree against fungi and microbes which use radicals to attack the tree, and against radicals formed by climate stress, e.g. temperature, snow load, wind and drought (Willför et al. 2003c, Pietarinen et al. 2006a). All these hypotheses

are, however, speculative and further studies are needed to understand the true role of lignans in knots.

For the living tree, the branches are of decisive importance, but industry considers them to be growth defects. The branches are cut when the trees are harvested, hence only the knots are problematic in further processing. In *Picea abies,* about 1% of the stem volume is knots. Considering that the density of the knots it twice that of normal wood, 2 mass percent of the dry stem is knots (Hakkila 1998). For Scots pine the corresponding amounts are 1 and 1.5%.

The physical and chemical properties of knots are different from those of normal wood (Wegelius 1946, Boutelje 1966). The knots have higher density, lower moisture content, high concentration of extractives and the fibre orientation differs from the surrounding stemwood. Furthermore, the knots contain short, stiff, compression wood fibres, which give paper poor technical properties.

In sawn timber, the knots dry faster than normal wood, causing cracks and holes, which decrease the strength. The knots are also known to impair the thermomechanical-pulp (TMP) quality and lead to an increased amount of rejected paper (Sahlberg 1995). Flake-like particles are formed during defibration, the energy consumption increase, and the heat can make the phenolic extractives change colour (Polcin & Rapson 1971, Holmbom 2005). In kraft pulping, the high density and resin content of the knots is problematic. It hinders the penetration of water and chemicals into the chips, both in cooking and bleaching. As a result, the chemical consumption and the amount of screen reject increases (Allison & Graham 1988).

When wood is chipped and screened in a pulp mill, approximately 90% of the knots end up in the so-called over-thick chip fraction (Sahlberg 1995). Eckerman and Holmbom (2001) developed a method, called ChipSep, for removal of knots from the over-sized chip fraction. The method is based on sedimentation of dried chips; the density of dry normal wood is lower than that of water, while the density of knots is higher. This Marcus Wallenberg Prize-rewarded process gives industry an opportunity to separate huge amounts of knots, a material that impairs the pulp and paper manufacturing, and is rich in lignans and other bioactive substances.

2.7 Wood extractives

The extractives constitute a heterogeneous substance group containing innumerable components. They are mainly extracellular, low-molar-mass substances that can be extracted from wood or pulp with neutral, polar or non-polar solvents (Fengel & Wegener 1989). The principle is *like dissolves like*, meaning that selective, non-polar solvents like hexane,

dichloromethane (DCM) and methyl *tert*-butyl ether (MTBE) dissolve lipophilic compounds, such as resin acids, fatty acids and sterols, while more polar solvents, such as ethanol and water, extract hydrophilic substances, i.e. simple sugars, phenols and inorganic salts. Acetone extracts both lipophilic and hydrophilic compounds (Fengel & Wegener 1989, Alén 2000b).

Tree species in the temperate regions typically contain 1–10% wood extractives, while the concentrations in some tropical species can be as high as 40% (Ekman & Holmbom 2000, Umezawa 2001). The amount and composition of extractives vary between tree species and within the species depending on place of growth, season, age and especially between types of tissue (Sjöström 1993, Willför et al. 2003a).

The extractives can be divided and classified in many ways: according to their synthesis, structure and function, or where they occur in the tree. In this text, the last-mentioned functionality approach is used. Generally, the extractives give colour, smell, or taste to the wood, constitute spare nutrient, work as plant hormones, or, when bound to metals, act as catalysts for biosynthesis, but above all, they protect the tree against bacteria, fungi and noxious insects, both physically and chemically. Some components are sticky, some form water-repellent protective layers, while other are toxic or hormonally inhibit the insect reproduction.

2.7.1 Oleoresin

The only softwood family containing regular resin canals in the wood is *Pinaceae*. The genera *Pinus*, *Picea*, *Larix*, *Pseudotsuga* and *Keteleeria* contain normal resin canals, while *Abies*, *Tsuga*, *Cedrus* and *Pseudolarix* only have traumatic resin canals. These canals are formed as a response to stress, wounding or infection. (Back 2000, p. 4).

The resin canals are filled with oleoresin, commonly also called resin or pitch. It is produced by the epithelium cells surrounding the resin canals, and it is a fluid mixture of resin acids (60–80%) and volatile terpenes (20–40%) (Back 2000). When the oleoresin comes in contact with air, the volatile terpenes evaporate and leave behind a hydrophobic, partly oxidized, mechanical seal. The oleoresin of genera *Larix* and *Pseudotsuga* contains a significant amount of fungi-toxic terpenyl alcohols that provide additional chemical protection. The solid form of oleoresin is called rosin.

Except normal and traumatic resin canals, additional resin pockets can be found inside stems of *Pinus* and *Picea*. The origin of these resin (or pitch) pockets is not clear. Presently, there are three hypotheses. The first claims that heavy wind blast causes bending stresses in the stem, which gives rise to cracks in the xylem close to cambium. These voids are then filled with resin from adjacent resin canals. The second explanation is that drought

causes the cracks, and the third explanation is based on pathogen attacks through the bark, which cause micro wounds. The resin pockets are then induced as a defence mechanism against the hostile assault. Resin pockets are detrimental defects in timber and veneer. (Seifert et al. 2010)

Stemwood of spruce normally contains 0.2–0.4% oleoresin, while pine heartwood has larger resin canals and, thus, contains about ten times more resin. In pine, additional resin acids are produced when the sapwood dies and transforms into heartwood. Heartwood in the lower parts of the pine stems can be soaked with resin - up to 40% of the wood weight can be resin. (Ekman 1979a, Back 2000)

Terpenes and terpenoids

The terpenes are, mainly head-to-tail condensation products of isoprene units formed mainly in the cambium (Back 2002). They are grouped according to the number of isoprene units $(C_5H_8)_n$ as outlined in Figure 21. If the terpene molecule contains one or more oxygen-containing functional groups it is called terpenoid. More information about the less abundant, nonresin-acid terpenoids is found in chapter 2.7.7.

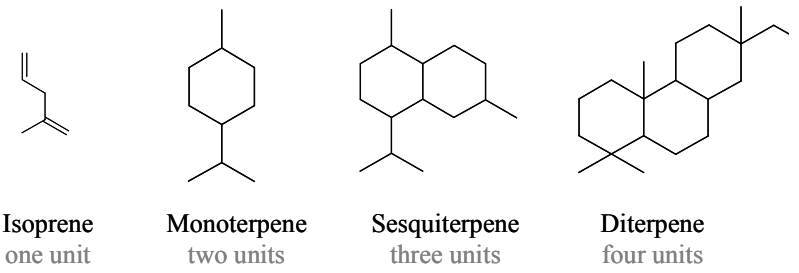
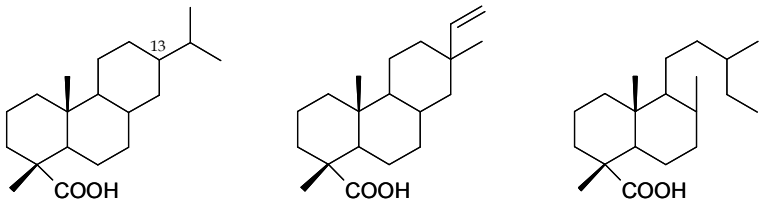


Figure 21 Basic structures of the terpene classes.

Monoterpenoids and sesquiterpenoids are volatile compounds that give the tree its characteristic odour. They can be extracted as turpentine by steam distillation, from digester relief condensates of the kraft process (Back 2000) or from collected oleoresin. Monoterpenoids can be used for preparation of flavours and fragrances (Sjöström 1993). These volatile compounds are, however, not studied in this thesis.

The major component group in the oleoresin is the resin acids. They are mainly tricyclic diterpenoids and the typical average amount is 0.2–0.8% of the wood weight (Holmbom & Ekman 1978, Conner et al. 1980c). Eight resin acids dominate in most of the softwood species. Depending on the substituent at the C_{13} position they can be divided into abietane (abietic) and pimarane (pimaric) type. The dominating, abietane-type has an isopropyl or an isopropenyl group as substituent, while the pimarane-type has a methyl and a vinyl substituent (Figure 22). Abietane-type acids with a

conjugated dienoic structure are less stable against oxidation and isomerization than dehydroabietic acid and the pimarane-type resin acids.



Abietane type Pimarane type Labdane type

Figure 22 Structures of resin acids of pimarane, abietane and labdane type.

There are also some less common resin acids with bicyclic structures. This type is called labdane (labdanoic). They are present in some pines, e.g. lambertianic (antidaniellic) acid in *Pinus lambertiana*, communic (elliotinoic) acid in *P. elliottii* and mercusic (dihydroagathic) acid in *P. mercusii* (Ekman & Holmbom 2000, p. 50). The structures of the most abundant resin acid are presented in Appendix C1.

The resin acids are weak acids with pK_a=5.7–6.4 (Nyrén & Back 1958). They have a hydrophilic carboxyl group and a hydrophobic skeleton that makes them good solubilizing agents in soap form. In kraft pulping and the following washing steps, resin-acid and fatty-acid soaps can solubilise the neutral, lipophilic components. In hardwood pulping, where no resin acids are present, tall oil or rosin soap is added to improve the removal of other lipophilic components (Assarsson 1969b). All resin acids are strongly toxic to fish (Leach & Thakore 1976) and abietane-type acids have antibacterial effects on Gram-positive bacteria (Söderberg et al. 1990).

Isomerization and oxidation of resin acids

The abietane-type resin acids with conjugated double bonds can easily isomerize when exposed to heat or mineral acid. This thermal isomerization is catalysed by the carboxyl group (Loeblich et al. 1955). The pimarane- and labdane-type resin acids, which lack conjugated double bonds, are unable to isomerize in this way.

The thermal isomerization of levopimaric (Loeblich et al. 1955), palustric (Joye & Lawrence 1961), neoabietic (Loeblich & Lawrence 1957) and abietic (Takeda et al. 1968) acids has been thoroughly studied. The reported equilibrium concentrations are 5–8% neoabietic, 7–14% palustric and 80–86% abietic acid. The equilibrium concentrations after acid-catalyzed isomerization of levopimaric (Ritchie & McBurney 1949, Baldwin et al. 1956), neoabietic (Ritchie & McBurney 1950) and abietic acid (Takeda et al. 1968) are reported to be 2–3% neoabietic, 3–4% palustric and 93–95%

abietic acid. There is also an alkali-catalysed isomerization (Schuller & Lawrence 1965), where the equilibrium concentrations are 3–7% neoabietic, 3–11% palustric, 46–73% abietic and 7–17% dehydroabietic acid. The content of levopimaric, abietic and dehydroabietic acid gives a good indication of the heating and oxidation the resin acids have undergone (Lawrence 1959).

Which changes do the resin acids undergo during wood storage, pulping and tall oil fractionation? No significant isomerization or oxidation occurs during a 2-week period of storing unbarked logs (Hemingway et al. 1971), but once the wood is chipped, the resin acids on the chips' surfaces are exposed to air and undergo a fast oxidation; within a few hours half of the levopimaric acid content is lost (Lawrence 1959). Elevated temperatures are known to speed up the resin acid isomerization. In chip piles, the metabolic processes of micro-organisms generate heat, so already after 7–14 days the temperature rises to 50 °C. Levopimaric acid is rapidly lost, along with a substantial amount of neoabietic acid. The abietic acid concentration is also reduced, while the dehydroabietic acid concentration is increased. The increase of dehydroabietic acid, however, account for only a minor part of the total losses of resin acids (Hemingway et al. 1971). After four weeks storing, the tall oil yield was reduced to less than 50% of what was originally present in the wood (Somsen 1962), and after six weeks all levopimaric acid was lost (Quinde & Paszner 1991, 1992).

The loss of resinous material can be either detrimental or beneficial depending on whether the tall oil and turpentine are recovered or not. In the kraft pulping industry, the resin acids are valuable by-products and, hence, losses are undesired. Therefore, effort is made to keep the chip storing as short as possible. Normally, chips for 5–10-days production is stored, but more modern mills tend to keep only 2–3 days' storage (Koskinen 2000, p. A418).

During kraft cooking, levopimaric acid is extensively isomerized and partial oxidation to dehydroabietic acid is observed (Foster et al. 1980, Zinkel & Foster 1980). About half of all levopimaric acid remains in the sulfate soap (Holmbom & Ekman 1978), but it disappears during the acid treatment to form CTO (Holmbom 1977).

Health effects of rosin

Rosin can cause contact allergy, dermatitis and asthma. Therefore, EU requires that all preparations containing ≥1% rosin are labelled with a skin sensitisation warning (1272/2008/EC). It can, however, be difficult to recognise the names of modified rosins, and the amounts are seldom declared on the packages, so in practice it is challenging to follow this regulation.

Unmodified rosin is known to cause contact allergy (Karlberg 2000, p. 512). The main allergenic components are, however, not the native resin acids, but the oxidized compounds, e.g. 15-hydroperoxyabietic acid (Karlberg 1988, Hausen et al. 1990). The allergenic activity of rosin can be altered by chemical modification; hydrogenation diminishes the allergenicity (Karlberg et al. 1988), while esterification with polyols increases it. Glyceryl monoabietate (Shao et al. 1993, Gäfvert et al. 1994) and maleopimaric acid (Karlberg et al. 1990, Gäfvert et al. 1995) are reported to be very allergenic modified rosin compounds.

Some occupations are more exposed to rosin than other; 22% of the electronic workers were reported to suffer from work-related respiratory symptoms and rhinitis due to rosin compounds in fumes from soldering flux (Burge et al. 1979). Other exposed occupations are: printers, newspaper dealers, rubber workers, carpenters, foundry workers, violinists, artists and secretaries (World Health Organization 2014). Adhesive plasters and bandages for treatment of leg ulcers are also known to cause skin irritation. Likewise can cosmetics such as eye shadow, rouge, lip preparations, mascara and hair products cause contact dermatitis. (Karlberg 2004, p. 316).

2.7.2 Parenchyma resin

The parenchyma resin is encapsulated in the pit ray parenchyma cells and serves as reserve nutrient and cell membrane substance (Sjöström 1993). In healthy living sapwood, the parenchyma resin consists of steryl esters, fats (i.e. di- and triacylglycerols) and waxes, but in the heartwood transition zone, where the cells die, the acylglycerols and steryl esters are enzymatically hydrolyzed by lipase and steryl esterases into free fatty acids, sterols and fatty alcohols (Back 2000). The same occurs when wood is stored. The total amount of fats in *Picea abies* is below 0.5% (Ekman 1979a), and approximately 1% in *Pinus sylvestris* (Saranpää & Nyberg 1987a).

In pulping, it is more difficult to remove parenchyma resin than oleoresin from the fibres. First, the alkaline pulping liquors must diffuse into the parenchyma cell via the pores so that the sterols and esters can form soap micelles with the surface-active substances. Thereafter, these fairly large micelles must diffuse out again through the pores[11]. This is a time-consuming process. By breaking the cell walls, the parenchyma resin can diffuse out more easily. This is also the case in mechanical pulping (Back 1969, Lunabba 1985).

[11] The pines are more easily deresinated than the other softwood genera because the pines have larger pits in their parenchyma cells. The pores in the pine are 10–30 μm in diameter, while the pores in spruce are 2–3 μm and in larch 3 μm (Back 1969).

Fatty acids and acylglycerols

Over 50 saturated and unsaturated fatty acids have been identified in *Picea abies* (Ekman & Pensar 1973, Ekman 1980). Straight-chain fatty acids with 16–24 carbon atoms are common, but unsaturated acids with 1–3 double bonds in *cis*-configuration dominate. The main fatty acids in softwoods are linoleic (9,12-18:2) and oleic (9-18:1) acids, but pinolenic (5,9,12-18:3) and palmitic (16:0) acids are also abundant (Ekman et al. 1979). Smaller amounts of sciadonic acid (5,11,14-20:3) and 14-methyl hexadecanoic acid (17:0ai) are also found (Figure 23).

The fatty acids of the parenchyma resin mainly occur in esterified form in the sapwood. Esters with glycerol (mono-, di- or triacylglycerols) are called fats, while esters with long-chain alcohols are called waxes. The waxes are, however, not so common in coniferous wood, they are more abundant in needles, bark and in hardwoods.

About 70% of all fatty acids in the triacylglycerols in pine are esters of 18:1 and 18:2, while 18:2 and 18:3 are the dominating fatty acids in the steryl esters (Saranpää & Nyberg 1987a).

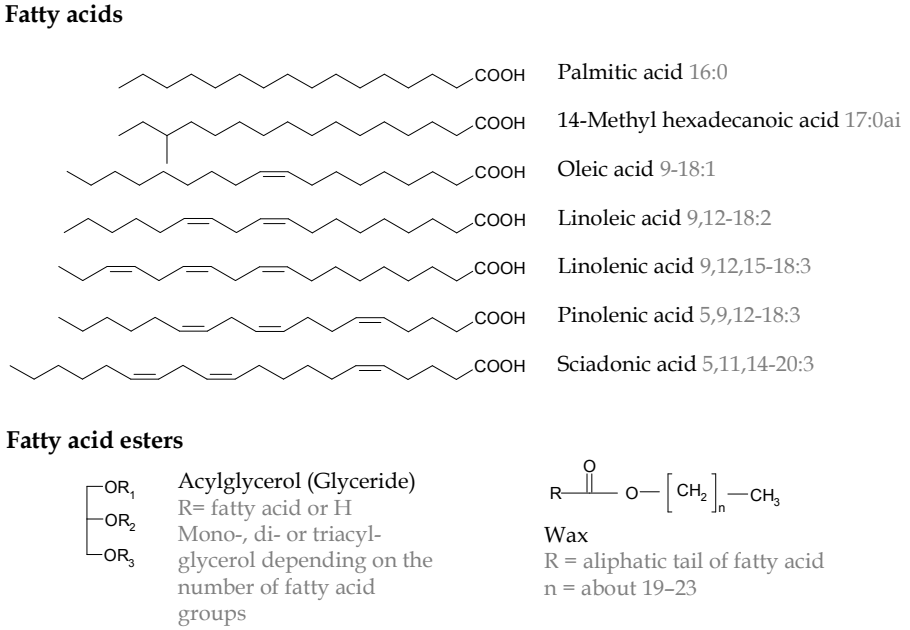


Figure 23 Structures of the most abundant fatty acids and fatty acid esters.

The fatty acids are synthesized in the plastids in the living ray parenchyma cells (Stumpf 1980, Saranpää 1988, 1990, p. 11). Thereafter, they are transported out to the cytosol and combined into triacylglycerols by enzymes located on the endoplasmic reticulum (Galliard & Stumpf 1966, Stumpf 1980). When the triacylglycerols have accumulated in sufficient

amounts, spherosomes (a.k.a. oleosomes or oil bodies) become visible in the parenchyma cells of the sapwood (Saranpää 1990).

In the sapwood, the triacylglycerols are regarded to be energy deposits (Lange et al. 1989). When heartwood is formed or when wood is stored, the triacylglycerols are partially hydrolyzed and monoacylglycerols, diacylglycerols and free fatty acids are formed. These compounds do not occur in substantial quantities in the living parenchyma cells in the sapwood (Ekman & Holmbom 2000, p. 48). The triacylglycerols can also hydrolyze into free fatty acids and these liberated acids can be deposited in cell lumens and on pit membranes and, thereby, decrease the permeability of the heartwood (Saranpää & Nyberg 1987a). It is, however, not normal to find large amounts of free fatty acids in fresh wood and this is regarded as an indication of a degradation of the endogenous lipids during the isolation process (Bethge & Lindgren 1962, Back 2000, p. 13).

Variations in parenchyma resin

Along the stem

There is no significant concentration gradient along the stem in the sapwood (Lange et al. 1989). The triacylglycerols do, though, show a slightly higher concentration at 4–5 m (Lange et al. 1989, Piispanen & Saranpää 2002). In heartwood, the highest concentrations are found at 1 and 14 m. The fatty acid concentration in between is only half as high. The composition of fatty acids is reported to be constant along the stem. (Lange et al. 1989)

Across the stem

In heartwood, the concentration of free fatty acids is reported to increase towards the pith (Hemingway & Hillis 1971, Saranpää & Nyberg 1987a, Fischer & Höll 1992). In sapwood, the fatty acids are mainly found as esters of glycerol or different sterols (more information about sterol esters later in this chapter). The glycerol esters are called glycerides or acylglycerols, and triacylglycerols are more abundant than diacylglycerols. The concentration of diacylglycerols is constant cross the stem, while the triacylglycerol concentration increases slightly from the cambial zone towards the inner parts of the sapwood. In the transition zone, the concentration, however, drops and rapidly approaches zero (Saranpää & Nyberg 1987a, Fischer & Höll 1992). This decline is associated with heartwood formation. When the parenchyma cells die, the tonoplasts of the vacuoles break and hydrolytic enzymes are released (Ziegler 1968). These lipases degrade the triacylglycerols into free fatty acids. All parenchyma cells do, however, not die simultaneously. Therefore, low triacylglycerol concentrations can be detected in the outer parts of the heartwood (Saranpää & Nyberg 1987a, Piispanen & Saranpää 2002).

Age and diameter

No differences in triacylglycerol concentrations have been found between young and old sapwood. There is, however, a difference correlating with the growth rate; slow-grown trees with narrow annual rings contain higher triacylglycerol and fatty acid concentrations. They also contain larger proportions of unsaturated fatty acids (Piispanen & Saranpää 2002). There is no correlation between the triacylglycerol concentration and the stem diameter in *P. sylvestris* (Piispanen & Saranpää 2002).

Geography

Several studies have showed that low temperatures and cold stress yield an increase in the sapwood lipid concentration and in the proportion of polyunsaturated fatty acids in the triacylglycerols (Ivanov 1928, Fuksman & Komshilov 1979, 1980, 1981, Piispanen & Saranpää 2002).

Annual variations

The amount of total and combined fatty acids is almost constant during the year (Swan 1968, Pensar 1969b, Saranpää & Nyberg 1987b, Ekman & Holmbom 1989a, Fischer & Höll 1992), only some minor changes have been reported in the amount of free fatty acids (Saranpää & Nyberg 1987b) and the triacylglycerols in the sapwood (Fischer & Höll 1992). The changes are, however, small, which indicates that the stored fat is not used for growth or needle formation (Piispanen & Saranpää 2002).

Some changes have been reported in the composition of total fatty acids; there are more short-chained fatty acids during early summer (May–June), and higher proportion of 18:3 during the winter (Swan 1968). The degree of unsaturation is also reported to be higher during the winter when the temperature is lower (Swan 1968, Yildirim & Holmbom 1978b, Fuksman & Komshilov 1979, 1980). It is believed that the change in lipids adjusts the fluidity trough the membrane and, thereby, regulates the cell functionality, which makes the organism more frost tolerant (Thompson 1992, pp. 14–16 and 210–211).

Storage of wood

Before mechanical and sulfite pulping, the wood is usually seasoned since it reduces the pitch problems in the pulp mill and in the paper making. In kraft pulping, however, fresh wood is preferred because prolonged storage makes the deresination more difficult and decreases the yield of the by-products turpentine and tall oil. Furthermore, extended storage increases the risk of attack by micro-organisms, which decrease both pulp yield and quality. (Nugent et al. 1977, Sjöström 1993)

Four processes occur during wood seasoning: enzymatic ester hydrolysis, autoxidation, metabolic oxidation trough cell respiration and microbial degradation. Hydrolysis caused by the trees own lipases and by attacking microbes proceed in the same way and they are, thus, difficult to distinguish. (Assarsson 1969a)

Wood can be stored as logs on land or under water, as chips or as sawdust, and the seasoning phenomena and rates differ according to the way of storage[12]. In logs, the access of oxygen is limited and the temperature is low. Therefore, only di- and triunsaturated fatty acids are oxidized. In chips, a larger surface area is exposed to oxygen under heat-preserving conditions. This causes degradation and disappearance of the unsaturated fatty acids (Donetzhuber & Swan 1965).

Logs

When spruce logs are stored on land, the amount of triacylglycerols decreases and the amount of free fatty acids increases due to fat hydrolysis. After four months, the unsaturated free fatty acids start to oxidize into insoluble substances and hence, the concentration of free fatty acids decreases back to its initial value, where it remains unchanged for 24 months. (Kahila 1957b, Assarsson et al. 1963)

When logs are stored under water, there is also a decrease in the concentration of triacylglycerols and a corresponding increase in the amount of free fatty acids. In water, however, the oxygen supply is limited so the fatty acids do not degrade. Therefore, the concentration of free fatty acids will continue to increase and after six months the concentration of free fatty acids is four times that in fresh wood (Assarsson & Åkerlund 1967) and it is even higher after two years (Kahila 1957b). After 24 months, there is no difference in triacylglycerol concentration between the logs stored on land and in water; the only difference is the significantly higher amount of free fatty acids in water-stored logs (Kahila 1957b).

Chips

The amount of free fatty acids reaches a maximum after one-week storage and then starts to decrease (Assarsson et al. 1963). The amount of fatty acid esters decreases by 50% when pine chips are stored 5 days in air at 60 °C or 3 days at 85 °C. Simultaneously, the amount of free fatty acids was doubled (Hemingway et al. 1971). After 10 days at 60 °C or 4.5 days at 85 °C, the total amount of both free and esterified fatty acids is decreased by 50% (Hemingway et al. 1971). After three months, 90% of the triacylglycerols and 70% of the waxes are hydrolyzed (Assarsson 1966), and the

[12] Two months of chip seasoning equals one summer on land or two summers under water for logs (Assarsson & Åkerlund 1967).

monoacylglycerols are decreased by one third. The reactions do, however, only concern the unsaturated components. The saturated free and esterified fatty acids remain more or less unchanged (Assarsson et al. 1963, Hemingway et al. 1971).

The amount of oxidized fatty acids reaches a maximum after two weeks, where after it decreases. After four weeks, however, it increases again (Assarsson et al. 1963). Some polymerization of unsaturated fatty acids is also reported during chip storage. These polymers are detrimental because they form deposits in the pulping process (Ohtani et al. 1986, Raymond et al. 1998).

The rapid drop in the content of esterified fatty acids during the two first weeks is caused by enzymatic hydrolysis, and the reactions accelerate as the temperature in the chip pile increases[13]. After four weeks the rate of hydrolysis diminishes (Assarsson et al. 1963), and after 12 weeks the main reaction is oxidation and degradation of the liberated fatty acids trough enzymatic and radical reactions (Assarsson & Croon 1963, Donetzhuber & Swan 1965). After one year, some free fatty acids still remain, probably because the temperature in the pile goes down after 5 months and this stop the reactions (Assarsson et al. 1963).

Reactions of fats and glycerides

Normally, autoxidation is a slow process, but it is significantly accelerated at higher temperatures. Light and metals also increase the rate of oxidation (Institute of Shortening and Edible Oils 2006) In fatty acid oxidation aldehydes (e.g. hexanal) are formed. These compounds give rise to odour problems e.g. in food packaging applications (Björklund Jansson 2000).

Saturated fatty acids are very stable. Double bonds, however, make the acids more sensitive to oxidation and addition reactions, and the more unsaturated the fatty acid is, the more susceptible it is to oxidation. In air at 37 °C, linoleic acid (9,12-18:2), which has two double bonds, is oxidize twenty eight times faster than oleic acid (9-18:1), which has only one double bond, and linolenic acid (9,12,15-18:3), which has three double bonds, is oxidized more than twice as fast as linoleic acid. The rate of oxidation does, however, also depend on the composition of the fats, not only on the degree of unsaturation (Holman & Elmer 1947). Triacylglycerols and other fatty acid methyl esters and are known to be more stable against oxidation than free fatty acids (Holman & Elmer 1947, Miyashita & Takagi 1986, Ogawa et al. 1995).

[13] The living cells in the sapwood continue to consume oxygen weeks after the tree is felled. This enzymatic combustion of fats and carbohydrates is an exothermic reaction, which increases the temperature in the chip pile and results in a net decrease of the total extractive content (Dahm 1964).

The polyunsaturated fatty acid esters belong to the so-called drying oils that undergo air oxidation and polymerization with the formation of tough films. These high molecular products contribute to the emergence of pitch problems (Lindgren & Norin 1969). The polymerization, however, only occur when the fats are exposed to extreme temperatures for long times.

Sulfate soap and tall oil

In the alkaline kraft pulping process, the esterified fatty acids are easily hydrolyzed into free fatty acids, and these acids form soaps, which aid the dispersion of other lipophilic compounds and, thereby, facilitate the pulp deresination. The fatty acid soaps are skimmed off the black liquor together with resin acids. When they are processed into CTO, appreciable amounts of the fatty acid are esterified (Vikström et al. 2005). The esters formed in the tall oil cooking and drying essentially show the same fatty acid composition as the free fatty acids of the tall oil. There is, however, a shift towards a lower degree of unsaturation; CTO from *Pinus sylvestris* is reported to contain 5% saturated, 32% monounsaturated, 46% diunsaturated and 17% triunsaturated fatty acids. About 3.5% of the CTO consists of esterified fatty acids. (Holmbom & Avela 1971a)

Further reading

There are innumerable studies on free and esterified fatty acids in the stemwood of pines and some of them are listed in Table 5. In these publications, the samples have been extracted with different solvents and, thereafter, the compounds can have been separated according to different fractionation methods. Some researchers have hydrolyzed their extracts and, thereby, analysed free fatty acids as well as fatty acids from steryl and glyceryl esters together. In some of the studies, the concentrations are given as percentage of dry wood, in other they are calculated as percentage of the total dried extract. All this should be kept in mind when the results are compared and interpreted.

No studies on fats in the stemwood of the *Tsuga* species studied in this work were found in the literature, probably because the overall concentrations are so low.

Table 5 Publications on fats in the stemwood of different conifer species.

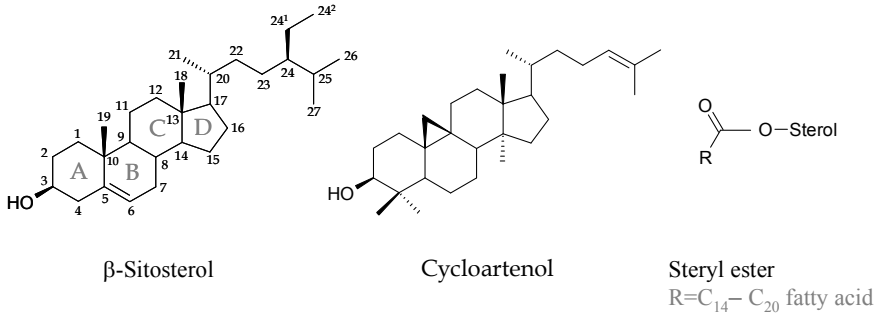
Species	Publication
Pinus	
P. banksiana	Hibbert & Phillips 1931, Buchanan et al. 1959, Rudloff & Sato 1963, Chapman et al. 1975, Nugent et al. 1977, Conner et al. 1980c, Chen et al. 1995
P. contorta	Anderson et al. 1969, Rogers et al. 1969, Conner et al. 1980a, Gao et al. 1995, Arshadi et al. 2013
P. elliottii	Buchanan et al. 1959, Thornburg 1963, Zinkel & Foster 1980
P. nigra	Hansen 1966, Yildirim & Holmbom 1978b, Hafizoğlu 1983, Uçar & Fengel 1995, Uçar & Balaban 2002
P. pinaster	Hemingway et al. 1973
P. radiata	Hansen 1966, Hemingway & Hillis 1971
P. resinosa	Levitin 1962
P. sibirica	Vodzinskii et al. 1969[14], Bardyshev et al. 1970b
P. strobus	Levitin 1962
P. strobus	Levitin 1962, Conner et al. 1980c
P. sylvestris	Bergström & Trobeck 1947, Bergström 1954, 1956, Bergström et al. 1956, Lehtinen et al. 1962, Assarsson & Åkerlund 1966, Hakkila 1969, Pensar 1969b, Vodzinskii et al. 1969, Bardyshev et al. 1970b, Manell & Pensar 1975, Holmbom 1977, Holmbom & Ekman 1978, Yildirim & Holmbom 1978a, 1978b, Hafizoğlu 1983, Saranpää 1990[15], Piispanen & Saranpää 2002, Willför et al. 2003b, Vikström et al. 2005, Arshadi et al. 2013
P. taeda	Buchanan et al. 1959, Zinkel 1975, Vikström et al. 2005
Picea	
P. abies	Bergström & Trobeck 1947, Bergström 1956, Bethge & Lindgren 1962, Assarsson & Åkerlund 1966, Pensar 1967, Swan 1968, Pensar 1969b, Vodzinskii et al. 1969[16], Ekman & Pensar 1971, Ekman & Pensar 1973, Bardyshev et al. 1974[17], Holmbom & Ekman 1978, Höll & Pieczonka 1978, Ekman 1979a, Ekman et al. 1979, Ekman 1980, Willför et al. 2003a, Vikström et al. 2005, Smeds et al. 2016
P. glauca	Rogers et al. 1969, Conner et al. 1980b, Chen et al. 1995
P. mariana	Nugent et al. 1977, Conner et al. 1980b, Chen et al. 1995
P. omorika	Däßler 1960
P. sitchensis	Caron et al. 2013
Abies	
A. sibirica	Lisina et al. 1967a, Vodzinskii et al. 1969
Larix	
L. gmelinii	Bardyshev et al. 1974[18]
L. lariciana	Nair & Rudloff 1959
L. sibirica	Bardyshev et al. 1970b, Ostroukhova et al. 2012, Vikström et al. 2005, Vodzinskii et al. 1969
Pseudotsuga	
P. menziesii	Graham & Kurth 1949, Dässler & Ding-Shjuä 1963, Campbell et al. 1965, Hancock & Swan 1965, Rogers et al. 1969, Foster et al. 1980

[14] *Pinus cembra* var. *sibirica* = *Pinus sibirica* Du Tour.
[15] PhD thesis which includes Saranpää & Nyberg 1987a, 1987b, Saranpää & Höll 1987, Saranpää 1988.
[16] *Picea excelsa* Link = *Picea abies* (L.) Karst.
[17] *Picea excelsa* Link = *P. abies.*
[18] *Larix dahurica* Turcz. = *L. gmelinii* (Rupr.) Kuzeneva.

Sterols, triterpenols and their esters

More than 260 different phytosterols have been found in various plants and marine materials (Akihisa et al. 1991). They are found in both gymnosperms and angiosperms, in liverworts, mosses, horsetails, ferns, fungi, algae, lichens and bacteria, and they occur in many parts of the plants; in roots, stems, bark, leaves, flowers, pollen, fruit and seeds (Grunwald 1980).

The sterols[19] have a very lipophilic, hydrocarbon skeleton combined with a hydroxyl group at C_3 position, methyl groups at C_{10} and C_{13}, and a side-chain of varying length at C_{17} (Figure 24 and Appendix C2). Stanols are the saturated analogues to sterols and their structure differ from the tetracyclic triterpenols (sometimes called methyl or dimethyl sterols), which have one or two methyl groups at C_4 (e.g. middle compound in Figure 24).



β-Sitosterol | Cycloartenol | Steryl ester R=C_{14}– C_{20} fatty acid

Figure 24 Structures of a sterol, a triterpeol and a steryl ester.

The sterols are very common in coniferous wood, but they are seldom found in large quantities (Kimland & Norin 1972). Most of them occur as esters combined with fatty acids (a.k.a. steryl esters), but they also occur in free form, as steryl glycosides or as acetylated steryl glycosides (Ekman 1979a, Höll & Lipp 1987). The free sterols mainly reside in the plasma membrane, but some is also present in the Golgi fraction and in the endoplasmic reticulum (Moreau et al. 1998). It has been suggested that their interaction with phospholipids stabilizes membranes and, thereby, controls the cell permeability[20] (Grunwald 1971) and that they take part in the temperature adaptation of membranes (Piironen et al. 2000).

The physiological function of the steryl esters is not well understood (Saranpää 1990). They are probably not membrane stabilizers like the free

[19] The name sterol comes from the Greek word stereos, which means solid, because the sterols are crystalline solids at room temperature.

[20] Only sterols with a flat configuration can penetrate the phospholipids of the membrane. Therefore, cholesterol has a stabilizing effect, while campesterol, which has a methyl group at C_{24} is less effective. β-Sitosterol, which has a somewhat more bulky ethyl group, is unable to penetrate deep enough to stabilize the membrane (Grundwald 1971).

sterols, but they might be involved in the intracellular sterol transport from the site of synthesis to the site of action in the membranes (Kemp et al. 1967). It has also been proposed that they are precursors to other steroids (Grunwald 1971) or function as an energy reserve in the sapwood (Lange et al. 1989).

Triterpenols are rare in softwoods (Ekman 1979a) and little is known about their cellular distribution (Ekman & Holmbom 2000, p. 65). The steryl glycosides and acetylated steryl glycosides have been found in trace amounts only (Saranpää & Höll 1987) and their role is not either clearly understood, but it has been suggested that they stimulate growth (Kimura et al. 1975).

Variations in the stem

Across the stem

There are different opinions about the radial distribution of sterols and triterpenols in the stem. Some say that they are almost uniformly distributed cross the stem (Manell & Pensar 1975, Ekman et al. 1979), while others argue that the highest sterol concentrations are found in the innermost heartwood (Höll & Goller 1982, Höll & Lipp 1987), or in both the outermost sapwood and in the innermost heartwood (Saranpää 1990).

Similar information is found about the radial distribution of steryl esters; they are either evenly distributed cross the stem (Höll & Lipp 1987) or then the innermost heartwood contain the highest concentrations (Höll & Pieczonka 1978, Höll & Goller 1982, Saranpää & Nyberg 1987b, Saranpää 1990).

Knots of *Pinus sylvestris* contain slightly higher steryl ester concentrations than the stem (Willför et al. 2003b), while knots of *Picea abies* are in the same range as the stemwood (Willför et al. 2003a).

Along the stem

Like with the radial distribution, there is some disagreement about the vertical distribution the free sterols and triterpenols. Some claim that they are uniformly distributed (Ekman 1979a, Ekman et al. 1979), while others have found more than twice as high concentrations at the base as in the top of the stem (Nugent et al. 1977). It has also been showed that slow-grown wood contains significantly much more sterols than fast growing (Uçar & Balaban 2002).

Age

The amount of free and esterified sterols in young trees without any heartwood is similar to that in the innermost heartwood of old trees (Höll &

Goller 1982). It has, therefore, been suggested that both free and esterified sterols are synthesized when the tree is young, and that the young, living wood needs higher sterol levels, while sapwood formed when the tree is older does not need that high sterol levels. Saranpää and Nyberg (1987a) write that the sterols probably decompose or transform during the heartwood formation, because there is a change in the free sterol composition in the transition zone. Höll and Lipp (1987), however, insist that the sterols are immobile and that the accumulation in the innermost part of the stem does not depend on the heartwood formation.

Trace amounts of steryl glycosides and acetylated steryl glycosides have been detected in *P. sylvestris*. The highest steryl glycoside concentrations were found in the outermost sapwood from where it decreased to zero in the inner heartwood. The concentration of acetylated steryl glycosides, on the other hand, increased slightly in the inner heartwood (Saranpää & Höll 1987).

Annual variations

The sterols do not show any notable seasonal variations (Ekman 1979a, Ekman et al. 1979). A small increase the concentration of sterols and/or triterpenoids esters was noted in August and March, but these changes are not large enough to be statistically significant (Saranpää & Nyberg 1987b).

Reactions of sterols and steryl esters

The sterols are fairly stable and the steryl esters in the heartwood are not easily hydrolyzed (Levitin 1962). The sterols may, however, undergo oxidation and other transformation reactions in the presence of light, heat, oxygen and metal contaminants (Kemmo 2008).

Both free and esterified campesterol, campestanol, sitosterol, sitostanol, cycloartenol and methylene cycloartanol are found in mechanical pulp and process waters (Ekman & Holmbom 1989a). In kraft pulping, part of the steryl and terpenoid esters remain unsaponified, i.e. they are not hydrolyzed to free sterols and fatty acids (Paasonen 1966, p. 97, Lindgren & Norin 1969). These esters are tacky and tend to form deposits, while the free sterols are incorporated in the sulfate soap and consequently into the CTO. The sterol content of the CTO is typically 3–5%, and through the distillation processes, the sterols are concentrated in the TOP residue[21]

[21] Typical concentrations (Holmbom & Ekman 1978, Holmbom 1978, p. 21):
spruce wood contains 6.3% sterols and triterpenyl alcohols, spruce soap 32%,
pine wood contains 5.3% sterols and triterpenyl alcohols, pine soap 52%,
CTO contains 4.4% sitosterol, 25% in esterified form,
TOP contains 0.4% sitosterol, 19% in esterified form, and
Distillate from pitch column (DI) contains 0.6% sitosterol, none in esterified form.

(Vikström et al. 2005). The high temperature during the TOP separation significantly degrades the non-esterified sterols and more than half of all sitosterol present in the CTO is destroyed (Huibers et al. 2000). The sterol concentration in TOP is, though, 5–15% (Cantrill 2008).

The sterols are detrimental in the tall oil. They cause a loss of fatty and resin acids during refining due to esterification and they decrease the acid number of the final product. They can, however, be collected from the pitch fraction and be used for production of therapeutic steroids, as additives in functional foods or in cosmetic applications like cream or lipstick (Fernandes & Cabral 2007).

Biological activity

In the 1950's, Best et al. (1954) found that phytosterols help to decrease the cholesterol level in man. By decreasing the level of low-density lipoprotein (LDL) in the blood, the absorption of cholesterol from food is reduced[22] and the amount of cholesterol produced by the liver is decreased (Jones et al. 1997, Plat & Mensink 2002). The first cholesterol-lowering product, a margarine, was launched in 1995 by the Finnish company Raisio under the trade name Benecol™. It contained sitostanol ester, a fatty acid ester of the hydrogenated form of sitosterol (review in Law 2000). Today, cholesterol-decreasing sterols are added to many different foods and there are several producers on the market. All sterols are, however, not equally good in food applications. Small amounts of campesterol are absorbed from the gut into the circulatory system, which is undesired. Sitosterol, on the other hand, is not absorbed and, therefore, a high ratio of sitosterol to campesterol is preferred in the raw material used for dietary products (Vikström et al. 2005).

Further reading

There are some publications on the concentration and composition of sterols and steryl esters in wood (Table 6). Most of these articles have studied the so-called unsaponifiable fraction, which includes both free and esterified sterols.

No publications about sterols or steryl esters in wood of *Pinus gerardiana, P. roxburghii, P. wallichiana, Picea koraiensis, P. pungens, Abies balsamea, A. concolor, A. lasiocarpa, A. pindrow, A. sachalinensis, A. sibirica, A. veitchii* or *Larix gmelinii* were found.

[22] LDL is generally known as "bad cholesterol". It is a protein that transports cholesterol in the blood stream and its concentration is strongly associated with cardiovascular diseases.

Table 6 Publications on sterols and steryl esters in stemwood

Species	Publication
Pinus	
P. banksiana	Hibbert & Phillips 1931, Buchanan et al. 1959, Rudloff & Sato 1963, Chapman et al. 1975, Nugent et al. 1977, Conner et al. 1980c, Chen et al. 1995
P. contorta	Conner et al. 1980a, Fischer et al. 1981, Gao et al. 1995, Hanneman et al. 2002
P. nigra	Yildirim and Holmbom 1978a, Fischer et al. 1981, Willför et al. 2007
P. pinaster	Desalbres 1959
P. radiata	Wallis & Wearne 1997
P. resinosa	Thompson et al. 2013
P. sibirica	Roshchin et al. 1978
P. strobus	Conner et al. 1980c, Fischer et al. 1981
P. sylvestris	Manell & Pensar 1972, 1975, Holmbom & Ekman 1978, Roshchin et al. 1978, Yildirim & Holmbom 1978a, Fischer et al. 1981, Saranpää & Höll 1987, Saranpää & Nyberg 1987a, Saranpää 1990, Willför et al. 2003b, Vikström et al. 2005
P. taeda	Buchanan et al. 1959, Stanley 1969, Zinkel 1975, Vikström et al. 2005
Picea	
P. abies	Pensar 1967, Kimland & Norin 1972, Holmbom and Ekman 1978, Höll and Pieczonka 1978, Ekman 1979a, Ekman et al. 1979, Fischer et al. 1981, Willför et al. 2003a, Vikström et al. 2005
P. glauca	Conner et al. 1980b, Chen et al. 1995
P. mariana	Nugent et al. 1977, Conner et al. 1980b, Chen et al. 1995
P. omorika	Däßler 1960
P. sitchensis	Kohlbrenner & Schuerch 1959, Fischer et al. 1981
Abies	
A. alba	Fischer et al. 1981
A. amabilis	Swan 1966
Larix	
L. decidua	Fischer et al. 1981
L. kaempferi	Fischer et al. 1981
L. lariciana	Nair & Rudloff 1959
L. sibirica	Vikström et al. 2005
Other species	
Pseudotsuga menziesii	Dässler & Ding-Shjuä 1963, Hancock & Swan 1965, Fischer et al. 1981
Tsuga canadensis	Fischer et al. 1981
Tsuga heterophylla	Swan 1966, Hanneman et al. 2002
Tsuga mertensiana	Fischer et al. 1981

2.7.3 Juvabiones and sesquiterpenes

The history of juvabiones started in 1940 when the Japanese researchers Tutihasi and Hanzawa (1940) isolated an unsaturated, monocyclic sesquiterpene carboxylic acid with one keto group from sulfite turpentine oil of *Abies sachalinensis*. This wood species is called todo matu in Japanese, and hence they named the compound todomatuic acid. A year later, Momose (1941) deduced the compound's structure and it was confirmed by Nakazaki and Isoe (1963) who also assigned its absolute configuration (*R,R*).

A few years later, the *Pyrrhocoris apterus* bugs at Harvard University suddenly started to behave strangely. Instead of developing into adult bugs, the larvae moulted an additional time and turned into giant larvae, thereafter they died. The behaviour resembled that of exposure to juvenile hormones, and an eager pursuit to find the source began. The cause revealed to be the tissue paper placed in the Petri dishes where the bugs lived and, thus, it came to be called "the paper factor"[23]. In order to identify the causing compound, the researchers received samples of American wood species from the university's herbarium and started to expose the bugs to different wood extracts. They found that *Abies balsamea*, *Tsuga canadensis* and *Larix lariciana* extracts showed high activity, but they were not able to identify the responsible component. (Sláma & Williams 1965, 1966)

Later that year, Bowers et al. (1966) isolated the active component from American balsam fir. Because of its juvenile hormone effect and the two keto groups they named it juvabione. They also verified that todomatuic acid was identical to the acid obtained on alkaline hydrolysis of juvabione, i.e. juvabione is the methyl ester of todomatuic acid (Figure 25). They also noted that the semipurified extract showed stronger effect on the bugs than the purified juvabione itself. They were, however, unable to detect significant activity in any other fraction from the purification procedure.

[23] Systematic tests of different paper qualities led to the conclusion that the New York Times and Wall Street Journal were lethal, while Nature was harmless. The first ones are printed on paper made of American pulp, while Nature is printed on paper of European pulp.

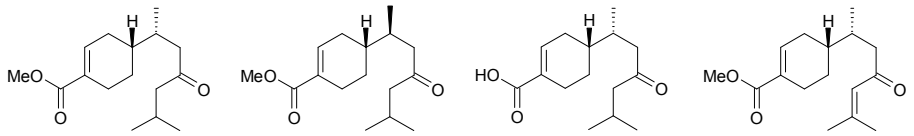


Figure 25 Structures of some juvabiones.

Sláma returned from Harvard to Czechoslovakia, where he together with professor Černý and co-workers found dehydrojuvabione, another compound with juvenile hormone effect, in a balsam fir growing in arboretum Banska Stianica (Černý et al. 1967). This specific tree has later caused a lot of confusion in literature. It was purported to be an *Abies balsamea*, but most likely it was a hybrid, which contained the diastereomer epijuvabione, not juvabione (Manville 1975). So when the scientists purified "natural (+)-juvabione" and distributed it to other research groups around the world, they actually sent (+)-epijuvabione instead. The groups which received this reference compound were confused, and some of them questioned the established configuration and tried to correct the structural assignment (Blount et al. 1969, Pawson et al. 1970, Sakai & Hirose 1973a, 1973b, Ficini et al. 1974, Rogers et al. 1974, Sláma et al. 1974). Manville (1975, 1989, 1992) has made three attempts to throw light on the mess and his conclusion is that juvabione has two asymmetric centres at C_4 and C_1' and hence it has four isomers[24]: (+)-juvabione (*R,R*), (+)-epijuvabione (*R,S*), (-)-epijuvabione (*S,R*) and (-)-juvabione (*S,S*). Only the (*R,R*)-isomer has been found in *Abies balsamea*, while other wood species contain either (*R,R*), (*R,S*) or a mixture of both epimers. Today, an abundance of different juvabione-type compounds have been identified in *Abies* and *Pseudotsuga* species and some of these structures are depicted in Appendix C4.

Biological activity

The effect of juvabiones on different kinds of insects, fish and fungi has been studied and reported in literature. It is known that juvabiones kill insects by upsetting their hormone balance and thereby disturbing their metamorphosis (Bowers et al. 1966, Williams & Sláma 1966). The insects cannot develop any resistance against the juvabiones since they die before attaining sexual maturity and if insect eggs are exposed to juvabiones the percentage of hatched eggs is reduced (Rogers et al. 1974). It has been noted that insects sensitive to juvabiones never occur in the vicinity of balsam fir vegetation (Sláma 1969). Therefore, synthetic juvabiones have been used as 3rd generation's pesticides. The effect of juvabiones is highly

[24] Juvabione and epijuvabione are diastereomers, while (+)- and (–)-juvabione, and (+)- and (-)-epijuvabione are enantiomers.

dependent on the insect species and, thus, the pest control is very selective (Rogers et al. 1974). The juvabiones are considered harmless to land-living animals of a higher order than insects and they are light sensitive i.e. they degrade in nature (Rogers et al. 1974).

Juvabiones also have an antifungal effect on the mycelia growth on wood-destroying fungi (Aoyama et al. 1991), on edible fungi (Yoneyama et al. 1990) and on fungi causing turfgrass diseases (Aoyama & Doi 1992). The last fungi cause large expenses on golf courses.

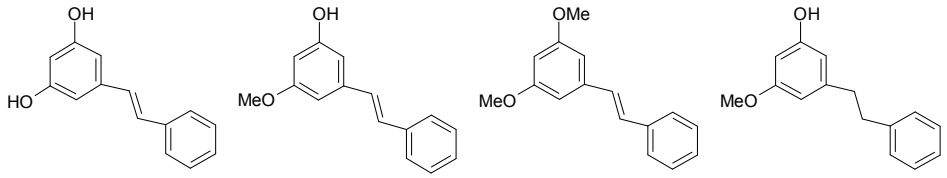
Juvabiones in water significantly increase the hepatic mixed-function oxygenase (MFO) activity in rainbow trout (Martel et al. 1997). The toxicity seems to decrease in the order 4′-dehydrojuvabione > juvabione > dihydrojuvabione > juvabiols (Leach et al. 1975). However, the juvabiones are not an actual threat to aquatic organisms outside pulp mills because the juvabiones originating from wood do not survive the alkaline kraft cook. Therefore, these components are found only in mechanical pulp mill effluents, and, to very low extent, in effluents from the sulfite process (Walden et al. 1986). Furthermore, when the effluents are treated in an activated sludge system, the juvabiones are biodegraded and hence the ethoxyresorufin-*O*-deethylase (EROD)-inducing potential is eliminated (Martel et al. 1997).

2.7.4 Stilbenes

Already in the 1920's, it was known that pine heartwood could not be pulped by the sulfite process[25]. For a long time it was believed to be a consequence of the high resin content, but Hägglund[26] (1927, 1928) stated that the reason was a substance in the heartwood, which was extractable with acetone and alcohol, but not with benzene or diethyl ether. Hägglund et al. (1936) studied this so-called "acetone resin" and showed that it was a mixture of substances, but did not contain fatty or resin acids.

Three years later, Erdtman (1939d) managed to isolate two optically inactive substances, which together constituted 0.5–1.0% of the dry heartwood of *Pinus sylvestris*. He named them pinosylvin and pinosylvin monomethyl ether. Later, also pinosylvin dimethyl ether (Cox 1940, Erdtman 1943), dihydropinosylvin (dihydropinosylvin) (Lindstedt 1950a) and dihydropinosylvin monomethyl ether (Lindstedt 1950c) were identified in pine. Structures of the most common stilbenes can be seen in Figure 26.

[25] Later it was shown that condensation products of pinosylvin and lignin, which are formed in acidic environment, inhibit the delignification in the sulfite cook. The macromolecules are large and not readily sulfonated and can, therefore, not be dissolved (Erdtman 1939, 1943).
[26] Professor at ÅAU 1920–1930.



Pinosylvin
PS

Pinosylvin
monomethyl ether
PSMME

Pinosylvin
dimethyl ether
PSDME

Dihydropinosylvin
monomethyl ether
Dihydro-PSMME

Figure 26 Structures of the most common stilbenes in pine wood.

First it was believed that the stilbenes were formed in the cambium and transported via the pith rays to the heartwood, where they were accumulated in the inner parenchyma cells of the latewood (Lindstedt 1951, Erdtman & Misiorny 1952). However, subsequent studies have asserted that the stilbenes are formed *in situ* in the dying parenchyma cells at the transition zone between heartwood and sapwood (Hillis 1977, Hart 1981). Their final location in the cell is not known, but most likely they enter the cell wall, where they bind to other wall components such as lignin (Hart 1981).

The stilbenes are not only produced during the heartwood formation, they can also be formed in the sapwood as an active response to infection or injury (Hart & Shrimpton 1979). Mechanical damage of cambium, bark, or fungal penetration of the sapwood causes formation of stilbenes, but only when the cells die slowly (Jorgensen 1961). The stilbene formation normally takes place during the late part of the growing season and during the dormant season, so a rapid cell death does not provide enough time for stilbene formation. The sapwood stilbenes are so-called phytoalexins because they are formed as a measure of active defence against micro-organisms. The heartwood stilbenes, on the other hand, are formed prior to injury and are, therefore, not phytoalexins (Hart 1981).

The stilbenes occur in two configurations, the planar *trans*-form and the aplanar *cis*-form. The *trans*-isomer is more stable and dominates in plant tissues, but interconversion occurs when they are exposed to heat or UV-light (Hart 1981). The hydroxystilbenes are also very unstable in light and coloured products are formed when they decompose; the more hydroxy groups, the darker the product, and this is the explanation to why pine heartwood turns dark when it is exposed to light (Morgan & Orsler 1968).

Variations in the stem

Across the stem

The distribution of stilbenes in *Pinus sylvestris* wood has been thoroughly studied. The heartwood contains 0.6–1.1% stilbenes and the concentration increases gradually from the pith towards the outer parts of the heartwood, (Erdtman & Rennerfelt 1944, Erdtman et al. 1951). Healthy sapwood contains only traces of stilbenes. Hillis and Inoue (1968) were the first to analyse stilbenes in knots. They isolated 0.2% pinosylvin and 0.1% pinosylvin monomethyl ether from knots of *P. radiata*. Later, Willför et al. (2003b) found significantly much more stilbenes, 1–7%, in knots of *P. sylvestris*. They reported that living knots contained more stilbenes than dead knots and that the concentration decreased markedly in the outer branch. This was in agreement with Erdtman and Rennerfelt (1944) who found 3% stilbenes in the heartwood of the branch. The roots are also rich in stilbenes; a concentration of 4.9% has been reported (Erdtman & Misiorny 1952).

Along the stem

The stilbenes are rather evenly distributed along the stem (Erdtman et al. 1951). Somewhat higher concentrations occur in the butt and the top, while the lowest concentrations are found in the middle, branch-free part (Erdtman & Misiorny 1952). The between-tree variations are, however, great. Pines growing side by side are reported to differ considerably in stilbene content, and there is no correlation with tree age, tree height, crown width, stem diameter or climatic conditions (Bergström et al. 1999). Erdtman et al. (1951) studied the stilbene content in 269 Swedish pines. They found that the stilbene content was highest in the southern parts of Sweden. The lowest content was found in the central parts, while the northern parts were just below the average value for the whole country. Spanish pines, on the other hand, contained twice as much stilbene as Swedish trees.

Biological activity

Erdtman and Rennerfelt (1944) found that there was a clear difference in decay resistance between pine heartwood and sapwood, and since the sapwood did not contain any stilbenes it seemed logical to conclude that they provided the resistance[27]. Tests with stilbenes in free form also pointed in the same direction when they revealed strong toxicity against several

[27] The fact that pine heartwood is significantly much more resistant to decay than sapwood has led to the misconception that pine heartwood is durable, but that is not true. In fact, pine heartwood in not durable at all (Rudman 1962), it is classed as slightly or even unresistant to decay (Scheffer & Cowling 1966).

different decay fungi[28] (Rennerfelt 1943, 1945, Rennerfelt & Nacht 1955, Välimaa et al. 2007, Belt et al. 2017). It has also been shown that pinosylvin is toxic to bacteria and mice (Frykholm 1945, Välimaa et al. 2007), fish (Erdtman 1939c, 1939d) and human lymphoblastoid cell lines (Skinnider & Stoessl 1986). Furthermore, the stilbenes show some insect (Wolcott 1951, 1953) and water repelling properties (Celimene et al. 1999). The stilbenes are toxic, but they do not alone provide decay resistance (Hart & Shrimpton 1979, Venäläinen et al. 2004). Bio-tests have shown that natural wood extracts, which contain several different phenols, exhibit much stronger effects than pure stilbene extracts, probably due to synergistic effects (Lindberg et al. 2004). So the decay resistance of pine heartwood is probably caused by several factors working together, not by the stilbenes alone.

2.7.5 Lignans

In an article on natural resins, Haworth (1936) mentions components consisting of two phenylpropane units with β,β'-linkage (i.e. 8,8'-linkage). This type of components was extracted from sulfite waste liquor (Lindsey & Tollens 1892, p. 353) and resin (Bamberger 1894) much earlier, but Haworth (1936) was the first to calls them "lignanes", later reduced to lignans without "e". Several efforts have been made to clarify the lignan nomenclature (Hearon & MacGregor 1955, Freudenberg & Weinges 1961, Gottlieb 1978, Weinges et al. 1978, IUPAC Recommendations 2000) and the current IUPAC recommendation is to quote the semisystematic names when the lignans and neolignans are encountered for the first time, thereafter, the trivial names may be used. However, since no new structures are introduced in this thesis, only trivial names are used. The lignan structures are, though, presented in Figure 27 and Appendix C5.

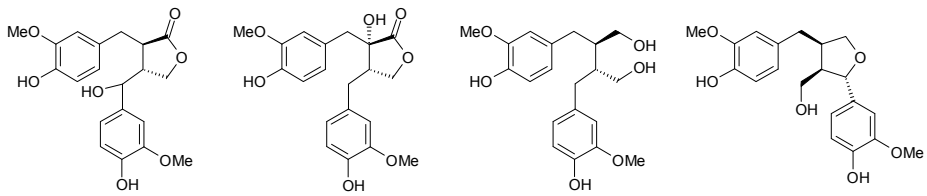


Figure 27 Structures of the most common lignans in softwood.

[28] Several different mechanisms have been proposed for the decay inhibition. Except limiting the fungal activity, some stilbenes are strong antioxidants and interfere with the degrading, free-radical mechanism of fungi (e.g. Ritschkoff 1996).

More than 200 lignans have been found in different parts of plants: roots, leaves, flowers, fruits and seeds. They often occur as glycosidic conjugates associated with fibre components, which make the isolation process difficult (Saarinen et al. 2000, Ward 2000). It has long been known that coniferous trees contain lignans in unconjugated form (Freudenberg & Knof 1957, Weinges 1960, Kimland & Norin 1972, Ekman 1976, 1979b, Ekman & von Weissenberg 1979, Lewis et al. 1998), but it was not until 1998 researchers realized how much lignans the (spruce) knots contain. Since then much research has been carried out (e.g. Ekman et al. 2002, Holmbom et al. 2003, Willför et al. 2003a, 2003b, Eklund et al. 2004b, Willför et al. 2004a, 2004b, 2004c, 2005a, 2005b, 2007, Smeds et al. 2011). Today, we believe that knots are the richest source of lignans in nature. The knots are available at saw and pulp mills in huge amounts[29] and the lignans are available in free form in the knots, which makes the extraction easy.

To demonstrate the extreme lignan concentrations in knots, a comparison of secoisolariciresinol concentrations in heartwood and knots of *Abies alba* and in different provisions are presented in Table 7.

Table 7 Amount of the lignan secoisolariciresinol in different provisions and in Abies alba (Mazur 1998, Willför et al. 2004b).

Source	Secoisolariciresinol mg/kg
Rye	0.47
Blackcurrant	3.9
Red wine, Cabernet Sauvignon (France)	6.9
Strawberry	15
China green tea, brewed	29
Heartwood of *Abies alba*	140
Flaxseed	3 700
Knots of *Abies alba*	32 000

Lignans are small, optically active molecules. They are formed in the transition zone between heartwood and sapwood (Fengel & Wegener 1989) through enantioselective dimerization of two coniferyl alcohol units and the reaction is controlled by a dirigent protein (Davin & Lewis 2000, Suzuki & Umezawa 2007). The lignans should not to be mixed up with lignin, a three-dimensional polymer, which is synthesized and polymerized in the differentiation zone close to the cambium (Lewis et al. 1998). The role of lignans in trees is not yet fully understood. In the core, they are believed to increase durability and life length. In the stem, they might take part in

[29] A paper mill using 1000 tons of spruce wood per day produces 8 tons of enriched knot fractions per day. The theoretical yield of HMR is 600 kg/d. In practice, 360 kg HMR can be purified per day i.e. 130 tons HMR per year (Holmbom et al. 2003).

controlling the plant growth and protect the tree against fungi and diseases (Raffaelli et al. 2002). Some lignans are phytoalexins, i.e. they are produced as a response when the tree is attacked by pathogens, such as bacteria or fungi.

Variations

Geographical variations

Piispanen et al. (2008) compared the lignan concentrations in *Picea abies* growing in northern and southern Finland. They found that knots contained significantly more lignans in north (14%) than in south (5.4%). This trend has also been proposed by Willför et al. (2003a). Ekman (1979b) showed that external stress, which caused eccentric growth, is associated with higher lignan concentration. This led Piispanen et al. (2008) to the hypothesis that the heavy snow load in Lapland causes the increases lignan concentration. They do, however, also support the growth-differentiation balance (GDB) hypothesis (Herms & Mattson 1992). According to that, the growth is limited by access to water and nutrients, while the production of secondary metabolites is restricted by the availability of carbohydrates.

Across the stem

The lignan concentrations in different parts of the stem have been studied. The concentration in sapwood of *Picea abies* is negligible, while the heartwood contain up to 0.5%. (Ekman 1979b, Willför et al. 2003a)

Along the stem

There are only two studies about the height distribution of lignans: Ekman (1979b) found the highest heartwood concentrations in *P. abies* below 1.5 m, while Sasaya and Ozawa (1991) found the maximum at 5.3 m in *Abies sachalinensis*. They did, however, only compare the concentrations at 1.3, 5.3 and 9.3 m, so no samples below 1.3 m were analysed; thus, it is possible that they missed the highest concentration if it occurred below 1.3 m.

Concentrations in the knots

The heartwood of branches and the roots contain more lignans than the stem (Ekman 1979b), but most lignan-rich are the knots. They can contain 20–50 times more lignans than the stemwood (Willför et al. 2004b). It seems that these lignans are not altered after maturation and heartwood formation. They can, however, due to their radical-scavenging properties, form sesquilignans and dineolignans (Willför et al. 2004c, 2005a).

When the lignan concentrations in knots at different heights in the stem are compared, the highest concentrations are found in the knots attached to the

branches with the largest biomass, i.e. the lowest living branches (at 8–12 m in southern Finland). From there, the concentrations decrease dramatically both towards the base and the top of the tree (Piispanen et al. 2008). Among the dead knots, the smallest knot in each branch whorl contain less lignans than the largest knot, while the opposite trend is observed among the knots from the living crown; there the larger knots contain more lignans than the smaller.

The lignan concentration inside the heartwood of a knot is lower at the knot base (close to the middle of the stem) than further along the knot fibres. The concentration reaches a maximum inside the stem, just before the outer-branch part, and in the branch it drops to normal stemwood levels within 20 cm from the stem. Inside the knot, the concentration decreased from the knot pith towards the outer parts. The concentration in the outermost annual rings of the knot was on the same level as in the surrounding stemwood. The same trend was observed inside the branches. (Willför et al. 2005b)

Reactions of lignans

Most of the lignans are fairly water soluble, so the main part is released during the chip washing and impregnation stage in pulp mills; only minor amounts are released later in the process. The lignans in the effluents show low acute toxicity compared to other extractives. They are biodegradable and completely removable by biological treatment. Sedimentation and chemical treatment are, however, not as effective. (Jørgensen et al. 1995)

Matairesinol is unstable at alkaline extraction conditions; the lactone ring opens (Milder et al. 2005). HMR undergoes base-catalyzed reactions at pH 9–12 and forms conidendric acid (Ekman & Holmbom 1989a). During alkaline peroxide bleaching of groundwood pulp, HMR is transformed to α-conidendric acid and there is a 70% decrease in the total lignan concentration (Ekman & Holmbom 1989b). At milder alkaline conditions (pH ~8), HMR forms small amounts of α-conidendric acid, *iso*-HMR and hydroxymatairesinolic acid (Eklund et al. 2004a).

In strong acidic conditions, HMR and α–conidendric acid are converted to α-conidendrin (Freudenberg & Knof 1957, Goldschmid & Hergert 1961), lariciresinol is converted to *iso*-lariciresinol (Erdtman 1939b), and secoisolariciresinol is converted to anhydrosecoisolariciresinol (Mazur et al. 1996).

Biological activity

In humans, certain lignans are converted into so-called enterolignans. They are claimed to exhibit antioxidant and anticarcinogenic properties, protect against osteoporosis, they are involved in the hormonal metabolism/availability and can reduce menopausal symptoms. They may

prevent/delay the onset of diabetes, they show hepatoprotective effects and they decrease the risk of coronary heart disease. There is an endless number of publications concerning health-promoting, antioxidant and antimicrobial properties of lignans, so only a reference to the reviews by Landete (2012) is given here.

Floccosoids and other lignan deposits in genus *Tsuga*

Normally, small amounts of lignans are dispersed throughout the tracheids, but in addition to that, there are irregular patches with large amounts of lignans in quite pure, deposited form. These deposits can differ in both physical and chemical form and they are often found in stemwood of genus *Tsuga* (Barton & Gardner 1962, Krahmer et al. 1970).

The floccosoids are white, opaque, crystalline deposits of conidendrin found in random clusters in the heartwood of *Tsuga heterophylla* (Barton 1963). The deposits are visible to the naked eye in dried and planed timber (Barton 1963, Krahmer et al. 1970). Near the heartwood-sapwood boundary, there are other, less common, clusters of clear, colourless deposits. They can be large enough to block the tracheid lumens and they mainly consist of HMR (Krahmer et al. 1970).

2.7.6 Flavonoids

The flavonoids are by far the most common group of phenolic plant compounds (Harborne 1989). They are found in almost all plants, from liverwort and algae to the most advanced angiosperms, and they are classified into an abundance of classes according to their functional groups. Most references regarding flavonoids in conifers are concerned with needles, bark or roots, but there are some older publications regarding the xylem. The structures of some flavonoids present in conifers are shown in Appendix C6.

Biological activity

In the early 1960's, the flavonoids were seen as metabolic waste products stored in the plant vacuoles, and were not considered to be of any major importance, except as flower pigment. Today, we know that the flavonoids are found in cell walls, in cytoplasm, in oil bodies and in the vacuoles. They are often protein-bound and have many key functions in different parts of the plant (Andersen & Markham 2006): they give colour to the flowers (Goto & Kondo 1991), attract and repulse insects, function as pollen and nectar guides, protect needles, shoots and seedlings from harmful radicals formed by UV radiation, drought or extreme temperatures (Jungblut et al. 1995), are involved in the auxin regulation in roots and buds, increase the heavy-metal tolerance, and work as probing stimulants and activation signals of nitrogen-fixing bacteria in the roots (Dixon et al. 1994). In the

tree stem they retard the heartwood decay (Scheffer & Cowling 1966, Venäläinen et al. 2006). It is, however, believed that the antioxidant properties play a more important role than the actual fungicidal effects (Schultz & Nicholas 2000).

Flavonoids in food are claimed to show health-promoting effects in humans[30]. They may protect against cancer, Parkinson disease, cardiovascular diseases, inflammations and provide antioxidant and estrogenic effects, but this far, the effects have been demonstrated *in vitro* only (Duthie et al. 2000, Manthey 2000, Pietta 2000, Birt et al. 2001, Gao et al. 2012).

Variations

Variations in the stem

The flavonoid concentration is reported to increase from the centre of the tree to the outer part of the heartwood, and to decrease higher up in the stem (Hancock 1957, Shostakovskii et al. 1969, Tyukavkina et al. 1972), but the opposite trend with higher flavonoid concentration in the centre of the tree has also been reported (Redmond et al. 1971).

Erdtman (1956) suggested that flavonoids are formed in cambium and transported to the heartwood via rays in the sapwood. Hergert and Goldschmid (1958) proposed another theory; they detected flavonoid glucosides in needles, cambium, sapwood and inner bark, and the corresponding aglycones in heartwood and outer bark. This led to the conclusion that synthesis and glycosylation occur in the needles, from where the flavonoid glycosides are transported down the inner bark, via sapwood rays and phloem to the heartwood-sapwood and inner-outer bark boundaries. There the sugar units are removed, the water solubility is reduced and, thus, the flavonoids are deposited. Today, it is believed that the flavonoids are formed enzymatically at the heartwood-sapwood transition zone, mainly in September–November (Magel et al. 1991).

Genetic variations

In genus *Pinus*, there is a clear division between subgenus *Pinus* and *Strobus*; the species in subgenus *Pinus* contain pinocembrin[31] and pinobanksin[32], while species in subgenus *Strobus* have a much more complex composition. This subgenus seems to be able to dehydrogenate the flavanones to flavones e.g. to chrysin and tectochrysin (Lindstedt 1951).

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[30] A high content of flavonoids is probably one of the reasons behind the health benefits of the Mediterranean diet (Vasilopoulou et al. 2005).
[31] Pinocembrin was first found in *P. cembra*, thereof its name (Erdtman 1944c).
[32] Pinobanksin was first isolated from *P. banksiana* (Erdtman 1944d).

Subgenus *Strobus* also contains 7-*O*-methylated flavones and flavanones, e.g. tectochrysin and pinostrobin. Furthermore, *P. lambertiana*, *P. monticola*, *P. strobus*, *P. parviflora* and *P. peuce* all contain *C*-methylated flavones and flavanones, e.g. stropopinin, cryptostrobin, strobochrysin and strobobanksin (Lindstedt 1951, Lindstedt & Misiorny 1951a). These five species belong to subsection *Strobus*; i.e. the *C*-methylated flavonoids have been detected only in subgenus *Strobus*, section *Quinquefoliae*, subsection *Strobus*.

Genus *Larix* contains taxifolin[33] (dihydroquercetin, DHQ), quercetin and dihydrokaempferol (Tyukavkina et al. 1972) and Douglas-firs (*Pseudotsuga menziesii*) contain taxifolin, dihydrokaempferol and pinocembrin (Dellus et al. 1997). The structures of some of these components are seen in Figure 28.

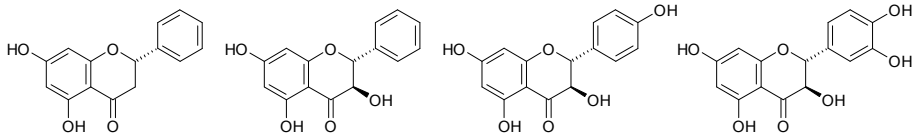

Figure 28 Structures of some flavonoids found in softwoods.

Reactions of flavonoids

In the beginning of the 20th century, it was well known that heartwood of pine and Douglas-fir could not be pulped using the sulfite method. Erdtman (1939a) showed that stilbenes caused the difficulties in pine, but no such compounds were detected in Douglas-fir. Instead, Pew (1948, 1949) detected another phenolic substance, the flavonoid taxifolin, which caused the difficulties. Later, flavonoids were found to inhibit the sulfite pulping of larch as well (Migita et al. 1952). Today, kraft pulping is an alkaline process, but the flavonoids continue to cause trouble, since they corrode the steel digesters (MacLean & Gardner 1953). Another issue is the discolouration of the surfaces of both air- and kiln-dried timber. The reason is catechin, which is transported from the inner sapwood to the surface along with the water. When the moist is evaporated, the remaining catechin reacts with air, and dark-coloured, polymerized tannins are formed (Barton & Gardner 1966). Catechin and pinobanksin are reported to cause loss of brightness in groundwood pulp as well (Redmond et al. 1971, Barton 1973).

[33] Taxifolin was first found in the heartwood of *Pseudotsuga menziesii*. It probably exists in *d*, *l*, and *dl* forms, but only the *d* form was isolated by Pew (1948).

Chalcones

Silylated flavanones and flavanonols give rise to double peaks in GC (Rudloff 1964). These extra peaks are so-called chalcones, which are formed when the ether bond is broken and the C-ring opens. The open ring can exist in both *cis*- and *trans*-form, but in some compounds the bulky trimethylsilyl (TMS) group hinders the formation of the *cis*-isomer and, thus, only one isomer is formed. Flavones and flavonols, which contain a double bond between C_2 and C_3 are more stable than the corresponding unsaturated compounds and do not exhibit any ring-opening reactions (structures in Appendix C6). The conversion of the TMS derivatives into the corresponding chalcones occurs both during the derivatisation process and during the GC analysis. The ratio between the flavanones and the chalcones depend on the derivatisation time and temperature, as well as on the injection technique (Creaser et al. 1991b). The proportion of the chalcone will increase e.g. when strong alkali is used (Lindstedt 1950b) or when the derivatisation mixture is stored at room temperature for several days (Creaser et al. 1991b).

2.7.7 Other extractives

Other lipophilic compounds

There are several other, less abundant, lipophilic compounds in conifers, and some of these structures are described in Figure 29. The most common group is terpenoids, which are terpenes substituted with at least one oxygen-containing functional group. (Information about the resin acids is found in chapter 2.7.1.) Other terpenes and fatty alcohols are of minor importance.

The diterpenoids is the most important group of terpenoids in conifers. Thunbergol and *cis*-abienol are most abundant in *Picea abies* wood, while pimarol and pimaral dominates in *Pinus sylvestris* wood (Holmbom & Ekman 1978).

Fatty alcohols are detected in almost all tree species. They can occur in both free and esterified form, and alcohols with an even number of carbon atoms dominate. Arachidyl (C_{20}), behenyl (C_{22}) and lignoceryl alcohols (C_{24}) are the most abundant fatty alcohols in Scandinavian softwood species (Lindgren & Norin 1969).

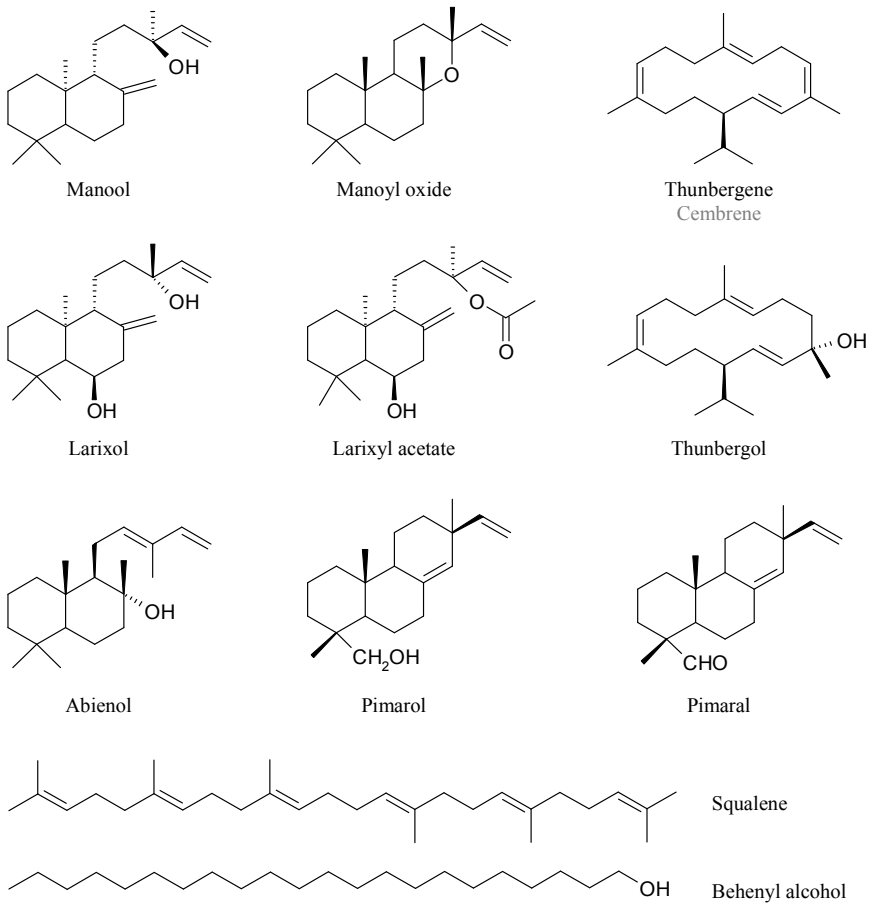

Figure 29 Structures of some additional lipophilic compounds.

Distribution in the stem

In *Pinus sylvestris* there are more fatty alcohols, diterpenyl alcohols and diterpenyl aldehydes in the heartwood than in the sapwood (Manell & Pensar 1975), but the concentrations are so low, that the differences in the radial distribution can be neglected.

The total concentration of diterpenyl alcohols in *Picea abies* is fairly constant across the stem, but there are some differences in the composition of individual components. Furthermore, there are slightly higher concentrations in the sapwood higher up in the stem compared to the lower parts (Ekman et al. 1979).

Reactions

During kraft pulping, *cis*-abienol is converted into two isomers of neoabienol and *trans*-abienol (Holmbom & Ekman 1978). During tall oil

distillation, the diterpene aldehydes do not change, but several other reactions are known to occur: thunbergol disappears completely, the fatty alcohols and the tricyclic diterpene alcohols (e.g. pimarol) are almost completely esterified and squalene is modified to a high extent (Holmbom & Avela 1971b, Holmbom & Ekman 1978). The esters are probably formed during the CTO recovery process (Holmbom & Avela 1971a) or during drying or long-term storage of CTO at elevated temperatures (Ivermark & Jansson 1970).

Further reading

There are innumerable studies on terpenes and other less abundant compounds in the wood, and some of them are listed in Table 8. The extraction methods, solvents and analytical techniques vary and, therefore, the results are a bit inconclusive. No publications regarding other lipophilic compounds in knots or stemwood were found for *Pinus elliottii*, *P. gerardiana*, *P. radiata*, *Picea omorika*, *P. pungens*, *P. sitchensis*, *Abies concolor*, *A. lasiocarpa*, *A. veitchii*, *Tsuga canadensis*, *T. heterophylla* or *T. mertensiana*.

Table 8 Publications on other lipophilic compounds in the stemwood.

Species	Publication
Pinus	
P. banksiana	Conner et al. 1980c, Pichette et al. 1998
P. contorta	Backlund et al. 2014
P. nigra	Yildirim & Holmbom 1978a, Hafizoğlu 1983, Khan et al. 1984a, Lange & Weiβmann 1987, 1989, Uçar & Balaban 2002, Rezzi et al. 2005, Willför et al. 2007
P. pinaster	Lange & Weiβmann 1987, 1989, Arrabal et al. 2002, 2005, Conde et al. 2013b
P. resinosa	Lange & Weißmann 1991
P. roxburghii	Shuaib et al. 2014
P. sibirica	Kashtanova et al. 1968, 1969, Raldugin & Pentegova 1971, Raldugin et al. 1984, Song et al. 1995
P. strobus	Bol'shakova et al. 1987, 1988a
P. sylvestris	Erdtman & Westfelt 1963, Assarsson & Åkerlund 1966, Holmbom & Avela 1971b, Manell & Pensar 1975, Holmbom & Ekman 1978, Yildirim & Holmbom 1978a Hafizoğlu 1983, Lange & Weiβmann 1987, 1988, 1989, Lange & Janežić 1993, Song et al. 1995, 1996, Willför et al. 2003b, Wajs et al. 2007, Salem et al. 2015
P. strobus	Conner et al. 1980c
P. taeda	Zinkel 1975, Carvalho et al. 1998
P. wallichiana	Song et al. 1995
Picea	
P. abies	Kimland & Norin 1972, Shmidt & Pentegova 1977, Holmbom & Ekman 1978, Ekman 1979a, Ekman et al. 1979, Bol'shakova et al. 1987, 1988a, Willför et al. 2003a, Wajs et al. 2006, 2007, Salem et al. 2015
P. glauca	Tomlin et al. 2000
P. koraiensis	Shmidt & Pentegova 1977
P. mariana	Pichette et al. 1998

Abies	
A. alba	Ribo et al. 1974, Bol'shakova et al. 1988a, Sekine et al. 2013
A. amabilis	Swan 1966
A. balsamea	Gray & Mills 1964, Carman & Dennis 1968, Pichette et al. 1998, Lavoie et al. 2013, Sekine et al. 2013
A. pindrow	Manral et al. 1987
A. sachalinensis	Numata et al. 1992
A. sibirica	Lisina & Pentegova 1965, Chirkova et al. 1966, 1967, Shmidt & Pentegova 1966, Chirkova & Pentegova 1969, Shmidt et al. 1975, Khan et al. 1984b, Radbil et al. 2002
Larix	
L. decidua	Wienhaus et al. 1960, Norin et al. 1965, Mills 1973, Bol'shakova et al. 1987, 1988a, Wajs et al. 2007, Pferschy-Wenzig et al. 2008, Salem et al. 2015
L. gmelinii var. *gmelinii*[34]	Lisina et al. 1969, Mills 1973, Shmidt & Pentegova 1974, Bol'shakova et al. 1980, 1986, D'yachenko et al. 1986, Wang et al. 2001, Radbil et al. 2002
L. gmelinii var. *japonica*	Bol'shakova et al. 1985a
L. gmelinii var. *olgensis*	Khan et al. 1983
L. kaempferi	Mills 1973, Bol'shakova et al. 1985b, 1986
L. lariciana	Mills 1973
L. sibirica	Shmidt et al. 1964, 1967, Shmidt & Pentegova 1966, Mills 1973, Bol'shakova et al. 1986, Ostroukhova et al. 2012
Pseudotsuga	
P. menziesii	Erdtman et al. 1968, Kimland & Norin 1968

Other phenols

In addition to the groups mentioned earlier, wood also contains small amounts of different monomeric phenols. It is believed that they are by-products or fragments from the lignin synthesis. Norway spruce, for example, contains vanillin, coniferyl alcohol, ferulic acid, *p*-hydroxybenzaldehyde, coniferyl aldehyde, guaiacyl glycerol, *p*-ethyl-phenol, coniferin and syringin (Kimland & Norin 1972, Ekman 1976). Some of these compounds were found also in *Tsuga heterophylla* and the Southern pines (Barton 1968, Traitler & Kratzl 1980).

Benzoic acid and its methyl ester are reported to be artefacts, produced e.g. by oxidative degradation of stilbenes or flavanones. They might be produced during milling (Rudloff & Sato 1963).

Mono- and disaccharides

The sap contains simple sugars like glucose, fructose, sucrose, and glucosides like coniferin. The amounts strongly vary with the season, and it is therefore not recommendable to compare sugar content in specimens sampled at different times of the year. No sugar data are included in this thesis.

[34] *L. dahurica* is a synonym of *Larix gmelinii* var. *gmelinii.*

3 Materials and methods

3.1 Samples, sampling and storage

Thirty nine species were examined: 14 pines, 7 spruces, 9 firs, 5 larches, a Douglas-fir and 3 hemlocks (Table 9). The sampling followed the same procedure for most of the species. There were, however, some exceptions that are pointed out later in the text. Comprehensive information on when and where all the samples were collected, as well as data on the trees are found in Appendix A2.

Table 9 Examined species

Pinus banksiana Lamb.	*Abies alba* Mill.
Pinus contorta Dougl.	*Abies amabilis* (Dougl.) J. Forbes
Pinus elliottii Engelm.	*Abies balsamea* (L.) Mill.
Pinus gerardiana Wall.	*Abies concolor* (Gord. & Glend.) Hildebr.
Pinus nigra Arnold.	*Abies lasiocarpa* (Hook.) Nutt.
Pinus pinaster Ait.	*Abies pindrow* (Royle ex D. Don) Royle
Pinus radiata D. Don	*Abies sachalinensis* (F. Schmidt) Mast.
Pinus resinosa Ait.	*Abies sibirica* Ledeb.
Pinus roxburghii Sarg.	*Abies veitchii* Lindl.
Pinus sibirica Du Tour	
Pinus strobus L.	*Larix decidua* Mill.
Pinus sylvestris L.	*Larix gmelinii* (Rupr.) Kuzeneva
Pinus taeda L.	*Larix gmelinii* var. *japonica* (Maxim. et Regel) Pilg.
Pinus wallichiana A.B. Jacks.	*Larix gmelinii* var. *olgensis* (Henry) Ostenf. & Syrach-Larsen
Picea abies (L.) H. Karst.	*Larix kaempferi* (Lamb.) Carr.
Picea glauca (Moench) Voss	*Larix lariciana* (Du Roi) K. Koch
Picea koraiensis Nakai	*Larix sibirica* Ledeb.
Picea mariana (Mill.) B.S.P.	
Picea omorika (Pančić) Purkyne	*Pseudotsuga menziesii* (Mirb.) Franco
Picea pungens Engelm.	
Picea sitchensis (Bong.) Carr.	*Tsuga canadensis* (L.) Carr.
	Tsuga heterophylla (Raf.) Sarg.
	Tsuga mertensiana (Bong.) Carr

Two healthy, mature trees of each species were felled. Samples of heartwood and sapwood were taken at 1.5 m height above the ground. Living and dead knots were cut out from each stem (Figure 30). The knots were classified as living if the outer branch was carrying living needles and dead if all the needles had fallen off. In some cases the branch was broken and had fallen off. Some larch samples were taken during the winter. Then the condition of the branch, the bark and the knots were studied in order to determine if the branch was living or dead. If the knots sampled were very

small, all knots were pooled together and the composite extract was analysed.

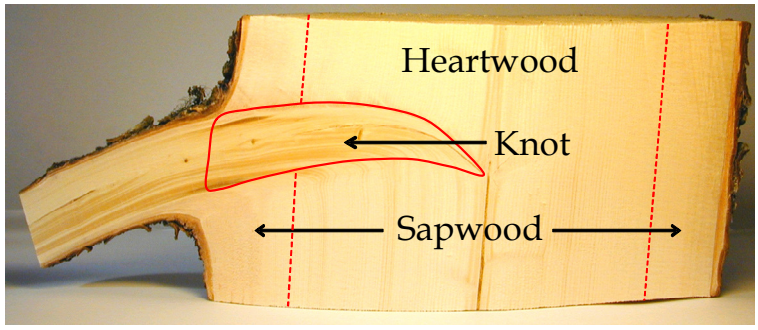

Figure 30 Cross-section of a Norway spruce stem with heartwood, sapwood and a knot (photo by Christer Eckerman).

All samples were frozen to –24 °C within 12 hours. Possible transport to the laboratory and storage therein was carried out in a frozen state.

Sampling exceptions

For *Pinus nigra*, *P. pinaster*, *Abies alba*, *Larix decidua* and *L. kaempferi*, three trees were felled. All knots from discs containing the lowest living and dead knots were analysed separately.

Only one tree of *Picea pungens* was felled. Discs were cut from 2 m and 11 m height. Stemwood was sampled from both discs. From the lower disc, nine dead knots were taken out, and from the higher disc seven living knots. All knots were extracted and analysed separately.

One tree was sampled also of *Picea abies* FRA and *Abies balsamea*. It was impossible to differentiate between heartwood and sapwood in *A. balsamea*. Therefore, the stemwood was divided into three parts: years 3–8, 9–18 and 18–39.

One knot was sampled from a wind fallen *Abies concolor*. The tree had fallen 2–3 weeks before sampling.

Bore samples were taken of *Pinus radiata*, *Picea koraiensis*, *P. omorika*, *Abies amabilis*, *A. sachalinensis*, *A. veitchii*, *Tsuga mertensiana* and *T. heterophylla* FI. The bore samples were taken from healthy, mature, standing trees. Stemwood samples were bored out 1.5 m above ground with a T-shaped, hand-operated increment borer. The diameter of the cores was 6 mm and the length varied from 2–15 cm. When possible, one living and one dead branch were cut close to the stem and cores were drilled out from the knots. If the tree had branches at 1.5 m height, the knots were sampled there. Otherwise the lowest branch was chosen. For *T. mertensiana* and *T. heterophylla* only one knot each was sampled. Additional samples were, however, taken from the outer branches, from the 5 cm closest to the stem.

The samples of *Pinus gerardiana*, *P. roxburghii*, *P. wallichiana* and *Abies pindrow* arrived at the laboratory as dry extracts. It is not known how many trees and knots were sampled, only the mass of the extracted wood is known.

3.2 Pre-treatment of wood samples

In the laboratory, the heartwood and the sapwood were manually separated according to their colour and moisture difference. The pith and the three innermost annual rings were removed from the heartwood sample. The fibres in the stemwood are perpendicular to those of the knots. That characteristic was used to carve out the knots. The separated samples were splintered and freeze-dried overnight (Figure 31). The dry splinters were ground in a Wiley mill, producing particles passing a 20-mesh screen, i.e. particles smaller than 0.87 mm. The bore cores were cut with a scalpel into pieces of the same size as the ground wood samples. After grinding, the wood was freeze-dried a second time to ensure complete removal of volatile compounds.

Figure 31 A whittled knot sample, splinter wood, ground wood and a 20-mesh screen (photo by Jarl Hemming).

3.3 Extraction

Sequential extractions were carried out in an accelerated solvent extractor (ASE), Dionex Corp. (Figure 32). About 4 g of wood was extracted with 50 ml of solvent or solvent mixture. First, the lipophilic extractives were extracted with hexane (90 °C, 13.8 MPa, 2 × 5 min). Then the phenolic extractives were extracted, either with acetone-water (95:5 v/v; 100 °C, 13.8 MPa, 2 × 5 min) or in the case of French *Abies alba*, *Pinus nigra* and *P. pinaster* in two steps, first with ethanol (100 °C, 13.8 MPa, 2 × 5 min) and then with acetone-water (95:5 v/v; 100 °C, 13.8 MPa, 2 × 5 min). In the

three-step extraction, the last acetone-water extraction was carried out to verify that all phenolics had been extracted in the prior ethanol step.

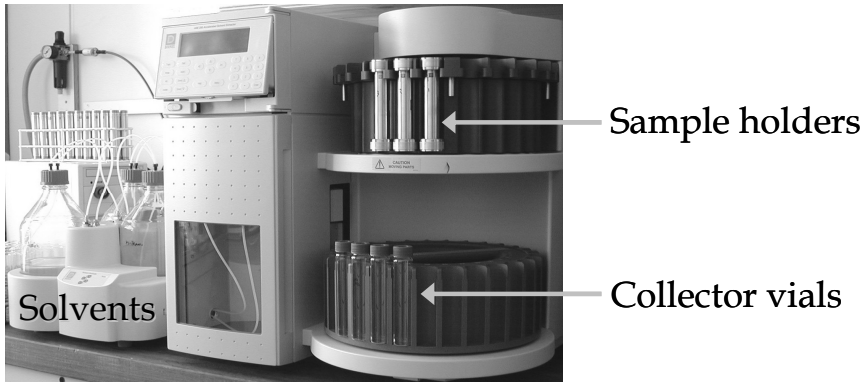

Figure 32 Accelerated solvent extractor (ASE 200) by Dionex Corp. (photo by Jarl Hemming).

3.4 Analysis of extracts

The internal standard compounds heneicosanoic acid (21:0), betulinol, cholesteryl heptadecanoate (Ch17) and 1,3-dipalmitoyl-2-oleyl-glycerol were added to each extract aliquot (Ekman & Holmbom 1989a). Thereafter, the samples were evaporated under a flow of nitrogen and dried in a vacuum desiccator (40 °C, 20 min) before silylation with 80 µl *N,O*-bis-(trimethylsilyl)trifluoro-acetamide (98%, Fluka), 20 µl trimethylchloro-silane (98%, Acros Organics) and 20 µl pyridine (99.0%, J.T. Baker). The samples were kept in an oven at 70 °C for 50 min, after which they were analysed by GC and GC-MS.

3.4.1 Long-column GC

Individual resin acids, fatty acids, sterols, diterpenoids, juvabiones, lignans, stilbenes and flavonoids were analysed with a Perkin-Elmer Autosystem XL (Wellesley, MA, USA) equipped with two flame ionization detectors (FIDs). Two columns with cross-linked liquid phases of different polarity were used in parallel for component separation: a dimethylpolysiloxane column (HP-1, 25 m, 0.2 mm i.d., film thickness 0.11 µm; Agilent) and a (5%-phenyl)-methylpolysiloxane column (HP-5, 25 m, 0.2 mm i.d., film thickness 0.11 µm; Agilent). The injection volume was 1 µl and the split ratio 1:20. The pressure of hydrogen carrier gas was constant at 14 psi and the air flow was 450 ml/min. The GC was programmed with an initial oven temperature of 120 °C (1 min hold) and a temperature increase at 6 °C/min to 300 °C (12-min hold). The injection temperature was 250 °C and the detector temperature 300 °C.

Due to procurement of a new GC, also this a Perkin Elmer Autosystem XL, the gas flow and temperature programmes were slightly changed. The injection temperature was increased by 10 °C to 260 °C and the flow of H_2 carrier gas changed to 0.60 ml/min. However, the effect of these changes on the results is negligible.

It was noticed that when the initial injector temperature was too high, triacylglycerols and steryl esters degraded and caused ghost peaks of fatty acids in the chromatograms. Therefore, a temperature program for the injector was introduced. The program started at 175 °C and was increased by 8 °C/min to 260 °C. Samples analysed with the new equipment and methods are: *Pinus gerardiana*, *P. roxburghii*, *P. wallichiana*, *P. strobus*, *P. nigra*, *P. pinaster*, *Abies alba* "FR 2", *A. pindrow*, *Larix decidua* FR, *L. gmelinii*, *L. gmelinii* var. *japonica*, *L. gmelinii* var. *olgensis*, *L. kaempferi*, *L. sibirica* FI, RU 2, RU 3 *Tsuga canadensis*, *T. heterophylla* and *T. mertensiana.*

3.4.2 Short-column GC

The steryl esters, triacylglycerols and oligolignans in the same silylated extracts were also analysed on a Varian 3400 GC system (Varian, Inc.) equipped with a Varian 8100 autosampler and FID. The on-column injection volume was 0.4 µl, the constant flow of hydrogen carrier gas was 18 ml/min at 100 °C and the air flow 330 ml/min. The extractives were separated on a DB-1/HP-1 column (Agilent) having the length of 5–7.5 m[35], inner diameter of 0.53 mm and film thickness of 0.15 µm in accordance with a method developed in our laboratory (Örså & Holmbom 1994). The injection temperature started at 80 °C. After 0.5 minutes it was increased by 200 °C/min up to 340 °C, where it was kept for 18 minutes. The detection temperature was 340 °C. The initial oven temperature 100 °C was kept for 1.5 minutes. Thereafter the temperature was increased by 12 °C/min up to 340 °C, where it was kept for 5 minutes. No FID correction factors were used.

In the course of the work also this gas chromatograph was replaced by a new instrument, a Perkin Elmer Clarus 500. The column was kept the same. The new injection volume was changed to 0.5 µl, the hydrogen gas flow to 45 ml/min and the air flow to 450 ml/min. A temperature program was applied to the injector. It started at 80 °C, increased by 50 °C/min to 110 °C, where after the gradient was decreased to 15 °C/min till the injector reached a final temperature of 330 °C. The oven temperature started at

[35] The original length of the column was 7.5 m. After 100–200 injections, non-volatile material had accumulated in the beginning of the column to such an extent that it was necessary to shorten the column by 20 cm. This was repeated now and then until the column had a final length of 5 m, thereafter it was replaced by a new 7.5-metre column.

100 °C (0.5-min hold), it increased by 12 °C/min to 340 °C where it was hold for 5 min. The detector temperature was unchanged.

3.4.3 Calculation of results

The chromatograms obtained were processed with a chromatographic software program (TotalChrom 6.2.1, Perkin-Elmer Inc.). The integration baseline was checked visually for each analysis, and corrected manually if necessary. The standard error of GC results is generally assumed to be approximately ±5%. All peaks were quantified by peak area. Fatty acids, resin acids, juvabiones, flavonoids and stilbenes were quantified against the heneicosanoic acid (C_{21}) standard, lignans and sterols against betulinol, steryl esters, sesquineolignans and dineolignans against cholesteryl heptadecanoate, and triacylglycerols and sesterneolignans against the 1,3-dipalmitoyl-2-oleyl-glycerol. According to Willför et al. (2003a), a correction factor of 1.2 was used for the lignans against betulinol. The limit of quantification was 0.005% (w/w), but compounds occurring in lower concentrations than this could be detected. Those concentrations are reported as trace amounts and are denoted with a plus sign (+) in the tables.

Some lipophilic compounds were not completely extracted with hexane, but were extracted also in the subsequent acetone-water step. For those compounds the amounts in the lipophilic and hydrophilic extracts were determined, added together and the sum is reported.

Silylation of certain flavanone and flavanol aglycones can cause artefact formation. When the ring-opening reaction occurs in alkaline environment, the compounds are partially converted into their corresponding chalcones (Creaser et al. 1991a). In this study, dihydrokaempferol was transformed into chalcone during derivatisation. The amount of chalcone was quantified, interpreted as an artefact formed from dihydrokaempferol, and the amount of chalcone was added to the amount of dihydrokaempferol.

3.4.4 GC-MS

For identification of individual components the samples were analysed by GC-mass spectrometry on an HP 6890-5973 GC-MSD system (Hewlett-Packard, Palo Alto, CA, USA) equipped with a 7683 autosampler. The temperature of the MS transfer-line was 300 °C. The MS ionisation mode was electron ionisation at 70 eV. The temperature of the MS ion source and quadrupole were 230 °C and 150 °C respectively. The mass range for analysis was 35 m/z to 800 m/z.

Two different columns were used. Free fatty acids, sterols, resin acids diterpenes, stilbenes, juvabiones, flavonoids and lignans were separated on the same type of HP-1 column as for GC-FID (25 m, 0.20 mm i.d., film thickness 0.11 µm). The injection volume was 1 µl and the split ratio was

1:20. Helium was used as carrier gas at a constant flow of 0.8 ml/min; the split flow was 15 ml/min. The injector temperature was 280 °C. The temperature program for separation started at 80 °C (hold 0.25 min), followed by an increase of 8 °C/min to 300 °C (10-min hold).

The steryl esters, triacylglycerols and oligolignans were separated on a MXT-65TG column (15 m × 0.25 mm i.d. × 0.10 µm film thickness; ResTek, USA) containing 65% diphenyl and 35% dimethyl polysiloxane. The injection volume for all samples was 0.5 µl, the split-less delay 0.3 min, and the injector temperature was 300 °C. The oven temperature program was started at 80 °C (1-min hold), followed by an increase of 10 °C/min to 350 °C (20-min hold). The carrier gas flow was 1.0 ml/min. The identification was based on comparing retention times and matching mass spectra with those in NIST98, WILEY275 and the laboratory's own unique database.

Some compounds were not included in any of the data bases mentioned above and only spectra of underivatized compounds have been reported in the literature. These extracts were, therefore, analysed by GC-MS in underivatized form and the mass spectra were compared to the spectra found in the literature.

3.5 Some remarks on materials and methods

3.5.1 Sampling

Variability

It is well known that trees growing at different sites have different chemical composition (Lindstedt 1950b, Erdtman et al. 1951, Nylinder & Hägglund 1954, Hakkila 1969, Piispanen et al. 2008, Neverova et al. 2014). It is also known that trees growing side by side can differ considerably (Erdtman et al. 1951, Manville & Rogers 1977). So is the chemical composition determined by genetic or environmental factors? By comparing clones and by cultivating seeds and clones at different sites it has been found that chemical composition is mainly under genetic control (Lindstedt 1951, Lee 1968, Fries et al. 2000, Klasnja et al. 2003, Miranda et al. 2007). The rest is influenced by the water and nutrient balance, and climatic conditions like temperature, light, wind exposure and snow load (Erdtman & Misiorny 1952, Piispanen et al. 2008).

According to the GDB, the growth (cell division and enlargement) is limited by water and nutrients, while the production of secondary metabolites (used for defence) is limited by the photosynthetic formation of carbohydrates (Herms & Mattson 1992). This could explain why trees growing further north are richer in polyphenols – the access to nutrients is

limited, but the sun is shining night and day during the growth period (Piispanen et al. 2008).

Age

It has been reported that older pines contain more resin than younger (Jayme & Blischnok 1938, Manville & Rogers 1977), but the real reason behind this is that older trees contain proportionally more heartwood than sapwood, and the heartwood is richer in resin. The actual influence of age is small (Buckland et al. 1953, Uprichard & Lloyd 1980). In this thesis, heartwood and sapwood were analysed separately, so the only age-related challenge was the juvenile trees that were sampled before they had formed any heartwood. This was the case with *Pinus radiata*.

Time of the year

There are some small differences in the extractive content of the sapwood depending on when the samples are taken (Swan 1968, Ekman et al. 1979, Höll 1985, Saranpää & Nyberg 1987b), but other researches claim that these differences are insignificant (Pensar 1969a, Pensar et al. 1981). The date when the wood was samples is, however, specified in Appendix A2.

Bore cores

Normally, stemwood samples are cut out as sectors, but for some species bore cores were sampled. Since the bore cores are equally thick rods, the portion of juvenile wood tends to be smaller compared to when sectors are sampled. This problem was, however, avoided since heartwood and sapwood were analysed separately.

3.5.2 Extraction

Several studies have showed that the ASE is well suited for extraction of wood and pulp, especially in sequential mode (Thurbide & Hughes 2000, Schoultz 2001, Sundberg et al. 2001, Bergelin et al. 2003). The method is fast, hence are the thermal degradation and isomerization of extractives is minimized (Bergelin et al. 2003). The total gravimetric yield with ASE is slightly higher than with Soxhlet, Soxtec, reflux and ultrasonic extraction techniques (Thurbide & Hughes 2000, Bergelin et al. 2003).

It has been showed that ASE is 30 times faster and consumes 75% less solvents compared to the Canadian Pulp and Paper Association's (CPPA's) standard Soxhlet method (Thurbide & Hughes 2000). This is a great advantage when a vast number of relatively small samples are extracted sequentially with different solvents.

3.5.3 Analysis of extractives

Tree extracts are complex mixtures containing many different types of components with both low and high molar mass. High-molar-mass components are heavily discriminated on GC, even when using an MXT column, so for analysing them HPLC is a better alternative. However, when it comes to separation of individual components with lower molar mass, GC is still superior. The separation is good enough up to C_{60} on short thin-film columns, so lipophilic compounds up to triacylglycerols and hydrophilic ones up to four lignan units and little above those are successfully analysed by GC.

Even though the HPLC equipment and methods have been developed; the resolution is still not high enough to separate the individual sterols and fatty acid in the same analysis. In addition, the personnel at the Laboratory of Wood and Paper Chemistry have great experience of GC methods for extractives, so the burden of history and force of habit weighed heavily upon the choice of method used in this study.

4 Results and discussion

This work compiles results from seven years of research carried out in several different projects. The objectives of these projects varied; in some the intention was to produce and characterize extracts for bio-testing, in some to check an analytical method or a potential raw material, and some studies were done out of sheer curiosity. This has led to a situation where the sampling and extraction methods differ somewhat from species to species. Some of the results are average values of several samples from trees growing in natural forests, while others are diminutive bore cores, or samples from trees growing under propitious conditions in arboretums. Anyhow, the natural variability is so large that it would be impossible to collect and study an adequate number of samples for reliable statistics. Therefore, this study only gives an overview of the composition and amounts of extractives in industrially important conifers. A somewhat critical attitude should be taken when interpreting the data, because more samples should have been analysed to get statistically reliable data.

4.1 Lipophilic compounds

4.1.1 Resin acids

The resin acids are principally found in the resin canals, which are a normal feature of genera *Pinus*, *Picea*, *Larix* and *Pseudotsuga*. The pines have the largest and most numerous resin canals, therefore they also contain the highest concentrations of resin acids. The other genera with resin canals, i.e. *Picea, Larix* and *Pseudotsuga,* contain resin-acid levels of the same magnitude. The resin canals in the pines are mainly located in the heartwood and the roots. Hence heartwood contains significantly more resin acids than sapwood. The difference is significantly less pronounced in other genera, where the resin canals are more evenly distributed throughout the whole stem.

Genera *Abies* and *Tsuga* lack resin canals. They can, however, form so-called traumatic resin canals as a response to injury. When the sampling was made, all injured areas were omitted and therefore, these samples contained only traces of resin acids. Accordingly, the resin acids in these species have been left out. The structures of all identified resin acids are presented in Appendix C1.

Pure, fresh oleoresin does not contain any oxidized or otherwise modified resin acids. They are artefacts formed during wood sampling, sample storage, extraction or GC analysis (Zinkel 1975). Traces of hydroxy-resin acids as well as abietadienoic, -trienoic and -tetraenoic acids were found in

some of the extracts analysed. They were, however, omitted since they do not occur in fresh, healthy wood.

Pinus

Heartwood of the pines contained considerably more resin acids than sapwood (Figure 33). The only exceptions were *Pinus sibirica* and *P. radiata,* were the sapwood contained equal or higher concentrations compared to the heartwood. Both samples of *P. sibirica* came from trees that were only 20 years old. The species is known to be slow-growing (Sannikov 2002, p. 414); it is therefore likely that the heartwood was too young, and that the difference between heartwood and sapwood will be more pronounced in more mature heartwood.

The pine species richest in resin acids were *P. resinosa* and *P. strobus*. Their heartwood contained more than 3% and 4% resin acids, respectively. The heartwood of *P. contorta*, *P. elliottii* and *P. taeda* contained 2–3% resin acids, the heartwood of *P. banksiana* and *P. sylvestris* 1–2%, and the heartwood of *P. nigra*, *P. pinaster*, *P. radiata* and *P. sibirica* contained less than 1% resin acids.

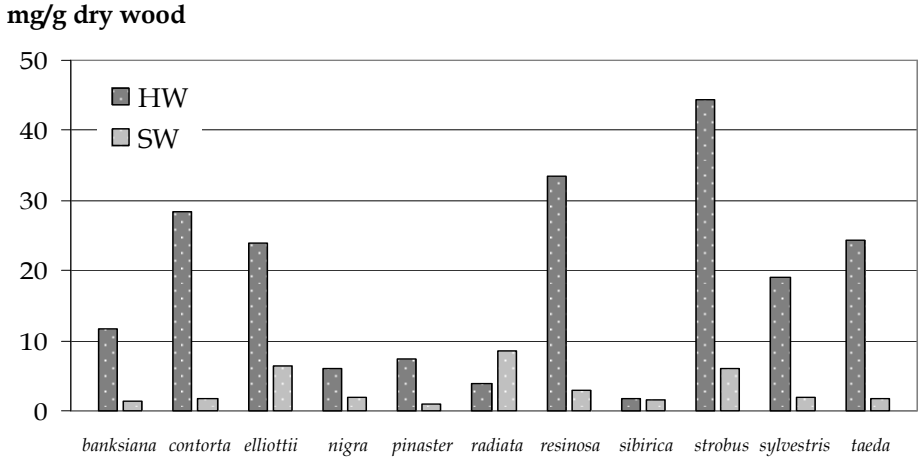

Figure 33 Total average concentrations of resin acids in stemwood of genus Pinus (HW=heartwood, SW=sapwood).

Generally, the knots contained much more resin acids than the heartwood (Figure 33 and 34, note the difference of scales).

For most species the dead knots contained more resin acids than the living knots (Figure 34). The only exceptions were the knots of *P. banksiana*, *P. resinosa* and *P. sylvestris*. Remarkable is that these species also had the highest resin-acid content in their knots. The living knots of *P. contorta* were rich in resin acids (10–20%). However, no dead knots of this species were analysed.

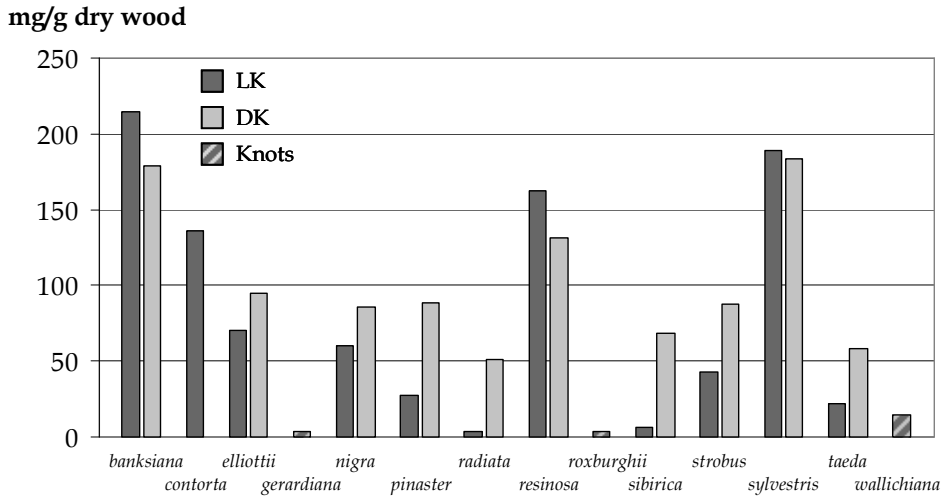

Figure 34 Total average concentrations of resin acids in knots of genus Pinus (LK=living knots, DK=dead knots, "Knots" is a mixture of dead and living knots).

The largest differences in the total resin acid content between living and dead knots were found in *P. radiata* and *P. sibirica*. In *P. radiata* the dead knots contained ten to fifteen times more resin acids than the living knots. In *P. sibirica* the dead knots contained ten times more resin acids. No previous studies on resin acids in knots of the pine species analysed here were found in the literature.

The composition and total amounts of resin acids in all studied species are found in Appendix D1 and the distribution of resin acids in all pine species can be seen in Figure 35. These values are used when discussing the different species.

Genus *Pinus* contained resin acids of abietane, pimarane and labdane type. The abietane type (blue bars in Figure 35) dominated in all species, with a share from 38% to 91%. The pimarane type (green bars) was the second most common group comprising 9–39% of all resin acids. In *P. roxburghii*, *P. sibirica*, *P. strobus* and *P. wallichiana,* the share of pimarane-type acids was exceptionally high. *P. gerardiana*, *P. sibirica*, *P. strobus* and *P. wallichiana* contained no, or very little, pimaric acid. Instead, the proportion of isopimaric acid was higher. These four species belong to subgenus *Strobus*, section *Quinquefoliae*. Song et al. (1995) studied oleoresin of 22 Chinese pine species and they noted that the content of isopimaric acid and abietic acid were much higher in the section *Quinquefoliae*[36]. However, in the present study the abietic acid content in section *Quinquefoliae* did not stand out in any way.

[36] They called the section *Strobus*, which is sometimes used in parallel with *Quinquefoliae*.

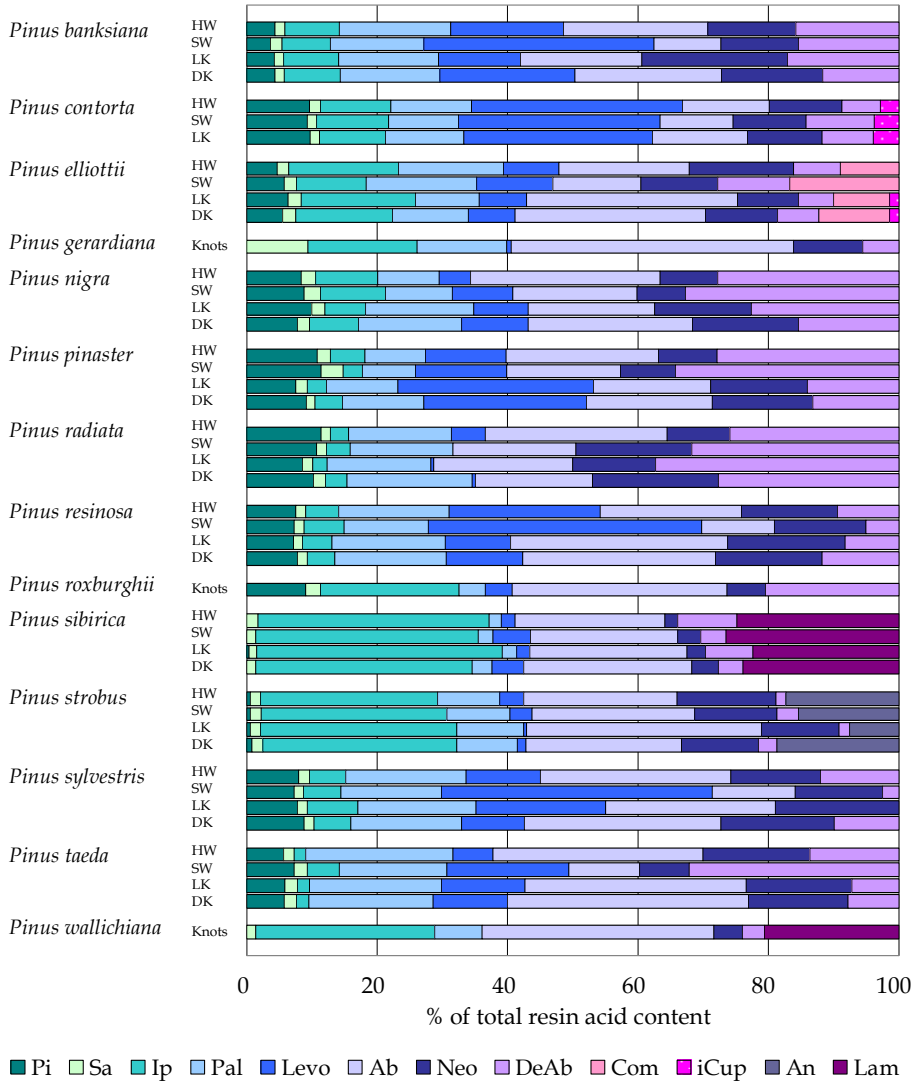

Figure 35 Composition of resin acids in genus Pinus in percent of the total resin acid content (HW=heartwood, SW=sapwood, LK=living knots, DK=dead knots). The resin acids of pimarane type are in green, of abietane type in blue, and of labdane type in pink/purple/grey. The complete names of the resin acids are found in the list of abbreviations.

Some species of genus *Pinus* contained resin acids of labdane type (pink/purple/grey bars in Figure 35). Their share was 0–26% of the total resin acids. Communic acid was found also in larch, while isocupressic, imbricatolic, anticopalic and lambertianic acid were found only in genus *Pinus*. The species containing labdane-type acids were: *P. contorta*, *P. elliottii*, *P. gerardiana*, *P. roxburghii*, *P. sibirica,* *P. strobus* and *P. wallichiana.* According to Song et al. (1995), high concentrations of

lambertianic acid are characteristic for section *Quinquefoliae*. They also reported traces in section *Pinus*. Here, a high content of lambertianic acid was found in *P. sibirica* and *P. wallichiana*, traces in *P. gerardiana* and *P. roxburghii,* but no was found in *P. strobus, P. sylvestris, P. resinosa, P. nigra* or *P. pinaster.* Therefore, it could not be confirmed, whether lambertianic acid is characteristic of any particular section or not.

In GC analysis on a HP-1 column, the resin acids of labdane type elute very close to other, better known, resin acids. However, on a HP-5 column, the peaks are well separated.

Pinus banksiana

The heartwood contained 1.0–1.4% resin acids, the sapwood 0.1–0.2%, the living knots 21–22% and the dead knot 18%. The pimarane-type acids constituted less than 15% of all resin acids, while the rest was rather equally distributed between the five acids of abietane type. The sapwood, however, contained more levopimaric acid and less abietic acid than the rest of the samples. The reason was probably that the oleoresin in the sapwood was fresher, less oxidised and therefore, still contained more levopimaric acid.

Rudloff and Sato (1963) made a comprehensive investigation of the heartwood extractives in *P. banksiana*, where they separated and identified 45 different compounds. They reported that the heartwood contained 2.1–2.2% resin acids and that isopimaric and abietic acids were the major resin acids, followed by dehydroabietic and neoabietic acid, as well as small amounts of pimaric and sandaracopimaric acids. The total amount of resin acids found in this thesis was roughly half of the amount they found in their heartwood. They also found considerably much more isopimaric acid and hardly any palustric or levopimaric acid. In this thesis, levopimaric and palustric acid together accounted for one third of all resin acids.

Conner et al. (1980c) studied the amount and distribution of resin acids in heartwood and sapwood of *P. banksiana*. They found 1.7–3.0% resin acids in the heartwood and 0.2–0.3% in the sapwood. This is roughly twice as much as reported in this thesis. Compared to the distribution presented here Conner et al. (1980c) found slightly more abietic acid in the heartwood. They also found much more dehydroabietic acid, somewhat less neoabietic acid and significantly less levopimaric acids in both heartwood and sapwood. The higher content of dehydroabietic acid was probably a result of isomerization reactions in the samples.

The most recent study of oleoresin from *P. banksiana* was made by Song (1998, p. 37). He found less dehydroabietic, pimaric and isopimaric acid than reported here. Song was not able to separate palustric acid from

levopimaric acid. He also found small amounts of communic acid. No communic acid was detected in this thesis.

Pinus contorta

P. contorta was rich in resin acids. The heartwood contained 2.6–3.1% resin acids, the sapwood 0.1–0.2% and the living knots 9–18%. The abietane-type acids amounted to more than 75% of all resin acids. Levopimaric acid dominated in all samples. It constituted one third of all resin acids. Abietic, neoabietic, palustric, pimaric and isopimaric acid were all equally abundant, 10–15%, while dehydroabietic and sandaracopimaric acid made up a minor part of the composition. Isocupressic acid[37], a labdane-type acid, was also found in the samples. The content was low and that probably explains why it has never been found in this species before.

Anderson et al. (1969) were first to analyse the resin acids in heartwood and sapwood of *P. contorta*. Compared to the composition presented in Figure 35, they found more abietic, dehydroabietic and isopimaric acid and less neoabietic and levopimaric acid. In their study, they also compared the resin acids of *P. contorta* and *P. attenuata* and concluded that there are no qualitative or quantitative differences between the two species.

Later, Conner et al. (1980a) analysed heartwood, sapwood and whole wood of *P. contorta*. Compared to the composition in this thesis they found significantly less levopimaric acid and significantly more dehydroabietic acid, i.e. their levopimaric acid had probably been isomerized to dehydroabietic acid. They also showed much less neoabietic acid in the heartwood and sapwood samples and a bit more palustric acid. The total part of pimarane-type acids was the same as in this thesis, but they showed less pimaric acid, which was compensated by more isopimaric acid.

Gao et al. (1995) found twice as much resin acids compared to the concentrations presented in this thesis; 4.0–5.6% in the heartwood and 0.3–0.4% in the sapwood. They also noticed that the total content of resin acids increased slightly from the inner to the outer heartwood. The most abundant resin acid in their study was palustric acid. It constituted 29% of all resin acids in the inner heartwood, 43% in the outer heartwood, 50% in the inner

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[37] Isocupressic acid was first isolated and identified in resin from the Mediterranean Cypress, *Cupressus sempervirens* (Mangoni & Belardini 1964). Later it was identified also in oleoresin of hoop pine, *Araucaria cunninghamii* (Caputo et al. 1974) in needles of Monterey cypress, *Cupressus macrocarpa* (Parton et al. 1996), in bark and needles of ponderosa pine, *P. ponderosa*, lodgepole pine, *P. contorta*, common juniper, *Juniperus communis* (Gardner et al. 1998) and bark of Utah juniper, *J. osteosperma* (Gardner et al. 2010). It is well documented that consumption of bark and/or needles from these species will cause abortions in pregnant domestic animals and isocupressic acid has been identified as the liable compound (Gardner et al. 1994, 1998, Parton et al. 1996).

sapwood and 52% in the outer sapwood. Gao et al. (1995) were apparently not able to separate levopimaric acid from palustric acid, and that is why they missed the fact that levopimaric was the dominating resin acid, not palustric acid. Furthermore, they found less pimaric acid in all samples and more abietic acid in the heartwood than reported in this thesis. They did not detect any isocupressic acid.

Natural hybrids of *P. contorta* and *P. banksiana* are found in Canada, where their areas of distribution overlap (Mirov 1961). The species can, however, be distinguished since *P. contorta* contains low amounts of isocupressic acid, an acid which is absent in *P. banksiana.*

Pinus elliottii

The total content of resin acids in *P. elliottii* was 2–3% of the heartwood, 0.6% of the sapwood and 4–13% of the knots. Zinkel and Foster (1980) found 0.57% resin acids in the sapwood, which is in good agreement with the results presented in this thesis. About 65% of all resin acids were of abietane type, 22% of pimarane type and 12% of labdane type.

Abietic acid dominated in the heartwood and the knots, while palustric and communic acid[38] dominated in the sapwood. Other major resin acids, in all of the samples, were neoabietic, levopimaric and isopimaric acid. Low contents of dehydroabietic, pimaric, sandaracopimaric and isocupressic acid were also found in all samples. Furthermore, the stemwood contained low proportions of imbricatolic acid[39]. This compound was not detected in the knots, neither was it found in any other species in this thesis. Bol'shakova et al. (1988b) have earlier identified imbricatolic acid in resin of the Swiss mountain pine, *P. mugo* K., from Transcarpathia, Ukraine.

Zinkel and Foster (1980) analysed resin acids in the sapwood. Their composition resembles the one presented here. The only differences was that they found a much higher percentage of isopimaric acid, a lower of

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[38] Communic acid was first found in the bark of common juniper, *Juniperus communis* L. (Arya et al. 1961a, 1961b), thence the name. Joye et al. (1963) found the same resin acid in oleoresin from *P. elliottii*, but they thought it was a new compound and named it elliotinoic acid. In a later study (Joye et al. 1965), they showed that elliotinoic acid was identical to communic acid. According to Erdtman (1963, p. 694), all diterpenoid acids found in Pinales have an equatorial carbonyl group at C_4 position. This is, however, not true for communic acid, which has an axial carbonyl group at C_4 position and it can, therefore, be of chemotaxonomic interest (Joye et al. 1965).

[39] Imbricatolic acid is the dihydro derivative of isocupressic acid. It was first isolated from the monkeypuzzle tree, *Araucaria araucana*, which also has been called *Araucaria imbricata*, thereof the compound's name (Weiβmann et al. 1965). Imbricatolic acid has been isolated from the resin of 18 Cupressus species growing in America and Asia, but it has not been found in the European species *C. sempervirens* (Gough & Mills 1970). Unripe berries of *Juniperus communis* ssp. *nana* contain imbricatolic acid, isocupressic acid and communic acid (Sakar et al. 2002).

communic acid, and that they did not detect imbricatolic nor isocupressic acid. They also observed that communic acid was present after the kraft pulping process, and it is, thus, not sensitive to isomerization. Joye and Lawrence (1963), on the other hand, claimed that communic acid was sensitive to oxidation.

There are at least four publications about resin acids in oleoresin of *P. elliottii* and the data presented in three of them there are almost identical (Joye et al. 1966, Joye & Lawrence 1967, Panda & Panda 1986). Compared to the results presented in this thesis, their composition is higher in isopimaric acid and levopimaric + palustric acid (they were not able to separate these two acids). They also found somewhat less dehydroabietic acid and an unidentified acid, which probably was imbricatolic acid (Joye et al. 1966).

The fourth publication on oleoresin is written by Song (1998, p. 52). His composition consists of much more levopimaric + palustric acid, a bit more sandaracopimaric acid and less abietic, dehydroabietic, pimaric and communic acid. He did not find any imbricatolic or isocupressic acid.

Pinus gerardiana

There is only one publication about resin acids in *P. gerardiana* (Panda & Panda 1986). The oleoresin composition presented there is richer in palustric + levopimaric, dehydroabietic and pimaric acid, while the knots studied in this thesis were richer in abietic, sandaracopimaric and isopimaric acid. It seems unlikely that the differences were caused merely by the different sample types studied, so additional work is needed on this species.

The total amount of resin acids in the knots was exceptionally low, only 0.4% of the dry wood weight. The most abundant acid was abietic acid, 43% of all resin acids, followed by isopimaric, palustric, neoabietic, sandaracopimaric, dehydroabietic, levopimaric and lambertianic acid in decreasing order. It is worth mentioning that the relative content of sandaracopimaric acid was exceptionally high in this species. It constituted 9% of all resin acids.

Pinus nigra

Pinus nigra is an industrially important softwood species and has been much studied. The nomenclature of the species is a bit confusing. *P. nigra* is divided into subspecies and variants and the division between the ranks may vary among botanists. There are, however, at least two subspecies of *P. nigra*: the eastern and the western. Below is an outline of the most commonly used subspecies and varieties. The samples trees in this study belonged to subsp. *salzmannii* var. *laricio.*

1. *Pinus nigra* subsp. *nigra*, the eastern subsp.
    - var. *nigra* = var. *austriaca* = subsp. *dalmatica*, Austrian pine
      Grows in Austria and on the Balkan peninsula (not in southern Greece)
    - var. *caramanica*, Turkish black pine
      Grows in Turkey, Cyprus and in southern Greece
    - var. *pallasiana*, Crimean pine
      Grows on Crimea

2. *Pinus nigra* subsp. s*alzmannii*, the western subsp.
    - var. *salzmannii,* Pyrenean Pine
      Grows in Southern France and Spain
    - var. *corsicana* = var. *maritima* = var. *laricio*, Corsican pine
      Grows on Corsica and in southern Italy
    - var. *mauretanica*, Atlas mountain black pine
      Grows in Morocco and Algeria

The resin-acid concentrations in the stem were fairly low: 0.6–0.7% in the heartwood and 0.2–0.3% in the sapwood. The knots contained much more resin acids than the stem, but the concentrations varied considerably, from 1.2% to 13%. About 80% of all resin acids were of abietane type. Abietic and dehydroabietic acid dominated. Equal amounts of neoabietic, palustric, levopimaric, pimaric and isopimaric acid and a smaller part of sandaracopimaric acid were found.

Bardyshev et al. (1970c) studied oleoresin of *P. nigra* grown in Bulgaria[40]. Their composition was similar to the one in this thesis. The only difference was that they found less dehydroabietic acid, which was compensated by a bit more neoabietic, palustric and sandaracopimaric acid. This implies that the samples in this thesis had undergone ageing.

The two varieties of *P. nigra* growing in Turkey (var. *caramanica* and var. *pallasiana*) have been studied by several scientists, and there are at least three publications about resin acids in Turkish *P. nigra*. Yildirim and Holmbom (1978b) analysed *P. nigra* var. *caramanica* (Loud.) Rehd. They extracted a mix of heartwood and sapwood and obtained 0.43–0.50% resin acids, which is well in accordance with this thesis. Their composition contained more neoabietic, palustric and levopimaric acid, and less dehydroabietic acid. Uçar and Fengel (1995) studied var. *pallasiana* and compared its stemwood extractives with var. *pyramidata*[41]. The samples

[40] Most likely *P. nigra* var. *nigra.*
[41] It is questionable whether these samples actually are two different varieties of *P. nigra* or if they are different subvarieties or forms of the same variety.

contained both heartwood and sapwood and they found the compositions to be quite similar. Compared to this thesis, they found more palustric acid and less abietic and dehydroabietic acid, i.e. their samples were less aged. Var. *pallasiana* and var. *pyramidata* contained less abietic acid and more palustric acid compared to *P. nigra* var. *caramanica* (Yildirim & Holmbom 1978b).

Uçar and Balaban (2002) compared slow- and fast-growing trees of *P. nigra* var. *pallasiana* from Turkey. The total concentration of resin acids was 1.1% and 1.2%, respectively, which is considerably much more than found earlier. The fast-growing trees were supposed to produce more resin acids and less sterols, but Uçar and Balaban (2002) did not find any larger differences. They did, however, find pinifolic acid in the wood. This compound is abundant in pine needles (Zinkel et al. 1985), and no one else has found it in *P. nigra* wood. Compared to the present study Uçar and Balaban (2002) found less abietic, dehydroabietic and pimaric acid in combination with more neoabietic, levopimaric, isopimaric and palustric acid.

Rezzi et al. (2005) studied the oleoresin of *P. nigra* var. *laricio* from Corsica (the same variety as studied in this thesis). They found less abietic and dehydroabietic acid, and more neoabietic, palustric and levopimaric acid, i.e. their samples were fresher.

Pinus pinaster

The total amount of resin acids in *P. pinaster* was among the lowest of all studied pines; 0.6–0.8% was found in heartwood and less than 0.2% in sapwood. The dead knots contained considerably much more resin acids than the living knots, 5–12% and 0.7–7.1%, respectively. The resin acid composition resembled that of *P. nigra*. The only difference was that the knots of *P. pinaster* contained more levopimaric acid. This is the first study where levopimaric and palustric acid have been separated in this species.

Joye and Lawrence (1967) compared oleoresin and rosin, and found their compositions to be fairly similar. The oleoresin contained more levopimaric + palustric acid, while more abietic acid was found in the rosin. Compared to this thesis they found less dehydroabietic acid, which was compensated by more neoabietic, isopimaric and levopimaric + palustric acid.

Hemingway et al. (1973) compared a 15-year-old tree with a 35-year-old. They found more levopimaric + palustric acid and less pimaric and dehydroabietic acid in the younger tree, which only contained sapwood. In the older tree they found more levopimaric + palustric at top of the stem than at base. This is quite natural since the top contained mostly sapwood. Hemingway et al. wrote that autoxidation of the labile resin acids occurred

in the older heartwood at the base of tree. The distribution of resin acids was the same as in a publication by Joye and Lawrence (1967).

Arrabal et al. (2002) compared the extractives in normal trees and in trees which produce extraordinary high amounts of oleoresin, so-called plus trees. The average plus tree produced 2.4 times more oleoresin than the normal tree, but the concentration of resin acids in the oleoresin was lower. However, the distribution of resin acids was the same, so obviously the production volume did not influence the composition of resin acids in the oleoresin. The composition of resin acids found by Arrabal et al. (2002) is the same as in the oleoresin analysed by Joye and Lawrence (1967).

Pinus radiata

P. radiata is extensively cultivated and it has become the most common pine in the southern hemisphere. The largest plantations are found in Australia, New Zealand, Spain, Argentina, Chile, Uruguay, Kenya and South Africa. It is favoured because it is fast-growing, e.g. on New Zeeland it can be harvested at the age of 25–35 years. Therefore, about 90% (1.6 million hectares) of New Zealand's forest plantations consist of *P. radiata.*

Two trees of *P. radiata* were sampled, but only one was old enough to contain any heartwood. The resin acid content in the heartwood was 0.4%, while the sapwood contained 0.9%, the living knots 0.3–0.4% and the dead knot 5%. About 85% of the resin acids were of abietane type. Abietic and dehydroabietic acid clearly dominated. They were accompanied by neoabietic, palustric and pimaric acid, as well as a low content of levopimaric, sandaracopimaric and isopimaric acid and traces of abietic acid.

Hemingway et al. (1971) found 1.5% resin acids in their wood chips. That is twice as much as reported in this thesis. Levopimaric + palustric acid (the peaks overlapped) were their dominating compounds. They found less abietic, dehydroabietic and pimaric acid than reported here. Hemingway and Hillis (1971) also studied the radial distribution of resin acids in *P. radiata* and they found that the total amount of resin acids decrease in the order: inner heartwood > outer heartwood > outer sapwood > inner sapwood.

Hemingway et al. (1971) also exposed chips to a heat treatment, which caused oxidative degradation of the extractives. They detected a rapid loss of levopimaric-palustric acid along with a significant loss of neoabietic acid. The content of abietic acid also decreased. However, the unconjugated, pimarane-type acids did not change at all. There was a significant increase in the amount of dehydroabietic acid during the treatment. This increase counted for approximately 15% of the loss of

abietane-type acids. The amount of dihydroresin acids did not increase during the treatment.

Song (1998, p. 87) analysed oleoresin of *P. radiata*. The dominating compound in his study was levopimaric acid. It constituted 43% of all resin acids. Song found less abietic, dehydroabietic, pimaric and isopimaric acid than reported in this thesis. Furthermore, he found 2.8% communic acid, a compound no one else has detected in oleoresin of *P. radiata.*

Pinus resinosa

The name *P. resinosa* hints that this species is very rich in resin, and that is true indeed. The heartwood contained 3.3% resin acids, the sapwood 0.3% and the knots 7.8–20%. The species is self-pruning (Burns & Honkala 1990) and in order to protect the stem, the knots contain a lot of resin. The sapwood layer is thick and easily penetrated by creosote, therefore, the wood is extensively used for poles, piling and railway ties (Hosie 1979, p. 48). Generally, the differences between wood samples of *P. resinosa* should be small, because *P. resinosa* is genetically the most uniformed (widely distributed) conifer. The species was reduced to a small surviving population during the last full-glaciation, and that is why it is so homogenetic (Eckenwalder 2009).

Abietic and levopimaric acid were the dominating resin acids. Levopimaric acid was especially abundant in the sapwood, where it constituted 42% of all resin acids. The content of neoabietic, palustric, dehydroabietic and pimaric acid was also fairly high, while the proportion of sandaracopimaric and isopimaric acid was low.

Sato and Rudloff (1964) studied the heartwood of *P. resinosa*. They stated that it contained 1.5% resin acids, which is only half of what is found in this thesis. They found less neoabietic and palustric acid, and significantly much more isopimaric acid. Their sample totally lacked levopimaric acid, but instead it contained an equivalent percentage of dehydroabietic acid, which indicated ageing.

Pinus roxburghii

This is the first study of resin acids in knots of *P. roxburghii*. Three other scientists (Panda & Panda 1986, Coppen et al. 1988, Song 1998) have analysed normal wood of *P. roxburghii*, but they arrived at different compositions.

The knots contained only 0.3% resin acids. The most dominating acids were abietic, dehydroabietic and isopimaric acid. Lower proportions of neoabietic, pimaric, palustric, levopimaric and sandaracopimaric acid were

detected along with traces of lambertianic acid. This is the first study where levopimaric and palustric acid were separated in this species.

Panda and Panda (1986) and Coppen et al. (1988) analysed oleoresin and rosin from *P. roxburghii*, which are the only sources of gum naval stores in India. When their normal wood is compared to the knots in this thesis one can conclude that they found more neoabietic and levopimaric + palustric acid, and less dehydroabietic acid. Coppen et al. (1988) did not find any sandaracopimaric acid at all, and Panda and Panda (1986) found less abietic acid in their oleoresin.

Song (1998, p. 90–91) analysed oleoresin. His composition was very different and the overlapping compounds palustric and levopimaric acid dominated. He found more sandaracopimaric acid and less abietic, pimaric and isopimaric acid. He also found two labdane-type acids: lambertianic acid, also detected in this thesis, and communic acid (3%), not detected in this work.

Pinus sibirica

The heartwood and sapwood of *P. sibirica* were very poor in resin acids, containing only 0.2%. The difference between the living and dead knots was significant, 0.4–1.4 was found in the living and 4.4–14% in the dead knots. The composition of resin acids clearly differed from that of previously describes pines. Here isopimaric acid dominated (32–39% of all resin acid), closely followed by abietic (23–27%) and lambertianic acid (20–27%). Low percentages of neoabietic, palustric, levopimaric, dehydroabietic and sandaracopimaric acid and traces of pimaric acid were also detected. This was the first study of *P. sibirica* where levopimaric and palustric acid were separated.

Oleoresin of *P. sibirica* is produced at industrial scale in Russia (Raldugin et al. 1984). Therefore, its extractives have been much studied. The publications are, however, written in Russian and they are not easily available (cf. Lisina et al. 1967c, Shmidt et al. 1970).

Kashtanova et al. (1967) were the first to isolate lambertianic acid from oleoresin of *P. sibirica*. This acid had previously been isolated from *P. lambertiana* (Dauben & German 1966). Later, lambertianic acid has been found in high concentrations in several pine species belonging to subsection *Strobus*.

Another Russian group (Lisina et al. 1972) studied the less abundant diterpene hydroxy acids in *P. sibirica*. They started with 6.5 kg oleoresin and managed to isolate 0.6 g isocupressic acid, 0.9 g *trans*-sciadopic acid and an unknown amount of pinusolic acid (labda-8(20),13-dien-16,15-olid-19-oic acid). They claim that isocupressic acid is a precursor of *trans*-

sciadopic acid, which in turn is a precursor of pinusolic acid and lambertianic acid.

There are two Chinese publications (Song et al. 1995, Song 1998, p. 94) about resin acids in the oleoresin of *P. sibirica* (Loud.) Mayr., which most likely is synonymous with *P. sibirica* Du Tour. The concentrations presented in these two studies are identical. The composition of their oleoresin resembles the sapwood of this thesis more than the heartwood. They found 25% lambertianic acid, and compared to this thesis they found a bit less isopimaric acid, more abietic and neoabietic acid, and traces of communic acid.

Pinus strobus

The stemwood of *P. strobus* contained the highest total concentration of resin acids of all species in this study, 3–6% in the heartwood and 0.6% in the sapwood. The total concentrations in the knots were below the average level of the pines, it was 4.0–4.6% in the living knots and 5.6–12% in the dead knots. Abietic and isopimaric acid dominated. High contents of anticopalic[42], neoabietic and palustric acid, as well as low proportions of levopimaric, dehydroabietic and sandaracopimaric acid were found. Only traces of pimaric acid were detected. This seems to be a feature that unites the pines of section *Quinquefoliae*.

P. strobus was the only species in this study which contained anticopalic acid. This is the first study where palustric and levopimaric acid were separated.

Santamour (1967) analysed the resin in wood of *P. strobus*. His resin acid composition resembled the sapwood's in this thesis. He did, however, make a mistake in the identification. He claimed that he found 12% elliotinoic acid (i.e. communic acid), when he in fact had found anticopalic acid.

Joye and Lawrence (1967) found communic acid in the oleoresin. They did not either find any anticopalic acid, but their abietic acid percentage was exceptionally high, so most likely the two compounds overlapped.

Zinkel and Spalding (1972) where the first to identify anticopalic acid in *P. strobus*. They discovered that it constituted 14–19% of the resin acids in sapwood and 61–96% of the resin acids in the needles.

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[42] Anticopalic acid was first identified in *P. monticola* and it is an enatiomer to copalic acid, which has been found in several members of the legume family (Zinkel et al. 1971).

Paraquat[43] is a pyridinium herbicide that is known to induce lightwood, i.e. to cause oleoresin-soaking of the stemwood. Conner et al. (1980c) studied whether paraquat treatment improves the yield and quality of tall oil. They found that paraquat stimulates the production of neutral and acidic diterpenes, while the sterol concentration remains unchanged. The composition of resin acids remained unchanged when the total concentration increased. Conner et al. (1980c) found 0.7% resin acids in the heartwood and 0.3% in the sapwood. It seems a bit odd that the concentrations differ that much; In this thesis six times more resin acids were found in the heartwood and twice as much in the sapwood. Their samples were fully 70 years old, so the difference is not due to too young heartwood. The trees were also growing under fairly similar conditions, so that explanation is also excluded. The composition of resin acids is, however, quite similar, they found somewhat less neoabietic acid and instead more abietic acid.

Bol'shakova et al. (1987, 1988b) studied the resin acid composition of the oleoresin and they found the same distribution as reported in this thesis. Additionally, they found traces of sclareolic acid.

Song (1998, p. 96) studied oleoresin and, once again, he presented a totally different resin acid composition. He did not find any anticopalic acid, but he claimed that 22% of his resin acids were lambertianic and 5% were communic acid. These acids have not been found by anyone else, except by Santamour (1967), who confused anticopalic acid and communic acid. If only acids of abietane and pimarane type are taken into consideration, the composition reported by Song (1998) resembles that of Joye and Lawrence (1967). It does, however, seem likely that Song (1998) mixed up some species or data.

Pinus sylvestris

The resin acid concentrations in *P. sylvestris* were 1.6–2.2% in the heartwood, 0.2% in the sapwood, 16–21% in the living knots and 18–19% in the dead knots. Abietic acid dominated in the heartwood and the knots, while levopimaric acid dominated in the sapwood. The same feature was observed in *P. banksiana*. Other major components in *P. sylvestris* were neoabietic and palustric acid. The heartwood and the dead knots contained dehydroabietic acid. Smaller parts of the three pimarane-type acids were also found.

[43] Paraquat is one of the most used herbicides in the world, but it was banned in EU in 2007 since it is harmful to human health (Court of First Instance of the European Communities 2007).

P. sylvestris is growing in northern Eurasia and is extensively used for pulp and tall oil production. Therefore, there are a countless number of publications about its resin acids. They describe the amount and/or the composition of resin acids in wood or oleoresin in trees e.g. from Finland (Holmbom & Ekman 1978), Sweden (Assarsson & Åkerlund 1966), Turkey (Yildirim & Holmbom 1978b, Lange & Weiβmann 1988), China (Song 1998, p. 98–102), Mongolia (Bardyshev et al. 1969), Yugoslavia (Lange & Janežić 1993), Bulgarian (Bardyshev et al. 1970c), Germany, Scotland and Spain (Lange & Weiβmann 1988). There are some variations in their data, but broadly they present the same composition pattern as described in Figure 35.

Pinus taeda

Pinus taeda is a main commercial pine species of south-eastern United States (Zinkel 1975). The heartwood contained 2.4% resin acids, the sapwood 0.2%, the living knots 0.2–5.2% and the dead knots 0.2–11%. About 90% of these acids were of abietane type, which is the highest percentage of all studied pines. Abietic acid dominated in all samples, except in the sapwood, where dehydroabietic acid was predominant. High contents of all abietane-type acids were found, as well as a significantly much lower content of all three pimarane-type acids. The knots contained traces of isocupressic acid. This acid was found also in *P. contorta* and *P. elliottii*.

There are five publications on the composition of resin acids in wood and oleoresin of *P. taeda* (Joye & Lawrence 1967[44], Hodges & Lorio 1975[45], Zinkel 1975[46], Panda & Panda 1986, Song 1998, p. 105–106) and they all show the same distribution pattern. The pattern is very similar to the sapwood composition in this thesis, with the exception that they found levopimaric acid instead of dehydroabietic acid, which indicated that their

[44] The oldest study (Joye & Lawrence 1967) compared the resin acid composition in oleoresin and rosin. They found that the oleoresin contained mainly levopimaric + palustric acid (the peaks overlapped) whereas it had turned into abietic acid in the rosin, probably as a result of the heat treatment during removal on volatile terpenes.

[45] Hodges and Lorio (1975) studied the effect of moisture stress on xylem oleoresin. It is known that moisture stress increases the susceptibility to the southern pine beetle, *Dendroctonus frontalis* Zimm, so they examined whether the stress caused some kind of change in the oleoresin that could explain the susceptibility. They found that the percentage of resin acids in the oleoresin decreased due to the drought. They could, however, not detect any change in resin acid composition. Therefore, they concluded that lower resin acid content simply implied lower physical resistance for the beetle to overcome.

[46] Zinkel (1975) studied the changes that occur in extractives when tall oil is produced, but he also paid attention to artefacts that are formed during extraction and the following component separation.

samples were fresher. Another minor difference is that Song (1998, p. 105–106) found only traces of pimaric acid, a compound that was present in 6–8% in all other studies. Zinkel (1975) found indications of trace amounts of communic acid, but he had problems in analysing it. Therefore, he concluded that the compound was readily polymerized inside the GC column and suffered from serious on-column losses. Song (1998, p. 105–106) also found communic acid. He claimed that 3% of the resin acids were communic acid. Unfortunately, no traces of communic acid were found in the wood of *P. taeda* analysed in this thesis.

Pinus wallichiana

Only knots were analysed of *P. wallichiana,* and the resin acid concentration was very low, only 1.4%. Abietic acid dominated, closely followed by isopimaric and lambertianic acid. Small parts of neoabietic, palustric, dehydroabietic and sandaracopimaric acid, as well as traces of Levopimaric and isocupressic acid were found. Like all other studied pine species from section *Quinquefoliae, P. wallichiana* lacked pimaric acid.

Coppen et al. (1988) studied the composition of xylem resin. They were unable to separate palustric and levopimaric acid, but otherwise their results were identical with the results presented in this thesis. It, therefore, seems plausible to assume that the composition of resin acids in stemwood and knots is equal. In their article Coppen et al. (1988) mention that *P. wallichiana* is growing at high altitudes (1800–3700 m above sea level) and, therefore, is unsuitable for commercial use.

Panda and Panda (1986) analysed oleoresin from *P. griffithii* McClelland, which is synonymous with *P. wallichiana*. They found significantly larger proportions of levopimaric + palustic acid, a bit more neoabietic acid, less isopimaric and no lambertianic acid at all.

Song et al. (1995) also studied the chemical composition of oleoresin from *P. griffithii*. Their resin acid composition was similar to the one in this thesis, except they claimed that 3% of the resin acids were communic acid. No communic acid was detected in this thesis.

Picea and *Pseudotsuga*

There were significant differences, both in total concentration and in composition of resin acids between different species of genus *Pinus*. No such differences were, however, observed within genus *Picea*; both the total amount of resin acids and the proportions of individual resin acids were roughly the same within and between the species. Furthermore, the resin canals are more evenly distributed throughout the stemwood of genus *Picea* than of *Pinus*. Therefore, no significant difference in the total resin acid concentration between the heartwood and the sapwood was observed. The

heartwood contained 0.05–0.2% resin acids and the sapwood 0.02–0.3% (Figure 36).

Several publications report that there are more resin acids in the sapwood than in the heartwood of *Picea abies* (Ekman 1979a, Ekman et al. 1979, Willför et al. 2005b), but the opposite has also been reported (Willför et al. 2003a). The sapwood samples of *P. abies*, *P. glauca*, *P. koraiensis* and *P. mariana* contained more resin acids than the heartwood, while the opposite was true for *P. omorika*, *P. pungens* and *P. sitchensis*. The differences were, however, generally small.

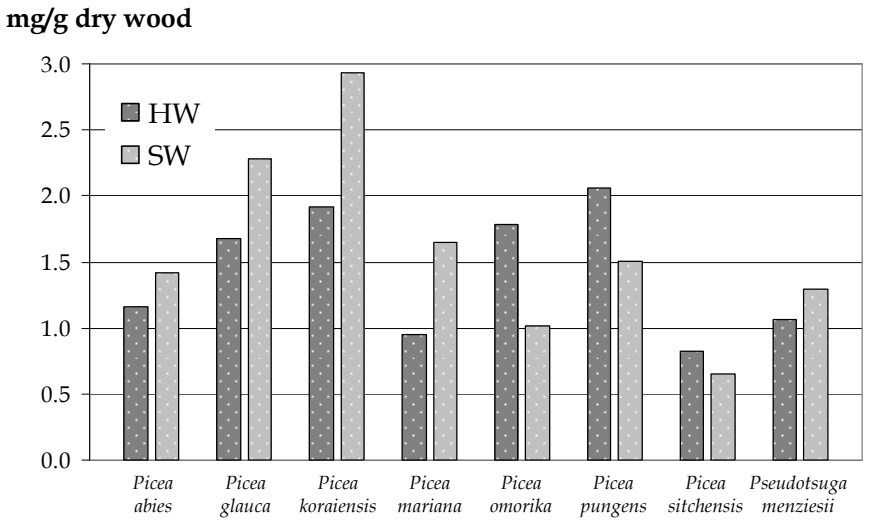

Figure 36 Total average concentration of resin acids in stemwood of genera Picea and Pseudotsuga (HW=heartwood, SW=sapwood).

The resin acid concentrations in the knots were on the same level as in the stemwood. The living knots contained less than 0.01% resin acids and the dead knots less than 0.02%, i.e. there was a weak trend towards more resin acids in the dead knots (Figure 37). The only exceptions were the small bore samples of *P. omorika*, were the living knots contained four times more resin acids compared to the dead.

Some of the knots contained significantly higher resin acid concentrations compared to the rest. These samples were: the dead knots from the French sample of *P. abies* (0.4% resin acids), the dead knots of *P. mariana* (0.9% and 1.4%, respectively), the knots of *P. omorika* (2.5% and 0.6%, respectively), the pooled dead knots from one tree of *P. sitchensis* (0.5%) and two of the nine dead knots of *P. pungens* (0.8% and 1.0%, respectively).

Resin acids in knots of genus *Picea* have previously only been studied in *P. abies*, not in any other species. Willför et al. (2003a) made similar

observations in *P. abies* as was seen in these *Picea* samples. They found that the knots in general contained less resin acids than the stemwood, the dead knots contained more resin acids than the living knots and that five of their fifteen dead knots contained exceptionally much, close to 2% resin acids.

At first, these aberrant dead knots might seem to be freaks of nature, but actually they all have something in common, they are all so-called loose knots[47] that are embedded in the stem! The death and pruning of spruce branches is a very slow process. It takes decades for the branch to piecemeal break, and during that time the knot shrinks and a protective resin layer is slowly formed around it. Only thereafter the surrounding stemwood grows over and covers the dead knot.

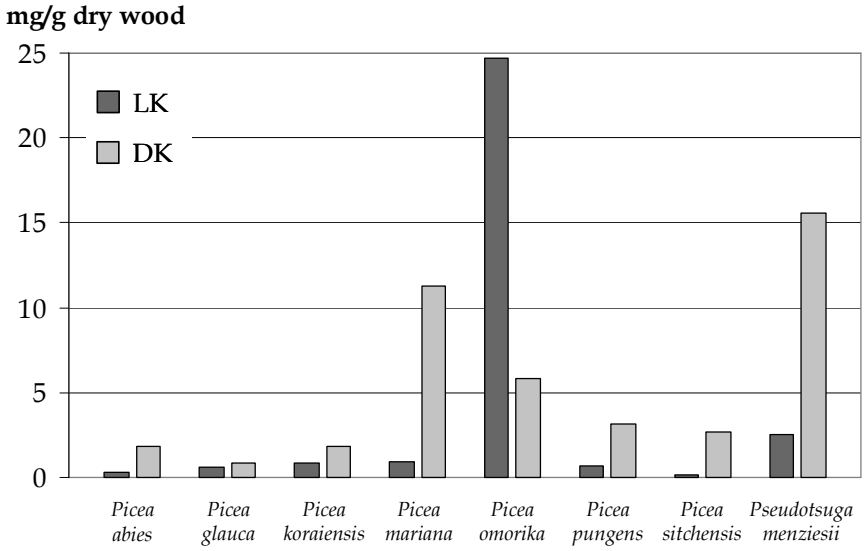

Figure 37 Total average concentration of resin acids in knots of genera Picea and Pseudotsuga (LK=living knots, DK=dead knots).

The dead knots with lower resin acid content were also physiologically dead, i.e. their branches had lost all their needles, but these knots had not yet been occluded. Hence, the observed difference in resin acid concentration could function as an indicator of how long ago the outer branch died. No analogous trends were observed for the dead knots of

[47] Loose knots are one of the most detrimental quality defects in timber; they influence both strength properties and visual appearance of wood and veneer. These ingrown knots are more common in the lower part of the stem, i.e. the part that normally goes to sawmills. The pulp mill receives the upper parts of the stem (the part with living branches and dead, not yet ingrown knots) and from the sawmill it obtains sawdust and the outer part of the stem, i.e. the sapwood. Thus, the resin acid content of knots is a more severe problem in sawmills than in pulp production.

genus *Pinus*, because the resin acid content in pine increases already when the sapwood is transformed into heartwood, i.e. long before the branch starts to die.

There were no striking differences between the resin acid compositions in the different *Picea* species (Figure 38). Between 72% and 86% of the acids were of abietane type. The remaining ones were of pimarane type. No labdane-type acids were detected. Dehydroabietic acid was the most abundant abietane-type acids. Significant proportions of palustric, levopimaric and abietic acid were also found. Isopimaric acid was the most abundant acid of pimarane type. Sandaracopimaric acid was more abundant than pimaric acid. The knots of *P. koraiensis* and *P. omorika* contained very small proportions of pimaric acid. The bore samples of heartwood, living and dead knots of *P. koraiensis* seemed to have been isomerized, because they contained extraordinarily much dehydroabietic acid and very small proportions of abietic, neoabietic, palustric and levopimaric acid.

The total concentration of resin acids in the stemwood of *Pseudotsuga menziesii* was in the same range as in genus *Picea*; 0.1% resin acids was found in both heartwood and sapwood (Figure 36). The knots contained more resin acids than the stemwood; the living knots contained 0.2% and the dead knots over 1.5% (Figure 37). About 75% of the resin acids were of abietane type, the rest of pimarane type (Figure 38). Palustric acid was the dominating acid followed by isopimaric acid, and significant proportions of abietic, neoabietic, levopimaric and dehydroabietic acid. Low concentrations of sandaraco-pimaric acid were also found, but no pimaric acid was detected.

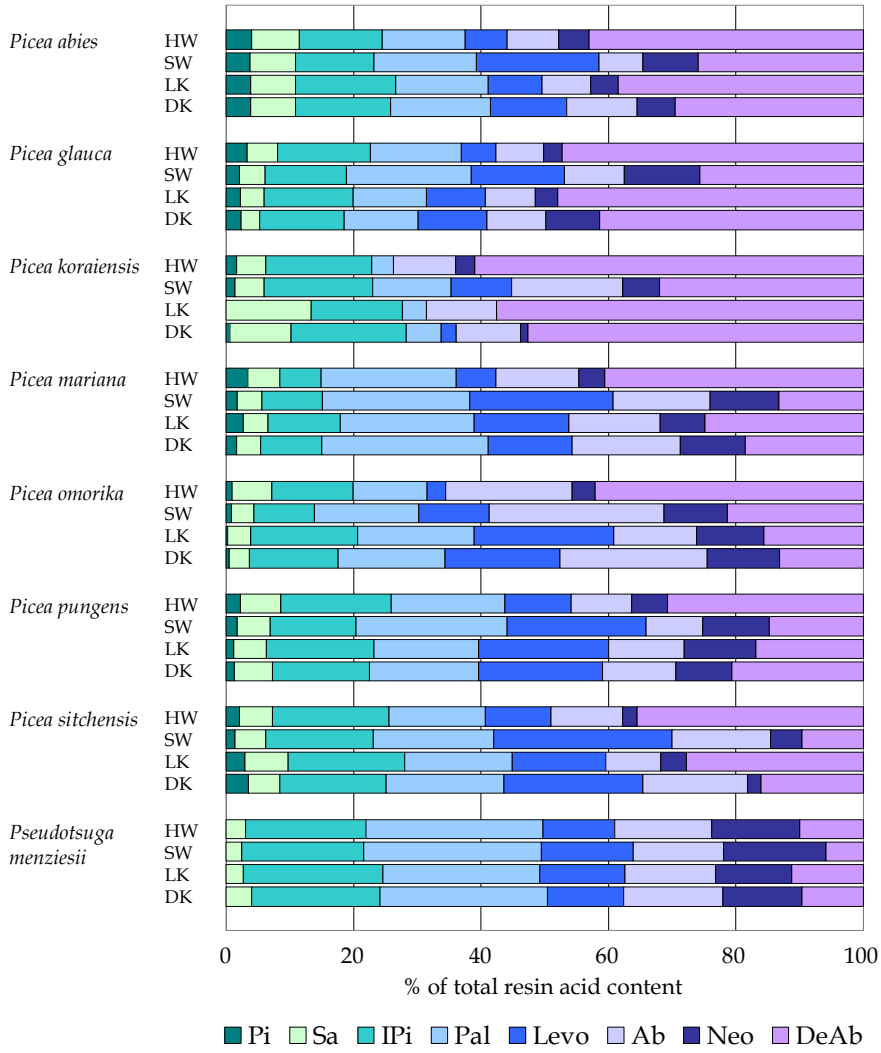

Figure 38 Composition of resin acids in genera Picea and Pseudotsuga in percent of the total resin acid content (HW=heartwood, SW=sapwood, LK=living knots, DK=dead knots). The resin acids of pimarane type are in green and of abietane type in blue. The complete names of the resin acids are found in the list of abbreviations.

Picea abies

The heartwood of *P. abies* contained 0.05–0.2% resin acids, the sapwood 0.06–0.2%, the living knots 0.02–0.05% and the dead knots 0.02–0.4%. This finding was supported by Bergström (1956), and Assarson and Åkerlund (1966) who also found 0.2% resin acids in the stem. Dehydroabietic acid was the predominating resin acid. Additionally, significant proportions of isopimaric acid, palustric acid and levopimaric

acid were found, as well as lower amounts of abietic, neoabietic, sandaracopimaric and pimaric acid (Figure 38).

Since *Picea abies* is an industrially important species, its resin acids have been thoroughly studied. Kahila (1957a) was one of the first to study the composition of gum oleoresin. Unfortunately, some of the resin acids known today were unidentified at that point, so his distribution was a bit distorted. Bruun and Gåsland (1960, p. 73) included palustric acid in their study and did, therefore, give a more accurate picture of the distribution. Proportionally they found more levopimaric and less dehydroabietic acid than reported here. They were, however, not able to separate pimaric and isopimaric acid, nor had sandaracopimaric acid been identified yet.

Bardyshev et al. (1970a) analysed balsam from more than 50 trees growing in the Soviet Union. This was the first publication where all resin acids known today were included. Their distribution was similar to the one reported in this thesis, except that they found more levopimaric acid and less dehydroabietic acid. The study by Kimland and Norin (1972) was less detailed and accurate than the Soviet study published two years earlier. They did, however, find resin acid methyl esters, which previously had been found only in the oleoresin of *Pseudotsuga menziesii* (Erdtman et al. 1968) and in spruce bark (Norin & Winell 1972). Kimland and Norin (1972) pointed out that the distribution of resin acids in the free and the esterified groups were different; the abietane-type acids dominated among the free acids, while the pimarane type dominated among the esterified acids.

Holmbom and Ekman (1978) made a detailed study on tall oil precursors in *Pinus sylvestris* and *Picea abies*. They found exactly the same distribution pattern as reported here, and they emphasized an important aspect - rosin from spruce contains less conjugated abietane-type acids than rosin from pine. Therefore, the losses during tall oil distillation are lower, but the obtained TOR is less suitable for products like paper size and resin acid dimers.

Ekman (1979a) was the first to analyse resin acids in heartwood and sapwood separately. He found more resin acids in the sapwood than in the heartwood, and his composition was very similar to the values reported in this thesis. Ekman (1979a) pointed out that levopimaric acid was most abundant in the sapwood, while dehydroabietic acid was most abundant in the heartwood. In a later publication Ekman et al. (1979) stated that the proportion of dehydroabietic acid increased with increasing age of tissue. They also found that the sapwood in higher parts of the stem contained slightly more resin acids than in the lower parts, and that the sapwood

contained slightly less resin acids during the summer months[48]. Ekman (1979a) found minor amounts, less than 0.005%, of the corresponding resin acid methyl esters.

One of the latest analyses of resin acids in wood of *P. abies* was done by Martin et al. (2002). They found significantly much more levopimaric acid than earlier studies; almost 40% of all their resin acids was levopimaric acid. The reason could be that their samples were very young or that they immediately froze the samples in liquid nitrogen and stored at them -80 °C, or then it was a combination of both.

The only publications on resin acids in *P. abies* knots are written by Willför et al. (2003a, 2005b). They found that the dominating resin acid varied between the dead knots. Dehydroabietic acid dominated in some knots, levopimaric acid in some, and levopimaric, palustric + isopimaric were most abundant in some (Willför et al. 2003a). Willför et al. (2005b) also separated the sapwood and the heartwood of living knots. There they found that the resin acid content in both heartwood and sapwood of the living knot was equal to that of the heartwood in the stem.

Picea glauca

The stemwood of *Picea glauca* contained more resin acids than the knots; 0.2% was found in the heartwood, 0.2–0.3% in the sapwood, 0.05–0.07% in the living knots and 0.08% in the dead knots. Previously Rogers et al. (1969) found 0.1% resin acids in the wood, while Conner et al. (1980b) found 0.3%. Dehydroabietic acid was the predominant resin acid, followed by palustric and isopimaric acid. Smaller proportions of abietic, neoabietic, levopimaric, pimaric and sandaracopimaric acid were also found. The composition presented by Conner et al. (1980b) for their whole wood was a combination of the composition of the heartwood and sapwood samples reported here.

Tomlin et al. (2000) studied the resistance of 331 trees to attack by pine weevil (*Pissodes strobi* Peck.). They found significantly much more resin acids in the xylem of resistant than in susceptible trees. They found more abietic acid, less dehydroabietic acid and no pimaric acid compared to the resin acid composition of this thesis.

Picea koraiensis

The stemwood of *P. koraiensis* was fairly resin acid rich. The heartwood contained 0.2% resin acids, the sapwood 0.3%, the living knot 0.09% and the dead knot 0.2%.

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[48] The hypothesis that the resin acid content decreases during early summer was proposed already by Swan (1968).

Dehydroabietic acid constituted more than half of all resin acids, so probably these bore samples had been oxidized. Other major resin acids were isopimaric and abietic acid, and in the knots also sandaracopimaric acid. Small proportions of pimaric, palustric and neoabietic acid were also detected.

Shmidt et al. (1978) identified the resin acids in Russian *P. koraiensis*. Their distribution was identical to the sapwood composition in this thesis, except that they did not separate levopimaric acid from palustric acid and proportionally they found more isopimaric acid.

Picea mariana

The heartwood of *Picea mariana* contained 0.1% resin acids, the sapwood 0.1–0.2%, the living knots 0.09% and the dead knots 0.9–1.4%. Wise and Moore (1945) extracted wood of seasoned *P. mariana* and they found 0.2% resin acids, which was well in accordance with the results presented here. Conner et al. (1980b) analysed heartwood and sapwood of *P. mariana* separately and found 0.2% and 0.5% resin acids, respectively, which was a bit more than reported here.

Palustric and dehydroabietic acid were the dominating resin acids in this thesis, but isopimaric acid and abietic were also important. The sapwood contained proportionally more levopimaric acid than the other samples. Some pimaric, sandaracopimaric and neoabietic acid were also detected.

Conner et al. (1980b) found the same resin acid composition in their heartwood and sapwood. It seems, though, like their samples were oxidized, because they had a lower proportion of abietic, neoabietic, palustric and levopimaric, and a higher proportion of dehydroabietic acid.

Picea omorika

Picea omorika is not industrially important and has therefore not been studied before. Here only bore samples were analysed and the resin acid concentration in the samples of living knots were exceptionally high and should be looked upon with some scepticism.

The heartwood contained 0.2% resin acids, the sapwood 0.1%, the living knots 2.5% and the dead knot 0.6%. Dehydroabietic, abietic, palustric and isopimaric acid were dominating. Additional large proportions of levopimaric acid were found in the knots. Some neoabietic and sandaracopimaric acid, as well as traces of pimaric acid were also found.

Picea pungens

This is the only study so far on resin acids in *Picea pungens*. The heartwood contained 0.2–0.3% resin acids, the sapwood 0.02–0.3% and the

living knots 0.05–0.09%. Seven of the dead knots contained 0.04–0.1% resin acids, while the two remaining contained 0.9% and 1.4% respectively. These resin-rich knots had been dead for a longer time than the other ones, and they were on their way to be over grown by the surrounding stemwood.

Isopimaric, palustric, levopimaric and dehydroabietic acid were the most prominent resin acids. Some abietic and neoabietic acid were also found along with minor proportions of sandaracopimaric and pimaric acid.

Picea sitchensis

The wood of *Picea sitchensis* contained least resin acids of all other spruce species in this study. The heartwood concentration was 0.07–0.09%, the sapwood 0.06–0.07% and the living knots contained less than 0.03% resin acids. The dead knots were divided into two groups, one containing only 0.01% resin acids and the other containing more than 0.5%. Dehydroabietic acid was the most abundant resin acid, followed by isopimaric acid, palustric, levopimaric and abietic acid. Small proportions of neoabietic, pimaric and sandaracopimaric acid were also found.

The only study so far on resin acids in *P. sitchensis* was made on cortical resin (Tomlin et al. 1996) and that composition is fairly different compared to that of the xylem. It will, therefore, not be any further commented.

Pseudotsuga menziesii

The total amount of resin acids in *Pseudotsuga menziesii* was of the same magnitude as in genera *Picea* and *Larix*. The stemwood (Figure 36) contained 0.1% resin acids and the living knots 0.2–0.3% (Figure 37). Compared to that, significantly much more resin acids were found in dead knots, 1.2–1.9%. Palustric acid was the most abundant resin acid (Figure 38), followed by isopimaric, abietic, neoabietic, levopimaric, dehydroabietic and sandaracopimaric acid in decreasing order.

Erdtman et al. (1968) studied pocket resin of *P. menziesii.* The resin acid composition of that resin was identical to the composition of the sapwood studied in this thesis (under the assumption that their unidentified resin acid was sandaracopimaric acid). Erdtman et al. (1968) also reported considerable amounts of resin acid methyl esters. They claimed that 3.6% of all pocket resin was resin acid methyl esters. No resin acid methyl esters were detected in the samples studied in this thesis.

Rogers et al. (1969) compared the interior and coastal varieties of *P. menziesii*. They found that the interior variety contained ten times more resin acids than the coastal variety, 0.5% and 0.05%, respectively. The tree in this thesis had grown in Solböle, Finland, but the seeds originated from Louis Creek in British Columbia, i.e. they were of the interior, more resin-rich variety.

Foster et al. (1980) found that the heartwood of *P. menziesii* contained 0.27% resin acids and the sapwood a bit less, 0.2%. Their resin acid composition was similar to this thesis, but they found more isopimaric acid, less levopimaric acid and small amounts of an unidentified compound.

Larix

As it appears in Figure 39, there were no striking differences between the total resin acid concentrations in heartwood and sapwood of genus *Larix*, except in *L. lariciana*, where the sapwood concentration was tree times higher than the heartwood concentration. In the stemwood, the resin acid concentration was 0.07–0.2% and in the knots 0.02–0.4%. The dead knots of *L. decidua*, *L. kaempferi* and the living knot of *L. sibirica* were richest in resin acids. This is the first study ever on resin acids in knots of genus *Larix*.

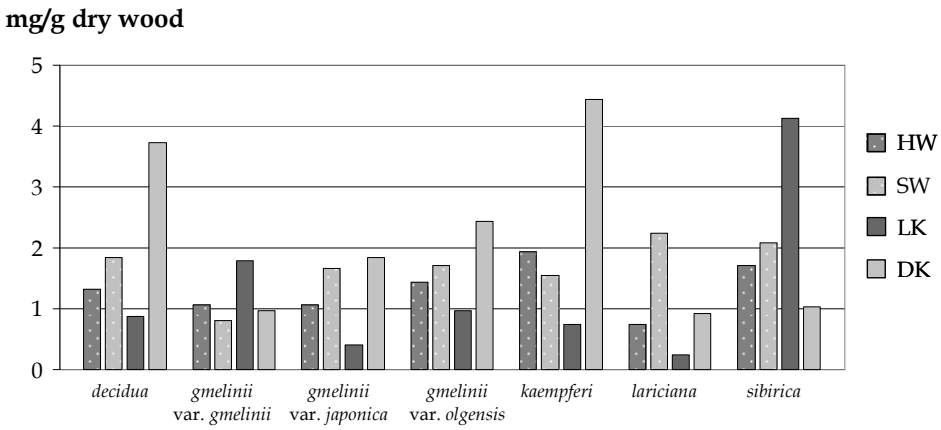

Figure 39 Total average concentration of resin acids in stemwood and knots of genus Larix (HW=heartwood, SW=sapwood, LK=living knots, DK=dead knots).

The composition of individual resin acids can be seen in Figure 40. The abietane-type acids constituted 39–53% of all resin acids, the pimarane-type 35–56% and the labdane-type 1–14%. Remarkable was that genus *Larix* contained a much larger proportion of pimarane-type acids than the other studied genera. The dominating resin acid in all species was isopimaric acid 33–53%, and like its closest relative *Pseudotsuga*, this genus also lacked pimaric acid. *P. menziesii* did, however, totally lack labdane-type acids, a resin acid type found in all *Larix* species.

Communic acid was found in all species. The proportions in the varieties of *L. gmelinii* were, however, much lower than in the rest of the larches, 1–2% and 3–13%, respectively. Furthermore, cupressic acid was found in *L. kaempferi* and *L. lariciana*. This labdane-type acid has previously been isolated from the Mediterranean cypress *Cupressus sempervirens* L.

(Mangoni & Belardini 1964). Mills (1973) identified epitorulosic acid in several larch species, and the structure of epitorulosic acid was identical to that of epicupressic acid. The two epimers were, however, not identified in this work and therefore, the name cupressic acid is used for the sum of the both epimers.

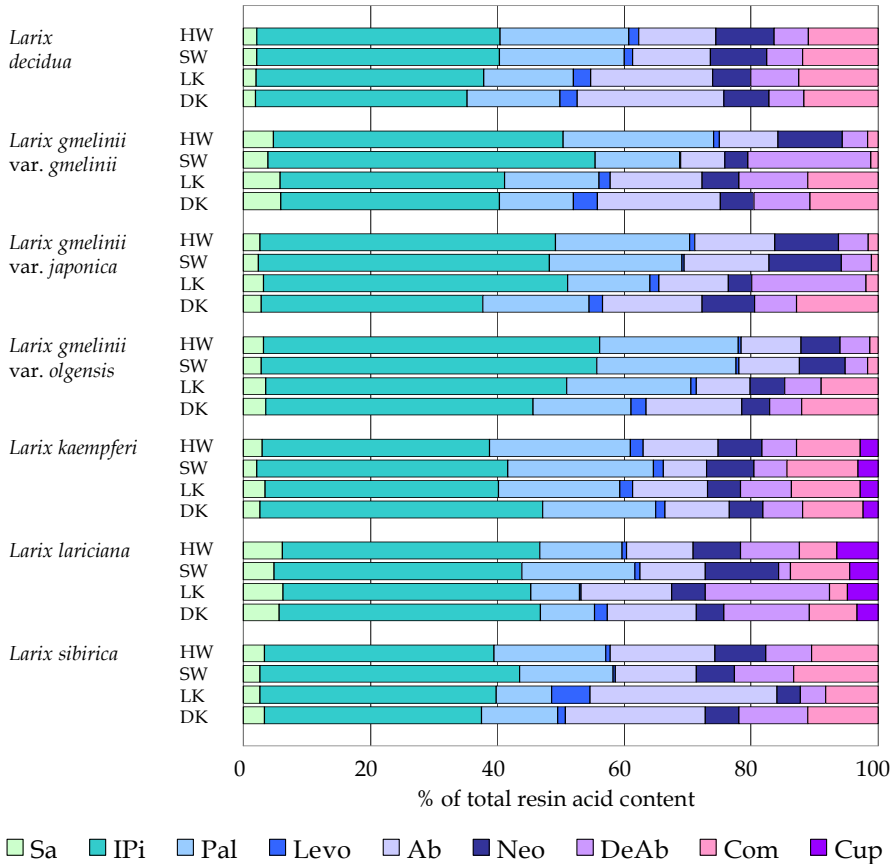

Figure 40 Composition of resin acids in genus Larix in percent of the total resin acid content (HW=heartwood, SW=sapwood, LK=living knots, DK=dead knots). The resin acids of pimarane type are in green, of abietane type in blue, and of labdane type in pink/purple. The complete names of the resin acids are found in the list of abbreviations.

Larix decidua

The stemwood of *Larix decidua* contained 0.1–0.3% resin acids. The concentration in the knots varied from 0.02% to 1.3%. Generally, the living knots contained less resin acid than the dead. Isopimaric acid was the dominating resin acid and it constituted 38% of all resin acids. The second most abundant resin acid was palustric acid, and it was followed by equal proportions of abietic, neoabietic and communic acid. Two isomers of communic acid were found in *L. decidua*. Normally, the later eluting peak

dominates, but in this species, the earlier eluting isomer was predominant. Small proportions of levopimaric, dehydroabietic and sandaracopimaric acid were also found.

Mills (1973) was first out to study the resin acids in oleoresin of *L. decidua*[49]. He compared samples from fourteen trees with a commercial bulk sample. His compositions resembled this thesis, but he did not find any communic acid, instead he reported a larger proportion of abietic acid and traces of pimaric acid.

Later, a research team from the Soviet Union (Bol'shakova et al. 1987) studied the oleoresin from trees growing in Transcarpathia (today's western Ukraine). They did not find any communic acid, but otherwise their resin acid composition is exactly similar to this thesis.

Holmbom et al. (2008) studied callus resin of *L. decidua* and compared it to normal oleoresin. The composition of their oleoresin differed a bit from the one reported here, but it was very close to that reported by Mills (1973). Holmbom et al. (2008) found low amounts of pimaric acid and lacked communic acid. The callus resin was almost resin acid free and its composition was very different from the oleoresin. The interested reader can find more information about callus resin in the article by Holmbom et al. (2008).

Larix gmelinii var. *gmelinii*

The stemwood of *Larix gmelinii* var. *gmelinii* contained 0.1% resin acid and the knots 0.03–0.2%. Isopimaric acid was the domination compound, but large proportions of palustric, abietic, dehydroabietic and communic acid, as well as some sandaracopimaric, levopimaric and neoabietic acid were also found. The percentage of communic acid was clearly higher in the knots than in the stemwood. Both of the sapwood samples contained less palustric and more dehydroabietic acid than expected. On the other hand, it was well in agreement with what Mills (1973) found. He studied four resin samples of *L. gmelinii* and the resin acid concentrations were presented as an average values for all of them. Unfortunately, only two of his samples were of var. *gmelinii*. The third sample was of var. *japonica* (Regel) Pilger and the forth of var. *principis-rupprechtii* (Mayr) Pilger. All these variants of *L. gmelinii* are, however, fairly similar, so it should not

[49] *Larix* oleoresin is tapped from the heartwood by boring, not trough the normal way of scarifying the sapwood (Mills 1973).The volatile part of oleoresin from *L. decidua* is called Venice turpentine. It is used for lithographic work, in sealing wax and varnishes. It is also highly appreciated for use in oil paintings since it maintains high gloss and brilliance, and doesn't turn yellow over time.

influence the results significantly. It should though be mentioned that Mills (1973) found more abietic acid and no communic acid at all.

Shmidt and Pentegova (1974) studied soft resin of *Larix dahurica* Turcz., which is a synonym of *L. gmelinii* var. *gmelinii*. It was a qualitative, not quantitative, study where they identified isopimaric, palustric, abietic, dihydroabietic, neoabietic and *cis*-communic acid. Shmidt and Pentegova (1974) claimed that *L. gmelinii* was similar to *L. decidua* (called *L. europea*), and that it strongly differed from *L. sibirica.* No similar trends were found in this work.

Bol'shakova et al. (1980) studied oleoresin from *Larix cajaderi* M.[50] growing in Kamchatka. They found isopimaric acid to be the dominating resin acid. It constituted 45% of all resin acids, which is well in agreement with the results of this thesis. They did, however, find significantly much more abietic acid, and they did not find any communic acid. Bardyshev et al. (1980) also found a high percentage of abietic acid in oleoresin from *Larix dahurica* Turcz, but they did not find any communic acid. They did, however, find some pimaric acid, which wasn't detected in any of the *Larix* samples in this thesis. Later, Bol'shakova et al. (1986) also identified low amounts of cupressic acid in Kamchatka larch. Cupressic acid was not found in any variety of *L. gmelinii* studied in this thesis.

Larix gmelinii var. *japonica*

The heartwood of *Larix gmelinii* var. *japonica* contained 0.05–0.2% resin acids, the sapwood 0.08–0.3%, the living knots 0.02–0.06% and the dead knots 0.03–0.3%. Also here isopimaric acid dominated, followed by palustric, abietic and neoabietic acid. Low proportions of levopimaric, dehydroabietic, sandaracopimaric and communic acid were found.

Bol'shakova et al. (1985a) studied "*Larix kamtschatica* (Rupr.) var. *kurilensis* (Kamchatkan or Kurile Dahurian larch)". This name is a bit contradictory, because both Kamchatkan and Dahurian larch is *L. gmelinii* var. *gmelinii,* while Kurile larch is *L. gmelinii* var. *japonica*. Since Bol'shakova et al. have emphasized that this is the Kurile variety, it was concluded that they had studied *L. gmelinii* var. *japonica*. Anyhow, as showed in Figure 40, the differences between the two varieties were quite small. The resin acid composition described by Bol'shakova et al. (1985a) was very similar to the one described in this thesis, but Bol'shakova et al. (1985a) were not able to detect any communic acid.

[50] *Larix cajaderi* Mayr is a synonym of *L. gmelinii* (Rupr.) Kuzen.

Larix gmelinii* var. *olgensis

Both the amount and the composition of resin acids in *L. gmelinii* var. *olgensis* were similar to those of the two other *L. gmelinii* varieties'. The heartwood of var. *gmelinii* contained 0.1% resin acids, the sapwood 0.1–0.2%, the living knots 0.03–0.2 and the dead knots 0.2–0.3%. The dominating resin acid was isopimaric acid and palustric acid, was the second most abundant compound. Lower amounts of abietic, neoabietic, levopimaric, dehydroabietic, sandaracopimaric and communic acid were also detected. There was seven times more communic acid in the knots than in the stemwood.

Khan et al. (1983) compared *L. gmelinii* var. *olgensis* with other larch species and concluded that its resin production was exceptionally low, and that only 42% of the oleoresin consisted of resin acids. Isopimaric acid was their main resin acid, it constituted more than 86% of all resin acids and the other abietane-type acids were present in considerably lower proportions. Khan et al. (1983) did not find any sandaracopimaric or communic acid.

Larix kaempferi

Both the heartwood and the sapwood of *L. kaempferi* contained 0.1–0.2% resin acids. There was, however, a major difference between the living and the dead knots. The living knots contained 0.06–0.1% resin acids, while the dead knots contained 0.3–0.6%. In the case of *L. kaempferi* the trend was quite clear, because thirty knots were analysed and none of the living knots contained more resin acids than any of the dead.

As in the other studied larch species, isopimaric acid was the dominating resin acid. One fourth was palustric acid. Lower proportions of sandaracopimaric, levopimaric, abietic, neoabietic, dehydroabietic, cupressic and communic acid were found. Two isomers of communic acid were detected and the earlier-eluting isomer was more abundant.

Mills (1973) was the first to study resin acids in *L. kaempferi.* He analysed four British oleoresin samples and his composition contained a higher proportion of abietic and dehydroabietic acid, and less palustric acid. He also claimed that he found traces of pimaric acid, but no communic acid. Mills is the only other scientist who has found cupressic acid in *L. kaempferi*, though he called it epitorulosic acid.

Bol'shakova et al. (1985b) studied the terpenoids in oleoresin from *L. leptolepis* (Siebold & Zucc.) Gord., which is synonym to *L. kaempferi*. Their composition contained even more abietic acid than reported by Mills (1973). They also found less palustric acid than reported in this thesis. Their proportion of sandaracopimaric acid, on the other hand, was unnaturally large, and since they didn't report finding any labdane-type

acids one cannot help but wondering if sandaracopimaric acid perhaps overlapped with communic acid.

Genetically *L. gmelinii* var. *japonica* and *L. kaempferi* are the closest related larch species (see cladogram in Appendix B6). Chemically, however, the composition of resin acids showed a distinct qualitative difference: *L. kaempferi* contained cupressic acid, which all three varieties of *L. gmelinii* lacked. Interesting is, though, that cupressic acid was present also in *L. lariciana*, one of the larch species genetically most distantly related to *L. kaempferi.*

Larix lariciana

There was a pronounced difference between the heartwood and the sapwood of *L. lariciana*. The heartwood contained 0.06–0.09% resin acids, while approximately three times more, 0.1–0.3% was found in the sapwood. Very low concentrations were found in the knots, 0.02–0.03% in the living knots and 0.04–0.1% in the dead knots. About 40% of all resin acids were isopimaric acid. It was found along with lower proportions of sandaracopimaric, palustric, abietic, neoabietic, dehydroabietic, communic and cupressic acid. Two isomers of communic acid were detected. The earlier eluting isomer dominated and only traces of the later were detected. Levopimaric was present in trace amounts.

Only one other study has been made on resin acids in *L. lariciana*. Mills (1973) analysed six oleoresin samples, four from cultivated and two from wild trees. The resin acid composition he presented was very similar to this thesis. The only differences were that he detected traces of pimaric acid, did not find any communic acid, and finally, he called cupressic acid epitorulosic acid.

Larix sibirica

The samples of *L. sibirica* were cut at three different Russian locations: Baikal in southern Siberia, Habarovsk in eastern Siberia and the Saint Petersburg region. The only chemical difference between the three geographical areas was that the stemwood from Habarovsk contained less communic acid than wood from the other regions.

The resin acid concentrations in the stemwood of *L. sibirica* were fairly high, from 0.09% to 0.3%. The living knot contained 0.4% resin acids and the dead knots 0.03–0.3% resin acids. Isopimaric acid dominated among the resin acids, but considerable proportions of abietic, palustric and communic acid, some neoabietic, dehydroabietic and sandaracopimaric acid, as well as traces of levopimaric acid were also found.

Mills (1973) studied oleoresin from two trees of *L. russica* (Endl.) Sabine ex Trautv., this is a synonym to *L. sibirica*. He claimed that he found traces

of pimaric acid and something that could have been traces of epitorulosic acid, i.e. cupressic acid. These two compounds were not detected in this thesis. Furthermore, Mills (1973) found only traces of neoabietic and no communic acid in his samples. He did, however, find significantly more sandaracopimaric and isopimaric acid, so perhaps one or both of these peaks overlapped with communic acid?

4.1.2 Fatty acids and acylglycerols

In this work, only free fatty acids, diacylglycerols and triacylglycerols were analysed. These compounds are hereafter collectively named fats. It was decided not to hydrolyze the esterified fatty acids into free fatty acids and hence, the fatty acid composition is given for free fatty acids only, no esterified fatty acids are included. This is a shortcoming, but the work was becoming too extensive, so it was decided that these experiments should be omitted.

The highest total concentrations of fats were found in genus *Pinus*, up to 2.7%. Genera *Picea*, *Abies*, *Larix* and *Pseudotsuga* contained 0.2–0.3% fats and *Tsuga* only 0.05%. The concentrations of fats were higher in the living cells of the sapwood than in the dead heartwood. In the sapwood, most of the fats occurred as triacylglycerols[51]. When parenchyma cells in the tree die, i.e. when heartwood is formed, triacylglycerols are hydrolyzed into free fatty acids. It was, however, found that young heartwood samples (e.g. *P. taeda*) still contained triacylglycerol concentrations close to those in the sapwood.

In the knots, the distribution of free and esterified fatty acids depended on the age of the knot; younger knots contained more triacylglycerols, while older knots contained more free fatty acids. In general, however, the fat composition of the knots resembled that of the heartwood.

Composition of free fatty acids

Oleic (9-18:1) and linoleic (9,12-18:2) acids were most abundant. Other detected free fatty acids were the saturated palmitic (16:0), 14-methylpalmitic (17:0ai), stearic (18:0), arachidic (20:0), behenic (22:0) and lignoceric (24:0) acids, the monounsaturated vaccenic acid (11-18:1) and the polyunsaturated pinolenic (5,9,12-18:3) and sciadonic (5,11,14-20:3) acids.

---

[51] According to the literature there should not be any free fatty acids in the sapwood. If they are detected it is a sign of early cell death, which should be regarded as an indication of degradation by endogenous lipids during the analysis (Bethge & Lindgren 1962, Ekman & Holmbom 2000, p. 13).

Unsaturated free fatty acids dominated in genera *Pinus*, *Picea*, *Larix* and *Pseudotsuga menziesii*, while saturated fatty acids dominated in *Abies* and *Tsuga*. Among the unsaturated acids, mono and dienoic acids were equally abundant in genus *Pinus*. Monoenoic fatty acids were the most abundant in *Pseudotsuga* and *Abies*, whilst dienoic fatty acids were the most abundant in *Picea*, *Larix* and *Tsuga*. Genus *Larix* contained higher proportions of trienoic acids (25%) compared to the other studied genera (7–15%).

When heartwood and sapwood were compared, there was a higher proportion of unsaturated free fatty acids in heartwood than in sapwood of *Pinus*, *Picea*, *Larix* and *Pseudotsuga*, while the opposite (higher proportion of saturated acids in heartwood than in sapwood) was found in *Abies* and *Tsuga.*

There were hardly any differences in fatty acid composition between living and dead knots. Saturated free fatty acids dominated in knots of genus *Abies*. In genus *Tsuga*, the proportions of saturated and unsaturated fatty acids were equal, while unsaturated acids dominated in the other studied genera. When only unsaturated fatty acids were taken into consideration, the monoenoic acids were most abundant in knots of *Pinus*, *Abies* and *Pseudotsuga*, while the dienoic acids dominated in *Picea*, *Larix* and *Tsuga.*

Ekman and Holmbom (2000, p. 47), have shown that *Picea* contains significantly higher proportions of saturated fatty acids than *Pinus* and that the dienoic acids are almost equally abundant in these genera. They did, however, find slightly lower proportion of trienoic acids in genus *Pinus* than in *Picea*. In the present work this statement was true for *Picea abies* and *Pinus sylvestris*, but when more species of each genus were taken into account, the proportions were found to be equal.

When samples of *Picea abies* grown in Finland and France were compared, the Finnish samples contained more unsaturated free fatty acids than the French. This is in accordance with earlier studies, which show that colder temperature yields an increase in the proportion of polyunsaturated fatty acids (Swan 1968, Yildirim & Holmbom 1978b, Fuksman & Komshilov 1979, 1980, 1981, Piispanen & Saranpää 2002). It is believed that the change in lipid composition adjusts the fluidity trough the cell membrane and, thereby, regulates the cell functionality, which makes the organism more frost tolerant (Thompson 1992, pp. 14–16 and 210–211).

Pinus

The heartwood of genus *Pinus* contained 0.09–1.8% free fatty acids, 0.01–0.15% diacylglycerols and 0.01–0.50% triacylglycerols (Figure 41). The concentrations in the sapwood were up to 0.89% free fatty acids, up to 0.17% diacylglycerols and up to 2.8% triacylglycerols. The knots contained

0.01–2.1% free fatty acids, up to 0.59% diacylglycerols and up to 3.0% triacylglycerols.

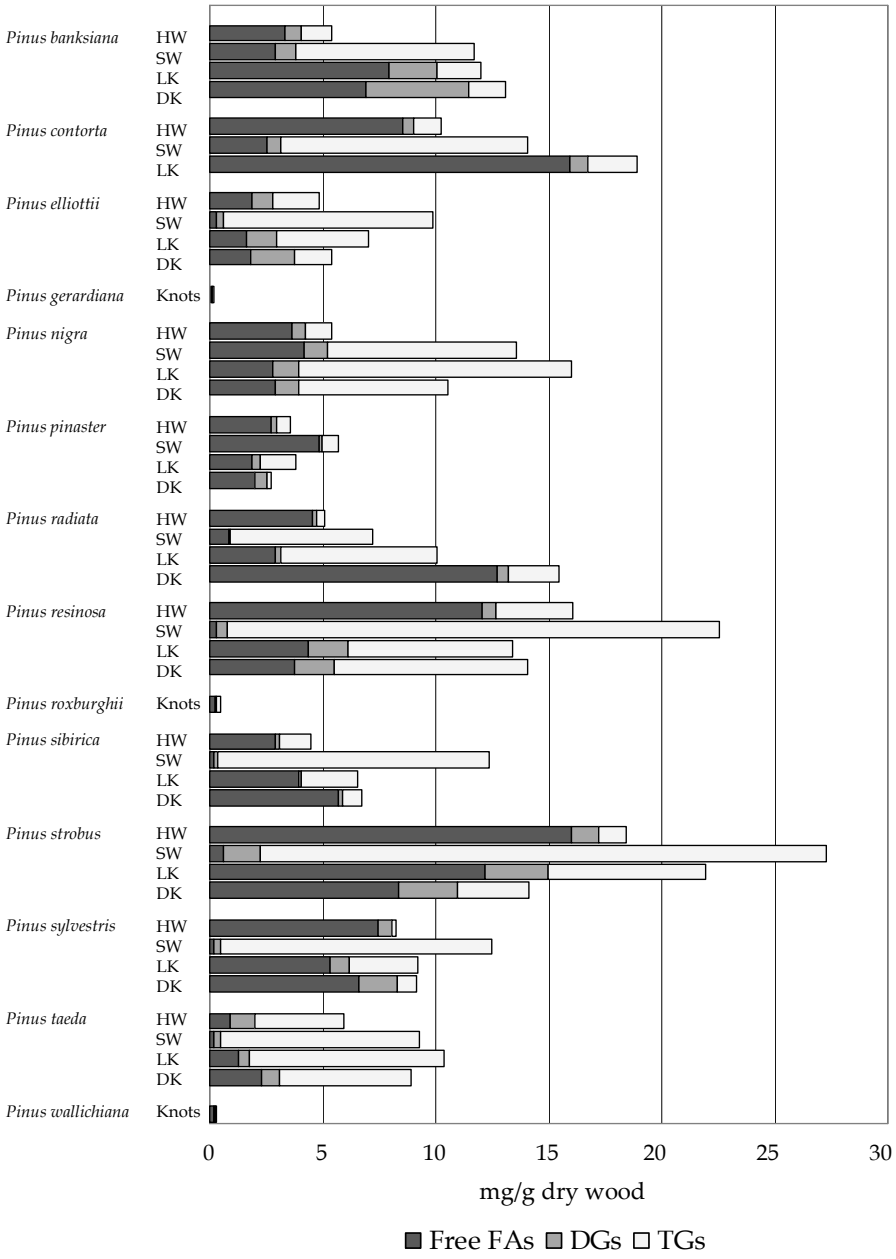

Figure 41 Average concentrations of free fatty acids (Free FAs), diacylglycerols (DGs) and triacylglycerols (TGs) in genus Pinus (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots, knots = mix of living and dead knots).

Earlier it has been suggested that the concentration of free fatty acids either is positively correlated to the stilbene concentration or is a result of seasoning (Ekman & Holmbom 1989a). Since no such correlation was found among the fourteen species analysed in this thesis, it presumably is a matter of storing.

Picea

The amount of fats was significantly lower in genus *Picea* than in *Pinus*. The heartwood contained 0.01–0.38% free fatty acids, 0.02–0.09% diacylglycerols and 0.01–0.16% triacylglycerols (Figure 42). The sapwood contained 0.01–0.06% free fatty acids, 0.01–0.06% diacylglycerols and 0.07–0.55% triacylglycerols, while 0.03–0.94% free fatty acids, 0.01–0.16% diacylglycerols and up to 0.30% triacylglycerols were detected in the knots.

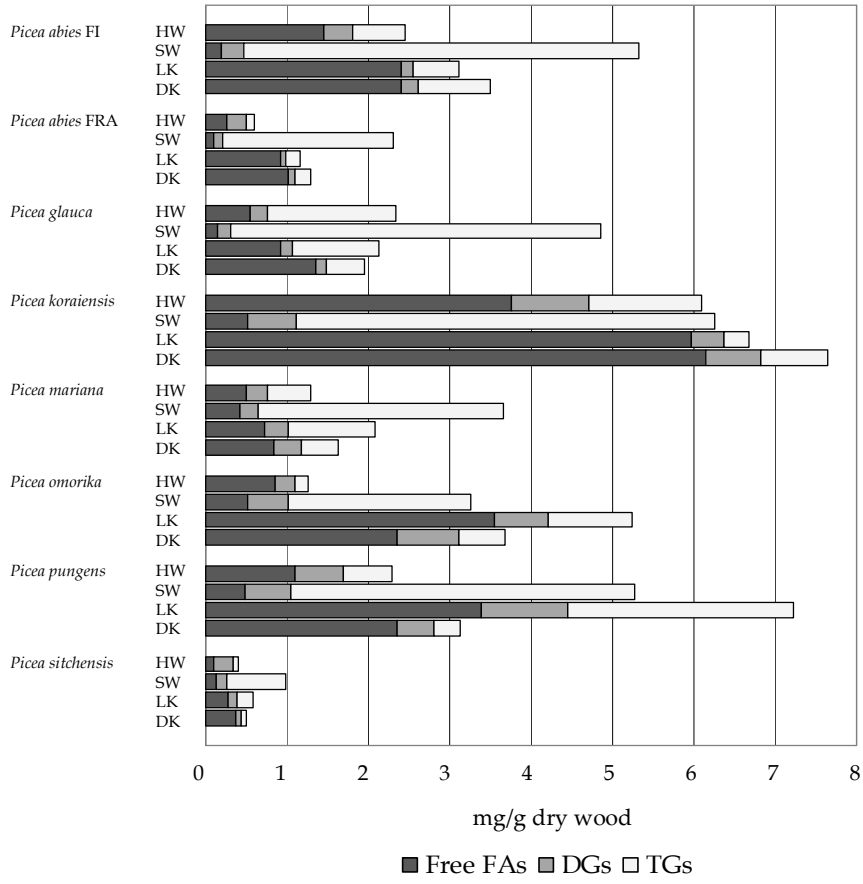

Figure 42 Average concentrations of free fatty acids (Free FAs), diacylglycerols (DGs) and triacylglycerols (TGs) in genus Picea (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Abies

The stemwood of genus *Abies* was low in fat. The heartwood contained 0.03–0.21% free fatty acids, 0.01–0.03% diacylglycerols and a maximum of 0.05% triacylglycerols (Figure 43). The concentrations in the sapwood were 0.01–0.16% free fatty acids, up to 0.04% diacylglycerols and up to 0.21% triacylglycerols. The knots were slightly richer in fat than the stem; they contained 0.07–3.9% free fatty acids, up to 0.47% diacylglycerols and up to 1.3% triacylglycerols.

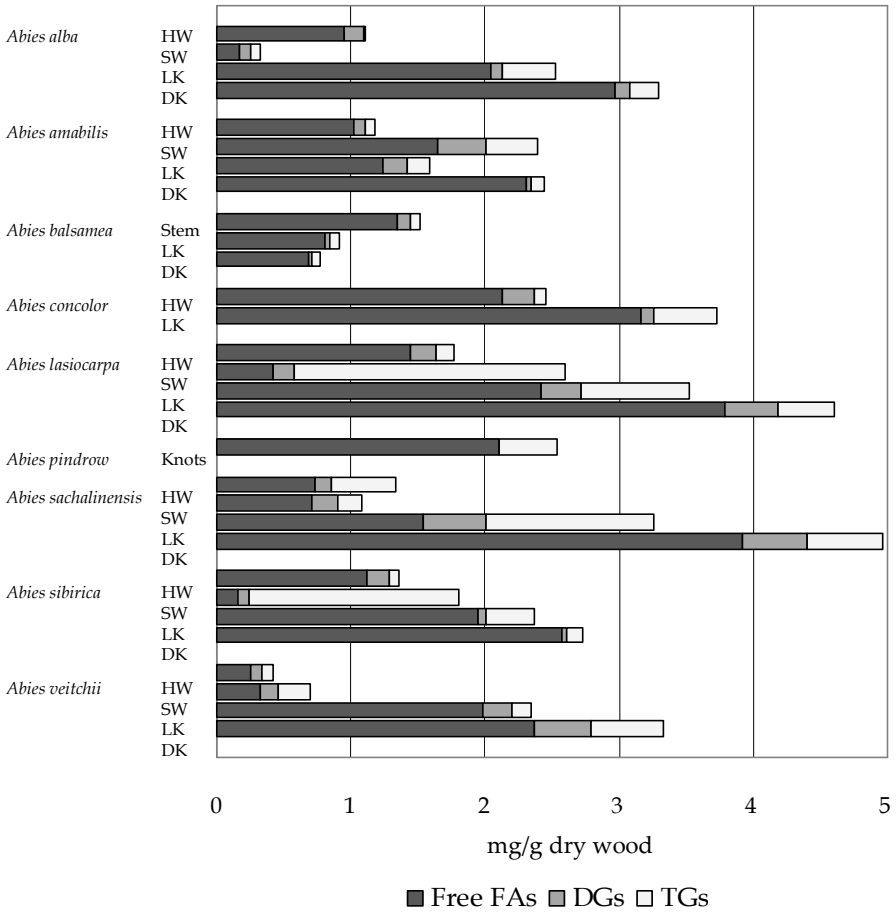

Figure 43 Average concentrations of free fatty acids (Free FAs), diacylglycerols (DGs) and triacylglycerols (TGs) in genus Abies (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots, stem = mix of heartwood and sapwood, knots = mix of living and dead knots).

Larix

The fat concentrations in genus *Larix* were in the same range as in genus *Picea*. The heartwood contained 0.04–0.42% free fatty acids and 0.01–0.11% triacylglycerols (Figure 44). The sapwood contained less free fatty acids (0.01–0.14%) and significantly much more triacylglycerols (0.04–0.63%). The knots contained 0.02–0.58% free fatty acids and up to 0.51% triacylglycerols. The concentration of diacylglycerols ranged up to 0.03% in all studied parts of the stem.

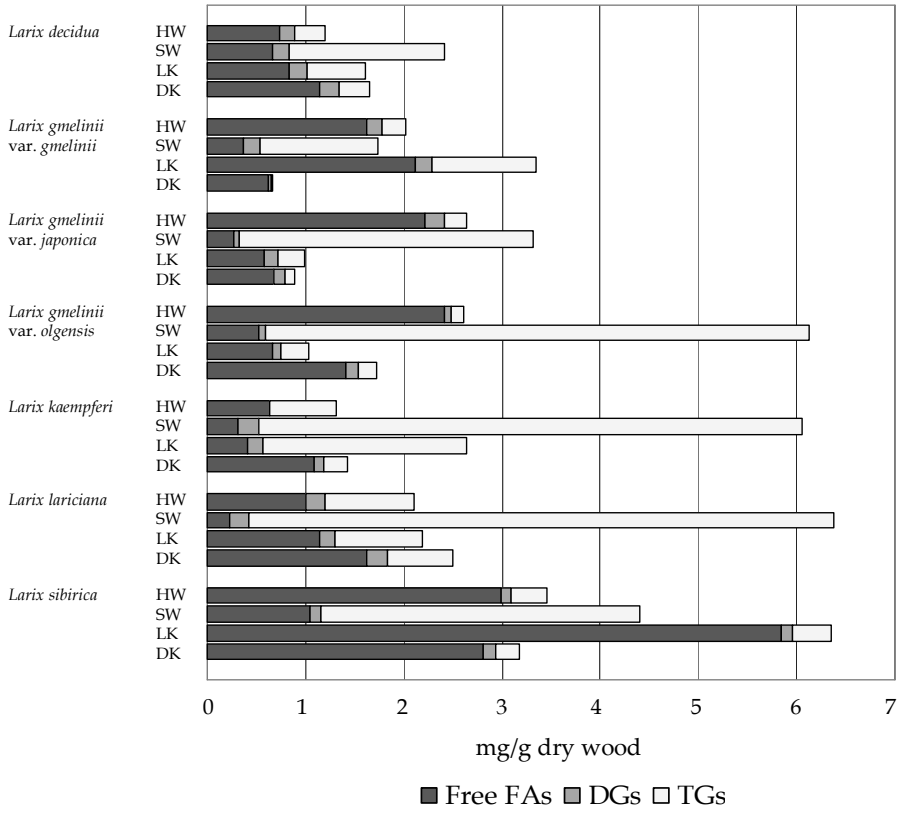

Figure 44 Average concentrations of free fatty acids (Free FAs), diacylglycerols (DGs) and triacylglycerols (TGs) in genus Larix (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Other species

The stemwood of genera *Pseudotsuga* and especially *Tsuga* was very low in fat (Figure 45). The heartwood contained 0.02–0.06% free fatty acids and less than 0.05% triacylglycerols; the sapwood 0.01–0.02% free fatty acids and 0.02–0.18% triacylglycerols. The concentration of free fatty acids in the knots of *Pseudotsuga menziesii* (0.23–0.40%) was in the same range as in genus *Larix*, while the concentrations in genus *Tsuga* were much lower (0.01–0.06%). Low concentrations of diacylglycerols and triacylglycerols were found in the knots of both *Pseudotsuga* and *Tsuga*, less than 0.02% diacylglycerols and a maximum of 0.04% triacylglycerols.

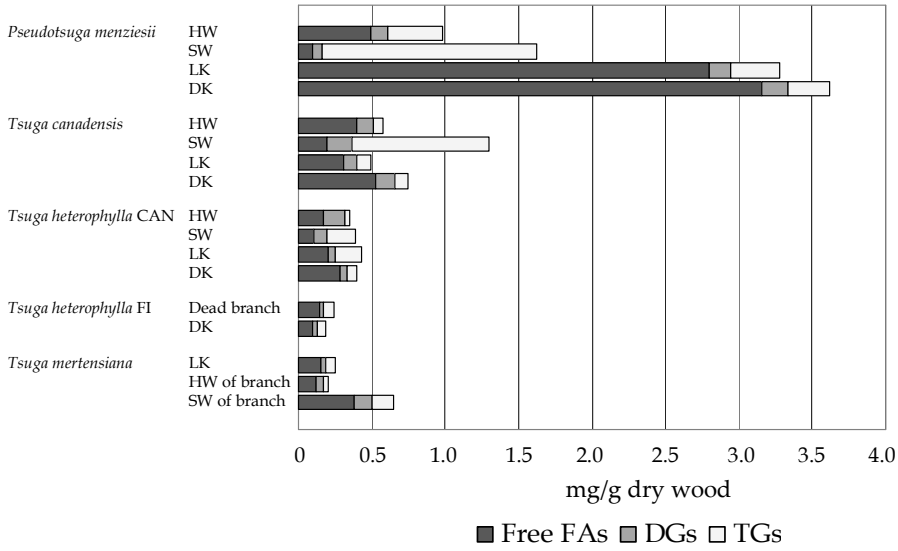

Figure 45 Average concentrations of free fatty acids (Free FAs), diacylglycerols (DGs) and triacylglycerols (TGs) in genera Pseudotsuga and Tsuga (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

4.1.3 Sterols, triterpenols and their esters

Extracts containing steryl esters are often hydrolyzed prior to analysis, so that the individual sterols can be identified and quantified. In this thesis, the extracts were *not* hydrolyzed. This means that the steryl esters were quantified as a group only, and that the sterol compositions presented in Appendix D3 are those of free sterols only, no esterified sterols were included. It is, however, known that steryl esters consist of approximately 60% sterols and 40% fatty acids, and that the compositions of free and esterified sterols are almost identical (Vikström et al. 2005). Therefore, a factor of 0.6 was used to calculate the amount of sterols in the steryl esters. These calculated sterol concentrations are presented in Figure 46–50.

Pinus

All wood samples of *Pinus* contained much more steryl esters than free sterols (Figure 46, Appendix D3). No free sterols, only steryl esters, were detected in knots of *P. gerardiana*, *P. roxburghii* and *P. wallichiana.*

Steryl esters are fairly stable and not easily hydrolyzed, and unlike the acylglycerols, they are not hydrolyzed when the cells die. Heartwood and sapwood, therefore, contain equal amounts of steryl esters, while the amount of free sterols was somewhat higher in heartwood and knots than in sapwood. The heartwood contained 0.01–0.03% free sterols, the sapwood 0.01% and the knots up to 0.04%. The steryl ester concentrations ranged up to 0.29% in the heartwood, up to 0.25% in the sapwood, up to 0.45% in the knots. This means that the total sterol concentration (free + esterified) was 0.01–0.19% in the stem and 0.02–0.29% in the knots.

Sitosterol was the dominating sterol in all samples (Appendix D3). The knots of *P. nigra* contained equal amounts of sitosterol and citrostadienol, and in the knots of *P. taeda* sitosterol was accompanied by almost equal concentrations of sitostanol. Small amounts of campesterol, campestanol, cycloartenol and methyl cycloartanol were detected in most of the samples.

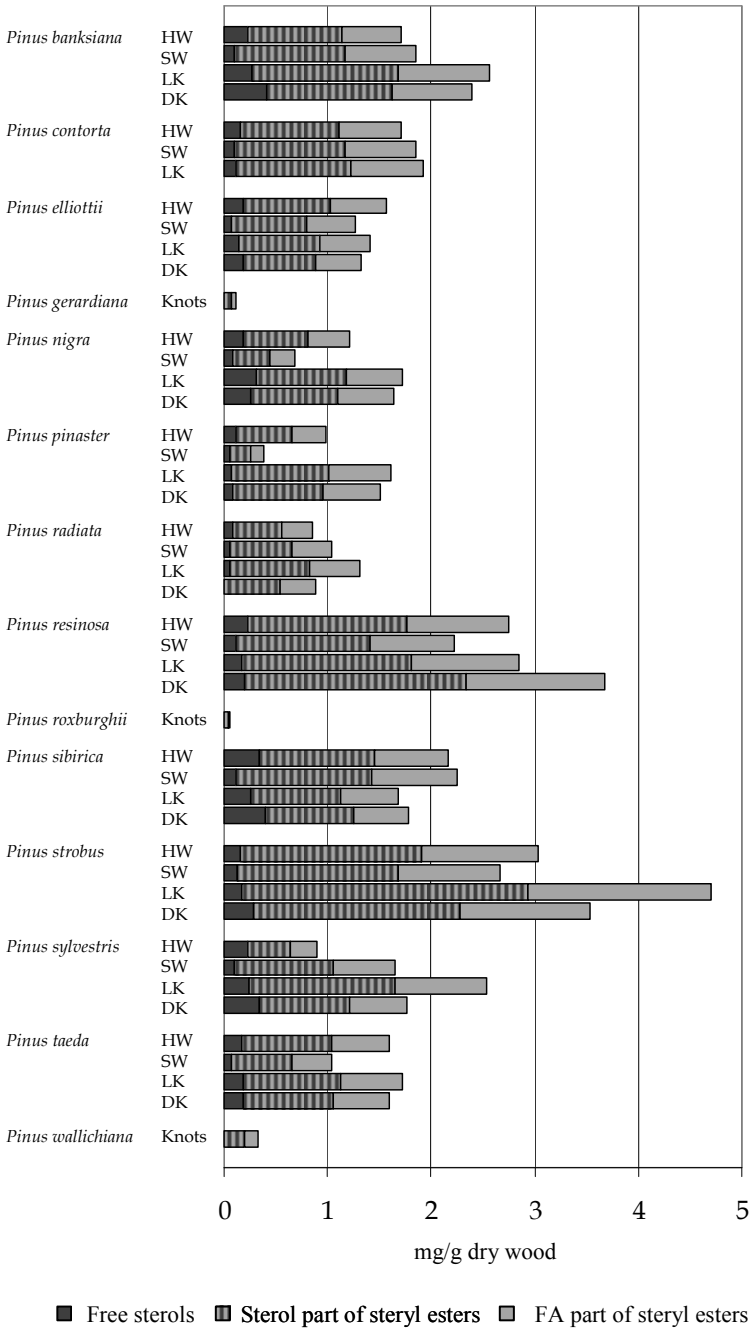

Figure 46 Average concentrations of free sterols and steryl esters in genus Pinus (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Picea

Genus *Picea* also contained much more steryl esters than free sterols (Figure 47). The only exception was the knots of the French *P. abies*; they contained more free sterols than esterified. The average concentrations of free sterols were higher in the heartwood (0.02–0.07%) and knots (0.01–0.17%) than in the sapwood (0.01–0.02%), while the average concentrations of steryl esters was higher in knots (0.04–0.32%) than in sapwood (0.10–0.21%) and heartwood (0.06–0.18%). The total concentration of free + esterified sterols was 0.06–0.18% in the stem and 0.05–0.21% in the knots.

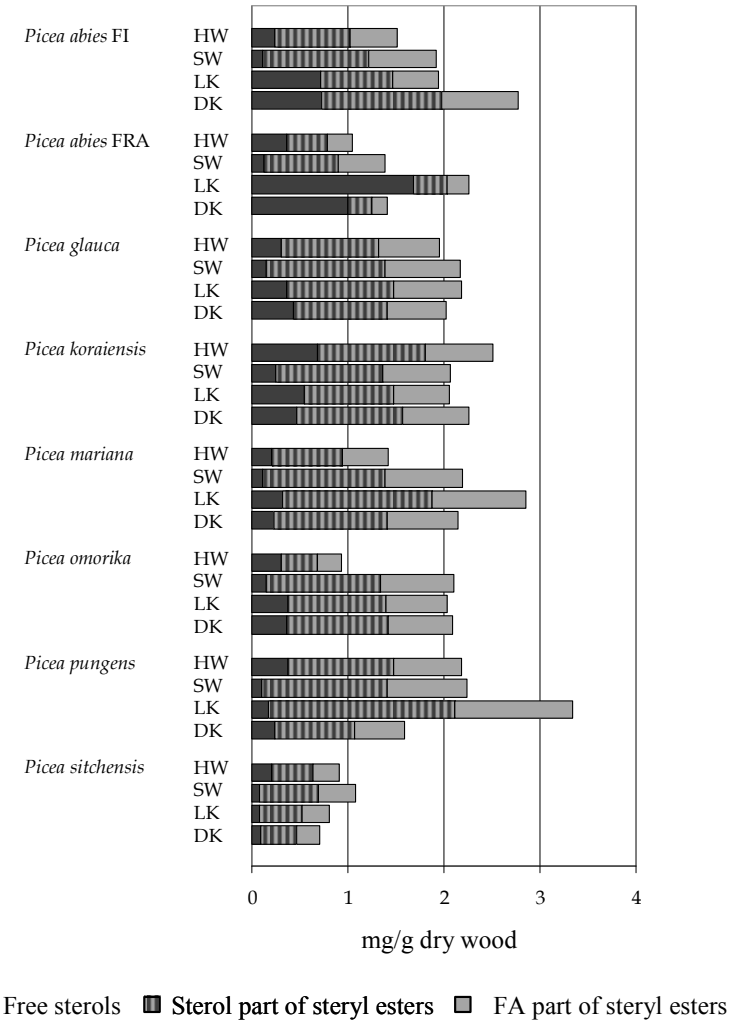

Figure 47 Average concentrations of free sterols and steryl esters in genus Picea (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Sitosterol was the most abundant sterol in all species. Other identified compounds were sitostanol, campesterol, campestanol, cycloartenol, methyl cycloartanol, citrostadienol and the ketone sitostadien-7-one.

Abies

Abies was the genus poorest in steryl esters, while the concentrations of free sterols were in the same range as in the other studied genera. In fact, this was the only genus which contained fairly equal amounts of free and esterified sterols (Figure 48), while the esterified form dominated in all other studied genera.

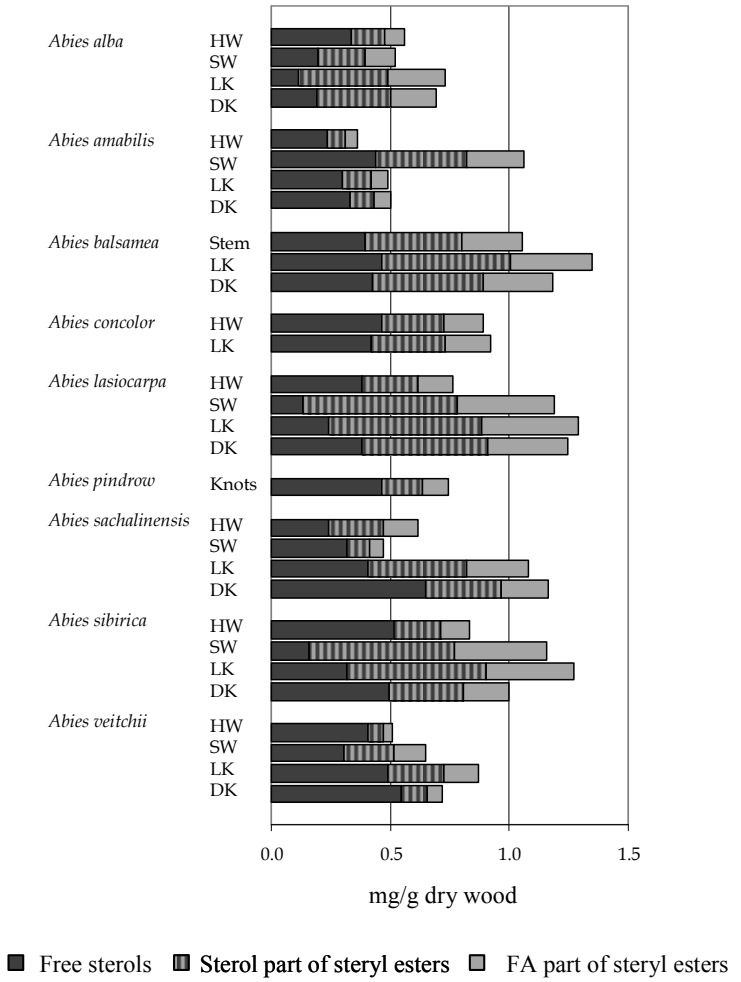

Figure 48 Average concentrations of free sterols and steryl esters in genus Abies (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

There were no significant differences between the average concentrations in stem and knots. The average concentration of free sterols was 0.01–0.05% in the stem and 0.01–0.07% in the knots. The average steryl ester concentration was 0.01–0.04% in the heartwood and 0.02–0.11% in the sapwood and knots. The calculated total sterol concentration (free + esterified) was 0.03–0.08% in the stem and 0.04–0.10% in the knots.

Sitosterol was the dominating sterol in all stemwood samples and in most of the knots. Campesterol was, however, equally or even more abundant in the knots of *Abies concolor*, *A. pindrow*, *A. sachalinensis* and *A. veitchii*. Other identified sterols and triterpenols were sitostanol, campestanol, cycloartenol, methyl cycloartanol and citrostadienol.

Larix

The *Larix* species contained much more steryl esters than free sterols (Figure 49). The only exception was the knots of *L. gmelinii* where the concentration of free sterols was higher, or equal, to the steryl esters concentration. This trend was observed only in the knots of the French *Picea abies*, not in any other species. The average concentrations of free sterols in the knots of *L. gmelinii* were 0.09–0.15%, while all other samples contained 0.01–0.03%. The average steryl ester concentrations were 0.07–0.17% in all samples. The calculated total sterol concentration (free + esterified) was 0.05–0.11% in the stem and 0.06–0.23% in the knots.

Sitosterol was the dominating compound in most of the samples. Campesterol was, however, more abundant than sitosterol in heartwood of *L. gmelinii* var. *olgensis*. Sitosterol and campesterol were equally common in knots of *L. lariciana* and in living knots of *L. sibirica*, while the dead knots of *L. sibirica* contained equal concentrations of sitosterol and sitostanol. Other identified sterols were campestanol, cycloartenol, methyl cycloartanol and citrostadienol. *L. decidua* and the knots of *L. kaempferi* additionally contained traces of stigmastadiene.

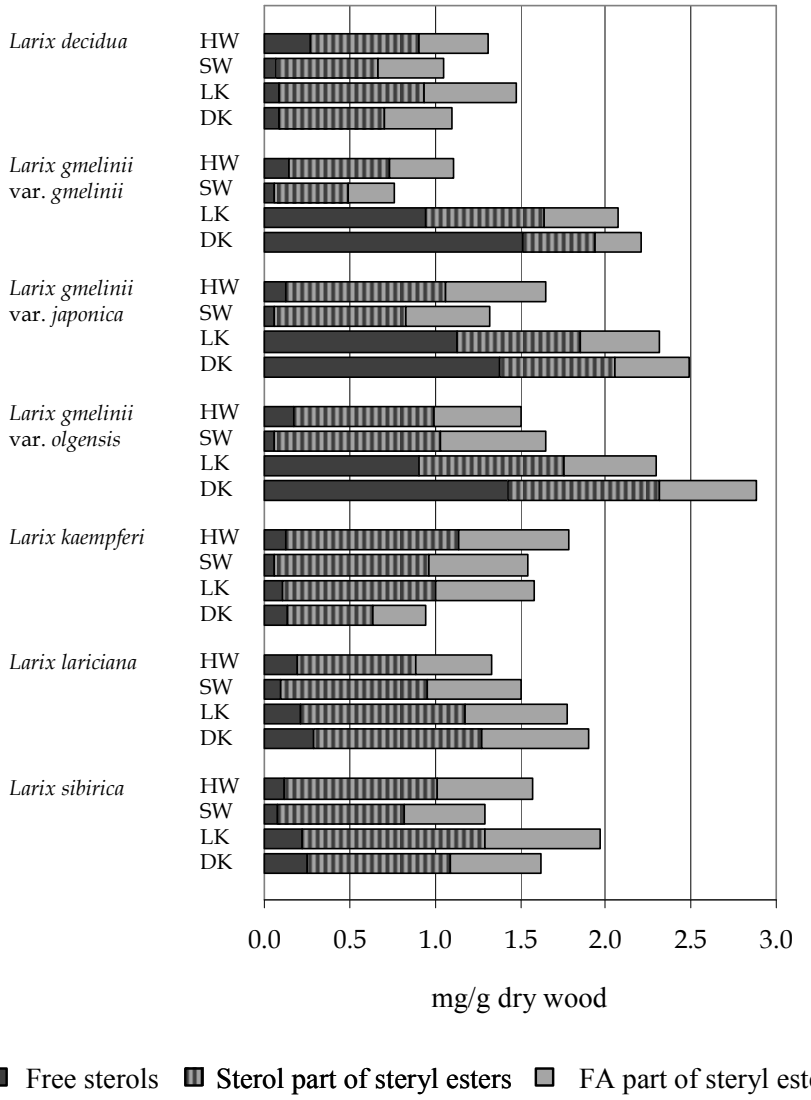

Figure 49 Average concentrations of free sterols and steryl esters in genus Larix (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Other species

Pseudotsuga menziesii contained significantly higher concentrations of esterified sterols than of free; the heartwood contained 0.01% free sterols, the sapwood traces and the knots 0.02–0.07%. The stemwood contained 0.20–0.24% steryl esters and the knots 0.35–0.45%. The calculated total amount of sterols was 0.15% in the heartwood and 0.26–0.32% in the knots (Figure 50). Sitosterol was most abundant in all samples, and other detected

sterols were sitostanol, campesterol, campestanol, cycloartenol, methyl cycloartanol and citrostadienol.

Stemwood and knots of genus *Tsuga* contained equal amounts of free sterols (0.01–0.04%) and steryl esters (0.01–0.05%). The Canadian knots of *T. heterophylla* were, however, fairly rich in steryl esters; they contained 0.20–0.25%[52]. The total calculated sterol concentrations were 0.01–0.05% in the stem and 0.02–0.17% in the knots.

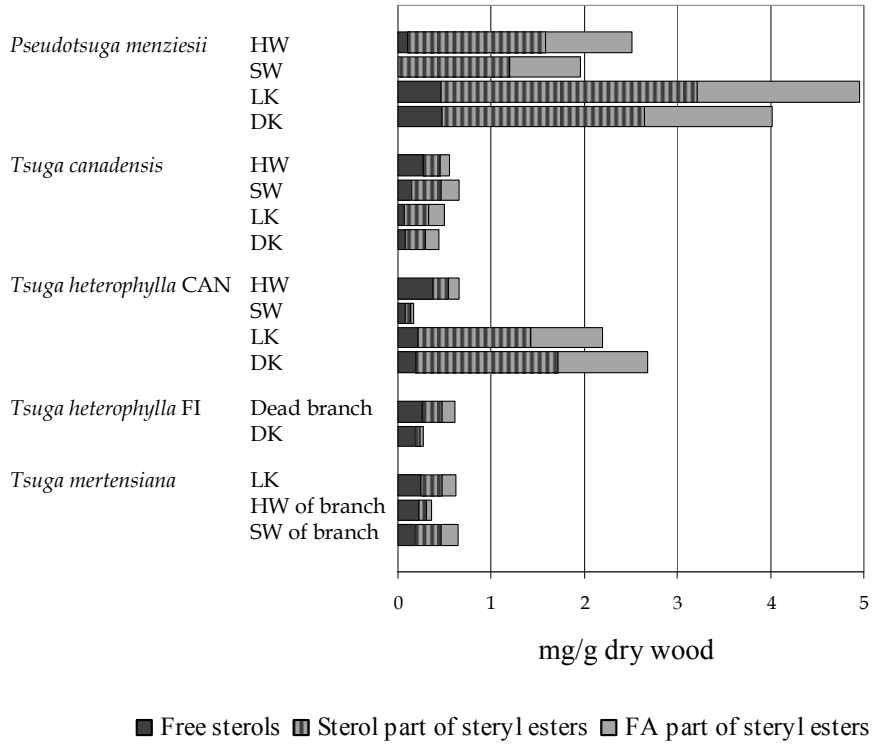

Figure 50 Average concentrations of free sterols and steryl esters in genera Pseudotsuga and Tsuga (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Sitosterol was the dominating sterol in all samples. Traces of sitostanol, campesterol, campestanol, cycloartenol, methyl cycloartanol and citrostadienol were also detected in all *Tsuga* species.

[52] A large, additional peak elutes right after the steryl ester area, so the researcher should pay attention not to include it in the group.

4.1.4 Juvabiones and other sesquiterpenoids

The juvabione-type components are characteristic of genus *Abies* and they were found in all *Abies* species studied in this work. Juvabiones have also been detected in a *Pseudotsuga* (Rogers & Manville 1972, Sakai & Hirose 1973a, 1973b, Rogers et al. 1974, Manville & Rogers 1977) and *Picea* (Willför et al. 2007) and a juvenile hormone effect on insects have been detected for a *Larix* and *Tsuga* (Sláma & Williams 1966) species. Therefore, also *Larix* and *Tsuga* are believed to contain juvabiones. However, juvabiones have never been reported in any *Pinus* species before this thesis.

In this work it was not possible to distinguish between the diastereomers of the juvabiones (structures in Appendix C4). Thus, the concentrations of e.g. juvabione and epijuvabione are reported as the sum of both diastereomers. It is possible to use chromatography to separate enantiomers, but for that purpose chiral columns are required.

Abies

The juvabiones are a group of extractives typically found in true firs. They are present in unique combinations, which make them useful for chemotaxonomic identification. As Manville (1992) points out – qualitative differences requires different biological factors to be present in the plant, whereas quantitative differences are a result of more or less active factors during the compound formation. Therefore, it is preferable to use the presence/absence criterion for classification rather than high/low concentrations. As can be seen in Figure 51, both the amounts and composition of juvabione-type components vary a lot between the *Abies* species.

In all species, except in *Abies balsamea*, the concentration of juvabione-type compounds was clearly higher in the knots than in the stemwood. The total content was very low in all samples of *A. alba*, *A. amabilis*, *A. balsamea*, *A. concolor* and *A. pindrow*. Knots of *A. lasiocarpa*, *A. sachalinensis*, *A. sibirica* and *A. veitchii* contained high concentrations of juvabiones. Lasiocarpenone, lasiocarpenonol and atlantone were typical of *A. lasiocarpa*, and 1′-dehydrojuvabione was found only in *A. balsamea*, *A. lasiocarpa* and *A. sibirica*. All three belong to the subsection *Laterales*. Other species in that subsection are *A. bifolia* and *A. kawakamii*. Manville (1989) have reported 1′-dehydrojuvabione in *A. bifolia*, but no one has studied non-volatile extractives in *A. kawakamii*. It is, however, very likely that 1′-dehydrojuvabione would be detected there too.

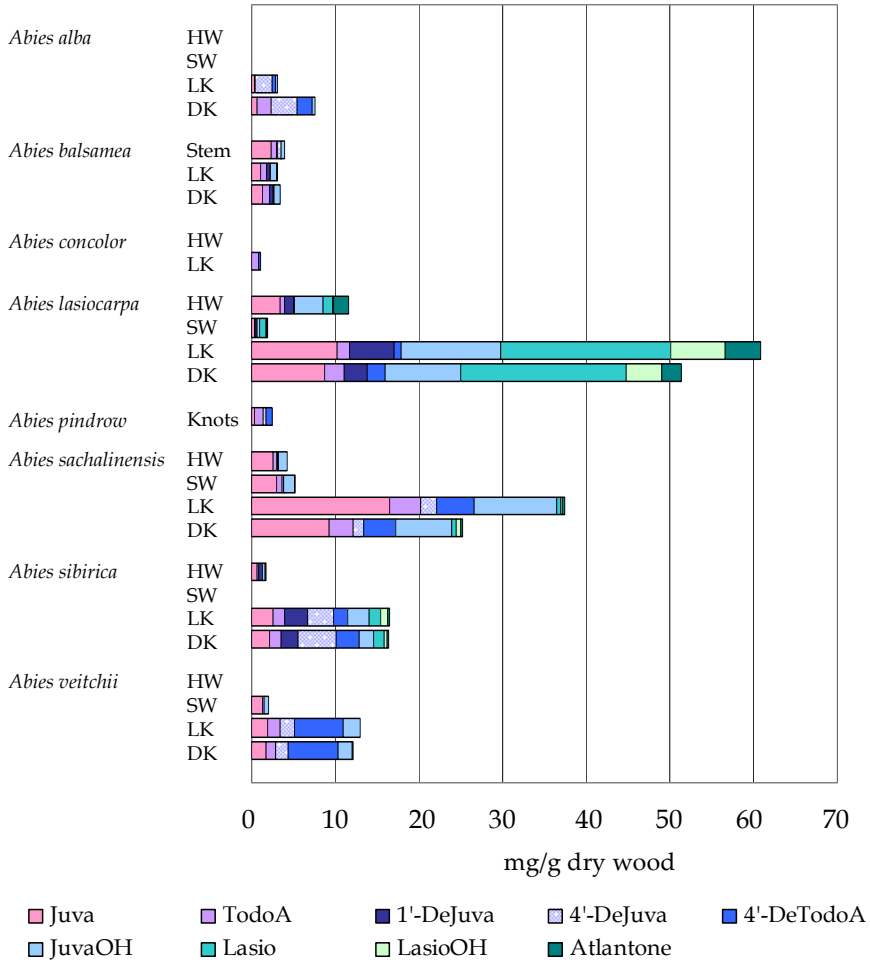

Figure 51 Average concentrations of juvabiones and other sesquiterpenoids in Abies species (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Willför et al. (2004b) also analysed samples of *Abies sibirica*, *A. lasiocarpa*, *A. balsamea*, *A. alba*, *A. amabilis*, *A. veitchii*, *A. sachalinensis* and *A. concolor*, but they did not find any lasiocarpenone, lasiocarpenonol, atlantones, or juvabiols in their samples.

Abies alba

The stemwood of *A. alba* contained traces of juvabione, todomatuic acid, 4′-dehydrojuvabione, 4′-dehydrotodomatuic acid, juvabiol and α-atlantone. The dominating juvabione in the knots was 4′-dehydrojuvabione (0.02–0.9%) followed by todomatuic acid (0–0.6%), 4′-dehydrotodomatuic acid (traces to 0.4%), juvabione (0–0.3%), juvabiol (traces to 0.06%) and

α-atlantone (traces to 0.01%). In most cases the dead knots contained more juvabiones than the living knots.

In this thesis, the samples of *A. alba* were collected at two different sites in France and it can be concluded that the difference between these two sites is greater than the differences within the site. Needle and twig analysis have disclosed that there are two phenotypes of *A. alba* (Manville et al. 1977), which could explain these differences.

Manville et al. (1977) studied *Abies alba* of North American origin. They found that the branch wood contained: juvabione, 4′-dehydrojuvabione, 4′-dehydroepijuvabione, juvabiol, isojuvabiol and epijuvabiol. The ratio 4′-dehydrojuvabione to 4′-dehydroepijuvabione was 3:1 and the ratio juvabiol:isojuvabiol:epijuvabiol was 7:3:2. Manville et al. (1977) did not detect any acids in *A. alba*. The reason is that they methylated the samples prior to analysis and thereby converted all acids into methyl esters.

Manville et al. (1977) points out that the quantitative variations of juvabione type compounds are larger in *A. alba* than in *A. balsamea* or in *A. lasiocarpa*. The results in this thesis support his statement.

Abies amabilis

The concentrations of juvabiones in *A. amabilis* were low. Traces of juvabione, todomatuic acid and 4′-dehydrotodomatuic acid were found in heartwood, sapwood and knots of all samples.

Abies balsamea

A. balsamea is the only species where the stemwood contained clearly more juvabiones than the knots. The dominating compound was juvabione, 0.2–0.3% was found in the stemwood and 0.1% in the knots. The stemwood and knots contained 0.06–0.09% todomatuic acid and low concentrations of 4′-dehydrojuvabione (0.01–0.06%), juvabiol (0.03–0.08%), 1′-dehydrojuvabione (0.01–0.04%), lasiocarpenone (traces), α- and γ-atlantone (traces).

Other scientists have found (+)-atlantone (Swan 1967), lasiocarpenone (Fraser & Swan 1975), (+)-juvabione, (+)-4′-dehydrojuvabione, juvabiol, isojuvabiol and 3′-dehydrojuvabi-5′-ol (Bowers et al. 1966, Manville 1975, 1976). The last component is, however, believed to be an artefact of the isolation procedure (Manville 1976). As in the case with *A. alba*, todomatuic acid was missed since the samples were methylated prior to analysis.

According to needle and twig analysis, there are two phenotypes of *A. balsamea* in eastern Canada (Hunt & Rudloff 1974). This affects both the composition and the concentration of extractives and the attentive

reader should bear this in mind when studying the constituents of *A. balsamea.*

Abies concolor

Traces of todomatuic acid and 4′-dehydrotodomatuic acid were found in the heartwood of *A. concolor*. The living knots contained 0.08% todomatuic acid and 0.02% 4′-dehydrotodomatuic acid.

Abies lasiocarpa

A. lasiocarpa contains much juvabiones and related sesquiterpenoids: 0.9–1.4% in the heartwood and 0.01–0.4% in the sapwood. Willför et al. (2007) have reported the largest amounts of juvabiones in knots of *Abies bornmülleriana* and *Abies cilicia,* 2.6–3.9% (w/w). The knots of *A. lasiocarpa* do, however, beat that record by a very comfortable margin since they contain 3.2–8.2% juvabiones.

Fraser and Swan (1975) isolated two new compounds from *A. lasiocarpa* and named them lasiocarpenone and lasiocarpenonol after the tree species where they occurred. Lasiocarpenone and lasiocarpenonol are juvabiones with a furan group in the side chain and they are foremost found in *A. lasiocarpa*. The concentration of lasiocarpenone was 0.06–0.2% in the heartwood, 0–0.1% in the sapwood and 1.5–2.5% in the knots. The amounts of lasiocarpenonol were lower: 0.01–0.02% in the heartwood, traces to 0.03% in the sapwood and 0.2–1% in the knots.

The second most abundant juvabione-type components in *A. lasiocarpa* were juvabione and juvabiol. The heartwood contained 0.3–0.4% of both compound. The sapwood contained traces to 0.06% of juvabione and 0–0.07% of juvabiol. The knots contained 0.8–1.3% juvabione and 0–1.6% juvabiol. Other compounds present were todomatuic acid (0.05% in the heartwood, traces to 0.01% in the sapwood and 0.08–0.3% in the knots), 4′-dehydrotodomatuic acid (0.01% in the heartwood, traces in the sapwood and 0.07–0.2% in the knots), and 1′-dihydrojuvabione (0.04–0.2% in the heartwood, traces to 0.04% in the sapwood and 0.1–1.0% in the knots).

Swan (1967) isolated two sesquiterpene ketones from a heartwood extract of *A. lasiocarpa*. The amounts were too low for identification, but he alleged that the compounds were susceptible to air and light degradation. Six years later, Fraser and Swan (1973) identified the compounds as the *Z*- and *E*-isomers of α-atlantone, of which the *E*-isomer is more stable and present in higher amounts. These sesquiterpenoids resemble the juvabione structure, but they lack the methyl ester and acid functions (for structures, see Appendix C4). The heartwood samples of this work contained 0.2% α-atlantone, the sapwood 0.01–0.02% and the knots 0.2–0.5%.

Manville (1989) studied branch wood of *A. lasiocarpa* and found juvabione, epijuvabione, 4′-dehydrojuvabione, 4′-dehydroepi-juvabione, 1′-dehydrojuvabione, juvabiol, epijuvabiol, 1′-dehydrojuvabiol, Z-α-atlantone, E-α-atlantone, lasiocarpenone (4*R*, 1′*S*) and lasiocarpenonol (4*R*, 5*R*, 1′*S*). He methylated the extracts before analysis and therefore, he did not find any acids, only their methyl esters. The amounts of their methyl esters are, however, well in accordance with this study's total sums of acids and methyl esters. No 1′-dehydrojuvabiol was identified in the samples of this thesis, but there were two unidentified components in the hexane extract, so presumable one of those unidentified peaks were derived from that alcohol.

It has been showed that mechanical pulping effluents of *A. lasiocarpa* contain juvabione, juvabiol, 1′-dehydrojuvabione and 1′-dehydrojuvabiol. These components are toxic to juvenile rainbow trout, but their toxicity is lower than that of the resin and fatty acids (Leach & Thakore 1976).

In the literature there are two schools: one claim that *A. bifolia* is a variety of *A. lasiocarpa*, the other that they are two separate species (Hunt 1993b, Earle 2009). They grow very close to each other and introgressive hybridization occurs in the north-south transect. Morphologically only minor characters distinguish them but their chemical composition differs. Epijuvabione, 4′-dehydrojuvabione, 4′-dehydroepijuvabione and lasiocarpenonol are present in *A. lasiocarpa*, but not in *A. bifolia* (Manville 1989). These compounds can, therefore, easily be used to distinguish between costal alpine fir (*A. lasiocarpa*) and Rocky Mountain alpine fir (*A. bifolia*). According to Manville (1989), some work concerning extractives in *A. lasiocarpa* has in fact been carried out on *A. bifolia* and this can cause some confusion.

Abies pindrow

No stemwood of *A. pindrow* was analysed. The knots contained 0.1% todomatuic acid, 0.07% 4′-dehydrotodomatuid acid, 0.04% 4′-dehydro-juvabione and 0.03% juvabione.

Abies sachalinensis

Only one tree of *A. sachalinensis* was studied. The concentrations in the heartwood and sapwood were comparable: 0.3% juvabione, 0.1% juvabiol, 0.05–0.07% todomatuic acid, 0.01% 4′-dehydrojuvabione and 0.01% 4′-dehydrotodomatuic acid. The knots contained much more juvabiones; 0.9–1.7% juvabione, 0.7–1.0% juvabiol, 0.3–0.4% todomatuic acid, 0.1–0.2% 4′-dehydrojuvabione and 0.4–.5% 4′-dehydrotodomatuic acid.

The knots of *A. sachalinensis* also contained 0.05–0.06% lasiocarpenone, 0.03–0.05% lasiocarpenonol and 0.02–0.03% α-atlantone. The stemwood contained only minor amounts of α-atlantone.

The wood of *A. sachalinensis* has been profoundly studied (Kawai et al. 1993b, Numata et al. 1983, 1990, 1992) and the following compounds have been found: (+)-juvabione, (+)-epijuvabione, epitodomatuic acid, (+)-dehydroepijuvabione, 4′-dehydroepitodomatuic acid, (-)-4′-dehydro-oxojuvabione, (+)-4′-dehydro-oxoepijuvabione, (+)- and (-)-oxojuvabione, (+)- and (-)-oxoepijuvabione, epijuvabiol, isoepijuvabiol, epijuvabienol ether, tetrahydrotodomatuic acid, 5′-hydroxyepijuvabione, *ar*-dihydroxy-epijuvabione, 3′-isodihydroepitodomatuic acid and 3′-dehydroepijuvabi-5′-ol. It should, though, be noted that several kilograms of wood were extracted in order to purify milligram-amounts of these compounds so the researchers were able to identify compounds occurring in very low concentrations (Numata et al. 1983, 1990, 1992). It has been showed elsewhere that 3′-dehydroepijuvabi-5′-ol is an artefact from the isolation/purification steps (Manville & Kriz 1977, Manville 1989) so it is possible that some of the other compounds are artefacts too.

Kawai et al. (1993a) studied nine trees of *A. sachalinensis* and found a tree-to-tree variation of stereoisomers. Seven of the trees were of juvabione-type (4*R*, 1′*R*) while the remaining two were of epijuvabione-type[53]. They also studied the essential oils of the needles but could not find any correlation with the chemical features of the wood. The content of volatile components in the needles was, however, influenced by temperature, rainfall and other growing conditions, while the constituents of the wood were formed under the influence of enzymes, which are under genetic control. Therefore, the wood constituents seem to provide a better, more invariable source for chemotaxonomic information than the needles.

Abies sibirica

There is only one report on juvabiones in *A. sibirica* and it is restricted to the total sum of juvabiones (Willför et al. 2004b). Thus the individual juvabiones in *A. sibirica* have never been identified. The heartwood contained 0.05–0.09% juvabione, 0.03–0.05% 1′-dehydrojuvabione, 0.02–0.04% juvabiol, 0.02% todomatuic acid and traces of both 4′-dehydrojuvabione and 4′-dehydrojuvabione. The sapwood contained traces of juvabione, todomatuic acid, 4′-dehydrojuvabione, 1′-dehydro-juvabione and juvabiol. The living and dead knots contained analogous

[53] There was one exception; a tree of epijuvabione-type contained the juvabione-type compound (–)-oxojuvabione. The side chain of that compound did, however, have a more thermodynamically stable, equatorial orientation and can, therefore, be described as an epijuvabione-type compound (Numata et al. 1990).

amounts; 0.2–0.3% juvabione, 0.1–0.3% juvabiol, 0.08–0.2% todomatuic acid, 0.1–0.7% 4′-dehydrojuvabione, 0.04–0.5% 4′-dehydrotodomatuic acid and 0.2–0.3% 1′-dehydrojuvabione.

Some other sesquiterpenoids were detected in *A. sibirica* as well. The stemwood contained traces of lasiocarpenone and the knots 0.06–0.2%. The heartwood contained 0.01% of lasiocarpenonol and the knots 0.03–0.1%. *A. sibirica* also contained low amounts of α- and γ-atlantone. The heartwood contained traces of atlantones and the knots 0.01–0.03%. α-Atlantone dominated in all samples.

Abies veitchii

The juvabiones in *A. veitchii* have not been studied earlier. In literature it is stated that *A. veitchii* and *A. sachalinensis* are very closely related (Zavarin et al. 1978, Isoda et al. 2000, Suyama et al. 2000), so one could expect that their juvabione patterns would be similar. This is, however, not the case. Both the total concentrations and the proportions are different. *A. sachalinensis* contains much more juvabiones than *A. veitchii*. Furthermore, juvabione is the dominating compound in *A. sachalinensis*, while 4′-dehydrotodomatuic acid dominates in *A. veitchii*. A common, extraordinary feature is that both species contain more juvabiones in the sapwood than in the heartwood.

The heartwood of *A. veitchii* contained 0.01% juvabione and traces of todomatuic acid, 4′-dehydrojuvabione, 4′-dehydrotodomatuic acid, juvabiol and lasiocarpenone. The sapwood contained 0.1% juvabione, 0.05% juvabiol, 0.02% todomatuic acid and traces of 4′-dehydrojuvabione, 4′-dehydrotodomatuic acid and lasiocarpenone. The dead and living knots correspond to each other. They contained 0.2% each of juvabione and juvabiol, 0.1–0.2% todomatuic acid, 0.2% 4′-dehydrojuvabione, 0.6% 4′-dehydrotodomatuic acid, and traces of lasiocarpenone and lasiocarpenonol. Small amounts of α-atlantone were detected in *A. sachalinensis*, but no atlantones were detected in the sampled tree of *A. veitchii.*

Pinus

Juvabiones have never before been found in stemwood or knots of any *Pinus* species (Pichette et al. 1998), but in this study they were found in six of fifteen species (Figure 52). However, the total amount of juvabiones in the stemwood was rather low. Remarkable is that the knots contained up to 330 times more juvabiones than the stemwood! The highest amounts of juvabiones were found in living knots of *P. banksiana* and both living and dead knots of *P. pinaster*. The most abundant compound in almost all pines was todomatuic acid.

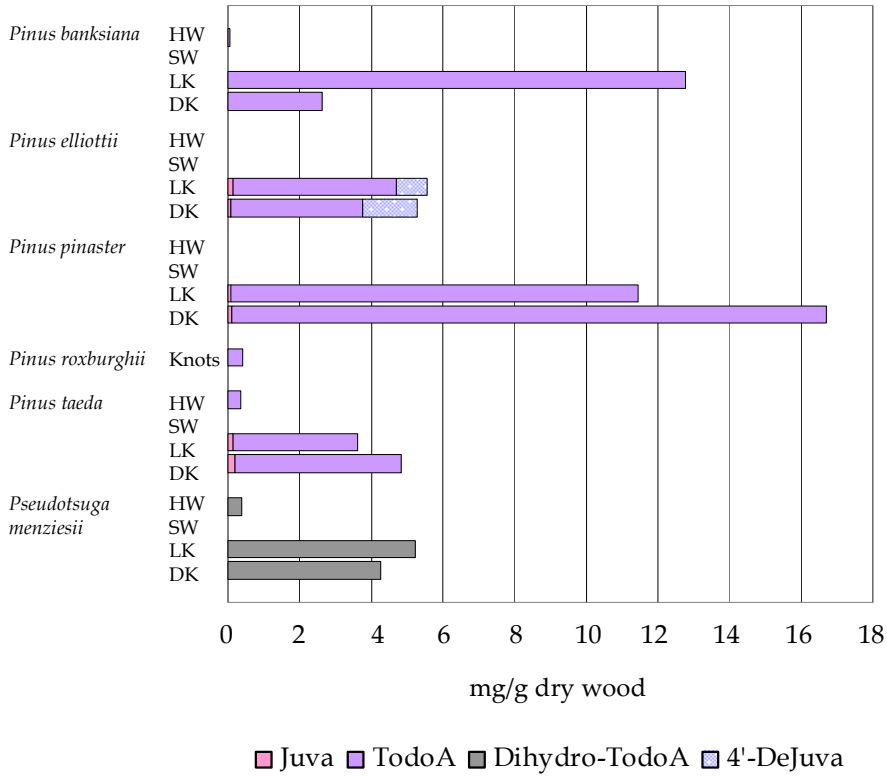

Figure 52 Average amounts of juvabiones in Pinus and Pseudotsuga species (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

Pinus banksiana

Pinus banksiana contained only one juvabione-type compound: todomatuic acid. In the stemwood only trace amounts were found, the living knots contained 1.3%, while the concentration in the dead knot was one fifth, i.e. only 0.3%.

Pinus elliottii

Traces of both juvabione and todomatuic acid were found in the stemwood of *P. elliottii*. The living and dead knots were rather similar: 0–0.3% 4′-dehydrojuvabione, 0.07–0.8% todomatuic acid and traces to 0.03% of juvabione.

Pinus nigra

Pinus nigra did not contain any todomatuic acid at all. Instead, it contained traces of juvabione, and the sapwood contained additional traces of 4′-dehydrotodomatuic acid.

Pinus pinaster

The heartwood of *P. pinaster* contained traces of juvabione, todomatuic acid and 4′-dehydrojuvabione. Traces of todomatuic acid and 4′-dehydrojuvabione were found in the sapwood. Todomatuic acid dominated in the knots, 0.6–2.6%, accompanied by 0–0.02% of juvabione and traces of 4′-dehydrojuvabione.

Pinus roxburghii

Only knots of *P. roxburghii* were analysed. They contained 0.04% of todomatuic acid and traces of dihydrotodomatuic acid (an acid which was found only in *P. roxburghii* and *Pseudotsuga menziesii*). It was unclear whether that was a coincidence or if these species are more closely related than one would expect.

Pinus taeda

The heartwood of *P. taeda* contained 0.04% of todomatuic acid and traces of juvabione. The sapwood contained traces of both juvabione and todomatuic acid. The knots contained up to 1% of todomatuic acid and traces to 0.04% of juvabione.

Picea

The only report on juvabiones in any *Picea* species is by Willför et al. (2007). They report traces of juvabiones in stemwood and knots of *Picea orientalis*. In this thesis, traces of juvabione were found in heartwood, sapwood and knots of *Picea koraiensis* and traces of α-atlantone were found in all analysed parts of *P. mariana*. No other juvabiones or sesquiterpenoids were found in the other *Picea* species.

Pseudotsuga

Pseudotsuga menziesii was the only studied species where dihydrotodomatuic acid was the dominating juvabione (Figure 52). This compound was found and isolated from *P. menziesii* already in the 1970's together with todomatuic acid (Rogers & Manville 1972, Rogers et al. 1974). Neither todomatuic acid nor any other juvabione-type compounds were, however, found in this study. The only juvabione detected was dihydrotodomatuic acid; 0.03–0.05% was found in the heartwood, traces in the sapwood and 0.3–0.5% in the knots i.e. ten times more in the knots than in the heartwood.

Manville and Rogers (1977) studied the juvabione content in stemwood and branches of *Pseudotsuga menziesii* var. *glauca* from costal, interior and mountain areas across British Columbia, Canada. They found most juvabiones in trees from the coastal region. According to their results the

concentrations in the branches paralleled the findings in the corresponding stemwood. This would imply that the branch wood is quite different from the knots. However, they also found one exception where a tree had exceptionally high concentrations in the branch wood and only traces in the stem, and in a previous study (Rogers & Manville 1972) they found a tree totally lacking dihydrotodomatuic acid. So there seems to be a distinct natural variability in the juvabione concentrations.

Volatile oil of the whole wood of *P. menziesii* is reported to contain: todomatuic acid, dihydrotodomatuic acid, *ar*-todomatuic acid, *ar*-pseudotsugonal, pseudotsugonal, dihydropseudotsugonal and dihydropseudotsugonol (Sakai & Hirose 1973a, 1973b). Since only the non-volatile components have been analysed in this work, several of these compounds were left out.

Larix

Low amounts of juvabiones were found in all *Larix* species except *L. kaempferi* and in *L. lariciana*. The concentrations in *L. decidua* were so low that the species was omitted from Figure 53. The acidic forms of the juvabiones dominated. Stemwood and knots of *Larix decidua* contained trace amounts of juvabione and todomatuic acid. Some of the dead knots contained traces of 4′-dehydrojuvabione.

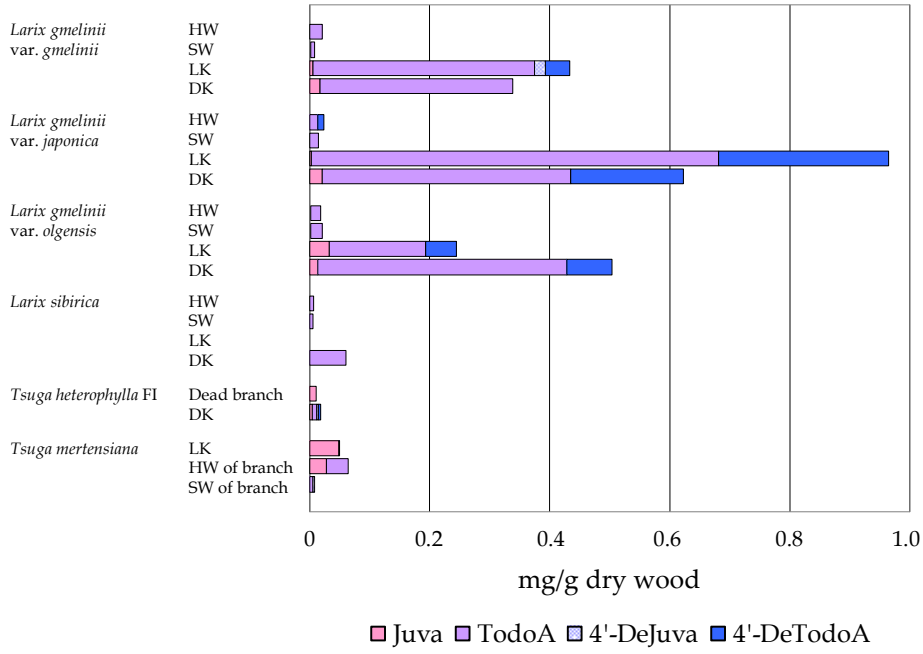

Figure 53 Average amounts of juvabiones in Larix and Tsuga species (HW = heartwood, SW = sapwood, LK = living knots, DK = dead knots).

The three varieties of *L. gmelinii* were fairly similar. The most abundant compound in all varieties was todomatuic acid. Traces of this compound were found in the stemwood and low concentrations, up to 0.08%, were found in the knots.

Sapwood and knots of all *gmelinii* varieties contained traces of juvabione, so did the heartwood of var. *olgensis*. Traces of 4′-dehydrojuvabione were found in the sapwood and living knots of var. *gmelinii* only. Traces of 4′-dehydrotodomatuic acid were found in heartwood of var. *gmelinii* and var. *olgensis*. The living knots of var. *gmelinii* and var. *olgensis* contained amounts below 0.01%, while var. *japonica* ranged between 0.02% and 0.03%. Stemwood and the dead knots of *L. sibirica* contained traces of todomatuic acid.

Sláma and Williams (1966) reported that *Larix lariciana* showed juvenile effect on the European bug, *Pyrrhocoris apterus*. No juvabiones were, however, detected in the wood samples of this species and the only unidentified compounds were a couple of diterpene alcohols.

Tsuga

The knots and branches of *Tsuga mertensiana* and *T. heterophylla* from Finland contained traces of juvabione and todomatuic acid. The dead knot of *T. heterophylla* also contained traces of 4′-dehydrojuvabione and 4′-dehydrotodomatuic acid. The living knot of *T. mertensiana* contained traces of 4′-dehydrotodomatuic acid, while the sapwood of the branch contained traces of 4′-dehydrojuvabione.

According to Sláma and Williams (1966) wood samples of *Tsuga canadensis* shows juvenile hormone effects of the European bug. No juvabiones were, however, detected in the samples of this thesis.

4.1.5 Other lipophilic compounds

The concentrations of thunbergol, thunbergene, manool, manoyloxide, larixol, larixyl acetate and squalene are presented in Appendix D5. There were, however, an abundance of other lipophilic compounds present in the wood. The concentrations of these compounds are not included in this thesis but data are available upon request.

Traces or very low concentrations of thunbergol occurred in many of the studied species. There were, however, some exceptions where the concentrations were higher. The dead knots of *Pseudotsuga menziesii* contained up to 0.10% thunbergol, the stem of *Pinus nigra* up to 0.15% and the dead knots of *P. sibirica* up to 0.40%. The knots of *Larix sibirica* from St Petersburg contained up to 0.32%, while only trace amounts were detected in the trees from Baikal and no thunbergol at all in the trees from

Habarovsk. The highest concentrations of thunbergol were found in the dead knots of *L. kaempferi* (up to 1.8%) and the knots of *P. nigra* (up to 3.7%).

Traces of thunbergene were often detected together with thunbergol, but the concentrations were significantly lower. The only samples which contained any concentrations worth mentioning were the dead knots of *P. nigra*. They contained up to 0.20% thunbergene. These samples also contained exceptionally high concentrations of thunbergol.

Manool was more abundant in genera *Picea*, *Abies* and *Larix* than in genera *Pinus*, *Pseudotsuga* and *Tsuga*. The concentrations were generally very low, and manool was often accompanied by traces of manoyl oxide. The dead knots of *Picea mariana, A. sibirica, A. veitchii, L. gmelinii* var. *japonica* and the knots of *L. gmelinii* var. *gmelinii* contained 0.1–0.2% manool. The living knot of *P. omorika*, the dead knots of *L. gmelinii* var. *olgensis* and some of the dead knots of *L. decidua* contained 0.2–0.5%. The dead knots of *A. alba* contained up to 0.78% manool and some of the dead knots of *L. kaempferi* contained up to 3.0%. These exceptional knots were found in two of three trees.

Larixol was detected in all three varieties of *Larix gmelinii*, *L. kaempferi* and in *L. sibirica*. The concentrations in the stem were lower than 0.02%, while the knots contained up to 0.67%. Low concentrations of larixyl acetate were detected in all studied *Larix* species. There were no concentration differences between the heartwood, sapwood and knots. Traces or very low concentrations of squalene were found in all species.

4.2 Hydrophilic compounds

4.2.1 Lignans and oligolignans

Concentrations of lignans and oligolignans are tabulated in Appendix D7.

Pinus

There were only little lignans in the stemwood of the pines. The average lignan concentrations in the heartwood of *P. contorta*, *P. radiata*, *P. resinosa*, *P. strobus* and *P. sylvestris* were lower than 0.05%. *P. banksiana*, *P. elliottii*, *P. nigra* and *P. pinaster* contained up to 0.10%, while 0.15% was found in the heartwood of *P. taeda* and 0.20% in *P. sibirica* (Figure 54). The total lignan concentrations in the sapwood samples were below 0.05%.

The knots, however, contained much more lignans; in some species even up to 60 times more than in the heartwood. The average lignan concentrations in the knots of *P. contorta*, *P. gerardiana, P. radiata*, *P. roxburghii*,

P. strobus, P. wallichiana and the dead knot of *P. banksiana* were up to 1.0%. The knots of *P. resinosa, P. sylvestris, P. taeda,* and the living knots of *P. banksiana* and *P. elliottii* contained up to 2.5%, while 3.2–5.0% was found in the knots of *P. nigra*, *P. pinaster*, *P. sibirica* and the dead knot of *P. elliottii.*

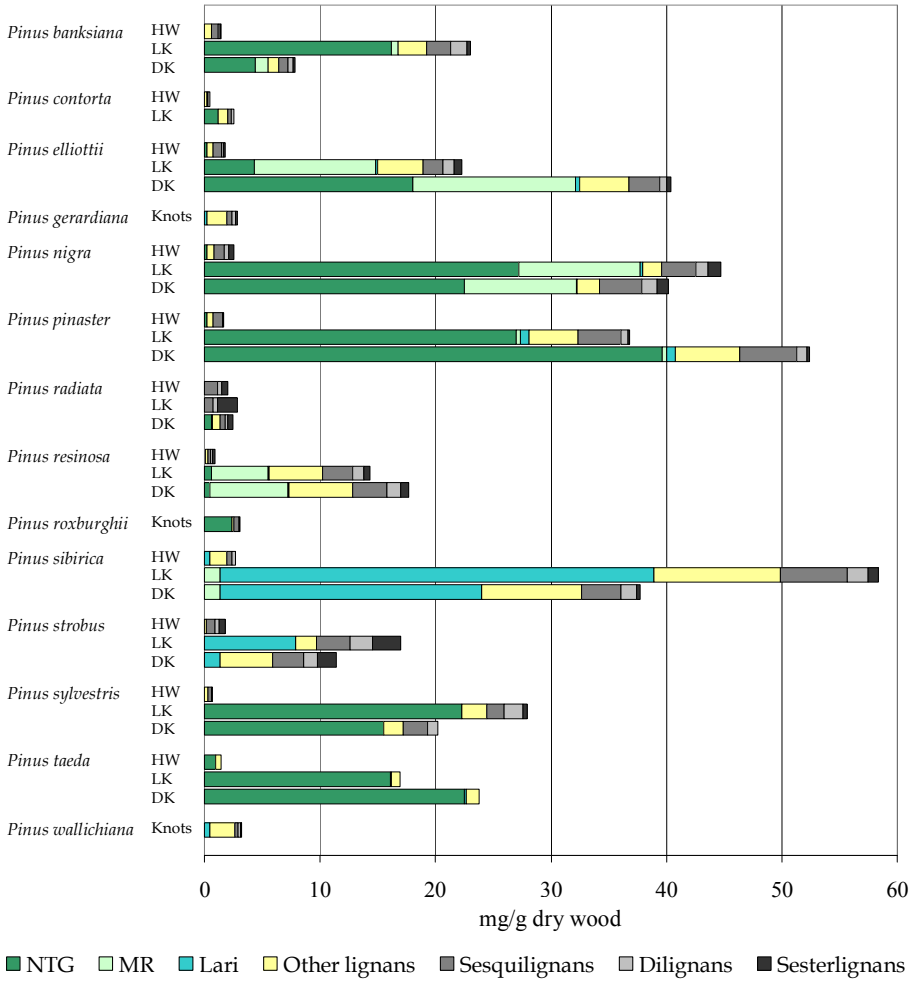

Figure 54 Average concentrations of lignans in genus Pinus (HW = heartwood, LK = living knot, DK = dead knot, NTG = nortrachelogenin, MR = matairesinol, Lari = lariciresinol).

There was a striking difference in the lignan distribution of the two subgenera (cladogram in Figure 16); Nortrachelogenin (NTG)[54] dominated in subgenus *Pinus*, while it was totally absent in subgenus *Strobus*. Instead, lariciresinol and cyclolariciresinol dominated in subgenus *Strobus*. There were some other genetic differences as well, but because of the limited number of species per subsections one should be careful in drawing too extensive conclusions. It did, nevertheless, seem like the heartwood of species from subsection *Contortae* (i.e. *P. banksiana* and *P. contorta*) contained mainly secoisolariciresinol and 7-todolactol A, while 7-todolactol A alone dominated in the heartwood of subsection *Pinus* (*P. sylvestris*, *P. resinosa* and *P. nigra*). NTG dominated in all knot samples from subgenus *Pinus*, except in *P. resinosa* and some of the knots of *P. elliottii*, where matairesinol dominated. Cyclolariciresinol dominated in the dead tissue (heartwood and dead knots) of *P. strobus*, while lariciresinol dominated in the living knots. Since cyclolariciresinol dominated in the knot extracts of *P. gerardiana* and *P. wallichiana* too, it is plausible that these knot extracts were mainly from dead knots. The ratio of fatty acids to triacylglycerols also supports this assumption. Lariciresinol and 7-todolactol A were equally abundant in the heartwood of *P. sibirica*, while lariciresinol dominated in the knots.

Small amounts of sesqui-, di- and sesterlignans were found in all samples, except in *P. taeda*. The sesquilignans were the most abundant oligolignans and like the lignans, the concentrations were higher in the heartwood than in the sapwood, except in *P. radiata*, where the sapwood contained slightly more oligolignans than the heartwood (0.20% and 0.22%, respectively). The heartwood of *P. elliottii*, *P. nigra* and *P. strobus* contained up to 0.20% oligolignans, the other stemwood samples less than 0.09%.

The oligolignan concentration was always higher in the knots than in the stemwood. The only exception was *P. radiata*, which was very poor in both lignans and oligolignans. The total average concentration in the knots of *P. contorta*, *P. gerardiana*, *P. roxburghii*, *P. taeda* and *P. wallichiana* was lower than 0.09%, *P. banksiana*, *P. elliottii*, *P. radiata* and *P. sylvestris* contained 0.11–0.38%, and up to 0.85% was found in the knots of *P. nigra*, *P. pinaster*, *P. resinosa, P. sibirica* and *P. strobus.* It could not be

[54] The name NTG was first given to a compound isolated from *Trachelospermum asiaticum* var. *intermedium* (Nishibe et al. 1971): A few years later, the stereochemistry of (–)-NTG was established (Nishibe et al. 1973) and the (+)-enantiomer, called wikstromol, was isolated from *Wikstroemia viridiflora* (Tandon & Rastogi 1976). Already Carnmalm (1959) isolated pinopalustrin from exhumed stumps of *Pinus palustris*. The results were, however, presented in Swedish only and therefore, passed unnoticed. It was not until Carnmalm et al. (1977) presented the stereochemistry of pinopalustrin in English that it became obvious that NTG and pinopalustrin were identical. By that time the name NTG was already established for the compound and, thus, remained prevalent.

concluded whether the lignan and oligolignan concentrations were higher in the living or in the dead knots.

Pinus banksiana

The total lignan concentration in heartwood of *P. banksiana* was 0.06–0.07% and 0.01–0.03% in the sapwood. The living knots contained 2.0% lignans, while only 0.65% was found in the dead knot. NTG was the dominating lignan in all knot samples. Lower concentrations of matairesinol, secoisolariciresinol, 7-todolactol A, cyclolariciresinol[55], two isomers of HMR, pinoresinol, α-conidendrin and lariciresinol were also found[56].

The heartwood contained 0.05–0.07% sesquilignans, 0.01% dilignans and 0.01% sesterlignans. Only traces of these three groups were detected in the sapwood. The living knots contained 0.20–0.21% sesquilignans, 0.14% dilignans and 0.03% sesterlignans. The concentrations in the dead knot were 0.08%, 0.04% and 0.02%, respectively. The sesquilignan NTG guaiacyl glyceryl ether was identified in the living knots.

The lignans in heartwood of *P. banksiana* have been studied by Rudloff and Sato (1963). They found cyclolariciresinol, secoisolariciresinol, lariciresinol, α-conidendrin, pinoresinol, olivil and three unknown lignans. Furthermore, they isolated a lignan trimer with the molar mass 573 g/mol. They conjectured that it was a lari-oligolignan, but considering the molar mass, it could have been the guaiacyl glyceryl ether of olivil or todolactol A. The molar mass of the sesquilignan identified in this thesis (NTG guaiacyl glyceryl ether) was 570 g/mol. Pietarinen et al. (2006a) studied knots of *P. banksiana* and found NTG and oligolignans.

Pinus contorta

The lignan concentrations in *P. contorta* were very low; 0.02–0.03% was found in the heartwood, traces in the sapwood and 0.10–0.35% in the living knots. NTG was the dominating lignan, followed by low concentrations of 7-todolactol A, secoisolariciresinol and pinoresinol.

Small amounts of oligolignans were detected in all samples. The heartwood contained very low concentrations of sesquilignans and dilignans, while the sapwood and the living knots contained traces of sesquilignans, dilignans and sesterlignans.

[55] Cyclolariciresinol is also known as isolariciresinol.
[56] Si et al. (2013) identified the neolignan cedrusin in branch wood from *P. banksiana*. No cedrusin was, however, identified in the samples analysed in this thesis.

The lignans in the stemwood of *P. contorta* have not been studied before. Willför et al. (2003c) reported the occurrence of NTG and liovil in the knots. They also saw some indications of oligomers, but they were not able to identify any oligolignans.

Pinus elliottii

The lignans in *P. elliottii* have not been studied before. The heartwood contained 0.05–0.11% lignans, the sapwood only traces, the living knots 0.95–2.8% and the dead knots 0.80–6.9%. NTG and matairesinol were the most abundant lignans. Lower concentrations of secoisolariciresinol, conidendric acid, 7-todolactol A, cyclolariciresinol, lariciresinol, pinoresinol, two isomers of HMR and α-conidendrin were also detected.

The heartwood contained low concentrations of sesquilignans, dilignans and sesterlignans. The sapwood contained only traces of oligolignans. The living knots contained 0.07–0.27% sesquilignans, 0.03–0.17% dilignans and 0.05–0.09% sesterlignans. The dead knots contained 0.09–0.40% sesquilignans, 0.03–0.13% dilignans and up to 0.13% sesterlignans.

Pinus gerardiana

Only knots of *P. gerardiana* were analysed and they did not contain any significant amounts of lignans, only 0.20% was found. Cyclolariciresinol was most abundant, but some lariciresinol, pinoresinol and traces of secoisolariciresinol were also detected. Less than 0.05% each of sesqui-, di- and sesterlignans were also found. There are no previous reports about lignans in the wood of *P. gerardiana*.

Pinus nigra

The heartwood of *P. nigra* contained 0.06–0.11% lignans and the sapwood less than 0.01%. The knots, on the other hand, were rich in lignans; 0.42–11% was found in the living knots and 1.1–6.6% in the dead. NTG was the most abundant lignan, but significant amounts of matairesinol were also detected in the knots. Low concentrations of 7-todolactol A, cyclolariciresinol, lariciresinol, secoisolariciresinol and an unknown lignan were found in all samples. The knot samples additionally contained small amounts of α-conidendrin, conidendric acid, and two isomers of HMR, pinoresinol and secoisolariciresinol monomethyl ether. Secoisolariciresinol dimethyl ether was detected in trace amounts in some heartwood and dead knot samples.

Low concentrations of sesqui-, di- and sesterlignans were found in the heartwood, only traces in the sapwood. The living knots contained 0.07–0.70% sesquilignans, 0.03–0.20% dilignans and 0.03–0.26% sesterlignans. The dead knots contained 0.16–0.57% sesquilignans, 0.08–0.19% dilignans

and 0.05–0.15% sesterlignans. Guaiacyl glyceryl ethers of secoisolariciresinol and NTG were identified in heartwood and knots.

Three other scientists have studied the lignans in *P. nigra*. Bamberger (1894) isolated pinoresinol from callus resin (also known as "Überwallungsharz" in German). Erdtman (1944a) concluded that there was no conidendrin in the stem. Willför et al. (2007) studied the lignans in heartwood, sapwood, as well as dead and living knots of *P. nigra* ssp. *pallasiana* (Austrian pine). Willför et al. (2007) also found that NTG dominated in all samples, but their concentrations in the knots were significantly higher than reported in this thesis. They found 9.2% NTG in the living knots and 5.3% in the dead. They also found much more secoisolariciresinol; 0.49% in the living knots and 0.26% in the dead. Their matairesinol concentration, on the other hand, was significantly lower, only 0.07% in the living knots and 0.54% in the dead. Willför et al. (2007) also detected the pinoresinol, sesquineo-, dineo- and higher oligolignans.

Pinus pinaster

The heartwood of *P. pinaster* contained 0.04–0.11% lignans and the sapwood up to 0.01%. The knots were fairly rich in lignans; 1.3–5.6% was found in the living knots and 3.7–5.3% in the dead. Also here was NTG the most abundant lignan; up to 5% of the dry knot wood weight was NTG. Pinoresinol was the second most abundant lignan followed by some secoisolariciresinol, lariciresinol, two isomers of HMR, cyclolariciresinol, lignan A, matairesinol, 7-todolactol A, α-conidendrin, 7-secoisolariciresinol monomethyl ether and secoisolariciresinol dimethyl ether.

The heartwood contained 0.06–0.10% sesquilignans, the sapwood 0.01–0.05%, the living knots 0.21–0.57% and the dead knots 0.36–0.65%. The most abundant sesquilignans in the heartwood and knots were NTG guaiacyl glyceryl ethers. Low concentrations of di- and sesterlignans were found in all samples.

Conde et al. (2013a) extracted heartwood, sapwood and knots with water. They identified and quantified NTG, pinoresinol, secoisolariciresinol, cyclolariciresinol and todolactol. Their concentrations were in the same range as the ones presented in this thesis.

Pinus radiata

The lignans in *P. radiata* have not been studied before, and one reason might be that the species is very poor in lignans. Only trace amounts were found in the stem and in the living knots, and the dead knot contained 0.14% lignans. NTG, secoisolariciresinol, 7-todolactol A, cyclolariciresinol, lariciresinol, pinoresinol and some unknown lignans were detected.

The heartwood contained 0.11% sesqui-, 0.04% di- and 0.05% sesterlignans. The sapwood contained less than 0.03% sesqui- and dilignans and 0.17% sesterlignans. The living knots contained 0.04–0.11% sesquilignans, 0.03–0.04% dilignans and 0.16–0.18% sesterlignans. Less than 0.05% of each type was found in the dead knot.

It is known that trees growing under favourable conditions use photosynthetic carbon for growth instead of defence (Herms & Mattson 1992 and references therein) and since these trees were remarkably fast growing, with annual rings exceeding 12 mm, it was only to be expected that they were poor in secondary metabolites.

Pinus resinosa

The heartwood of *P. resinosa* contained 0.04–0.05% lignans, the sapwood less than 0.01%, the living knots 0.71–1.5% and the dead knots 0.87–2.0%. The composition of lignans differed from the other studied pine species, since matairesinol was the dominating compound, followed by 7-todolactol A. Some secoisolariciresinol, HMR, NTG, 9′-hydroxylariciresinol, pinoresinol, cyclolariciresinol and traces of lariciresinol, as well as α-conidendrin and some minor, unknown lignans were also detected.

Low concentrations of sesqui-, di- and sesterlignans were found in the stemwood. The knots contained 0.09–0.40% sesqui-, 0.04–0.15% di- and 0.03–0.07% sesterlignans.

Sato and Rudloff (1964) studied the heartwood of *P. resinosa*. They found three trimeric oligolignans which were guaiacyl glycerol derivates of lariciresinol. The same trimers have previously been detected in *Pinus banksiana* (Rudloff & Sato 1963). Pietarinen et al. (2006a) identified todolactol A, isoliovil, NTG and oligolignans in the knot extracts.

Pinus roxburghii

Only knots of *P. roxburghii* were studied and the total lignan concentration was 0.26%. NTG was the dominating compound, but traces of pinoresinol, secoisolariciresinol, lariciresinol and cyclolariciresinol were also detected. The knots also contained low amounts of sesqui-, di- and sesterlignans. Pinoresinol has been found earlier in the oleoresin (El-Shaer 2002), but the lignans in wood have not been studied before.

Pinus sibirica

P. sibirica was the pine species richest in lignans in this study; 0.19–0.21% was found in the heartwood, less than 0.01% in the sapwood, 5.0% in the living knots and 2.1–4.4% in the dead knots. This species was different from the pines described earlier because it lacked NTG, which was the most

abundant compound in most of the other species. Lariciresinol was the dominating compound in *P. sibirica*; up to 4% was found in the knots. Cyclolariciresinol, secoisolariciresinol, matairesinol, two isomers of HMR, pinoresinol, 7-todolactol A, conidendric acid and α-conidendrin were also found.

The heartwood contained low amounts of sesqui- and dilignans, the sapwood traces of sesqui-, di- and sesterlignans. Up to 0.61% sesquilignans were found in the living knots and up to 0.43% in the dead. The guaiacyl glyceryl ethers of secoisolariciresinol, lariciresinol and anhydroisolariciresinol were identified. The knots also contained some unidentified di- and sesterlignans.

There are no previous reports of lignans in the stemwood. Willför et al. (2003c) studied the antioxidant activity of knot extracts. They found lariciresinol, cyclolariciresinol, secoisolariciresinol and oligolignans consisting of the guaiacyl glycerol ethers of the main lignans in their extracts.

Pinus strobus

The lignan concentrations in *P. strobus* were fairly low and the composition was very simple. The total concentration was 0.01–0.03% in the heartwood; only traces were found in the sapwood, 0.67–1.3% in the living knots and 0.49–0.68% in the dead knots. The only lignans detected were lariciresinol and cyclolariciresinol. Lariciresinol dominated in the living knots and cyclolariciresinol in the dead. Some sesqui-, di- and sesterlignans were detected in all samples.

Carvalho et al. (1996) analysed wood of *Pinus strobus* var. *chiapensis* Martinez. They isolated 0.19 g lariciresinol per kg wood. In this thesis, the equivalent amount of cyclolariciresinol, not lariciresinol, was detected. It is known that lariciresinol forms cyclolariciresinol when treated with acid (Erdtman 1939b), but the samples did not come in contact with any acid, so it is not likely that the cyclolariciresinol was isomerized lariciresinol.

Pietarinen et al. (2006a) also identified both lariciresinol and cyclolariciresinol in their knot extracts and they stated that lariciresinol was more abundant. They did, however, not report whether the extracts originated from living or dead knots.

Pinus sylvestris

The heartwood of *P. sylvestris* contained 0.04% lignans, the sapwood only trace amounts, the living knots 1.4–3.5% and the dead knots 0.70–2.8%. The most abundant lignan was NTG, but low concentrations of secoisolariciresinol, 7-todolactol A, cyclolariciresinol, pinoresinol, larici-

resinol, two isomers of HMR and some minor unknown lignans were also detected. Sesqui-, di- and sesterlignans were also found in all samples, except in the dead knots where only the two first were detected. The sesquilignan NTG guaiacyl glyceryl ether was identified in the living knots.

Erdtman (1939b) was the first to study lignans in *P. sylvestris*. He isolated pinoresinol from callus resin. He also stated that there was no conidendrin in the sapwood (Erdtman 1944a). Later, Ekman et al. (2002) identified NTG in knots and in the heartwood of branches. They found 2–4% NTG in the knots, but they did not detect any NTG in the normal stemwood. Willför et al. (2003b) also studied the lignans in *P. sylvestris*. They found 0.4–3% in the knots, but no lignans in the stemwood. Neither did they find any lignans 10 cm out in the branch. Like Ekman et al. (2002), they stated that NTG was the most abundant lignan. They did, however, also find smaller amounts of matairesinol, secoisolariciresinol, liovil and two unidentified lignans, as well as 0.1–0.7% of a complex mixture of oligolignans. The oligolignans were mainly of trimeric type and it seemed like they were formed at an early age, and that mainly lignans were formed as the trees grew older. Later, Willför et al. (2004c) identified the oligolignans as β-*O*-4-linked guaiacyl glyceryl ethers of NTG and secoisolariciresinol.

Holmbom et al. (2008) studied the callus resin and found matairesinol, pinoresinol and unidentified lignan esters therein. This shows that the lignan composition of the wood differs significantly from that of callus resin.

Pinus taeda

The heartwood of *P. taeda* contained 0.15% lignans, the sapwood trace amounts, the living knots 0.02–4.8% and the dead knots 0.02–4.9%. The dominating lignan was NTG. Very low concentrations of secoisolariciresinol, conidendric acid, 7-todolactol A, pinoresinol, lariciresinol, cyclolariciresinol, α-conidendrin, HMR and matairesinol were also detected. This was the only species where no oligolignans were detected.

The enzymatic biosynthesis of lignans in *P. taeda* has been frequently studied, e.g. Eberhardt et al. (1993) detected low concentrations of matairesinol (0.02%) and pinoresinol in cell suspension cultures of *P. taeda.*

Pinus wallichiana

Only knots of *P. wallichiana* were analysed and they contained only 0.26% lignans. As in the related species *P. sibirica* and *P. strobus*, NTG did not dominate; instead cyclolariciresinol and lariciresinol were most abundant. Traces of pinoresinol and secoisolariciresinol were also detected, as well as

low concentrations of sesqui-, di- and sesterlignans. There are no previous reports of lignans in wood of *P. wallichiana.*

Picea

The lignan concentrations in genus *Picea* were much higher than in genus *Pinus*. A reason could be that the pines contain other protective, polyphenolic compounds and oleoresin as well, while the lignans constitute the main group of phenols in spruce.

The average lignan concentrations in the heartwood of *P. glauca* and *P. abies* grown in Finland were lower than 0.09%, while the other species contained up to 0.40% (Figure 55). The heartwood of *P. abies* grown in France was an outlier with a remarkably high heartwood concentration - fully 1.5%. All sapwood samples contained less than 0.05% lignans.

The average lignan concentrations in the knots of *P. pungens* and *P. sitchensis* were only 1.5–1.7%. The related species *P. omorika* and *P. mariana* contained 2.2–4.8%, while *P. glauca* and the dead knot of *P. abies* grown in France contained 5.9–9.5%. *P. abies* and *P. koraiensis* were closely related and contained the highest average lignan concentrations, 11–13%.

The average total oligolignan concentrations in heartwood of the Finnish *P. abies*, *P. mariana* and *P. glauca* were 0.05% at the most. The heartwood of *P. omorika* and *P. sitchensis* contained 0.13–0.14% oligolignans, while *P. pungens*, *P. abies* from France and *P. koraiensis* contained 0.22–0.29%. The sapwood of *P. koraiensis* was the richest in oligolignans (0.25%). *P. omorika* and *P. pungens* contained less than 0.09% and the remaining species less than 0.05%.

Like the lignan concentrations, the oligolignan concentrations were remarkably much higher in the knots than in the normal stemwood. The average oligolignan concentrations in the knots of *P. glauca*, *P. mariana*, *P. omorika*, *P. sitchensis* and the living knots of *P. pungens* were 0.8–1.6%. *P. abies*, *P. koraiensis* and the dead knots of *P. pungens* contained 2.3–4.6% oligolignans.

The lignan HMR dominated in almost all spruce species, however, with two exceptions: *P. pungens*, where 7-todolactol A dominated in the heartwood and secoisolariciresinol in the knots, and *P. sitchensis* where 7-todolactol A dominated in all samples.

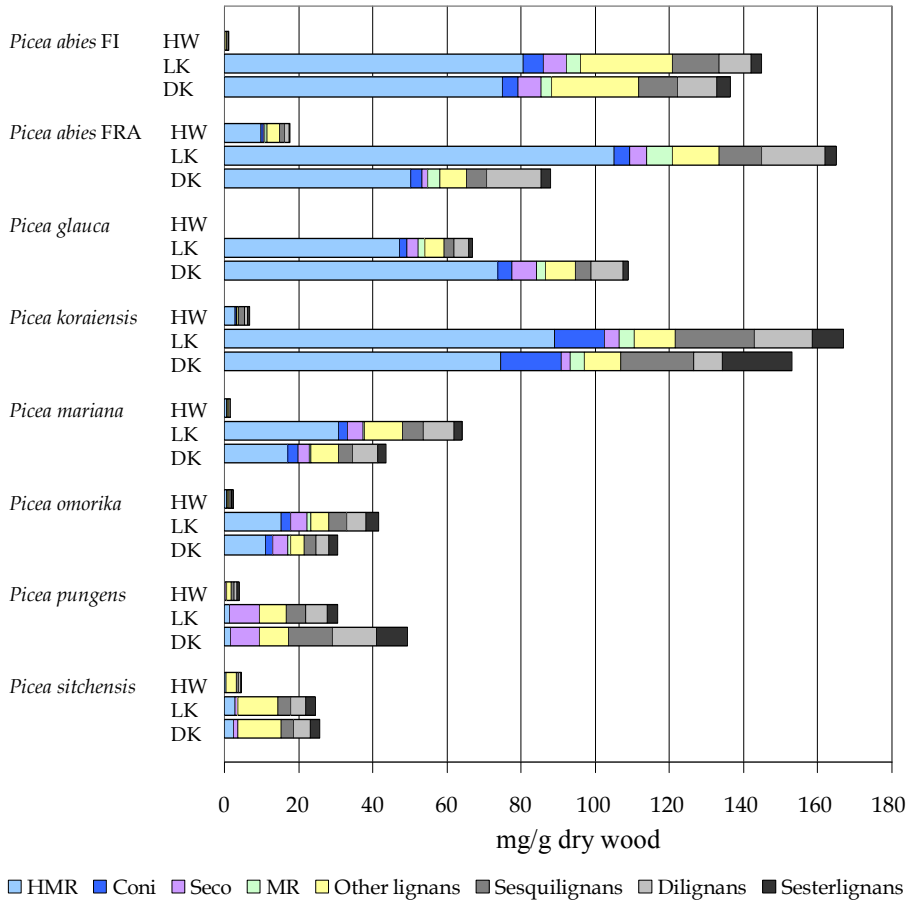

Figure 55 Average concentrations of lignans in genus Picea (HW = heartwood, LK = living knot, DK = dead knot, HMR = hydroxymatairesinol, Coni = α-conidendrin, Seco = secoisolariciresinol, MR = matairesinol).

Picea abies

Two trees of *P. abies* grown in Finland and one tree grown in France were sampled. The French heartwood was exceptionally rich in lignans; 1.5% compared to 0.06–0.12% in the Finnish samples. The French sapwood, on the other hand, was poorer in lignans than the Finnish. The Finnish knots contained 11–12% lignans, the French living knot 13% and the French dead 6.5%.

The composition of lignans was similar in the Finnish and French trees. HMR dominated and low concentrations of 7-todolactol A, matairesinol, secoisolariciresinol, α-conidendrin, conidendric acid, lariciresinol, as well as traces of lignan A, pinoresinol, cyclolariciresinol, 7′-oxolariciresinol and some unidentified lignans were detected.

Trace amounts of sesqui-, di- and sesterlignans were found in the stemwood of the Finnish trees. The French heartwood contained low concentrations. The total average oligolignan concentrations in the Finnish and French knots were fairly similar. They contained 0.53–1.4% sesquilignans, 0.82–1.7% dilignans and 0.15–0.41% sesterlignans. The guaiacyl glyceryl ethers of 7-todolactol A, secoisolariciresinol, HMR and lariciresinol were identified.

Many scientists have identified and quantified the lignans in different parts of *P. abies*. Erdtman (1944a) was first out, and he found conidendrin in the stem and branches. Freudenberg and Knof (1957) found 0.6% lignans in the wood. They identified two isomers of HMR, which constituted 0.25% of the wood, liovil, α-conidendrin, pinoresinol, matairesinol, lariciresinol, oxomatairesinol and 3,4-divanillyltetrahydrofuran. They also detected an unidentified lignan.

Weinges (1960, 1961) studied callus resin (Überwallungsharz), from which he isolated pinoresinol, *epi*-pinoresinol, lariciresinol, cyclolariciresinol and secoisolariciresinol. Several years later, Holmbom et al. (2008) also analysed callus resin. They found pinoresinol, lariciresinol, secoisolariciresinol, lariciresinol coumarate and some unidentified lignan esters. They did not find any *epi*-pinoresinol or cyclolariciresinol, and explained that these compounds were formed from pinoresinol and lariciresinol in acidic solution. These reactions have also been shown earlier (Haworth & Kelly 1937, Lindberg 1950).

Kimland and Norin (1972) found pinoresinol, with small amounts of lariciresinol, cyclolariciresinol and secoisolariciresinol in the oleoresin. Omori et al. (1983) isolated and identified traces of *p*-coumaric acid, (+)-pinoresinol and lariciresinol *p*-coumarate from resin.

Some years later, Ekman (1976) did a comprehensive study of the lignans in the stemwood. His total lignan content was 0.5%, which was closer to the concentrations found in the French specimen than in the Finnish. Ekman (1976) detected 19 lignans: two isomers of HMR, α-conidendrin, liovil, secoisolariciresinol, lariciresinol, pinoresinol, matairesinol, cyclolariciresinol, α-conidendric acid, lignan A[57], lignan B and seven unidentified lignans. Ekman (1976) did not detect any oxomatairesinol, which Freudenberg and Knof (1957) did. Therefore, he suggested that their oxomatairesinol was an auto-oxidation product from HMR. Ekman (1976) did, however, find α-conidendric acid. The explanation proposed was that α-conidendric acid was an artefact from hydrolyzed α-conidendrin formed

[57] The lignan was first isolated from spruce roots (Andersson et al. 1975). The name Lignan A was given by Ekman (1976), but a few years later he changed it to picearesinol (Ekman 1979b). The name 7′-hydroxylariciresonol was introduced by Smeds et al. (2012).

during the extraction procedure. The concentrations reported by Erdtman (1976) were obtained for a mix of heartwood and sapwood, and were well in accordance with the results of this thesis.

Jørgensen et al. (1995) compared the lignans found in stemwood and in TMP effluents. Their total lignan content was 1.0 mg/g oven-dried wood (o.d.w.) and the composition was very similar to this thesis.

Willför et al. (2003a, 2004a, 2005a) have studied the lignans in stemwoos and knots. They found 5–24% lignans in the knots. Their composition was very similar to this thesis, they did, though, find some NTG, or its enantiomer wikstromol, in trees from northern Finland. This compound was not detected in any sample from the southern part of Finland. They also found 2–6% oligolignans in the knots (Willför et al. 2003a). The amount of oligolignans was normally 20–30% of the lignan amount. In young trees, however, it amounted to 30–60%. According to the authors, this suggested that the oligolignans were formed at an early age, while the lignans appeared later. The β-*O*-4-linked guaiacyl glyceryl ethers of HMR, secoisolariciresinol, lariciresinol, cyclolariciresinol, lignan A, liovil, conidendrin and pinoresinol were identified, as well as 5-5-*bis*-secoisolariciresinol and either 5-5-*bis*-cyclolariciresinol or 5-5-*bis*-lariciresinol (Willför et al. 2004a, 2004c). In a later study, Smeds et al. (2016) identified several di-, sester-, tri-, sesquar- and tetralignans. Some of them were combinations of various units, while others consisted of several units of the same type. They also detected lignans linked to one or two guaiacyl glycerol units by β-*O*-4 or β-5 bonds.

Holvestad et al. (2006) analysed lignans in *P. abies* grown in Norway. They did not detect any significant lignan amounts in stemwood, but the total content in the knots was 6.5%. They identified and quantified two isomers of HMR and liovil.

Several studies have focused on identifying the less abundant lignans in knots. Among them, Eklund et al. (2004b) identified two isomers of *iso*-HMR. They were detected in spruce species where HMR was a major compound. Smeds et al. (2011) identified 7*S*- and 7*R*-todolactol A, 7*S*-isoliovil, the 7′*S*,8′*R*,8*R*,7*S*-isomer of lignan A and two stereoisomers (9′*R*,8′*R*,8*R*,7*S* and 9′*R*,8′*R*,8*R*,7*R*) of 9′-hydroxylariciresinol. Additionally, they identified two stereoisomers of lignan A, four stereoisomers of liovil, 7-hydroxylariciresinol, 7-hydroxydivanillyl tetrahydrofuran and 9-hydroxypinoresinol tentatively. The compound previously identified as liovil was proven to be 7*R*-todolactol A and 7*R*-isoliovil. 7*R*-Todolactol A was unstable in aqueous solution and formed 7-isoliovil, a stereoisomer of 9′-hydroxylariciresinol (probably 7*S*-todolactol A), todolactol B, 7-hydroxydivanillyl tetrahydrofuran and didehydrodivanillyl tetrahydrofuran.

Picea glauca

The heartwood of *P. glauca* contained less than 0.02% lignans and only traces were detected in the sapwood. The living knots contained 4.5–6.7% lignans and the dead knots 9.4–9.5%, i.e. the concentrations in the knots were 390–620 times higher than in the heartwood. The two isomers of HMR dominated in all samples. Some NTG, secoisolariciresinol, α-conidendrin, 7-todolactol A, matairesinol, and traces of lariciresinol, conidendric acid, cyclolariciresinol, pinoresinol and some unknown lignans were also detected.

Traces of oligolignans were found in the stemwood. The knots contained 0.17–0.43% sesquilignans, 0.31–0.97% dilignans and 0.07–0.15% sesterlignans. The guaiacyl glyceryl ethers of 7-todolactol A, secoisolariciresinol, HMR and lariciresinol were identified.

Willför et al. (2004a, 2005a) made a thorough investigation of the lignans and oligolignans in *P. glauca* and their results were well in accordance with this thesis. The only minor differences were that they detected lignan A, while NTG was found in this thesis. Their heartwood concentrations were also a bit higher and their knot concentrations somewhat lower. The predominant sesquilignans were the guaiacyl glyceryl ethers of HMR and lariciresinol (Willför et al. 2004a).

Hart et al. (1975) injured sapwood of *P. glauca* with an increment borer, but they could not detect any significant changes in composition or amount of lignans compared to sound wood. The lignans they quantified in heartwood and sapwood were HMR, liovil and conidendrin. Pietarinen et al. (2006a) detected HMR, secoisolariciresinol, matairesinol, todolactol A, isoliovil, α-conidendrin and oligolignans in their knot extracts.

Picea koraiensis

P. koraiensis was very rich in lignans; 0.39% was found in the heartwood, 12% in the living and 11% in the dead knot. HMR was the dominating lignan, followed by α-conidendrin. Some matairesinol, 7-todolactol A, secoisolariciresinol, lariciresinol, conidendric acid and cyclolariciresinol were also detected. Low concentrations of sesqui-, di- and sesterlignans were found in the normal stemwood; the knot concentrations were higher and varied from 0.76% to 2.1% for each oligolignans type.

Leont'eva et al. (1974b) made a comprehensive analysis of the lignans in the stemwood. The concentrations they found were in accordance with the heartwood concentrations in this thesis, they did, however, detect some other compounds as well: 3,4-divanillyltetrahydrofuran, liovil, pinoresinol

and ketomatairesinol[58]. On the other hand, they did not find any conidendric acid, cyclolariciresinol, 7-isoliovil, secoisolariciresinol or 7-todolactol A. Willför et al. (2004a, 2005a) studied heartwood, sapwood and knots of *P. koraiensis* and their data were almost identical with the results presented in this thesis.

Picea mariana

Picea mariana was not as rich in lignans as the previously described spruce species. The heartwood contained 0.07–0.19%, the sapwood less than 0.03%, the living knots 2.4–7.2% and the dead knots 2.0–4.1%. HMR was the dominating compound, some 7-todolactol A, secoisolariciresinol, α-conidendrin, NTG, lariciresinol, and traces of cyclolariciresinol, matairesinol pinoresinol and several minor, unknown compounds were also found. The stemwood contained very low oligolignan concentrations, while the knots contained 0.36–0.77% sesquilignans, 0.55–1.1% dilignans and 0.15–0.28% sesterlignans. The guaiacyl glyceryl ethers of 7-todolactol A, secoisolariciresinol, HMR and lariciresinol were identified.

Erdtman (1944a) found conidendrin in branches of *P. mariana.* Sixty years later Willför et al. (2004a, 2005a) made a thorough study of heartwood, sapwood and knots. Their concentrations were fairly similar to those in this thesis. Willför et al. (2004a, 2005a) did, however, identify lignan A, while NTG and some unidentified compounds were found in this thesis. They also identified the guaiacyl glyceryl ethers of HMR and liovil.

Pietarinen et al. (2006a) identified HMR, todolactol A, isoliovil, conidendrin, lignan A, secoisolariciresinol, lariciresinol and oligolignans in the knots.

Picea omorika

Picea omorika is closely related to *P. mariana* and consequently both lignan composition and concentrations were rather similar. The heartwood of *P. omorika* contained 0.13% lignans, the sapwood 0.02%, the living knots 2.8% and the dead 2.2%. HMR was the most abundant lignan, followed by secoisolariciresinol, α-conidendrin, 7-todolactol A, matairesinol, conidendric acid, NTG, and traces of lariciresinol, cyclolariciresinol, pinoresinol and oxomatairesinol. The stemwood contained very low concentrations of sesqui-, di- and sesterlignans, the knots 0.23–0.51% of each compound type.

Erdtman (1944a) found some conidendrin in branches of *P. omorika*. Willför et al. (2004a, 2005a) made a more comprehensive study of the

[58] Ketomatairesinol is synonymous with oxomatairesinol.

heartwood, sapwood and knots. Their results are almost identical with the results presented in this thesis.

Picea pungens

The heartwood of *P. pungens* contained 0.06–0.31% lignans, the sapwood less than 0.02%, the living knots 1.0–2.2% and the dead knots 0.76–2.8%. Here HMR was not the dominating lignan, instead secoisolariciresinol was most abundant and 7-todolatol A was second most abundant. Some HMR, 9′-hydroxy lariciresinol (also found in *P. sitchensis*), lignan A, and traces of lariciresinol, NTG, pinoresinol, cyclolariciresinol, lignan B and some unknown lignans were also detected.

The concentrations of oligolignans were high in ratio to the fairly low lignan concentrations. Up to 0.14% each of sesqui-, di- and sesterlignans were found in the heartwood. The sapwood contained less than 0.07% of each type, while the living knots contained up to 0.99% of each group and the dead knots up to 1.8%.

Erdtman (1944a) stated that *P. pungens* did not contain any conidendrin. Willför et al. (2004a, 2005a) studied stemwood and knots of and their results were equal to the results of this thesis, with the exception that no traces of conidendric acid were found in this thesis.

Picea sitchensis

P. sitchensis had the lowest lignan concentrations of all studied spruce species. The heartwood contained 0.14–0.50%, the sapwood trace amounts and the knots 1.2–1.8%. 7-Todolactol A was the dominating compound in all samples. Some HMR, 9'-hydroxy lariciresinol (also found in *P. pungens*), secoisolariciresinol and NTG were also found, as well as traces of hydroxy-NTG[59], lariciresinol, cyclolariciresinol and pinoresinol.

The stemwood contained very low concentrations of oligolignans. The knots contained 0.26–0.38% sesquilignans, 0.37–0.46% dilignans and 0.22–0.31% sesterlignans. The guaiacyl glyceryl ethers of todolactol A, secoisolariciresinol, HMR and lariciresinol were identified.

Erdtman (1944a) tried to find conidendrin in *P. sitchensis*, but he did not succeed. Willför et al. (2004a, 2005a) analysed heartwood, sapwood and knots. They found a bit lower concentrations than reported in this thesis. They also identified lignan A, but no NTG or hydroxy-NTG. Pietarinen et al. (2006a) found todolactol A, isoliovil, HMR, lignan A and oligolignans in the knot extracts.

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[59] 7′-Hydroxynortrachelogenin was first identified by Yang et al. (1999).

Abies

The average lignan concentrations in genus *Abies* were in the same range as in genus *Picea*. The average oligolignan concentrations were, though, a bit higher in genus *Abies* than in *Picea.*

The average lignan concentration in the heartwood of section *Balsamea* was lower than in the other sections; *A. lasiocarpa*, *A. sibirica*, *A. sachalinensis* and *A. veitchii* contained less than 0.10% and *A. balsamea* 0.17% (Figure 56). The average lignan concentration in the heartwood of *A. alba* was 0.49%, 0.81% in *A. concolor* and 0.86% in *A. amabilis*. The concentrations in the sapwood of *A. alba*, *A. amabilis*, *A. lasiocarpa* and *A. sibirica* were lower than 0.03%, while *A. sachalinensis* and *A. veitchii* contained 0.07% and 0.10% lignans, respectively.

The knots of *A. lasiocarpa* contained fairly low average lignan concentrations, 1.1–1.5%. The knots of *A. sachalinensis* and *A. veitchii*, the living knots of *A. alba* and *A. sibirica* and the dead knot of *A. amabilis* contained 2.2–4.3% lignans. *A. concolor*, *A. balsamea* and the dead knots of *A. sibirica* contained 6.2–9.0%, while 11–13% was found in the dead knots of *A. alba*, the living knot of *A. amabilis* and the knots of *A. pindrow.*

The average oligolignan concentration in the heartwood of *A. veitchii* and *A. sibirica* was lower than 0.10%. Less than 0.30% was found in *A. sachalinensis*, *A. lasiocarpa* and *A. alba*, while *A. amabilis* and *A. concolor* contained fully 0.60%. The average oligolignan concentration in the sapwood was lower than 0.10%, except in *A. lasiocarpa, A. sachalinensis* and *A. veitchii* which contained 0.14%, 0.29% and 0.31%, respectively. The knots of *A. lasiocarpa*, the living knots of *A. alba* and the dead knots of *A. amabilis* contained fully 1% oligolignans, the remaining knots 3.2–6.1%.

The lignan composition in genus *Abies* differed from that in genus *Picea*. HMR dominated in the spruces, while 7-todolactol A was the most abundant in the stemwood of *Abies* and secoisolariciresinol in the knots. The only exception was the heartwood of *A. amabilis*, where HMR dominated.

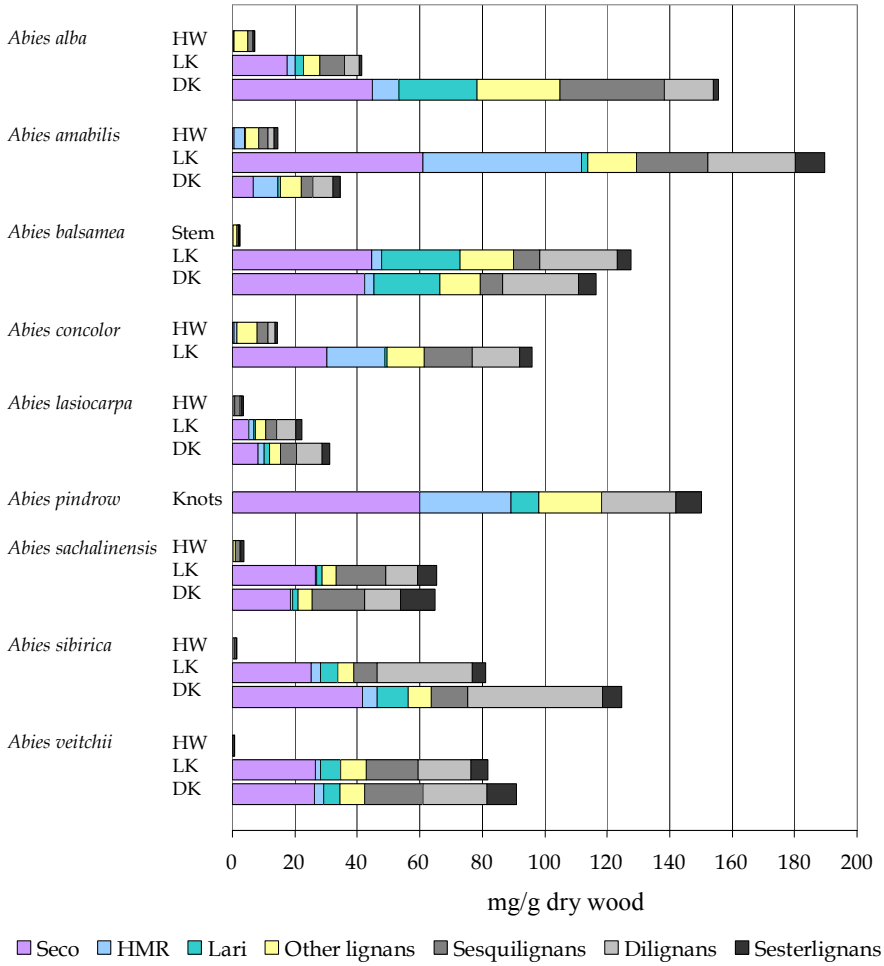

Figure 56 Average concentrations of lignans in genus Abies (HW = heartwood, LK = living knot, DK = dead knot, Seco = secoisolariciresinol, HMR = hydroxymatairesinol, Lari = lariciresinol).

Abies alba

The lignan concentration in the heartwood of *A. alba* was 0.31–0.79%, trace amounts were found in the sapwood, 1.3–6.6% in the living knots and fully 7.4–14% in the dead knots. The dominating compound in the heartwood was 7-todolactol A. Secoisolariciresinol was most abundant in the knots, but significant amounts of lariciresinol were also found, especially in the dead knots. Other compounds were the two isomers of HMR, cyclolariciresinol, lignan A, pinoresinol, secoisolariciresinol monomethyl ether, secoisolariciresinol dimethyl ether, matairesinol,

9′-hydroxy lariciresinol and traces of α-conidendrin as well as conidendric acid and some unknown lignans.

The heartwood contained low concentrations of sesqui-, di- and sesterlignans; traces were found in the sapwood. The living knots contained up to 1.4% sesqui- and dilignans and up to 0.28% sesterlignans. The amounts in the dead knots were fairly high; up to 4.5% sesquilignans, up to 1.9% dilignans and up to 0.31% sesterlignans were found.

The sesquilignan lariciresinol coumarate was identified in the heartwood, secoisolariciresinol guaiacyl glyceryl ether and lariciresinol coumarate were found in the sapwood, while the guaiacyl glyceryl ethers of secoisolariciresinol, lariciresinol and 7-todolactol A, as well as lariciresinol coumarate were detected in the living knots. The dead knots contained the same sesquilignans as the living knots in addition to the guaiacyl glyceryl ethers of anhydrosecoisolariciresinol and HMR.

Erdtman (1944a) searched for conidendrin in *A. alba*, but did not find any. In this thesis, some very small amounts were detected and the conjecture is that the distinction could be genetic; Erdtman's trees grew in Sweden, while the trees in this thesis grew in France.

Jørgensen et al. (1995) analysed the lignans in wood of *A. alba* and in TMP effluents of the same. The concentrations they report were for the whole stemwood, thus, their values lie between the sapwood and heartwood values. There were some differences between the lignans present; they identified liovil, lignan B and *allo*-HMR, while 7-todolactol A, secoisolariciresinol monomethyl ether and secoisolariciresinol dimethyl ether were found in this thesis.

Willför et al. (2004b) also analysed heartwood, sapwood and knots. The lignan distributions were similar, but they found NTG[60] while lignan A, conidendrin and conidendric acid were found here. Furthermore, they wrote that the dineolignans was the most abundant group of oligolignans, while sesqui- and dilignans were almost equally abundant in this thesis.

Pietarinen et al. (2006a) detected secoisolariciresinol, HMR, 7-todolactol A, isoliovil, lariciresinol, matairesinol and oligolignans in their knot extracts.

Abies amabilis

The heartwood *of A. amabilis* contained 0.86% lignans, the sapwood traces, the living knots 12–14% and the dead knot 2.2%. HMR was the dominating lignan in the heartwood and the dead knot, while secoisolariciresinol

[60] Presuming that 27% NTG in the dead knot is a typing-error.

dominated in the living knots. 7-Todolactol A, matairesinol, α-conidendrin, conidendric acid, NTG, lariciresinol, cyclolariciresinol, 7-hydroxy secoisolariciresinol, lignan A and pinoresinol were also detected. Low concentrations of sesqui-, di- and sesterlignans were detected in the heartwood and the dead knot, trace amounts in the sapwood and 0.9–2.8% of each type in the living knots.

Hergert (1960) found HMR in heartwood of *A. amabilis*. Barton and Gardner (1962) found matairesinol, conidendrin and HMR in the heartwood and negligible amounts of matairesinol in the sapwood. Willför et al. (2004b) studied heartwood, sapwood and knots and their results were identical with those in this thesis.

Abies balsamea

The stem of *A. balsamea* contained 0.10–0.22% lignans, the living knot 9.0% and the dead knot 7.9%. 7-Todolactol A was the most abundant compound in the heartwood, while secoisolariciresinol dominated in the knots. Significant amounts of lariciresinol were also found in the knots. Other compounds detected were matairesinol, cyclolariciresinol, HMR, pinoresinol, conidendric acid and lignan A.

Traces of sesqui-, di- and sesterlignans were found in the stem. The knots contained low amounts of sesqui- and sesterlignans and 2.4–2.5% dilignans. The sesterlignans lariciresinol coumarate and the guaiacyl glyceryl ethers of 7-todolactol A, secoisolariciresinol and lariciresinol were identified.

Willför et al. (2003c, 2004b) also analysed heartwood, sapwood and knots of *A. balsamea*. Their results resembled those in this thesis, except that they found secoisolariciresinol monomethyl ether and dimethyl ether in their dead knot.

Abies concolor

The heartwood of *A. concolor* contained 0.81% lignans and the living knot 6.2%. 7-Todolactol A was most abundant in the heartwood, while secoisolariciresinol dominated in the knot. A significant amount of HMR was also found in the knot. Other identified lignans were matairesinol, cyclolariciresinol, lignan A, lariciresinol, secoisolariciresinol monomethyl ether, pinoresinol and 7-methoxymatairesinol.

The heartwood contained 0.35% sesquilignans, 0.21% dilignans and 0.07% sesterlignans. The living knots contained 1.5% sesqui- and dilignans and 0.40% sesterlignans.

Erdtman (1944a) looked for, but could not find any conidendrin in *A. concolor*. Willför et al. (2004b) studied heartwood and a living knot.

Their results were in line with this thesis, except that here lignan A and secoisolariciresinol monomethyl ether were found, while they found NTG.

Abies lasiocarpa

The total lignan concentrations in *A. lasiocarpa* were low; 0.06–0.09% in the heartwood, traces in the sapwood, 0.31–1.8% in the living knots and 1.0–2.0% in the dead knots. 7-Todolactol A dominated in the heartwood, while secoisolariciresinol was predominant in the knots. Other identified lignans were HMR, lariciresinol, matairesinol, lignan A, cyclolariciresinol, pinoresinol, 9′-hydroxy lariciresinol, 7-isoliovil, and in the stemwood additional traces of α-conidendrin.

The stemwood contained low concentrations of sesquilignans and traces of di- and sesterlignans. The dilignans dominated in the knots. The knots contained 0.18–0.60% sesquilignans, 0.25–1.0% dilignans and 0.14–0.29% sesterlignans. The guaiacyl glyceryl ethers of 7-todolactol A, secoisolariciresinol, HMR, lariciresinol, as well as lariciresinol coumarate were identified.

Willför et al. (2004b) studied heartwood, sapwood and knots of *A. lasiocarpa* and their result were very similar to those in this thesis. Pietarinen et al. (2006a) detected secoisolariciresinol, todolactol A, isoliovil, HMR and oligolignans in the knots.

Abies pindrow

The knots of *A. pindrow* were very rich in lignans; the total concentration was 12%. Secoisolariciresinol was the dominating compound, but a significant amount of HMR was also found. Other identified lignans were lariciresinol, lignan A, 7-todolactol A, cyclolariciresinol, pinoresinol, secoisolariciresinol monomethyl ether, α-conidendrin and matairesinol. No sesquilignans were detected, but 2.4% dilignans and 0.81% sesterlignans. There are no previous reports of lignans in *A. pindrow*.

Abies sachalinensis

The heartwood of *A. sachalinensis* contained 0.10% lignans, the sapwood 0.07%, the living knots 3.3% and the dead knot 2.6%. The predominant lignan in the stem was 7-todolactol A, while secoisolariciresinol was most abundant in the knots. Low concentrations of lariciresinol, lignan A, cyclolariciresinol, HMR, and traces of pinoresinol, α-conidendrin, conidendric acid and matairesinol were also detected.

The heartwood contained 0.15% sesquilignans, 0.05% dilignans and 0.09% sesterlignans. The sapwood contained 0.12% sesquilignans, 0.05% dilignans and 0.12% sesterlignans. The knots contained 1.6–1.7% sesquilignans, 1.0–1.1% dilignans and 0.61–1.1% sesterlignans.

Takehara et al. (1980) detected three lignan esters in the compression and opposite wood of *A. sachalinensis*. They found lariciresinol *p*-coumarate[61] lariciresinol ferulate[62] and secoisolariciresinol di-*p*-coumarate. The last compound has not been reported earlier. Sasaya et al. (1980) also studied compression and opposite wood of *A. sachalinensis*, but they concentrated on lignans, not sesquilignans. They found conidendrin, cyclolariciresinol, pinoresinol, lariciresinol, lignan A and teterahydro-2-(4-hydroxy-3-methoxyphenyl)-4-(4-hydroxy-3-methoxybenzoyl)-3-furanmethanol. They did, however, not find the lignan that is most abundant in the stemwood, i.e. 7-todolactol A.

Ozawa and Sasaya have written a series of articles where they isolated and determined the structures of lignans from the normal wood of *A. sachalinensis*. They found todolactol B (Ozawa & Sasaya 1987), which existed as a mixture of epimers, as well as todolactol C and D (Ozawa & Sasaya 1988a). They were, however, uncertain whether todolactol D was a natural compound or an artefact. They also isolated pinoresinol, *epi*-pinoresinol, conidendrin and todolactol A (Ozawa & Sasaya 1988b). They stated that todolactol A was unstable in pure form, at room temperature, and that it was dehydrated to todolactol B in wood. Ozawa et al. (1988) also isolated lariciresinol, lariciresinol-*p*-coumarate and lignan A, and pointed out that the distribution and accumulation of the extractives was closely associated with the heartwood formation.

Sasaya and Ozawa (1991) also studied the radial and height distribution of cyclolariciresinol, todolactol A-D, lariciresinol, conidendrin and pinoresinol in the stem. They found an increase in the lignan concentration from cambium to the heartwood-sapwood boundary, where it reached its maximum. Todolactol A was, however, an exception. It seemed like that lignan had been converted into some other compound, possibly todolactol B, at the sapwood-heartwood boundary.

In a subsequent publication they isolated two new sesquilignans, which they named abiesol A and B (Ozawa & Sasaya 1991). Abiesol A consisted of a lariciresinol and a coniferyl alcohol unit, abiesol B occurred as a mixture of four tautomers. Unfortunately, no attempts were made to identify the oligolignans in the samples of *A. sachalinensis* studied in this thesis. That was a pity, since *A. sachalinensis* is one of the few species where a lot of work has been done on identification of sesquilignans and it would have been useful to compare the results.

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[61] Lariciresinol p-coumarate was earlier found in heartwood of *L. kaempferii* (Miki et al. 1979a), *A. sibirica* and *A. nephrolepis* (Leont'eva et al. 1976).
[62] Earlier found in heartwood of *A. sibirica* and *A. nephrolepis* (Leont'eva et al. 1976).

Willför et al. (2004b) studied heartwood, sapwood, as well as living and dead knots of *A. sachalinensis*. Both their composition and concentrations were similar to those in this thesis.

Abies sibirica

The stemwood of *A. sibirica* was poor in lignans. Only 0.07–0.09% was found in the heartwood and traces in the sapwood. The knots contained 50–80 times higher lignan concentrations than the heartwood; the living knots contained 3.8–4.0% and the dead knots 5.5–7.3%. 7-Todolactol A was the dominating lignan in the heartwood and secoisolariciresinol in the knots. Lariciresinol was the second most abundant lignan in all samples. Some HMR and matairesinol was also found along with trace amounts of cyclolariciresinol, pinoresinol, α-conidendrin, conidendric acid, lignan A and several minor, unknown compounds.

Traces of sesqui-, di- and sesterlignans were found in the stemwood. The living knots contained 0.61–0.90% sesquilignans and the dead knots 0.90–1.4% Guaiacyl glyceryl ethers of secoisolariciresinol and lariciresinol, as well as lariciresinol coumarate were identified as the main sesquilignans. The dominating type of oligolignans in the knots was the dilignans; 2.2–3.9% was found in the living knots and 3.5–5.1% in the dead ones. The sesterlignans occurred in fairly low concentrations; 0.39–0.49% in the living knots and 0.54–0.71% in the dead ones.

Medvedeva et al. (1971) were the first to isolate liovil from *A. sibirica*. Later, Leont'eva et al. (1974a) detected secoisolariciresinol, 3,4-divanilyltetrahydrofuran, lariciresinol, pinoresinol, olivil, matairesinol and HMR. They also found 2.5% lariciresinol *p*-coumarate, 0.83% lariciresinol ferulate (Leont'eva et al. 1976) and low concentrations of a lariciresinol ester, two olivil esters and two HMR esters (Leont'eva et al. 1977).

Willför et al. (2003c, 2004b) have studied lignans and oligolignans in heartwood, sapwood, as well as living and dead knots of *A. sibirica.* Generally, their concentrations were a bit lower than in this thesis, but the compositions were identical.

Abies veitchii

The heartwood of *A. veitchii* contained only traces of lignans. The sapwood, on the other hand, was richer in lignans and contained 0.10%. This was the only species where the concentration was higher in the sapwood than in the heartwood. The total concentration in the knots was 4.2–4.3%.

Secoisolariciresinol was the most abundant lignan in all samples. Low concentrations of lariciresinol, 7-todolactol A, HMR, lignan A, cyclolariciresinol, and traces of pinoresinol, conidendric acid and

α-conidendrin were also detected. The heartwood contained traces, and the sapwood very low concentrations of sesqui-, di- and sesterlignans. The knots contained 1.6–1.9% sesquilignans, 1.7–2.0% dilignans and 0.55–0.94% sesterlignans

Willför et al. (2004b) also studied heartwood, sapwood and knots of *A. veitchii*. Their results were very similar to the ones reported here.

Larix

The total lignan concentrations in stemwood of genus *Larix* were lower than in genera *Picea* and *Abies*, but higher than in genus *Pinus*. The average concentrations in the heartwood were 0.04–0.19% and less than 0.03% in the sapwood (Figure 57).

The knots of *L. lariciana* and *L. sibirica* were the poorest in lignans; their average concentrations were 0.60–3.8%. *L. decidua*, *L. gmelinii* var. *japonica*, the dead knots of *L. kaempferi* and the living knots of *L. gmelinii* var. *gmelinii* and *L. gmelinii* var. *olgensis* contained 5.7–8.7%. The dead knots of *L. gmelinii* var. *gmelinii* and var. *olgensis,* and the living knots of *L. kaempferi* contained 11–12% lignans.

Cyclolariciresinol was the dominating lignan in the heartwood of all species, except in *L. lariciana* and *L. sibirica* where 7-todolactol A dominated.

Secoisolariciresinol dominated in the knots of genus *Larix*, like in the knots of *Abies*. In genus *Abies,* secoisolariciresinol was accompanied by HMR and lariciresinol, in *Larix,* however, it was accompanied by lariciresinol, cyclolariciresinol and NTG.

On average, the heartwood of the larches contained less than 0.09% oligolignans. *L. decidua* was an exception; its heartwood contained 0.69% oligolignans. The average oligolignan concentration in the sapwood was 0.02–0.35%.

The knots of *L. lariciana* and *L. sibirica*, which were poorest in lignans, also contained least oligolignans, 0.26–1.2% on average. The other knots contained 1.8–3.2%.

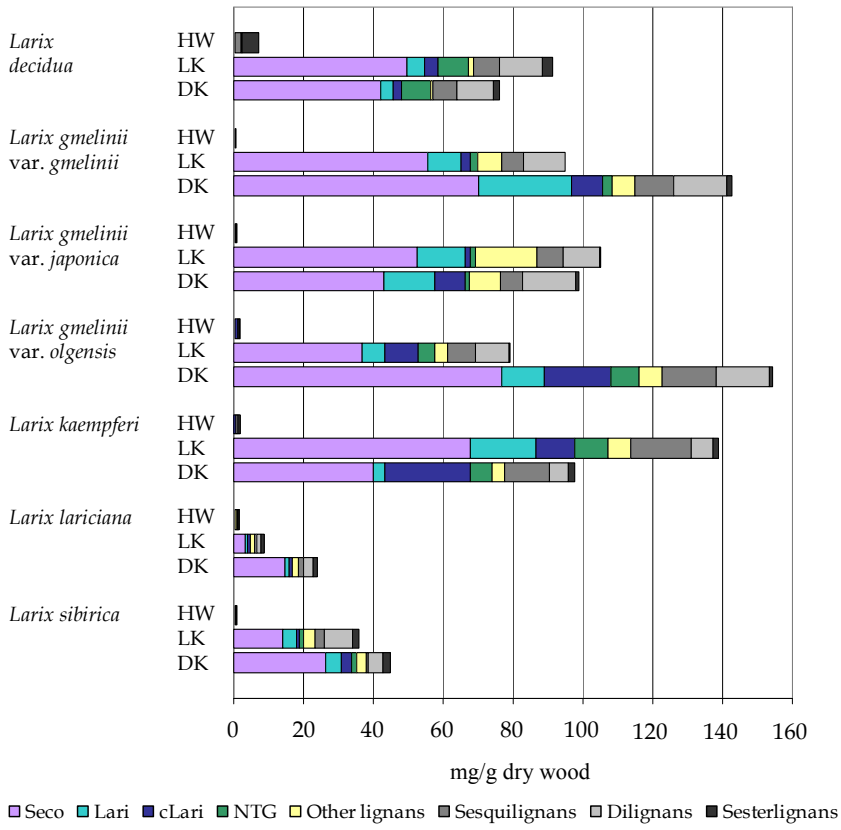

Figure 57 Average concentrations of lignans in genus Larix (HW = heartwood, LK = living knot, DK = dead knot, Seco = secoisolariciresinol, Lari = lariciresinol, cLari = cyclolariciresinol, NTG = nortrachelogenin).

Larix decidua

The lignan concentration in the heartwood of *L. decidua* varied from trace amounts to 0.11%. The sapwood contained traces, the living knots 3.2–9.7% and the dead knots 1.9–9.0%. Cyclolariciresinol was the most abundant lignan in the heartwood, while secoisolariciresinol dominated in the knots. Lower concentrations of NTG and lariciresinol were also detected, as well as traces of HMR, matairesinol, 7-todolactol A, pinoresinol, α-conidendrin, lignan A and secoisolariciresinol dimethyl ether.

The heartwood contained low concentrations of sesqui- and dilignans and up to 1.0% sesterlignans. Trace amounts of all three groups were found in the sapwood. The knots contained 0.27–1.4% sesquilignans, 0.47–2.2% dilignans and 0.09–0.42% sesterlignans. Guaiacyl glyceryl ethers of secoisolariciresinol and lariciresinol were detected.

Bamberger and Landsiedl (1897, p. 500) were the first to isolate lignans from *L. decidua*. They isolated lariciresinol from callus resin (Überwallungsharz). Freudenberg and Weinges (1959) isolated secoisolariciresinol and liovil from the wood, and Erdtman and Tsuno (1969) isolated pinoresinol from the resin. Holmbom et al. (2008) also analysed callus resin. They detected pinoresinol, secoisolariciresinol, lariciresinol-9-acetate, lariciresinol, NTG, lariciresinol-coumarate and some unidentified lignan esters.

Willför et al. (2003c) were the first to analyse lignans in knots of *L. decidua*. They presented the proportions of some lignans (secoisolariciresinol, lariciresinol, cyclolariciresinol) and oligolignans in a hydrophilic knot extract. Zule and Holmbom (2008) analysed stemwood, knots and branches of *L. decidua*. They found secoisolariciresinol, lariciresinol and NTG in the knots.

Larix gmelinii

Three varieties of *L. gmelinii* were studied: var. *gmelinii*, var. *japonica* and var. *olgensis*. They were all fairly similar, both regarding concentrations and lignan compositions. The heartwood of var. *gmelinii* contained 0.07–0.08% lignans, var. *japonica* contained 0.02–0.10% and var. olgensis 0.17–0.21%. The concentrations in all sapwood samples were lower than 0.03%. The concentration in the knots of var. *gmelinii* was 3.1–15%, var. *japonica* contained 6.5–11% and var. olgensis 5.0–12%.

Cyclolariciresinol was the dominating lignan in the stemwood and secoisolariciresinol in the knots. The knots also contained some lariciresinol and NTG, along with lower concentrations of pinoresinol, α-conidendrin, HMR, 7-todolactol A, lari-9-acetate, matairesinol and secoisolariciresinol dimethyl ether. The oligolignan concentrations in the stemwood were very low. On average, the knots contained 0.6–1.6% sesquilignans, 1.0–1.5% dilignans and a maximum of 0.14% sesterlignans.

Lapteva et al. (1971) analysed wood of *L. gmelinii* and detected secoisolariciresinol, lariciresinol, cyclolariciresinol, pinoresinol, conidendrin and 3,4-divanillyltetrahydrofuran. They stated that lariciresinol dominated in fresh extracts, while cyclolariciresinol was predominant in long-time stored extracts. There are no previous studies of lignans in the knots.

Larix kaempferi

The heartwood of *L. kaempferi* contained 0.07% lignans and the sapwood trace amounts. The knots, on the other hand, were fairly rich in lignans; the living knots contained 2.7–22% and the dead knots 1.6–17%. Cyclolariciresinol was the most abundant lignan in the heartwood, while

secoisolariciresinol dominated in the knots. No traces of secoisolariciresinol were detected in the stemwood. Other lignans present in the knots were lariciresinol, NTG, lignan B, HMR, 7-todolactol A and traces of matairesinol and α-conidendrin in some of the living knots. Very low concentrations of pinoresinol were found in all samples. Traces of di- and sesterlignan were found in the stemwood. The knots contained 0.29–3.2% sesquilignans, 0.10–1.3% dilignans and up to 0.73% sesterlignans. NTG guaiacol glyceryl ether and lariciresinol guaiacol glyceryl ether were identified.

Erdtman (1944a) looked for, but did not find any conidendrin in the stemwood of *L. kaempferi*. In this thesis, it was not either found in the stemwood, but traces were found in some of the knots, though not in all.

Takehara and Sasaya (1979c) analysed sapwood and found lariciresinol, secoisolariciresinol and pinoresinol. They also isolated three new neolignans of dihydrobenzofuran type (Takehara & Sasaya 1979a, 1979b).

Miki et al. (1979b, 1980a, 1980b) found lariciresinol, secoisolariciresinol, cyclolariciresinol, pinoresinol, 2-(4-hydroxy-3-methoxyphenyl)-3-hydroxy-methyl-4-(4-hydroxybenzyl)-tetrahydrofuran, earlier found also in *Picea abies*, (Ekman 1976) and lariciresinol *p*-coumarate in the heartwood of *L. kaempferi*[63] (1979a). They also isolated seven neolignans from the wood.

Sakakibara et al. (1987) found lariciresinol, lariciresinol-p-coumarate, 2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-4-(4-hydroxybenzyl)-tetra-hydrofuran, cyclolariciresinol, secoisolariciresinol, pinoresinol and four neolignans in the wood, but they could not detect any conidendrin or HMR. In their article they also discussed the relationship between Braun's lignin and lignans. They reached the conclusion that lignans exist in a wide molecular range, from dimers to polymers, and that the polymeric fraction corresponded to Braun's lignin. They did, however, not agree with Haworth's definition that lignans are phenyl propane units linked by a β-β bond; instead they follow a definition by McCredie et al. (1969) according to which the term "lignan" covers all natural products of low molar mass that arise primarily from the oxidative coupling of *p*-hydroxyphenylpropane units, i.e. also other bonds than β-β are included.

Nabeta et al. (1991) found pinoresinol and a neolignan in the callus tissue of *L. kaempferi*. There are no previous reports on lignans in knots of this species.

[63] *Larix leptolepis* Gord. is a synonym of *L. kaempferi* (Lamb.) Carr.

Larix lariciana

The heartwood of *L. lariciana* contained 0.10–0.11% lignans, the sapwood traces, the living knot 0.46–0.74% and the dead knots 0.82–2.9%. These were the lowest lignan concentrations in the studied *Larix* species.

7-Todolactol A was the most abundant lignan in the heartwood, while secoisolariciresinol dominated in the knots. Very low concentrations of cyclolariciresinol, lariciresinol, and traces of HMR, matairesinol, pinoresinol, conidendric acid, α-conidendrin and some unidentified lignans were also detected.

The stemwood contained trace amounts of sesqui-, di- and sesterlignans. The knots contained 0.06–0.18% sesquilignans, 0.11–0.36% dilignans and 0.08–0.12% sesterlignans. Secoisolariciresinol guaiacyl glyceryl ether was the only identified sesquilignan.

No one else has studied lignans in stemwood of *L. lariciana*. Pietarinen et al. (2006a), however, identified secoisolariciresinol, cyclolariciresinol, todolactol A, isoliovil and oligolignans in their hydrophilic knot extracts.

Larix sibirica

The heartwood of *L. sibirica* contained 0.05–0.10% lignans, the sapwood trace amounts, the living knot 2.3% and the dead knots 1.0–6.4%. 7-Todolactol A was the most abundant lignan in the heartwood, while secoisolariciresinol dominated in the knots. Low concentrations of lariciresinol, 7-todolactol A, NTG, and traces of HMR, conidendric acid, pinoresinol, α-conidendrin and lignan A were also identified.

The stemwood contained traces of sesqui-, di- and sesterlignans. The concentrations in the knots had a maximum of 0.28%, 0.80% and 0.33% of each type. The guaiacyl glyceryl ethers of secoisolariciresinol and lariciresinol were identified.

Lapteva et al. (1971) analysed lignans in wood of *L. sibirica* and they identified secoisolariciresinol, conidendrin, lariciresinol, pinoresinol, cyclolariciresinol and 3,4-divanillyltetrahydrofuran. Pietarinen et al. (2006a) identified secoisolariciresinol, lariciresinol, todolactol A, isoliovil, NTG and some unidentified oligolignans in their hydrophilic knot extracts.

Other species

The average lignan and oligolignan concentrations in the heartwood of *Pseudotsuga menziesii* were 0.24% and 0.17% respectively (Figure 58). The corresponding values in *Tsuga canadensis* were 0.39% and 0.25%, and in Canadian *Tsuga heterophylla* 1.1% and 0.03%, respectively.

The lignan concentrations in the knots and branches were remarkably much higher than in the stem. The average lignan concentration of the knots was 3.8–4.6% in *P. menziesii,* 11–15% in *T. canadensis*, 8.2–12% in Canadian *T. heterophylla*, 0.32–2.5% in Finnish *T. heterophylla* and 5.2–11% in *T. mertensiana.*

The average oligolignan concentration of the knots was 0.60–0.79% in *P. menziesii*, 2.4–2.6% in *T. canadensis*, 0.54–0.94% in Canadian and Finnish *T. heterophylla* and 1.7–2.4% in *T. mertensiana.*

The lignan composition in *P. menziesii* differed from all other studied species; this was the only species where cyclolariciresinol dominated in all samples. The composition in the *Tsuga* species was fairly similar to that of genus *Picea;* HMR dominated, accompanied by lower concentrations of α-conidendrin, secoisolariciresinol and 7-todolactol A. The neolignan cedrusin was found in genus *Tsuga* only.

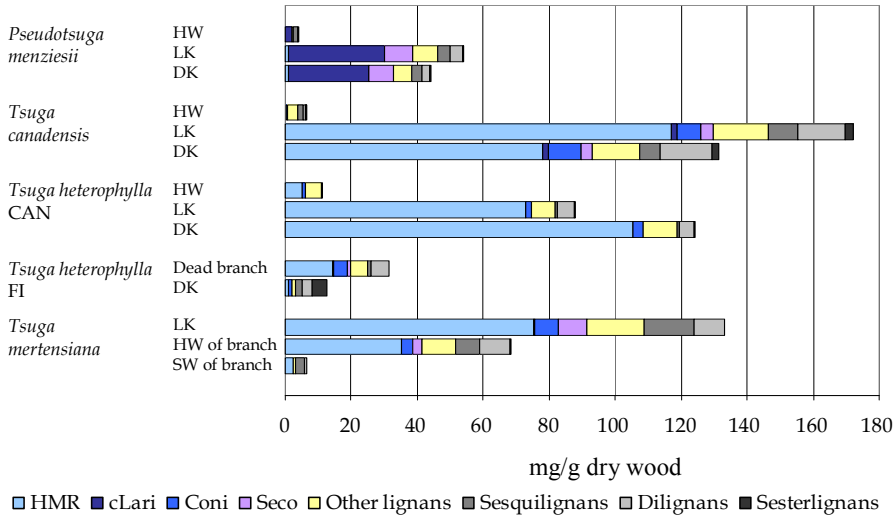

Figure 58 Average concentrations of lignans in genera Pseudotsuga and Tsuga (HW = heartwood, LK = living knot, DK = dead knot, HMR = hydroxymatairesinol, cLari = cyclolariciresinol, Coni = α-conidendrin, Seco = secoisolariciresinol).

Pseudotsuga menziesii

The lignan concentrations in *Pseudotsuga menziesii* were low, approximately on the same levels as in genus *Pinus*. The heartwood contained 0.24–0.25% lignans, the sapwood less than 0.02%, the living knots 1.1–8.1% and the dead knots 0.72–6.9%.

The lignan composition did not resemble that of any other species in this study. Cyclolariciresinol was the dominating compound in all samples. Secoisolariciresinol was the second most abundant followed by NTG,

lariciresinol, HMR and 7-todolactol A. Traces or very small amounts of matairesinol, pinoresinol and α-conidendrin were also detected. Syringaresinol was identified, but not quantified. The stemwood contained 0.10–0.14% sesquilignans, and very low concentrations of di- and sesterlignans. The knots contained 0.21–0.57% sesquilignans, 0.14–0.38% dilignans and 0.02–0.07% sesterlignans.

Erdtman (1944a) tried to find conidendrin in *P. menziesii* but he could not detect any. In this thesis, traces were found in some samples. Dellus et al. (1997) purified pinoresinol from the sapwood. Their yield was 0.02%, which was surprisingly high. They also found and purified a neolignan glucoside, which was found earlier in needles of *Picea abies* (Lundgren et al. 1981) and *Pinus sylvestris* (Popoff & Theander 1975), as well as in the inner bark of *P. sylvestris* (Pan & Lundgren 1996) and *Larix kaempferi* (Miki & Sasaya 1979).

Willför et al. (2003c) have studied the proportions of lignans in the hydrophilic knot extracts. They found very different compositions in the two trees they studied. One tree contained NTG and lariciresinol, while the other contained cyclolariciresinol and secoisolariciresinol. Furthermore, they detected secoisolariciresinol guaiacyl glycerol ethers, which had not been found earlier in any *Pseudotsuga*.

Holmbom et al. (2008) detected pinoresinol, lariciresinol-9-acetate, lariciresinol, cyclolariciresinol, lariciresinol-coumarate and some unidentified lignan esters in the callus resin of *P. menziesii*.

Tsuga canadensis

The heartwood of *T. canadensis* contained 0.17–0.61% lignans, the sapwood 0.05–0.09%, the living knots 14–16% and the dead knots 11%. 7-Todolactol A was the most abundant lignan in the heartwood, while HMR was predominant in the knots. Some α-conidendrin, NTG, secoisolariciresinol, matairesinol, lariciresinol, pinoresinol, some unknown lignans and traces of oxomatairesinol and the neolignan cedrusin[64] were also detected. The knots also contained cyclolariciresinol, but the heartwood did not.

The heartwood contained 0.12–0.21% sesquilignans, 0.04–0.08% dilignans and 0.03% sesterlignans. The sapwood contained 0.04–0.07% sesquilignans and traces of the two other types. The knots contained 0.61–0.89% sesquilignans, 1.1–2.0% dilignans and 0.11–0.28% sesterlignans.

[64] The heartwood contained 0.02–0.04% cedrusin, the sapwood 0.04%, and the dead knots up to 0.04%.

Erdtman (1944a) found conidendrin in a branch and Pietarinen et al. (2006a) found HMR, α-conidendrin, matairesinol, lignan A, todolactol A, isoliovil and oligolignans in a hydrophilic knot extract.

Tsuga heterophylla

Samples from three specimens of *Tsuga heterophylla* were analysed; two trees were from Canada and one from Finland. There was a great difference between the Finnish and the Canadian knots.

The total lignan concentration in the Canadian heartwood was 1.0–1.3%, only traces were found in the sapwood, 7.2–9.5% in the living knots and 11–13% in the dead knots. The dead Finnish knot contained only 2.5% lignans and the dead branch even less, only 0.32%. HMR dominated in all samples, except in the dead Finnish knot where α-conidendrin and HMR were almost equally abundant. Very low concentrations of 9′-hydroxy lariciresinol, 7-todolactol A, 7-isoliovil, lignan A, lariciresinol, pinoresinol and some unknown compounds were also detected. The Finnish samples additionally contained secoisolariciresinol, matairesinol, NTG, cyclolariciresinol and oxomatairesinol.

Low concentrations of sesqui-, di- and sesterlignans were found in the Canadian stemwood. The knots contained 0.07% sesquilignans, 0.47–0.52% dilignans and a maximum of 0.02% sesterlignans. The dead Finnish knot contained 0.18%, 0.32% and 0.43% of respective group. The dilignans dominated in the dead branch (0.52%), there was some sesquilignans (0.11%) and traces of sesterlignans.

The first studies on lignans from *T. heterophylla* were on native lignin (Brauns 1945) and spent sulfite liquor (Pearl 1945). Both were shown to contain conidendrin. Hergert (1960) identified HMR in native lignin.

Goldschmid and Hergert (1961) were the first to analyse lignans in the wood. They found HMR, pinoresinol, oxomatairesinol and conidendrin. The concentration of conidendrin was 0.05% in the sapwood, 0.15–0.20% in the heartwood and 0.5% in the spent liquor from sulfite pulping. They thereby understood that a part of the conidendrin did not originate from the wood, but must have been formed during the cook. They discovered that conidendrin is formed by dehydration of HMR, and that oxomatairesinol is an auto-oxidation product of HMR[65].

Barton and Gardner (1966) studied the distribution of lignans in the stem. They found that the inner heartwood was characterized by high concentrations of HMR and matairesinol and some conidendrin. The concentrations dropped in the transition zone between the heartwood and

[65] Six months exposure of HMR to air gives oxomatairesinol.

sapwood, and only trace amounts were found in the sapwood. The HMR concentration was 2.9% in the transition zone and 0.004% in the sapwood. The corresponding concentrations of matairesinol were 0.5% and 0.005%, respectively. They also noticed that there was more matairesinol and HMR in the sapwood during April–May than during the rest of the year. According to a later publication (Barton 1970), the sapwood contained 0.10% HMR, 0.02% matairesinol, 0.01% α–conidendrin, 0.01% liovil and 0.05% of a new neolignan.

Pietarinen et al. (2006a) are the only ones who have analysed knots of *T. heterophylla*. They found HMR, todolactol A, isoliovil, lignan A and some oligolignans in their hydrophilic knot extract.

Barton (1963) found whitish flecks, so-called floccosoids, which were readily visible in dried and planed timber. The white cells appeared in random clusters in the tracheids, never in the ray cells and they consisted of pure conidendrin. Krahmer et al. (1970) also studied cellular inclusions in the heartwood and found four different physical forms of deposits. Each type contained relatively pure matairesinol, HMR, conidendrin and an unknown compound. More information about the lignan deposits are found in chapter 2.7.5, the part about floccosoids.

Kawamura et al. (1996a) have studied discolouring of sapwood. Catechin is reported to be the main discolouring component (Barton 1968), but the catechin concentration was very low in the sapwood where the discolouration mainly took place. Therefore, Kawamura et al. (1996b) suggested that several other components interacted and caused the photodiscolouration. According to them, the main discolouring constituents were: HMR, oxomatairesinol, α–conidendrin, pinoresinol and the neolignan cedrusin[66]. Less significant were three other lignans (8-hydroxy-α-conidendrin, 8-hydroxy-α-conidendric acid methyl ester and 8-hydroxy-oxomataoresinol) and two sesquilignans (7′-hydroxylappaol E + *epi*-7′-hydroxylappaol E) (Kawamura et al. 1997, 2000). The lignans did not cause photodiscolouration separately, but together they interacted and gave rise to brown colour (Kawamura et al. 1998). Barton, however, opposed this and wrote that the lignans lacked vicinal hydroxyl groups and that the stable ring systems should prevent formation of coloured oxidation products (Barton 1968).

[66] In this thesis 0.01–0.03% cedrusin was found in the heartwood and 0.02–0.04% in the sapwood.

Tsuga mertensiana

No stemwood of *Tsuga mertensiana* was analysed, only a living knot and an outer branch. The living knot contained 11% lignans and the heartwood of the branch 5.2%. HMR was the dominating lignan. Some secoisolariciresinol, α-conidendrin, 7-todolactol A, pinoresinol, lariciresinol, lignan A, NTG, oxomatairesinol[67], matairesinol, cyclolariciresinol and *iso*-HMR were also found, as well as traces of the neolignan cedrusin.

The living knot contained 1.5% sesquilignans and the heartwood of the branch 0.72%. Both samples contained fully 0.9% dilignans and very low concentrations of sesterlignans.

Barton and Gardner (1962) found matairesinol, conidendrin and HMR in the heartwood. The amount of matairesinol in the sapwood was negligible. They also analysed ring shakes of *T. mertensiana*, where they found colourless, crystalline deposits of pure matairesinol. Erdtman (1944a) found conidendrin in a branch, but there are no previous reports of lignans in knots of *T. mertensiana.*

4.2.2 Stilbenes

The stilbenes are characteristic of pine heartwood and only two pine species, *P. lambertiana* and *P. peuce*, have been reported to lack stilbenes (Lindstedt 1951). Up to now, the compositions in more than fifty pine species have been analysed. Most of these studies have dealt with heartwood only; the knots have been neglected even though for many species they are even richer in stilbenes than the heartwood (Figure 59).

Heartwood of *P. nigra*, *P. resinosa* and *P. taeda* were richest in stilbenes; all containing more than 2%. More than 1% was found in the heartwood of *P. elliottii*, *P. strobus* and *P. sylvestris*. The remaining species contained between 0.1% and 0.8%. The concentrations were always higher in heartwood than in sapwood. In fact, the concentrations in the sapwood were so low that all sapwood samples were omitted from Figure 59, but are given in Appendix D6.

The knots of *P. sibirica* and *P. strobus* were the richest in stilbenes; they contained 9–12% and 8–15%, respectively. *P. nigra*, *P. resinosa* and *P. sylvestris* contained 3–6%, while the knots of *P. banksiana*, *P. elliottii*, *P. taeda* and *P. wallichiana* contained 1–2%. The knots of *P. contorta*, *P. gerardiana*, *P. pinaster*, *P. radiata* and *P. roxburghii* contained the lowest stilbene concentrations of the studied species.

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[67] Is this a true wood component or an artefact? Ekman (1976) has suggested that oxomatairesinol is an auto-oxidation product of HMR.

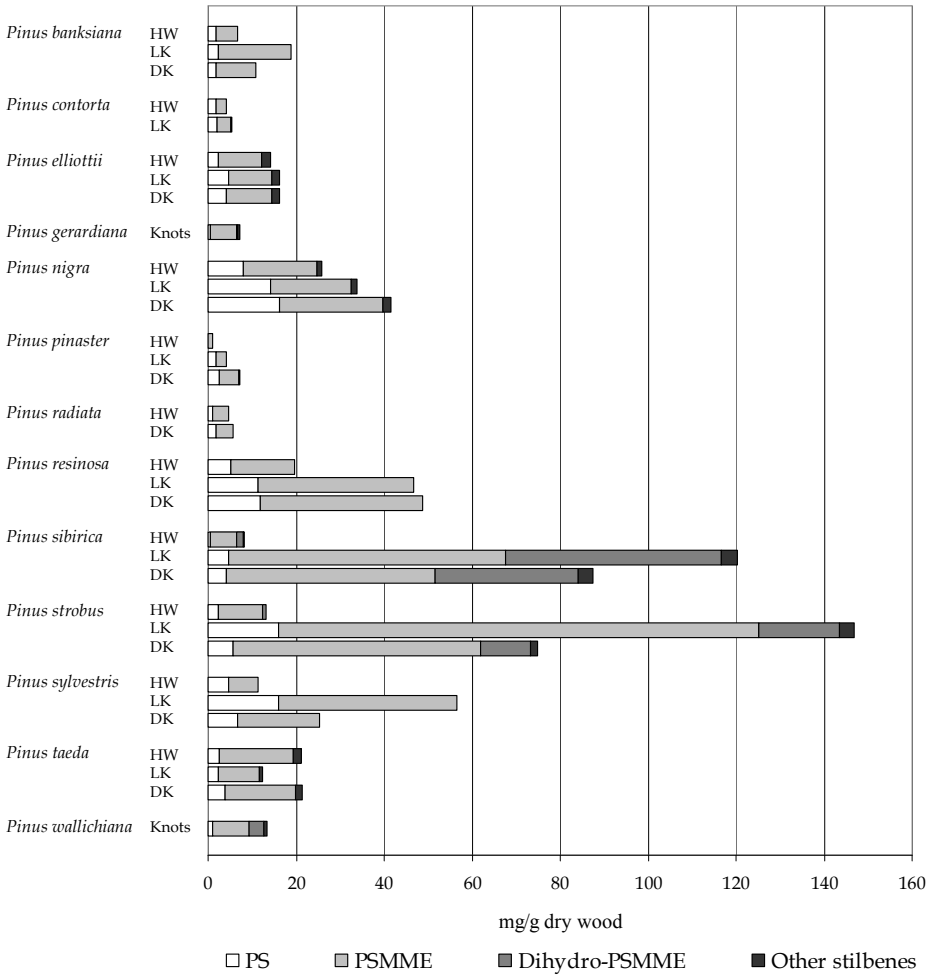

Figure 59 Average concentrations of stilbenes in genus Pinus (HW = heartwood, LK = living knot, DK = dead knot, PS = pinosylvin, PSMME = pinosylvin monomethyl ether, Dihydro-PSMME = dihydropinosylvin monomethyl ether).

Generally, the stilbene content in the knots was in the same range as in the heartwood. There were, though, some exceptions. The amount of stilbenes in the knots of *P. resinosa* was more than twice as large as in the heartwood. Furthermore, the concentration in the living knots of *P. sylvestris* was five times higher than in the heartwood and in the dead knots it was twice as high as in the heartwood. Willför et al. (2003b) also found more stilbenes in knots than in heartwood of *P. sylvestris*.

The knots of *P. sibirica* and *P. strobus* also contained much more stilbenes than the heartwood. They contained 10–15 and 6–11 times more, respectively.

For most species, there was no considerable difference between the concentrations in the living and dead knots. The differences in *P. sibirica*, *P. strobus* and *P. sylvestris* were, though, significant, especially in the last two species, where the living knots contain twice as much as the dead ones. Willför et al. (2003b) also stated that living knots of *P. sylvestris* contained more stilbenes than dead knots.

Pinosylvin monomethyl ether was the predominating stilbene in all species, except for the knots of *P. roxburghii* where pinosylvin dominated. *P. roxburghii* was, though, so poor in stilbenes (less than 0.02% in total), so it was left out of Figure 59.

It has been reported earlier (Erdtman & Misiorny 1952) that the periphery of heartwood from older trees contains proportionally more pinosylvin, while younger specimens contain proportionally more pinosylvin monomethyl ether. This trend was visible also in this thesis. The ratio in the heartwood of trees older than twenty years was 1.2–4.3, while the ratio in younger trees was 3.6–13, i.e. younger trees contained proportionally more pinosylvin monomethyl ether than the older ones.

The ratios of pinosylvin monomethyl ether to pinosylvin in knots varied significantly between the pine species, from 1.3 up to 15. There was no significant difference between living and dead knots, but trees with a high ratio in the heartwood generally also showed high ratios in the knots. *P. pinaster*, though, was an exception. There the heartwood ratio was 11 and the average knot ratio was 1.6. Willför et al. (2003b) have stated that the ratio of pinosylvin monomethyl ether to pinosylvin was higher in knots than in stemwood, 1.1–2.3 and 1.8–4.4, respectively. This was indeed true for *P. sylvestris* and a few other species, but it was equally common that the ratio was higher in the stemwood, and in some species there was no difference at all, so the ratio seems to depend on the species.

It was not possible to draw any unambiguous conclusions about the total stilbene content and the relationship, but it seemed like the concentrations in the knots of closely related species were on the same level. For example, the knots of *P. nigra*, *P. resinosa* and *P. sylvestris* all belonged to subsection *Pinus* (Appendix B2), and they were all rich in stilbenes. Another example was *P. sibirica* and *P. strobus*. Their knots contained the highest stilbenes concentrations of all samples and they both belonged to subsection *Strobus* (Appendix B3). *P. wallichiana*, however, also belonged to this subsection, but its concentration was very modest, so there was no absolute rule.

The occurrence of dihydrostilbenes, on the other hand, seemed to be genetically determined. Quantifiable amounts were found in section *Quinquefoliae* only[68], and the concentrations were especially high in subsection *Strobus*, i.e. in *P. sibirica*, *P. strobus* and *P. wallichiana.* Traces were found in some species from subgenus *Pinus*, but these amounts were barely detectable. The explanation according to Erdtman et al. (1966) is that subgenus *Strobus* has a more powerful methylation and hydrogen transferring system than subgenus *Pinus*.

Pinus banksiana

The heartwood of *P. banksiana* contained 0.6–0.8% stilbenes, the living knots 1.8–2.0 and the dead knot 1.1%. Erdtman (1944d), who was the first to study stilbenes in heartwood of *P. banksiana* identified the dominating compound as pinosylvin monomethyl ether. Later, Lindstedt and Misiorny (1951b) used paper chromatography to detect pinosylvin monomethyl ether and pinosylvin in both heartwood and sapwood. Celimene et al. (1999) detected also a third stilbene, Pinosylvin dimethyl ether, in the sapwood, but no traces of pinosylvin dimethyl ether were detected in this thesis, only pinosylvin monomethyl ether and pinosylvin. The heartwood contained 0.5% pinosylvin monomethyl ether and 0.1–0.3% pinosylvin. The living knots contained 1.6–1.7% pinosylvin monomethyl ether and 0.2–0.3% pinosylvin, and the dead knots 0.9% pinosylvin monomethyl ether and 0.2% pinosylvin.

Pinus contorta

P. contorta was fairly poor in stilbenes, only 0.4% was found in the heartwood and 0.3–0.8% in the living knots. The heartwood contained 0.2% each of pinosylvin monomethyl ether and pinosylvin, small amounts of pinosylvin dimethyl ether and traces of hydroxypinosylvin monomethyl ether. The knots contained 0.2–0.5% pinosylvin monomethyl ether, 0.1–0.3% pinosylvin, low concentrations of pinosylvin dimethyl ether and traces of hydroxypinosylvin monomethyl ether.

Lindstedt (1949a) analysed the mountain variety, *P. contorta* var. *latifolia*, and he found 0.01% pinosylvin and 0.004% pinosylvin monomethyl ether in the heartwood. His separation procedures were, however, tedious and, therefore, the yields remained low. Interesting is, though, that he found pinosylvin to be more abundant than pinosylvin monomethyl ether. Some

[68] It should be noted that no pines from section *Parraya* were analysed. It can, therefore, not be verified whether the occurrence of dihydrostilbenes was characteristic for the whole subgenus *Strobus* or only for section *Quinquefoliae*, but according to Erdtman et al. (1966) it should be valid for the whole subsection *Parraya*.

years later Lindstedt and Misiorny (1951b) analysed sapwood, but they did not detect any stilbenes at all therein.

Willför et al. (2003c) analysed a hydrophilic knot extract of *P. contorta* and found both pinosylvin monomethyl ether and pinosylvin. They did not detect any pinosylvin dimethyl ether, but that was quite logical since pinosylvin dimethyl ether is a component found in the lipophilic extract, which they did not analyse.

Pinus elliottii

The heartwood of *P. elliottii* contained 0.9–2.0% stilbenes and the knots 0.4–2.9%. Pinosylvin monomethyl ether was the dominating stilbene in all samples and it was accompanied by pinosylvin. The heartwood also contained some pinosylvin dimethyl ether and traces of dihydropinosylvin, dihydropinosylvin monomethyl ether, hydroxypinosylvin monomethyl ether and hydroxypinosylvin dimethyl ether. In the knots hydroxypinosylvin dimethyl ether was more abundant than pinosylvin dimethyl ether, and it was accompanied by traces of hydroxypinosylvin monomethyl ether. No dihydrostilbenes were detected in the knots. This was the first time the stilbenes in *P. elliottii* were analysed.

Pinus gerardiana

No stemwood of *P. gerardiana* was analysed in this thesis, but Lindstedt and Misiorny (1952) did. They found pinosylvin and pinosylvin monomethyl ether in the heartwood. In this thesis, the pooled knots contained 0.7% stilbenes. Pinosylvin monomethyl ether dominated (0.6%) followed by smaller amounts of pinosylvin, dihydropinosylvin monomethyl ether, pinosylvin dimethyl ether, hydroxypinosylvin monomethyl ether, hydroxypinosylvin dimethyl ether and traces of dihydropinosylvin.

Pinus nigra

The heartwood of *P. nigra* contained 1.3–3.7% stilbenes, the living knots 0.5–7.6% and the dead knots 2.3–5.5%. Pinosylvin monomethyl ether was the dominating compound, but all samples were also rich in pinosylvin. The mass ratio pinosylvin monomethyl ether to pinosylvin was 2.1 in the heartwood and 1.3–1.4 in the knots. All samples also contained some hydroxypinosylvin dimethyl ether, pinosylvin dimethyl ether and hydroxypinosylvin monomethyl ether. Traces of dihydropinosylvin were found in some of the knots.

The stilbenes in *Pinus nigra* have been studied on several occasions. Erdtman (1943) found pinosylvin and pinosylvin dimethyl ether in the heartwood. In a later survey (Erdtman 1944d), he supplemented the list with pinosylvin monomethyl ether. Alvarez-Nóvoa et al. (1950b) studied

P. nigra var. *calabrica*, which was a synonym of var. *laricio*, the variety studied in this thesis. They found only 0.4% pinosylvin monomethyl ether and no pinosylvin at all in the heartwood. Lindstedt and Misiorny (1951b) found pinosylvin and pinosylvin monomethyl ether, while Yildirim and Holmbom (Yildirim & Holmbom 1978a) determined the pinosylvin dimethyl ether content of the heartwood to be 0.03%, which was well in agreement with this thesis.

Pinus pinaster

Pinus pinaster was very poor in stilbenes and that corresponded well to the fact that it exhibits very low resistance to decay (Alvarez-Nóvoa et al. 1950b). Only 0.09–0.1% stilbenes were found in the heartwood, 0.2–0.7% in the living knots and 0.5–0.8% in the dead knots. Pinosylvin monomethyl ether dominated in all samples. The proportion of pinosylvin was very low in the heartwood. In the knots, the proportion was significantly higher; about 40% of all stilbenes in the knots was pinosylvin. Small amounts of hydroxypinosylvin monomethyl ether and hydroxy pinosylvin dimethyl ether were detected in the knots. These compounds were not detected in the stemwood.

Alvarez-Nóvoa et al. (1950b) analysed heartwood of *P. pinaster*, but did not find any stilbenes at all. They did, however, not exclude the possibility that the wood contained very small amounts of stilbenes. Lindstedt and Misiorny (1951b) were able to detect pinosylvin monomethyl ether and pinosylvin by paper chromatography, while Hemingway et al. (1973) found pinosylvin monomethyl ether and pinosylvin in mass ratios between 8:1 and 3:1. In this thesis, the heartwood ratio was greater than 10:1. Erdtman and Misiorny (1952) reported that the proportion of pinosylvin in the outer heartwood increase with age, and, thus, could the lower proportion of pinosylvin in this thesis be a consequence of the very young heartwood samples.

Pinus radiata

There were no significant differences between the heartwood and the dead knot of *P. radiata*, but it was remarkable that no stilbenes could be detected in the living knots. There was only one other species without any significant stilbene concentrations in the knots and that was *P. roxburghii*. These two species are not closely related, so the low content in knots was not typical for a specific section or group.

The heartwood of *P. radiata* contained 0.5% stilbenes and the dead knot 0.6%. Pinosylvin monomethyl ether was the dominating compound in all samples and it was accompanied by pinosylvin. It has been written two publications on stilbenes in heartwood of *P. radiata* (Lindstedt 1949b,

Lindstedt & Misiorny 1951b). They found 0.08% pinosylvin monomethyl ether and some pinosylvin, which was considerably less than what is reported here. Hillis and Inoue (1968) have analysed heartwood, sapwood and knots. They found even less stilbenes; 0.04% pinosylvin monomethyl ether and 0.003% pinosylvin in the heartwood, and 0.1% pinosylvin monomethyl ether and 0.2% pinosylvin in the knots. Their extraction procedure consisted of several steps and it is possible that they lost some pinosylvin monomethyl ether during the purification procedure. Furthermore, they compared healthy sapwood with mechanically damaged and insect attacked. They did not detect any stilbenes in healthy sapwood. The mechanically damaged sample contained 0.02% pinosylvin monomethyl ether, while the *Sirex*-affected sapwood contained 0.07% pinosylvin and traces of pinosylvin monomethyl ether; i.e. there were more stilbenes in the infested sapwood than in the mechanically damaged, and pinosylvin was the dominating stilbene in *Sirex*-attacked wood and knots, while pinosylvin monomethyl ether dominated in the other samples.

Pinus resinosa

P. resinosa contained much stilbenes, 1.6–2.4% in the heartwood and 3.2–5.8% in the knots. Lindstedt and Misiorny (1951b) found two stilbenes: pinosylvin monomethyl ether and pinosylvin, and they stated that pinosylvin monomethyl ether constituted three-fourths of the total amount. This was confirmed in this thesis.

Celimene et al. (1999) studied the composition of stilbenes in the sapwood and they found stilbenes in the proportions: 55% pinosylvin monomethyl ether, 35% pinosylvin and 9% pinosylvin dimethyl ether. No pinosylvin dimethyl ether was detected in this thesis, and all heartwood and sapwood samples contained proportionally more pinosylvin monomethyl ether than theirs.

Pinus sibirica

The heartwood of *P. sibirica* contained 0.8% stilbenes. The knots, however, were exceptionally rich in stilbenes. The living knots contained 11–13% and the dead knots 7.4–10%. Pinosylvin monomethyl ether was the dominating stilbene, but the knots also contained significant amounts of dihydropinosylvin monomethyl ether. Furthermore, small proportions of pinosylvin, dihydropinosylvin and pinosylvin dimethyl ether were detected. Large amounts of dihydrostilbenes were found only in the pines of subsection *Strobus*.

Lisina et al. (1967b) found pinosylvin dimethyl ether and a compound they called “3,5-dimethoxybibenzyl” in the oleoresin. In this thesis, pinosylvin, dihydropinosylvin, pinosylvin monomethyl ether and dihydropinosylvin monomethyl ether were found, but not the hydrogenated form of pinosylvin

dimethyl ether. Perhaps the "3,5-dimethoxybibenzyl" reported by Lisina et al. (1967b) was, in fact, dihydro pinosylvin dimethyl ether?

Willför et al. (2003c) analysed a hydrophilic knot extract and found pinosylvin monomethyl ether, dihydropinosylvin monomethyl ether, pinosylvin and dihydropinosylvin. They did not find any pinosylvin dimethyl ether, because they did not analyse the lipophilic extract.

Pinus strobus

The heartwood of *P. strobus* contained 1.1–1.6% stilbenes. The living knots contained the highest stilbene concentrations detected in this work, 11–18% and about half of that amount, 5.8–9.1%, was found in the dead knots. Pinosylvin monomethyl ether constituted more than three-fourths of the stilbenes in all samples. In the heartwood, pinosylvin monomethyl ether was accompanied by pinosylvin, some dihydropinosylvin monomethyl ether and traces of dihydropinosylvin. In the knots, the second most abundant compound was dihydropinosylvin monomethyl ether, followed by pinosylvin and dihydropinosylvin. As mentioned earlier, a large amount of dihydrostilbenes in the knots is a typical feature of subsection *Strobus*.

Lindstedt and Misiorny (1951) found pinosylvin, pinosylvin monomethyl ether and dihydropinosylvin monomethyl ether in the heartwood, and pinosylvin monomethyl ether and dihydropinosylvin monomethyl ether in the sapwood. Carvalho et al. (1996) complemented the list by adding pinosylvin dimethyl ether and dihydro pinosylvin dimethyl ether. Both studies mentioned above were qualitative, not quantitative.

Pinus sylvestris

pinosylvin and pinosylvin monomethyl ether were first isolated from the heartwood of *P. sylvestris* (Erdtman 1939d), and, thus, this has become the most studied species regarding stilbenes. Erdtman was a pioneer in the field and he wrote a large number of publications regarding e.g. the distribution of stilbenes in the stem and between-tree variations (Erdtman & Rennerfelt 1944, Erdtman et al. 1951, Erdtman & Misiorny 1952). After studying a vast number of trees Erdtman arrived at the conclusion that the average stilbene concentration in the heartwood of Swedish *P. sylvestris* was 0.9%, and that only about 3% of all trees contained more than 1% (Erdtman et al. 1951). The trees in this thesis were obviously part of that minor fraction, since the heartwood concentration was 1.1–1.2%.

Erdtman and Rennerfelt (1944) reported high stilbene concentrations in the branches and Willför et al. (2003b) were the first to study stilbenes in knots of *P. sylvestris*. There they found 1.2–7.0% stilbenes and the highest concentrations were found in the living knots. In this thesis, the living knots

contained 5.1–6.3% stilbenes and the dead knots 1.8–3.2%, which corresponded well with Willför's results.

Two other groups have studied heartwood and knots of *P. sylvestris*. Holvestad et al. (2006) found 0.23–2.0% stilbenes in the heartwood and 2.0–8.4% in the living knots. They also noticed that knots higher up in the tree contained more stilbenes than those at lower levels. Karppanen et al. (2007) made an extensive study which comprised forty trees. They found 0.09–2.1% stilbenes in the heartwood and 2.8–6.5% in the knots. Their average values were 1.0% in the stem and 4.6% in the knots.

Pinosylvin monomethyl ether dominated in all samples of this thesis. Pinosylvin constituted 42% of the stilbenes in the heartwood and 27–28% in the knots. Additionally, traces of pinosylvin dimethyl ether were detected in all samples. Pinosylvin dimethyl ether has previously been identified by Cox (1940) and quantified by Yildirim and Holmbom (1978a).

Erdtman et al. (1951) reported that the ratio of pinosylvin monomethyl ether to pinosylvin varied from 2 to 4. Willför et al. (2003b) found a much lower heartwood ratio, 1.1–2.3. The ratio in Willför's knots was 1.8–4.4, which was in the same range as in Erdtman's heartwood. Holvestad et al. (2006) found an even lower ratio, 1.1–1.4 in the heartwood and below one in the knots. In this thesis, the heartwood ratio was 1.5 and the ratio in the knots ranged from 2.5 to 2.7, which was in agreement with Willför's results.

Pinus taeda

The heartwood of *P. taeda* contained 2.1% stilbenes, the living knots 0.01–3.1% and the dead knots 0.02–4.3%. The composition of stilbenes in the heartwood and the knots were very similar. Pinosylvin monomethyl ether dominated and it was accompanied by some pinosylvin, pinosylvin dimethyl ether and traces of hydroxy pinosylvin dimethyl ether. Additionally traces of dihydropinosylvin monomethyl ether were found in the heartwood and hydroxypinosylvin monomethyl ether in the knots. Lindstedt and Misiorny (1951b) have identified pinosylvin and pinosylvin monomethyl ether in the heartwood.

Pinus wallichiana

Only knots of *P. wallichiana* were analysed in this thesis, but heartwood as well as sapwood have been analysed earlier (Lindstedt 1949d, Lindstedt & Misiorny 1951b). In the heartwood they found 1.4% pinosylvin monomethyl ether, some pinosylvin and dihydropinosylvin monomethyl ether. In the sapwood they found pinosylvin monomethyl ether and dihydropinosylvin monomethyl ether, no pinosylvin.

The knots in this study contained 1.3% stilbenes. Pinosylvin monomethyl ether dominated, followed by dihydropinosylvin monomethyl ether and pinosylvin. Low concentrations of dihydropinosylvin and traces of pinosylvin dimethyl ether and hydroxypinosylvin monomethyl ether were also found.

Other species

It has been reported that *Pseudotsuga menziesii*, like the pines, is a difficult raw material for the sulfite process. Therefore, one could easily jump to conclusions and assume that Douglas-fir also contains stilbenes, but this is not the case. The wood did not contain any stilbenes. The processing problems are caused by flavonoids (Pew 1948, Erdtman 1949, Gripenberg 1952). More information about the flavonoids can be found in chapters 2.7.6 and 4.2.3.

4.2.3 Flavonoids

High flavonoid concentrations were found in genera *Pinus*, *Larix* and *Pseudotsuga*. Only traces were found in *Picea* and *Tsuga*. No flavonoids at all were detected in *Abies*. Generally, the concentrations and compositions of flavonoids in heartwood and knots were fairly equal, while hardly any flavonoids were detected in sapwood. There were, however, some significant differences between the species, and they are discussed in the following section. The tabulated concentrations are found in Appendix D8.

Pinus

Heartwood of *P. elliottii* contained more than 3% flavonoids, *P. taeda* 2–3%, and *P. banksiana*, *P. contorta* and *P. radiata* 1–2% (Figure 60). The other species contained less than 1%. The knots of *P. sibirica* and *P. strobus* were richer in flavonoids than the stemwood; less than 1% was found in the stemwood, while the knots contained 2–4% flavonoids.

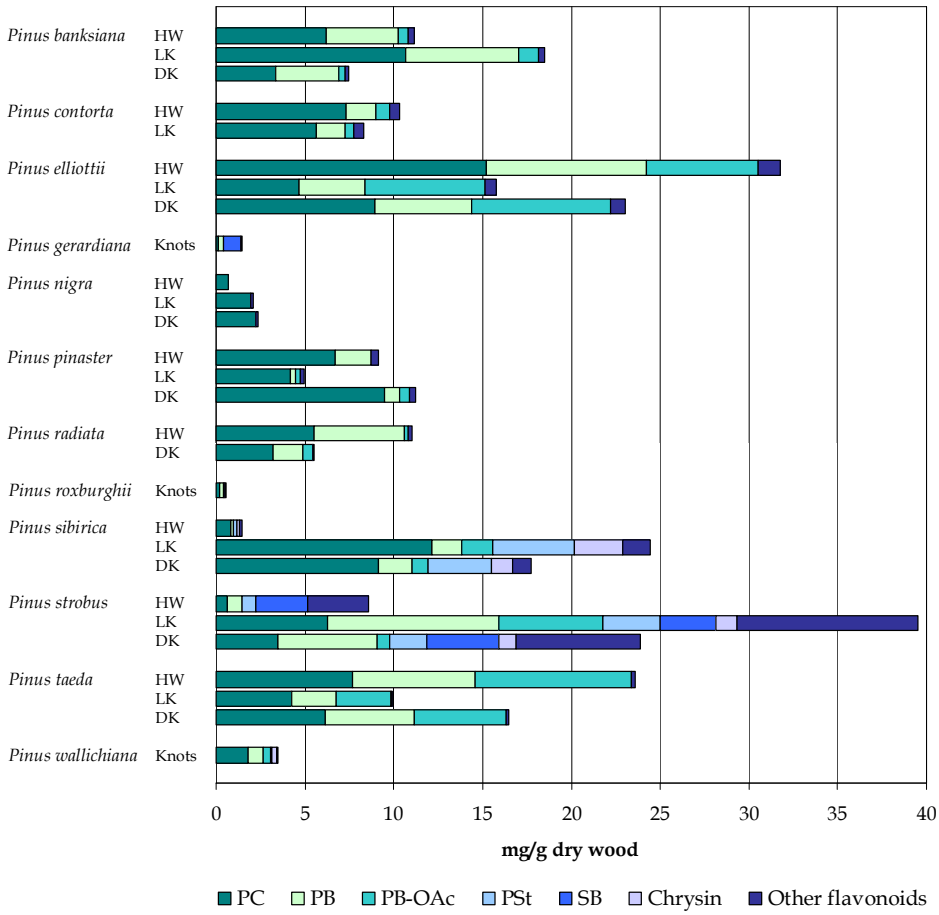

Figure 60 Average concentrations of flavonoids in genus Pinus (HW = heartwood, LK = living knot, DK = dead knot, PC = pinocembrin, PB = pinobanksin, PB-OAc = pinobanksin-3-acetate, PSt = pinostrobin, SB = strobobanksin).

Pinus banksiana

The heartwood of *P. banksiana* contained 0.8–1.4% flavonoids, the living knots 1.7–2.0% and the dead knot 0.8%. Pinobanksin and pinocembrin were almost equally abundant and were accompanied by lower amounts of pinobanksin-3-acetate and dihydrokaempferol.

Erdtman (1944d) isolated pinobanksin and pinocembrin from heartwood of *P. banksiana.* He was the first to isolate pinobanksin and named it after this species[69]. The presence of pinobanksin and pinocembrin was later confirmed by others (Lindstedt & Misiorny 1951b, Rudloff & Sato 1963).

[69] Pinocembrin was isolated earlier that year from heartwood of *Pinus cembra* (Erdtman 1944c).

Neacsu et al. (2007) identified pinobanksin, pinobanksin-3-acetate and pinocembrin from the knots. Their proportions were similar to the present study.

Redmond et al. (1971) determined the total concentration of pinobanksin and pinocembrin across a stem of *P. banksiana*, and found that the content decreased from the pith towards the heartwood-sapwood boundary. This pattern differs from that of stilbenes, where the concentration reaches its maximum in the transition zone between the heartwood and the sapwood.

Pinus contorta

The heartwood of *P. contorta* contained 0.8–1.3% flavonoids and the knots 0.5–1.2%. Pinocembrin was the most abundant flavonoid, followed by lower concentrations of pinobanksin, pinobanksin-3-acetate and dihydrokaempferol.

Lindstedt (1949a) was the first to study the flavonoids in *P. contorta*. He found 0.02% pinocembrin and 0.003% pinobanksin in heartwood. Later, other groups verified the presence of these two compounds (Lindstedt & Misiorny 1951b, Loman 1970, Conner et al. 1980a, Hanneman et al. 2002), and Willför et al. (2003c) found them in the knots. No one else has detected pinobanksin-3-acetate or dihydrokaempferol in *P. contorta* wood. *P. contorta* is closely related to *P. banksiana*, so it is not surprising that they contain the same flavonoids.

Pinus elliottii

There are no previous observations on flavonoids in *P. elliottii*. This is surprising considering the high concentrations now found and the fact that *P. elliottii* is such an industrially important species! The heartwood contained 2.0–4.3% flavonoids and the knots 0.5–3.2%. Pinocembrin accounted for almost half of the flavonoids in heartwood and one third in knots. Significant amounts of pinobanksin and pinobanksin-3-acetate were also detected, as well as lower concentrations of dihydrokaempferol and taxifolin. The stemwood also contained some dihydrokaempferol-3-acetate and catechin.

Pinus gerardiana

No stemwood of *P. gerardiana* was analysed in this thesis. The knots were poor in flavonoids, the total concentration being mere 0.1%. The most abundant flavonoid was strobobanksin, but low concentrations of pinobanksin, pinocembrin and an unidentified flavonoid were also detected.

Lindstedt and Misiorny (1952) found the same compounds and some pinostrobin in their samples. They were a bit surprised, because they had expected to detect chrysin and tectochrysin too, like in the other species

belonging to the subgenus *Strobus*. They did, however, find the same trend in *P. burgeana* Zucc. and therefore, Lindstedt and Misiorny (1952) concluded that subsection *Gerardianae* was unable to dehydrogenate flavanones to flavones, a reaction considered to be characteristic for the subgenus *Strobus*. In this thesis, only one species of the subsection *Gerardianae* and three species of the subsection *Strobus* were studied, and it is therefore difficult to draw any far-reaching conclusions. It would, however, be very interesting indeed to analyse the flavonoids in other species from subgenus *Strobus*, because it would be interesting to verify whether it is true that only subsection *Strobus* can dehydrogenate flavanones to the corresponding flavones.

Pinus nigra

P. nigra was poor in flavonoids; only 0.07–0.08% was found in the heartwood and 0.05–0.5% in the knots. Pinocembrin was the dominating compound, accompanied by traces of dihydrokaempferol. The living knots also contained traces of catechin.

Neither Erdtman (1944d) nor Alvarez-Nóvoa et al. (1950b) did find any flavonoids in their studies. Lindstedt and Misiorny (1951b) on the other hand succeeded in detecting pinocembrin by using paper chromatography.

Pinus pinaster

The heartwood of *P. pinaster* contained 0.7–1.3% flavonoids. There was a significant difference between living and dead knots; 0.3–0.8% was found in the living knots and 0.8–1.5% in the dead. Pinocembrin dominated in all samples. Some pinobanksin, as well as traces of pinobanksin-3-acetate, dihydrokaempferol and taxifolin were also found. Furthermore, the sapwood and knots contained traces of catechin.

Alvarez-Nóvoa et al. (1950b) detected 0.08% pinocembrin and 0.02% pinobanksin from the heartwood, which was only one tenth of what was found in this thesis. The presence of pinocembrin and pinobanksin was confirmed by Lindstedt and Misiorny (1951b) and Hemingway et al. (1973), who additionally detected small amounts of dihydrokaempferol and taxifolin.

Pinus radiata

The heartwood of *P. radiata* contained 1.1% flavonoids. Only traces were found in the living knots, while 0.6% was found in the dead knot. Pinobanksin and pinocembrin were equally abundant and were accompanied by pinobanksin-3-acetate and dihydrokaempferol.

Lindstedt (1949b) isolated 0.08% pinobanksin and 0.08% pinocembrin from the heartwood. That was about one tenth of the amount detected in

this thesis. Lindstedt and Misiorny (1951b) also identified these two compounds by paper chromatography. Hillis and Inoue (1968) studied heartwood, sapwood and knots of *P. radiata*. They did not find any flavonoids in the sapwood, but the knots contained 2–3 times more pinocembrin and pinobanksin than the heartwood. Their heartwood concentrations were, however, significantly much lower than the ones presented in this thesis. They found 0.06% pinobanksin in heartwood and 0.16% in knots. The heartwood contained 0.04% pinocembrin and the knots 0.12%. They also studied damaged sapwood and found that it contained 0.06% pinocembrin. Insect infestation did, however, not induce flavonoid synthesis.

Pinus resinosa

P. resinosa was the only pine where no flavonoids were detected. Other studies (Lindstedt 1951, Lindstedt & Misiorny 1951b) also have expressed doubt whether this species actually contains any flavonoids. Sato and Rudloff (1964), however, claimed that they detected small amounts of pinocembrin in the heartwood.

Pinus roxburghii

Only knots of *P. roxburghii* were analysed and they contained only 0.05% flavonoids. Pinocembrin was most abundant, closely followed by pinobanksin, pinobanksin-3-acetate and traces of strobobanksin, chrysin and an unknown flavonoid. No one else has studied flavonoids in this species.

Pinus sibirica

The concentration of flavonoids was much higher in the knots than in the heartwood of *P. sibirica*; the heartwood contained only 0.3%, while 2.1–4.3% was found in the knots. Pinocembrin was the dominating compound in all samples. The knots additionally contained significant amounts of pinostrobin, some pinobanksin and chrysin, as well as low concentrations of pinobanksin-3-acetate, dihydrokaempferol and tectochrysin. Willför et al. (2003c) also found that pinocembrin was the dominating flavonoid in the knots.

Tyukavkina et al. (1968b) isolated chrysin and tectochrysin from the heartwood of *P. sibirica*. Later, also the hydrogenated analogues of these compounds, i.e. pinocembrin and pinostrobin (Lutskii et al. 1968), as well as small amounts of dihydrokaempferol, apigenin and kaempferol (Lutskii et al. 1971) were isolated. No apigenin or kaempferol were detected in this thesis.

Pinus strobus

The flavonoid concentrations of *P. strobus* were significantly higher in the knots than in the heartwood, as in its relative *P. sibirica*. The heartwood contained 0.4–1.3% flavonoids, the living knots 3.9–4.0% and the dead knots 2.0–2.8%. The composition of flavonoids differed somewhat between the heartwood and the knots; strobobanksin dominated in the heartwood, while pinobanksin dominated in the knots. Other abundant compounds were pinocembrin, pinostrobin, strobobanksin, and in the living knots also pinobanksin-3-acetate. Lower concentrations of stropobinin[70], cryptostrobin, tectochrysin, chrysin and tree unknown flavonoids were also detected.

Erdtman (1944b) isolated flavonoids from the heartwood of *P. strobus*. He separated 0.1% chrysin, 0.1% tectochrysin, 0.004% pinostrobin, 0.07% stropobinin and traces of pinobanksin. Alvarez-Nóvoa et al. (1950a) additionally found 0.08% cryptostrobin. They could, however, not determine whether it was a naturally occurring compound or if it was formed from stropobinin under the influence of alkali during the isolation process. The structures were later corrected by Matsuura[71] (1957).

Lindstedt and Misiorny (1951a) identified two new constituents in the heartwood: strobobanksin and strobochrysin[72]. Furthermore, they found that stropobinin and cryptostrobin were in equilibrium with the same chalcone and, therefore, could be converted into each other if they were heated in diluted alkali, so a mixture of these two components was always obtained. In a subsequent publication (Lindstedt & Misiorny 1951b) they used paper chromatography to detect pinocembrin, chrysin, pinostrobin, tectochrysin, pinobanksin, strobobanksin, stropobinin and cryptostrobin in heartwood.

Pinus sylvestris

Pinus sylvestris was very poor in flavonoids. The stemwood and the dead knots contained traces of catechin and dihydrokaempferol, while only dihydrokaempferol was detected in the living knots. Lindstedt and Misiorny (1951b) found pinocembrin and pinobanksin in the heartwood; while Willför et al. (2003b) found traces of pinocembrin in the heartwood and in the knots, but they did not either detect any pinobanksin.

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[70] Stropobinin has also been found in heartwood of *P. monticola* (Lindstedt 1949c), *P. lambertiana*, *P. parviflora*, and *P. peuce* (Lindstedt & Misiorny 1951) i.e. in species from subsection *Strobus*. It has, though not been detected in *P. walliciana* (Lindstedt 1949d).

[71] Stropobinin is 6-methyl cryptostrobin.

[72] Strobochrysin is 6-methylchrysin. No MS-spectra of strobochrysin was found in the literature, so the presence of strobochrysin in *P. strobus* could not be verified.

Pinus taeda

P. taeda was not as rich in flavonoids as its relative *P. elliottii*, but the compositions were almost identical. The total concentration of flavonoids was 2.4% in the heartwood and 0.02–3.0% in the knots. Pinocembrin, pinobanksin and pinobanksin-3-acetate were equally abundant and they were accompanied by traces of dihydrokaempferol. Lindstedt and Misiorny (1951b) also detected pinocembrin and pinobanksin in the heartwood.

Pinus wallichiana

Only knots of *P. wallichiana* were analysed in this work and they contained 0.3% flavonoids. Pinocembrin was the most abundant, but lower concentrations of pinobanksin, pinobanksin-3-acetate and chrysin, as well as traces of an unknown flavonoid were also detected.

Lindstedt (1949d) isolated 0.13% pinobanksin, 0.01% pinocembrin, 0.07% chrysin and 0.07% tectochrysin from the heartwood of *P. wallichiana*. No tectochrysin was detected in the knots.

Larix and other species

The flavonoid concentration was higher in the knots than in the heartwood in all studied *Larix* species (Figure 61). The heartwood of *L. decidua* and *Pseudotsuga menziesii* contained 2–3% flavonoids, the heartwood of *Larix gmelinii* var. *olgensis* and *L. kaempferi* 1–2%, while the remaining species contained less than 1%.

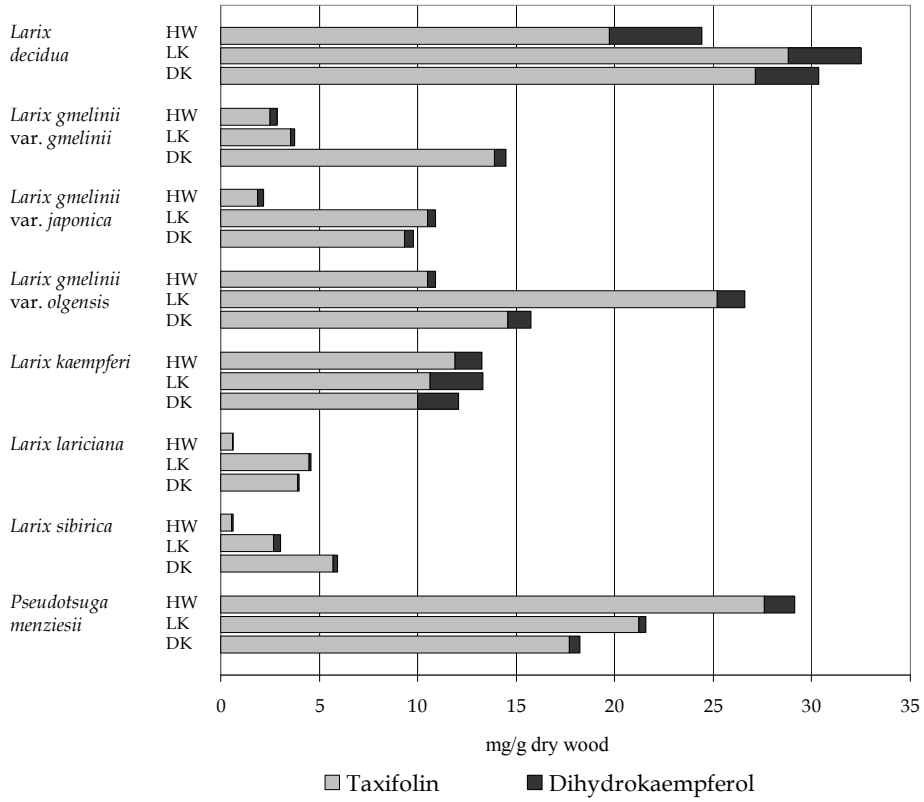

Figure 61 Average concentrations of flavonoids in genus Larix (HW = heartwood, LK = living knot, DK = dead knot).

Larix decidua

L. decidua was very rich in flavonoids. The concentration in heartwood was 1.5–3.6% and in knots 1.3–3.9%. The predominant flavonoid was taxifolin, but some dihydrokaempferol was also detected. The stemwood contained traces of catechin.

Gripenberg (1952) was the first to isolate taxifolin and dihydrokaempferol from the heartwood of *L. decidua*. He did, however, call dihydrokaempferol aromadendrin. He reported that the total flavonoid concentration was about 0.7% and that the ratio of aromadendrin to taxifolin was approximately 2:1. Brewerton (1956) also detected the same compounds.

Zule (2010) studied the flavonoids in stem and knots of two *L. decidua* trees. She found that the total concentration of flavonoids was highest in the lower parts of the stem and decreased higher up. The total flavonoid

concentration was 0.5–1.6% in the heartwood[73], 0.01% in the sapwood and 3.3–7.0% in the knots. The heartwood contained 0.6–1.1% taxifolin and 0.4–0.8% dihydrokaempferol. The knots contained 2.9–6.2% taxifolin and 0.3–1.0% dihydrokaempferol. Traces of naringenin and quercetin were found in heartwood, sapwood and knots. Zule's results are well in line with the results presented in this work.

Larix gmelinii

The heartwood of *L. gmelinii* var. *gmelinii* contained 0.2–0.4% flavonoids, the living knots 0.3–0.4% and the dead knots 0.6–2.2%. The concentrations in the heartwood samples of *L. gmelinii* var. *japonica* varied more than within the other varieties, from 0.05% to 0.5%. The knots contained 0.7–1.5%. *L. gmelinii* var. *olgensis* was the variety richest in flavonoids; the heartwood contained 0.8–1.4%, the living knots fully 2.5–2.8% and the dead knots 1.5–1.7%.

Wang et al. (2005) also determined the total concentration of flavonoids in *L. gmelinii* (Rupr.) Rupr. They found 1.2% in the xylem and 1.7% in the branches thinner than 5 mm in diameter. Based on the high concentrations they reported, it may be assumed that they in fact analysed *L. gmelinii* var. *olgensis*.

Tyukavkina et al. (1967b) analysed heartwood of *L. gmelinii* and found dihydrokaempferol, quercetin and taxifolin[74]. Later, they determined that taxifolin accounted for 69% of all flavonoids and quercetin for 11% (Tyukavkina et al. 1967a). Small amounts of kaempferol (Tyukavkina et al. 1968a), pinostrobin, pinocembrin, naringenin and pinobanksin (Lapteva et al. 1974) were also identified. In the present study taxifolin was also found to be the most abundant compound. It was accompanied by lower concentrations of dihydrokaempferol, and the sapwood of *L. gmelinii* var. *gmelinii* contained traces of catechin. The other compounds mentioned by Lapteva et al. (1974) were, however, not detected.

Larix kaempferi

The heartwood of *L. kaempferi* contained 1.1–1.9% flavonoids. The concentration in the living knots was 0.4–2.4% and 0.5–2.3% in the dead knots. Taxifolin was the dominating compound and dihydrokaempferol constituted about 10–20% of all flavonoids. The sapwood contained only trace amounts of catechin.

[73] The total flavonoid concentration 0.5 m above the ground varied from 1.4% to 1.6%.
[74] Taxifolin is a synonym of dihydroquercetin.

Hasegawa and Shirato (1951) isolated something they called distylin from *L. kaempferi*[75]. Kondo (1951) claimed that distylin was a racemic mixture of taxifolin, but Gripenberg (1952) received a sample of Hasegawa's distylin and he showed that it actually was a mixture of taxifolin and dihydrokaempferol. Brewerton (1956) also found taxifolin and dihydrokaempferol[76] in *L. kaempferi.*

Kondo and Furuzawa (1953, 1954a, 1954b, 1955), and Furusawa and Kondo (1959) have studied flavonoids in heartwood of *L. kaempferi.* They identified taxifolin and dihydrokaempferol[77], and determined the heartwood concentrations to be 2.4–4.3% and 0.2–0.4%, respectively. The concentrations found in this thesis are lower, but the proportions were the same. Kondo and Furuzawa (1955) also found that the concentrations depended on the growth location as well as on the position in the stem; the outer part of the heartwood contains more taxifolin and dihydrokaempferol than the inner part. Furthermore, they found that decayed heartwood contains higher flavonoid than healthy heartwood (Furusawa & Kondo 1959).

Larix lariciana

The flavonoid concentration in heartwood of *L. lariciana* was low, only 0.06–0.08%. The knots, however, contained about six times more flavonoids, 0.4–0.5%. Taxifolin was predominant, but traces of dihydrokaempferol and naringenin were also detected. Nair and Rudloff (1959) isolated 0.3% taxifolin, 0.05% dihydrokaempferol[78] and trace amounts of quercetin from the heartwood.

Larix sibirica

The flavonoid concentrations in *L. sibirica* were also low: between 0.01 and 0.1% in the heartwood, 0.3% in the living knot and 0.1–0.9% in the dead knots. Taxifolin was the dominating compound and it was accompanied by low concentrations of dihydrokaempferol. Traces of catechin were detected in the sapwood.

Tyukavkina and Antonova (1969) used hot water to extract up to 1.5% flavonoids from pulp of a 185-years-old specimen of *L. sibirica.* They also found that taxifolin was the main component (84% of total), but they claimed that it was accompanied by quercetin and kaempferol, the unsaturated form of the compounds found in the present study.

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[75] *Larix leptolepsis* is a synonym of *L. kaempferi*.
[76] Dihydrokaempferol is a synonym of aromadendrin.
[77] Dihydrokaempferol is a synonym of katsuranin.
[78] Dihydrokaempferol is a synonym of aromadendrin.

Venäläinen et al. (2006) studied the flavonoids in fast-growing juvenile heartwood. They found 0.4% flavonoids in total, and more than half of that was taxifolin. They did, however, observe that there were very large between-tree variations.

Pseudotsuga menziesii

The flavonoid concentrations in *P. menziesii* were relatively high; 2.6–3.2% in the heartwood, 0.1–4.2% in the living knots and 0.4–3.2% in the dead knots. As in genus *Larix*, taxifolin was predominant, but some dihydrokaempferol was also detected.

Pew (1948, 1949) isolated taxifolin from the heartwood of *P. menziesii*. His average yield was 1%, but concentrations up to 2.2% were reported. He did, however, point out that some taxifolin could have been lost during the purification steps and that the actual concentration might have been higher (Pew 1948). Later, several other groups (Graham & Kurth 1949, Barton & Gardner 1958, Gardner & Barton 1960) also determined the taxifolin content, and they found concentrations up to 1.5% in the heartwood. Squire et al. (1967) detected some additional compounds; at most they found 1.0% taxifolin, 0.3% dihydrokaempferol, 0.2% pinobanksin and 0.1% quercetin. Dellus et al. (1997) added pinocembrin to the list of compounds detected in *P. menziesii.*

Other species

Low amounts of flavonoids were detected also in some other species. Traces of catechin, dihydrokaempferol, pinocembrin and taxifolin were found in all samples of *Picea sitchensis*. Hernes and Hedges (2004) also analysed wood of *P. sitchensis* and found 0.01% epicatechin. Traces of catechin were also detected in the heartwood of *Picea mariana* and in the stemwood of *Tsuga canadensis.* Low concentrations of catechin were found in the stemwood of *T. heterophylla* and its knots contained 0.1–0.2%. This was supported by Barton (1970) who found 0.05% catechin in the sapwood of *T. heterophylla*.

4.3 Summary of results

Resin acids

Resin canals are a normal feature of genera *Pinus*, *Picea*, *Larix* and *Pseudotsuga*, while *Abies* and *Tsuga* lack resin canals. It is known that heartwood of genus *Pinus* has the largest and most numerous resin canals and, as expected, this genus also had the highest resin acid concentrations. *Picea, Larix* and *Pseudotsuga* all contained resin acid levels of the same magnitude and their resin canals are more evenly distributed throughout the whole stem. Thus, there were no concentration differences between the heartwood and sapwood.

The knots of *Pinus* contained significantly much more resin acids than the heartwood, and the dead knots contained even more resin acids than the living knots (Table 10). In *Picea*, the death and pruning of branches is a very slow process. It was noticed that dead, loose knots that were totally embedded in the stem were exceptionally rich in resin acids. There were also other physiologically dead knots, i.e. their branches had lost all their needles, but the outer branch itself had not yet fallen off. These knots were significantly lower in resin acids. The resin acid content can, thus, function as an indicator of how long ago the outer branch died. No analogous trends were observed for genus *Pinus*, probably because the resin acid content in pine increases already when sapwood is transformed into heartwood, i.e. long before the branch starts to die.

Table 10 Lowest and highest average concentrations of resin acids per genus (HW = heartwood, SW = sapwood).

	Concentration		
	mg/g dry wood		
	HW	SW	Knots
Pinus	2.4–44	0.91–8.5	3.3–215
Picea	0.48–2.1	0.65–2.9	0.13–25
Abies	tr–0.13	tr–0.07	tr–1.2
Larix	0.75–1.9	0.81–2.2	0.25–4.4
Pseudotsuga	1.0	1.3	8.9
Tsuga	tr	tr	tr–0.09

tr = traces

Genera *Pinus* and *Larix* contained resin acids of abietane, pimarane and labdane type, while only abietane- and pimarane-types were found in *Picea* and *Pseudotsuga*. In *Pinus*, there were significant differences, both regarding concentration and composition, between the species. No such differences were observed within genus *Picea*. The resin acids in *Pseudotsuga menziesii* were very similar those in *Picea*. Genus *Larix*

contained larger proportions of pimarane-type acids than the other studied genera. There were also some disparities in the resin acid composition.

First time studied/reported

- Resin acids in stemwood of *Picea omorika, Picea pungens* and *Picea sitchensis*
- Resin acids in knots of genera *Pinus* and *Larix*, in *Picea glauca*, *P. koraiensis, P. mariana, P. omorika, P. pungens, P. sitchensis* and *Pseudotsuga menziesii*
- Isocupressic acid in *Pinus contorta*
- Isocupressic and imbricatolic acid in *P. elliottii*
- Lambertianic acid in *P. gerardiana*
- Sandaracopimaric and communic acid in *Larix gmelinii* var. *olgensis*
- Two isomers of communic acid in *L. kaempferi* and *L. lariciana*
- First study where levopimaric and palustric acid have been separated in *Pinus pinaster, P. sibirica, P. strobus* and *L. gerardiana*

Chemotaxonomic significance

- No or only traces of pimaric acid in section *Quinquefoliae* of genus *Pinus*, while it constituted about 10% of the resin acids in the other sections. The content of isopimaric acid was also notably higher in section *Quinquefoliae*
- Communic acid in *Pinus elliottii* and in all larch species
- Isocupressic acid in *Pinus contorta*, *P. elliottii*, *P. taeda* and *P. wallichiana*
- Imbricatolic acid in stemwood of *Pinus elliottii* only, not in knots or in any other species
- Anticopalic acid in *P. strobus* only
- Lambertianic acid in *Pinus gerardiana*, *P. roxburghii*, *P. sibirica* and *P. wallichiana*
- The habitats of *Pinus contorta* and *P. banksiana* overlap (Mirov 1961). The species can, however, be distinguished since *P. contorta* contains low amounts of isocupressic acid, an acid which is absent in *P. banksiana*
- Cupressic acid in *L. kaempferi* and *L. lariciana*. These two species are *not* closely related. All three varieties of *L. gmelinii* lack cupressic acid
- No pimaric acid in *Pseudotsuga menziesii*

Fatty acids and acylglycerols

The highest total concentrations of fats were found in genus *Pinus*, while *Picea*, *Abies*, *Larix* and *Pseudotsuga* contained significantly smaller amounts and *Tsuga* even less (Table 11). The total concentrations of fats were higher in the living cells of the sapwood than in the dead heartwood. In the sapwood, most of the fats occur as acylglycerols, while they have been hydrolyzed into free fatty acids in the heartwood. The enzymatic process is, however, fairly slow, so young heartwood still contains acylglycerol concentrations close to those in the sapwood. The same trend is observed also in the knots - younger knots contain more acylglycerol, while older knots contain more free fatty acids.

Table 11 Lowest and highest average concentrations of fatty acids and acylglycerols per genus (DGs = diacylglycerols, TGs = triacylglycerols, HW = heartwood, SW = sapwood).

	Concentration								
	Free FAs			DGs			TGs		
	HW	SW	Knots	HW	SW	Knots	HW	SW	Knots
	mg/g dry wood								
Pinus	0.91–16	0.18–4.8	0.07–16	0.14–1.2	0.07–1.6	0.06–4.6	0.21–4.0	0.70–25	tr–12
Picea	0.10–3.8	0.10–0.52	0.27–6.1	0.20–0.95	0.12–0.61	0.07–1.1	0.07–1.6	0.73–5.1	0.06–2.8
Abies	0.26–2.1	0.15–1.6	0.69–3.9	0.08–0.24	0.09–0.36	tr–0.47	tr–0.48	0.07–2.0	0.06–1.3
Larix	0.63–3.0	0.23–1.0	0.41–5.8	n.d.–0.20	0.06–0.21	tr–0.22	0.13–0.90	1.2–6.0	tr–2.1
Pseudotsuga	0.49	0.10	3.0	0.12	0.07	0.16	0.37	1.5	0.31
Tsuga	0.17–0.40	0.11–0.19	0.10–0.53	0.11–0.15	0.09–0.17	tr–0.13	tr–0.06	0.19–0.93	tr–0.18

tr = traces

n.d. = not detected

Unsaturated free fatty acids dominated in genera *Pinus*, *Picea*, *Larix* and in *Pseudotsuga menziesii*, while saturated fatty acids dominated in *Abies* and *Tsuga*. Monoenoic and dienoic acids were equally abundant in the stemwood of genus *Pinus*. In *Pseudotsuga* and *Abies* were monoenoic fatty acids most abundant, while dienoic fatty acids dominated in *Picea*, *Larix* and *Tsuga*. Genus *Larix* contained higher proportions of trienoic acids than the other studied genera.

There was a difference in the proportion of polyunsaturated fatty acids between *Picea abies* trees growing in Finland and France, because colder temperature yields an increase in polyunsaturated fatty acids (Swan 1968, Yildirim & Holmbom 1978b, Fuksman & Komshilov 1979, 1980, 1981, Piispanen & Saranpää 2002).

First time studied/reported

- Fats in stemwood of *Picea koraiensis*, *P. pungens, Abies alba, A. amabilis, A. balsamea, A. concolor, A. lasiocarpa, A. sachalinensis, A. veitchii, Larix decidua, L. kaempferi, Tsuga canadensis* and *T. heterophylla*

- Fats have been studied in knots of *Pinus sylvestris* and *Picea abies*, but not in the other species in this thesis

Sterols, triterpenols and their esters

The sterols can occur in free and esterified form, and the esterified form normally dominates. The steryl esters are fairly stable and they are not easily hydrolyzed. So unlike the acylglycerols they are not hydrolyzed when the cells die. The heartwood and sapwood, therefore, contain similar amounts of steryl esters, while the amount of free sterols is somewhat higher in the heartwood and knots than in the sapwood (Table 12). The only exception was genus *Abies,* which contained fairly equal amounts of free and esterified sterols.

Table 12 Lowest and highest average concentrations of free and esterified sterols per genus (HW = heartwood, SW = sapwood).

	Concentration					
	Free sterols			Steryl esters		
	HW	SW	Knots	HW	SW	Knots
	mg/g dry wood					
Pinus	0.09–0.34	0.06–0.13	n.d.–0.42	0.66–2.9	0.33–2.5	0.06–4.5
Picea	0.20–0.68	0.08–0.25	0.08–1.7	0.63–1.8	1.0–2.1	0.41–3.2
Abies	0.24–0.52	0.13–0.44	0.11–0.65	0.10–0.42	0.15–1.1	0.17–1.1
Larix	0.12–0.27	0.06–0.09	0.08–1.5	0.96–1.7	0.70–1.6	0.69–1.7
Pseudotsuga	0.11	tr	0.47	2.4	2.0	4.0
Tsuga	0.28–0.38	0.08–0.15	0.07–0.26	0.28	0.08–0.50	0.09–8.9

n.d. = not detected

tr = traces

Sitosterol was the most abundant sterol in all species. It was accompanied by campesterol and small amounts of sitostanol and campestanol.

First time studied/reported

- Sterols, triterpenols and/or steryl esters in stemwood of *Picea koraiensis, P. pungens, Abies balsamea, A. concolor, A. lasiocarpa, A. sachalinensis, A. sibirica, A. veitchii* and *Larix gmelinii*
- Previously sterols, triterpenols and/or steryl esters have been studied in knots of *Pinus nigra, P. sylvestris* and *Picea abies* only. This is the first study on knots in all other species

Juvabiones

Juvabiones are characteristic of genus *Abies* and were found in all species of that genus. They were also found in most *Larix* species, in *Pseudotsuga menziesii*, in six *Pinus* species, and traces were detected in some *Picea* and *Tsuga* species. The juvabione concentrations were clearly higher in the knots than in the stemwood (Table 13). The knots of *A. lasiocarpa* contained 3.2–8.2% juvabiones, which is the largest amount ever reported in a fir.

Table 13 Lowest and highest average concentrations of juvabiones per genus (HW = heartwood, SW = sapwood).

	Concentration		
	mg/g dry wood		
	HW	SW	Knots
Pinus	n.d.–0.38	n.d.–tr	n.d.–17
Picea	n.d.–tr	n.d.–0.05	n.d.–tr
Abies	tr–12	tr–5.2	0.06–61
Larix	n.d.–tr	n.d.–tr	n.d.–0.96
Pseudotsuga	0.38	tr	4.7
Tsuga	n.d.	n.d.	n.d.–0.06

n.d. = not detected

tr = traces

First time studied/reported

- Juvabiones have not been detected before in stemwood or knots of any *Pinus* species. Here they were found in *Pinus banksiana*, *P. elliottii*, *P. nigra*, *P. pinaster, P. taeda* and *Pinus roxburghii.* The total amount in the stemwood was rather low, but the knots contained up to 330 times more juvabiones than the stemwood!
- Juvabiones were also detected for the first time in stemwood and knots of *Picea koraiensis*, *P. mariana*, *Abies alba*, *A. amabilis*, *A. concolor*, *A. veitchii*, *Larix decidua*, *L. gmelinii* and *L. sibirica*, and for the first time in knots of, *Abies balsamea*, *A. lasiocarpa*, *A. pindrow*, *A. sachalinensis*, *Pseudotsuga menziesii*, *Tsuga heterophylla* and *T. mertensiana*.

Chemotaxonomic significance

- Juvabiones are characteristic of genus *Abies*, low concentrations or traces were, however, detected in all genera;
- The juvabiones are present in unique combinations, making them useful for chemotaxonomic identification;

- Lasiocarpenone, lasiocarpenonol, atlantone and 1′-dehydrojuvabione were found in genus *Abies*, subsection *Laterales;*
- *A. veitchii* and *A. sachalinensis* are closely related. Both species contained more juvabiones in the sapwood than in the heartwood. α-Atlantone was detected in *A. sachalinensis*, but no atlantones were detected in the sampled tree of *A. veitchii*;
- Traces of juvabione were found in *Picea koraiensis* and traces of α-atlantone were found in *P. mariana*. No other juvabiones or sesquiterpenoids were found in any other *Picea* species; and
- *Pseudotsuga menziesii* was the only studied species where dihydrotodomatuic acid was the dominating juvabione.

Other lipophilic compounds

A wide range of other lipophilic compounds were also analysed. The concentrations were normally very low (Table 14), e.g. were traces of the aliphatic hydrocarbon squalene found in all species.

Table 14 Lowest and highest average concentrations of other lipophilic compounds per genus (HW = heartwood, SW = sapwood).

	Concentration		
	mg/g dry wood		
	HW	SW	Knots
Pinus	tr–1.1	0–0.48	n.d.–21
Picea	tr–0.08	tr–0.19	tr–5.3
Abies	tr	tr–0.07	tr–1.9
Larix	0.05–1.7	0.13–2.0	tr–11
Pseudotsuga	tr	tr	0.42
Tsuga	tr	tr	tr

tr = traces

Very low concentrations of the monocyclic diterpenoid thunbergol were detected in more than half of the species, and it was often accompanied by traces of thunbergene. Higher concentrations of thunbergol were found in the dead knots of *L. kaempferi* (up to 1.8%) and in the knots of *P. nigra* (up to 3.7%).

The labdane terpenoid manool was more abundant in genera *Picea*, *Abies* and *Larix* than in *Pinus*, *Pseudotsuga* and *Tsuga*. The concentrations were generally very low, but some of the dead knots of *L. kaempferi* contained up to 3.0%. Manool was often accompanied by traces of manoyl oxide.

Larixol was detected in the three varieties of *Larix gmelinii*, *L. kaempferi* and *L. sibirica*. The concentrations in the stem were lower than 0.02%, while the knots contained up to 0.67%. Low concentrations of larixyl acetate were detected in stemwood and knots of all *Larix* species.

Lignans and oligolignans

Lignans were found in all studied genera. The total concentration of lignans in the heartwood decreased in the order: *Tsuga* > *Picea* ≈ *Abies* > *Pseudotsuga* > *Larix* ≈ *Pinus*, and for the knots in the order: *Tsuga* > *Larix* > *Abies* > *Pseudotsuga* > *Picea* > *Pinus*. The lignans and oligolignans were much more abundant in the knots than in the heartwood. There were hardly any lignans in the sapwood of any species (Table 15).

Table 15 Lowest and highest average concentrations of lignans and oligolignans per genus (HW = heartwood, SW = sapwood).

	Concentration					
	Lignans			Oligolignans		
	HW	SW	Knots	HW	SW	Knots
	mg/g dry wood					
Pinus	tr–2.0	tr–0.20	tr – 50	n.d.–2.0	n.d.–2.2	n.d.–8.5
Picea	0.15–15	0.05–0.45	15 – 133	tr–3.0	0.09–2.5	7.5–46
Abies	0.21–8.6	0.10–0.99	11 – 129	0.62–6.2	0.50–3.1	12–61
Larix	0.41–1.9	tr–0.23	6.0 – 123	0.06–6.9	0.20–3.5	5.1–32
Pseudotsuga	2.4	0.15	42	1.7	1.4	7.0
Tsuga	3.9–12	tr–0.71	3.2–146	0.22–2.5	0.66–0.72	5.4–26

n.d. = not detected

tr = traces

Different lignans were predominant in the heartwood and in the knots. 7-Todolactol A was most abundant in *Pinus* and *Abies* heartwood, HMR in *Picea*, and cyclolariciresinol in *Larix* and *Pseudotsuga.* NTG was the most abundant lignan in knots of genus *Pinus*. HMR dominated in most *Picea* species and in *Tsuga*, while secoisolariciresinol was the most abundant in the knots of *Abies* and *Larix*. The lignan composition in *Pseudotsuga menziesii* differed from all other studied species with cyclolariciresinol dominating in both heartwood and knots.

Small amounts of sesqui-, di- and sesterlignans were found in almost all samples. The sesquilignans were the most abundant oligolignans.

First time studied/reported

- Lignans and/or oligolignans in stemwood of *Pinus contorta, P. elliottii, P. radiata, P. sibirica, Larix lariciana* and *Tsuga canadensis*
- Lignans and/or oligolignans in knots of *Pinus elliottii, P. gerardiana*, *P. radiata, P. roxburghii, P. taeda, P. wallichiana*, *Abies pindrow, Larix gmelinii, L. kaempferi* and *Tsuga mertensiana*

Chemotaxonomic significance

- NTG dominated in knots of subgenus *Pinus*, while it was totally absent in knots of subgenus *Strobus*. Instead, lariciresinol and cyclolariciresinol dominated in the knots of subgenus *Strobus*;
- 7-Todolactol A and secoisolariciresinol dominated in *Picea pungens* and 7-todolactol A in *Picea sitchensis*;
- HMR dominated in the heartwood of *A. amabilis*; and
- The neolignan cedrusin was found in genus *Tsuga* only.

Stilbenes

The stilbenes are characteristic of pine heartwood, and generally the stilbene content in the knots is in the same range as in the heartwood (Table 16). There were, though, four exceptions (*P. resinosa, P. sibirica, P. strobus and P. sylvestris*) where the knots contained up to 15 times more stilbenes than the heartwood.

Table 16 Lowest and highest average concentrations of stilbenes per genus (HW = heartwood, SW = sapwood).

	Concentration mg/g dry wood		
	HW	SW	Knots
Pinus	1.0–26	tr–0.29	0.18–147
Picea	n.d.–tr	n.d.–tr	n.d.–0.06
Abies	n.d.–tr	n.d.–tr	n.d.–0.79
Larix	n.d.	n.d.–tr	n.d.
Pseudotsuga	n.d.	n.d.	n.d.
Tsuga	n.d.–tr	n.d.	n.d.–tr

n.d. = not detected

tr = traces

For most species there was no significant difference between the concentrations in living and dead knots. The living knots of *P. sibirica*, *P. strobus* and *P. sylvestris* were, however, much richer in stilbenes compared to the dead knots. The living knots of *P. sibirica* and *P. strobus* contained 12% and 15% stilbenes, respectively, which were the highest stilbene concentrations detected.

First time studied/reported

- Stilbenes in stemwood of *Pinus elliottii*
- Stilbenes in knots of *Pinus banksiana*, *P. gerardiana*, *P. nigra*, *P. pinaster*, *P. resinosa*, *P. roxburghii*, *P. strobus*, *P. taeda* and *P. wallichiana*

Chemotaxonomic significance

- Large amounts of dihydrostilbenes were found in pines of subsection *Strobus*. According to Erdtman et al. (1966) this subgenus has a more powerful methylation and hydrogen transferring system.

Flavonoids

The highest flavonoid concentrations were found in genera *Pinus*, *Larix* and *Pseudotsuga*. Only traces were found in genera *Picea, Abies* and *Tsuga* (Table 17). The concentration and composition of flavonoids in heartwood and knots were fairly equal, and hardly any flavonoids were detected in the sapwood. The flavonoid concentration was, however, higher in knots than in heartwood of all studied *Larix* species.

Table 17 Lowest and highest average concentrations of flavonoids per genus (HW = heartwood, SW = sapwood).

	Concentration		
	mg/g dry wood		
	HW	SW	Knots
Pinus	n.d.–32	n.d.–0.25	n.d.–41
Picea	n.d.–0.38	n.d.–tr	n.d.–0.40
Abies	n.d.–0.11	n.d.–0.10	n.d.–tr
Larix	0.62–25	n.d.–0.09	3.0–33
Pseudotsuga	29	tr	20
Tsuga	n.d.–tr	n.d.–0.11	n.d.–1.7

n.d. = not detected

tr = traces

The heartwood of *P. elliottii* contained more than 3% flavonoids, the heartwood of *P. taeda* 2–3%, the heartwood of *P. banksiana*, *P. contorta* and *P. radiata* 1–2% and the remaining species less than 1% flavonoids. The knots of *P. sibirica* and *P. strobus* were the richest in flavonoids. They contained 2–4%.

First time studied/reported

- Flavonoids in stemwood of *Pinus elliottii*, *Picea mariana* and *Tsuga canadensis*
- Flavonoids in knots of *Pinus elliottii*, *P. gerardiana*, *P. nigra*, *P. pinaster*, *P. roxburghii*, *P. strobus*, *P. taeda*, *P. wallichiana*, *Picea sitchensis*, *Larix gmelinii*, *L. kaempferi*, *L. lariciana*, *L. sibirica*, *Pseudotsuga menziesii* and *Tsuga heterophylla*
- Pinobanksin-3-acetate and dihydrokaempferol in *Pinus contorta*

Chemotaxonomic significance

- Subsection *Strobus* can dehydrogenate flavanones to the corresponding flavones, a feature that is missing from subsection *Gerardianae* (Lindstedt & Misiorny 1952); and
- *P. resinosa* was the only pine where no flavonoids were detected.

4.4 Utilization potential

4.4.1 Tall oil potential

fatty acids, sterols and resin acids are dissolved or dispersed in alkaline pulping liquors and can be recovered in the form of crude tall oil (CTO). Depending on the wood species used, 30–50 kg CTO is produced per tonne of pulp, and the global production is about 1.4 Mt/a. More than half is produced in the USA and one fifth in Scandinavia (Holmbom 2011, p. 187, Norlin 2011, p. 594).

CTO can be vacuum distilled into several fractions (Table 18). Tall oil fatty acids (TOFA) and tall oil rosin (TOR) are valuable raw materials for a variety of chemical products. TOR represents 35% of the total global rosin production. The rest is gum rosin tapped from living trees (64%) and wood rosin distilled from old stumps (1%). The total global rosin production was 1.2 Mt in 2008 (Turner 2010).

Table 18 Principal composition and yields of crude tall oil fractions (Norlin 2011, p. 592, RA = resin acids, FAs = fatty acids).

Fraction	Yield	Composition		
		RA	FAs	Neutrals
	%	%		
Heads	5–12	<0.5	30–50	40–60
TOFA	35–45	<2	95–98	1–2
DTO	May-15	20–30	65–70	4–7
TOR	20–35	85–96	1–5	1–7
TOP	20–40	5–13	5–10	40–60

The tall oil potential of the studied species was calculated as resin acids + free fatty acids + the fatty acid part of acylglycerols and steryl esters (Table 19). *P. strobus* and *P. resinosa* showed the highest tall oil potential, 2–6%. *P. contorta*, *P. elliottii*, *P. sylvestris* and *P. taeda* yielded 1–4%, but the concentration difference between heartwood and sapwood was pronounced in this group. One should, however, bear in mind that less than 45% of the tall oil available in the living tree can be recovered as tall oil (Drew &

Propst 1981, p. 10). Calculated per tonne dry pulp the yield is about half, i.e. only about 20% of the tall oil available in the tree can be recovered.

Table 19 Tall oil potential of studied pine species (FAs = fatty acids, RAs = resin acids, HW = heartwood, SW = sapwood).

Potential	Species	FAs + RAs	
		kg/t dry wood	
		HW	SW
High	*P. strobus*	64	32
	P. resinosa	50	24
Moderate	*P. contorta*	39	15
	*P. elliottii**	29	16
	P. sylvestris	28	14
	*P. taeda**	30	10
Low	*P. banksiana*	18	13
	P. nigra	12	15
	P. radiata	9	15
	P. sibirica	7	14
	P. pinaster	11	7

*trees are harvested before heartwood formation i.e. they contain sapwood only and can therefore not be considered as high-potential raw material.

It can be concluded that the tall oil potential is strongly dependent on the wood raw material used in the pulp mill. Fast-growing species like *P. radiata*, *P. elliottii* and *P. taeda* have not formed any heartwood when they are harvested. This increases the sapwood to heartwood ratio and, thereby, decreases the tall oil potential. The same is true when large quantities of saw mill residues are utilized in the pulp mill.

4.4.2 Sterols

Phytosterols are used in cholesterol-lowering food and dietary supplements, cosmetics, and as starting material for manufacturing of pharmaceutical steroid hormones. The raw materials for sterol production are tall oil pitch (TOP) and soybean oil deodorizer distillate (SODD) (Table 20). SODD is a by-product of soybean oil refining, where the sterols are isolated together with tocopherols (vitamin E). This means that the profitability is highly dependent on the vitamin-E market. The global phytosterols production is 13 000–15 000 t/a, and 55–60% of that originated from TOP (Arboris 2016), so about 80 500 tons TOP per year is utilized for sterol production.

Table 20 Sterol sources (Cantrill 2008, Thomas 2011, p. 8, Yan el al. 2012).

Source	Sterols
	%
Pine trees	0.1
Crude tall oil (CTO)	>2
Tall oil pitch (TOP)	5–15
Soybeans	0.05
Crude soybean oil	0.2–0.4
Soybean oil deodorizer distillate (SODD)	4–9

The sterol potential of the studied species was calculated as free sterols + the sterol part of steryl esters. The pines richest in sterols were: *Pinus strobus* (which is used for sterol production in the USA), *P. sibirica* and *P. resinosa* (Table 21).

Table 21 Sterol potential in stemwood of studied pine species (HW = heartwood, SW = sapwood).

Potential	Species	Sterols	
		kg/t dry wood	
		HW	SW
High	*P. strobus*	1.9	1.6
	P. sibirica	1.4	1.4
	P. resinosa	1.7	1.4
Moderate	*P. contorta*	1.1	1.1
	P. banksiana	1.1	1.1
	P. sylvestris	0.6	1.0
	P. elliottii	1.0	0.8

Picea pungens, *P. mariana*, *P. glauca*, *P. koraiensis*, *P. omorika*, *P. abies* (grown in Finland), *Pseudotsuga menziesii* and *Larix gmelinii* var. *olgensis* also contained more than 0.1% sterols, while all *Tsuga* and *Abies* species were poor in sterols and cannot be used as raw material for sterol production.

4.4.3 Juvabiones

Juvabiones are insect juvenile hormones that interfere with the metamorphosis and prevent the insects from reaching maturity. Juvabione derivatives can, thus, be used as insecticides.

The juvabione potential presented is the sum of all juvabiones (Table 22). The best raw material for juvabione utilization is knots of *A. lasiocarpa* (5–6%), but knots of *A. sachalinensis* (3–4%) could also be considered.

Heartwood of *A. lasiocarpa* yields 1% juvabiones. This was the only stemwood sample that contained any significant amounts, thus, only concentrations in knots are included in Table 22.

Table 22 Potential yield of juvabiones (LK = living knots, DK = dead knots.

Potential	Species	Juvabiones	
		kg/t dry wood	
		LK	DK
High	*A. lasiocarpa*	61	51
	A. sachalinensis	37	25
Moderate	*A. sibirica*	16	16
	Pinus pinaster	11	17
	A. veitchii	13	12

4.4.4 Stilbenes

Stilbenes show unique features combining fluorescence, phosphorescence, photochrome, photochemical and photophysical properties. Stilbene derivatives are, thus, used in dyes, optical brighteners, phosphors, scintillators and as pH indicators (Smith 1997, p. 925, Likhtenshtein 2012). Stilbene moieties have also been used as building blocks for preparation of machaeriols, which are structurally related to cannabinoids used for medication (Xia & Lee 2008).

The estimated production volume of stilbene dyes is almost 4 000 t/a (Smith 1997, p. 930). Commercial stilbene dyes for cotton and cellulose are, however, mostly manufactured from 4-nitrotoluene-2-sulfonic acid, not from natural stilbenes (Smith 1997, p. 922).

Willför et al. (2003b) have shown that heartwood of *Pinus sylvestris* contains 12 kg pinosylvin + pinosylvin monomethyl ether per ton dry wood and knots 68 kg/t. Accordingly, the stilbene potential of the species studied in this thesis was calculated as the sum of all pinosylvin and pinosylvin monomethyl ether isomers (Table 23). The highest yields were detected in heartwood of *Pinus nigra*, *P. resinosa* and *P. taeda* (2–3%) and in knots of *P. strobus* and *P. sibirica* (9% and 6%, respectively). The knots of *P. resinosa*, *P. sylvestris* and *P. nigra* can also be considered as potential sources of pinosylvin and pinosylvin monomethyl ether. They yield 4–5%.

Table 23 Potential yield of pinosylvin (PS) and pinosylvin monomethyl ether (PSMME) in heartwood (HW) and knots.

Potential	Species	PS + PSMME	
		kg/t dry wood	
		HW	knots
High	*P. resinosa*	20	48
	P. nigra	25	36
Knots high	*P. strobus*	12	94
	P. sibirica	6	60
	P. sylvestris	11	41
Moderate	*P. taeda*	19	16
	P. elliottii	12	14
	P. banksiana	7	15

4.4.5 Lignans

The lignan HMR has received dietary ingredient clearance by the American Food and Drug Administration (FDA 2004) and is sold as dietary supplement since 2006. HMR is also used as ingredient in cosmetics and constitutes a potential raw material for large-scale semisynthesis of other lignans.

Picea knots have been reported to contain 0.6–12% lignans (Willför et al. 2004a) and *Abies* knots 3–7% (Willför et al. 2004b). The only commercial lignan so far is HMR. It is extracted from *Picea abies* knots, which contain 3–18% HMR (Willför et al. 2003a). A large pulp mill can, thus, sort out knots and extract up to 100 tons of HMR per year (Holmbom et al. 2007).

The yields of HMR and secoisolariciresinol were calculated and it was found that knots of *Tsuga canadensis* and Canadian *T. heterophylla* were the best raw materials for extraction of HMR (Table 24). Their potential yield ranged from 7% to 12% HMR, while knots of *Picea koraiensis*, *P. abies, Tsuga mertensiana* and *P. glauca* contained 5–11% HMR. The yield of secoisolariciresinol was the highest in *Larix gmelinii* (all three varieties), *Abies pindrow*, *L. kaempferi* and *L. decidua.* Their yields ranged from 4% to 8%.

Table 24 Potential yield of hydroxymatairesinol (HMR) and secoisolariciresinol (seco) in living knots (LK) and dead knots (DK).

Species	HMR		Species	Seco	
	kg/t dry wood			kg/t dry wood	
	LK	DK		LK	DK
Tsuga canadensis	117	78	*Larix gmelinii* var. *gmelinii*	55	70
Tsuga heterophylla CA	73	105	*Abies pindrow*	60	
Picea koraiensis	89	75	*Larix gmelinii* var. *olgensis*	37	77
Picea abies FI	81	75	*Larix kaempferi*	68	40
Picea abies FR	105	50	*Larix gmelinii* var. *japonica*	53	43
Tsuga mertensiana	75	n.a.	*Larix decidua*	50	42
Picea glauca	47	74	*Larix gmelinii* var. *gmelinii*	37	77

n.a. = not analysed

4.4.6 Flavonoids

Taxifolin or dihydroquercetin (DHQ) is used in a wide range of commercial products in Russia, e.g. in cosmetics, as dietary supplement, in pharmaceutics, as preservative and antioxidant in foods, in feed and as biostimulator for crops. In the USA, taxifolin is marketed as food supplement.

Taxifolin is extracted from roots, butt logs and stumps of *Larix gmelinii* and *L. sibirica*, and the average yield is 2–3% (Taxifolia 2017). Considering that the annual Russian larch harvesting is 30 million m^3, this implies that 40,000 tons taxifolin could be produced annually (Fitopanacea 2017). At the moment, the production is below 100 t/a, but European Food Safety Authority (EFSA 2017) has recently approved taxifolin as a novel food ingredient in EU, so the market has a potential to grow.

Usually lower parts of the stem are used to extract taxifolin, but this thesis clearly shows that also heartwood and knots of *Larix decidua* and *Pseudotsuga menziesii* are suitable raw materials for taxifolin production (Table 25).

Table 25 Potential yield of taxifolin in studied Larix species (HW = heartwood).

Potential	Species	Taxifolin	
		kg/t dry wood	
		HW	knots
High	*Pseudotsuga menziesii*	28	19
	Larix decidua	20	28
Moderate	*Larix gmelinii* var. *olgensis*	11	20
	Larix kaempferi	12	10
Low	*Larix gmelinii* var. *gmelinii*	2	9
	Larix gmelinii var. *japonica*	2	10
	Larix lariciana	1	4
	Larix sibirica	1	4

Larix and *Pseudotsuga* were not the only genera containing high flavonoid concentrations. The antimicrobial dietary supplement propolis (bee glue) contains significant amounts of pinocembrin, a component found in several of the studied pines. The potential yields in Table 26 are calculated as the sum all flavonoids. Pinocembrin, pinobanksin and pinobanksin acetate were, however, the dominating compounds.

The richest were the Southern pines *P. elliottii* and *P. taeda*. Their heartwood contained 1–2% and the knots 2–3%. The knots of *P. sibirica* and *P. strobus* contained 3–4% flavonoids and could also be used as raw material for flavonoid extraction.

Table 26 Potential yield of flavonoids (mainly pinocembrin, pinobanksin and pinobanksin acetate) in studied Pinus species (HW = heartwood).

Potential	Species	Flavonoids	
		kg/t dry wood	
		HW	knots
High	*Pinus elliottii*	32	19
	Pinus taeda	24	13
Knots high	*Pinus sibirica*	3	36
	Pinus strobus	9	32
Moderate	*Pinus banksiana*	11	13
	Pinus contorta	10	8
	Pinus radiata	11	3
	Pinus pinaster	9	8

5 Concluding remarks and future perspectives

All studied species exhibited a specific composition of extractives and the amounts differ not only from tree to tree, but also within parts of the individual trees. Therefore, it is almost impossible to draw any general conclusions about extractives in softwoods. Fortunately, that has not been the purpose of this thesis. The goal has been to gather comparable data, which other researchers can use for reference in their research. This reference book does not cover all industrially important softwood species, but at some point one just has to stop and let others continue.

If these conclusions are the only part of this thesis that you read, beware of the simplified picture presented! The values in the figures below are average concentrations based on the mean values for all species within that genus, and the intervals in the text are the smallest and largest average concentrations for that genus. Accordingly, there are values and compounds that have been omitted because they are not typical for the genus as a whole, but can still be unique identifiers for a specific species. More information about these compounds is found in chapter 4.

For most studied species, the heartwood contains more extractives than the sapwood, and the knots contain much more extractives than the stemwood.

Pinus

The pines are very rich in extractives, especially in lipophilics. The average concentrations for the heartwood in this thesis were 2.3–8.9% (Figure 62). The sapwood contained 0.76–3.7% extractives and the knots 0.82–30%. In general, there were about three times more extractives in knots than in heartwood. The most abundant compounds in heartwood and knots were resin acids, while esterified fatty acids dominated in sapwood. Significant amounts of stilbenes and flavonoids were found in heartwood and knots. In addition, there were a few per cents of lignans in the knots. There were hardly any lignans in the stemwood.

Stilbenes are characteristic of pine heartwood, but this study has shown that they can be even more abundant in knots than in heartwood. Some knots contained up to 15% stilbenes.

Flavonoids were found in some pines, larches and in Douglas-fir. Commonly the concentrations were equally high in the heartwood and the knots, but some species were observed to differ from that pattern; the concentration could be up to 16 times higher in the knots. Some knots contained up to 3% flavonoids.

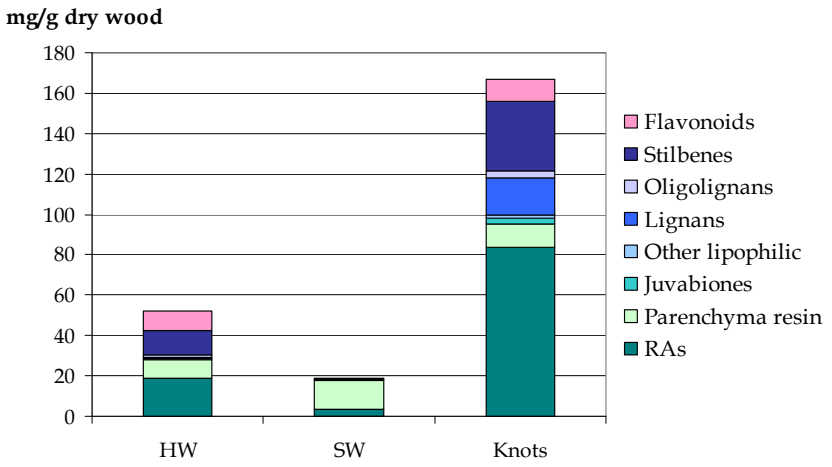

Figure 62 Average composition of extractives in heartwood (HW), sapwood (SW) and knots of genus Pinus.

Picea

The spruces were significantly lower in extractives than the pines. The heartwood contained 0.54–2.0%, the sapwood 0.30–1.4% and the knots 2.6–18%, i.e. there were about five times more extractives in the knots than in the stemwood (Figure 63). The extractives in the heartwood consisted of equal parts of parenchyma resin and lignans. There were also some resin acids and oligolignans. Most of the extractives in the sapwood were esterified fatty acids and sterols. The concentration of resin acids was higher in the knots than in the heartwood, but the resin acids were, however, not as abundant as the lignans and oligolignans.

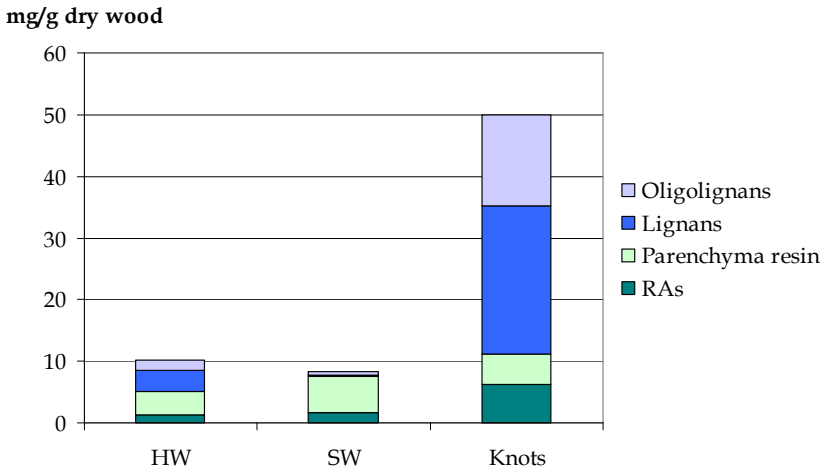

Figure 63 Average composition of extractives in heartwood (HW), sapwood (SW) and knots of genus Picea.

Abies

The total average concentration of extractives in fir was very similar to that in spruce. It was found 0.19–1.8% extractives in the heartwood, 0.20–1.0% in the sapwood and 3.7–19% in the knots (Figure 64). The firs lack resin canals and, thus, lack resin acids. Instead, the heartwood is protected by juvabiones, lignans and oligolignans. Additionally some parenchyma resin was found in all tissue types. There were up to ten times more extractives in the knots than in the heartwood.

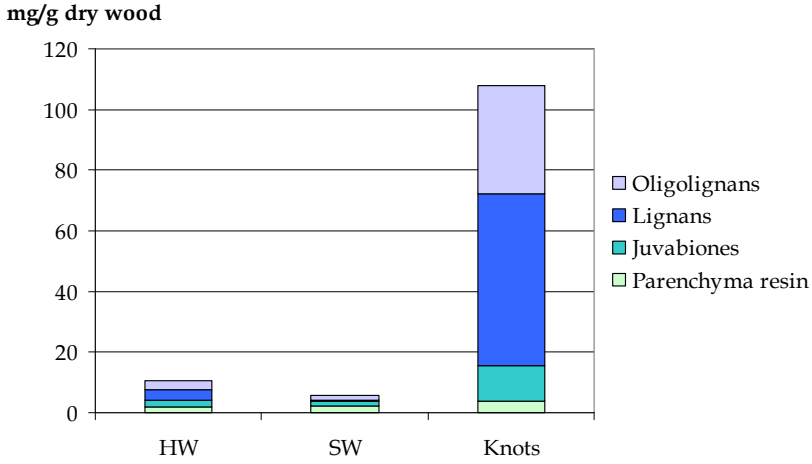

Figure 64 Average composition of extractives in heartwood (HW), sapwood (SW) and knots of genus Abies.

The juvabiones are characteristic of fir and Douglas-fir. In this study, all firs contained juvabiones, some knots even more than 8%.

Larix

The heartwood of the larches contained 0.64–3.6% extractives, the sapwood 0.54–1.5% and the knots 1.7–19%. On average, there were seven times more extractives in the knots than in the heartwood (Figure 65). This was the only genus where heartwood, sapwood and knots all contained fairly equal total concentrations of lipophilic extractives, i.e. resin acids, parenchyma resin and other lipophilic compounds. In the other studied genera, the knots were richer in lipophilic extractives than the stem.

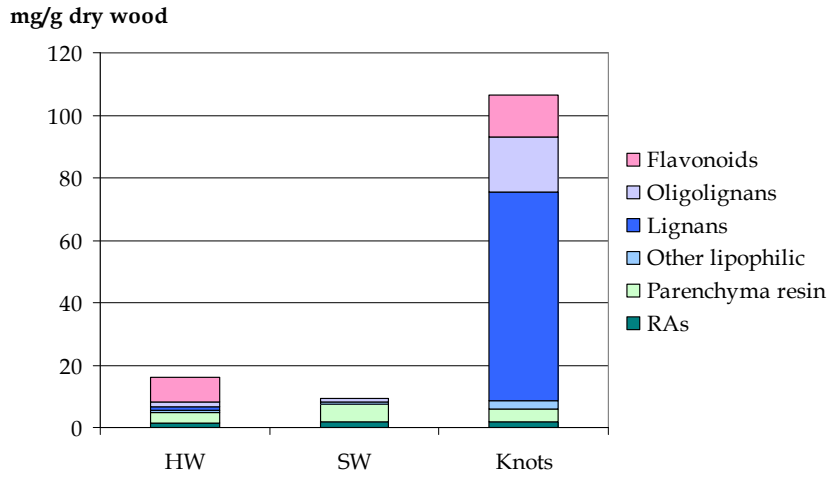

Figure 65 Average composition of extractives in heartwood (HW), sapwood (SW) and knots of genus Larix.

Half of the extractives in the heartwood were flavonoids. Some species contained up to 3% flavonoids. The rest were parenchyma resin and lower concentrations of resin acids, lignans, oligolignans, and the lipophilic compounds thunbergol, manool, larixol and larixyl acetate. The extractives in the sapwood were mostly esterified fatty acids.The lignans dominated in the knots, but there were also 1–2% oligolignans and flavonoids.

Pseudotsuga

The heartwood of Douglas-fir was almost as rich in extractives as the heartwood of the pines; 3.8% was found in heartwood, 0.06% in sapwood and 9.1% in the knots (Figure 66). Exceptional for this species was that most of the extractives in the heartwood were flavonoids. The concentrations in the heartwood even exceeded those of the knots. The knots, on the other hand, were very rich in lignans. There were also some oligolignans, resin acids, parenchyma resin and juvabiones. All this amounted to concentrations two times as high as in the heartwood.

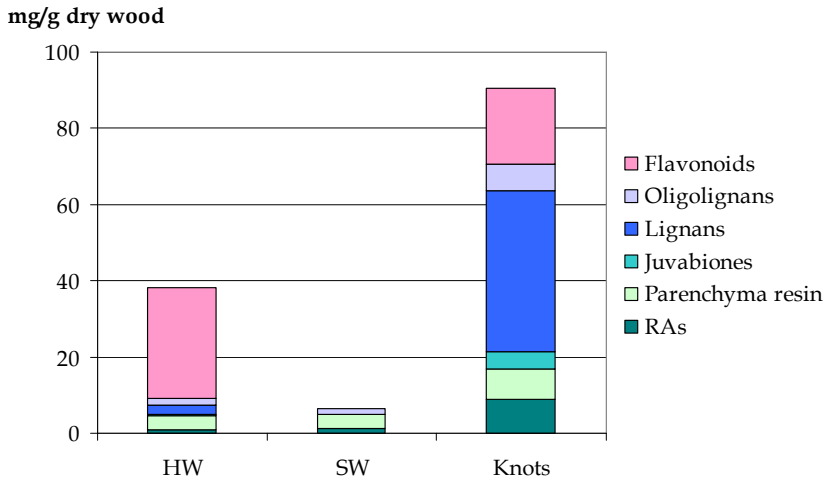

Figure 66 Average composition of extractives in heartwood (HW), sapwood (SW) and knots of genus Pseudotsuga menziesii (only one species of genus Pseudotsuga was studied).

Tsuga

The average total extractive concentrations in hemlock were on the same level as in the firs; 0.76–1.3% was found in the heartwood, 0.13–0.34% in the sapwood and 0.80–17% in the knots (Figure 67). The hemlocks have no resin canals and, therefore, do not benefit from the protection provided by the resin acids. Instead, the heartwood is preserved by lignans and some oligolignans. The concentration of extractives was ten times higher in the knots is than in the heartwood; some knots contained up to 15% lignans and fully 2% oligolignans.

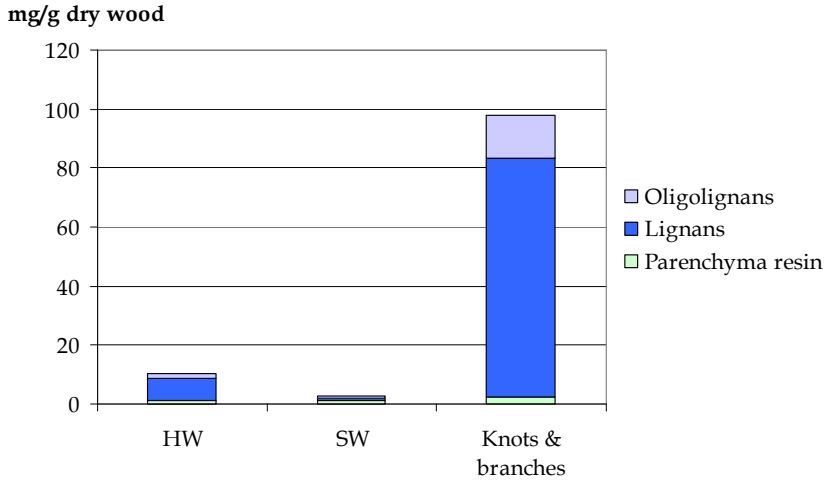

Figure 67 Average composition of extractives in heartwood (HW), sapwood (SW) and knots of genus Tsuga.

Final remarks

In this work, the chemical compounds in stemwood and knots of several important softwood species were systematically mapped. The data can be used at pulp and paper mills to understand problems that appear during the pulping process or in the end product, and thereby reduce losses, number of breaks and stoppages of production. It can also be used by R&D chemists and engineers who are trying to identify the best raw material for new chemical products, or to increase the yield in already existing processes.

This work clearly shows that some species are better suited for production of tall oil and sterols, while others contain significant concentrations of bioactive compounds, which can be used in insect repellents, as antioxidants in functional foods or cosmetics. The aim of this work was not to give any straight answers as to what could be used where, or how much the profits could be increased, it merely provides a fundamental knowledge base for developing a more sustainable, natural chemical world. All in all, this is, however, probably one of the most comprehensive surveys ever published on non-volatile extractives in softwoods.

Acknowledgements

This has been a long journey along a very winding road, and I must admit, I have not always been able to see the goal, because there have been so many trees in the way. Nevertheless, here I am, finally, looking down at the forest of test tubes I have accumulated during the years. Some are yellow, some are brown and about half of them are sticky, very sticky indeed. It will probably take me another eternity to clean them, but it doesn't matter. Not now. I just feel a great relieve. I finally made it!

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Åbo, January 12, 2018

Linda

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Appendices

Appendix A Samples

A1 Names of studied species in Latin, English, Swedish and Finnish
A2 Sample information

Appendix B Cladograms

B1 Pine section *Trifoliae*
B2 Pine section *Pinus*
B3 Pine sections *Quinquefoliae* and *Parraya*
B4 Genus *Picea*
B5 Genus *Abies*
B6 Genera *Larix*, *Tsuga* and *Pseudotsuga*

Appendix C Chemical structures

C1 Resin acids
C2 Diterpenes and diterpenoids
C3 Sterols and triterpenols
C4 Juvabiones
C5 Lignans
C6 Flavonoids
C7 Stilbenes

Appendix D Concentrations of compounds

D1 Resin acids
D2 Fatty acids and acylglycerols
D3 Sterols, triterpenols and their esters
D4 Juvabiones
D5 Other lipophilic compounds
D6 Stilbenes
D7 Lignans and oligolignans
D8 Flavonoids

Appendix E Chromatograms

E1 Short-column GC
E2 Long-column GC

Appendix F Plant synonyms

Appendix A Samples

A1 Names of studied species in Latin, English, Swedish and Finnish

Latin	English	Swedish	Finnish
Pinus			
Pinus banksiana Lamb.	jack pine	banksianatall	banksinmänty
Pinus contorta Dougl.	lodgepole pine, shore pine	contortatall, strandtall	kontortamänty
Pinus elliottii Engelm.	slash pine	-	elliotinmänty, etelänkeltamänty
Pinus gerardiana Wall.	chilgoza pine	-	-
Pinus nigra Arnold.	black pine, Austrian pine	svarttall	mustamänty
Pinus pinaster Ait.	maritime pine	medelhavstall, havstall, terpentintall	rannikkomänty
Pinus radiata D. Don	Monterey pine	radiatatall	Montereynmänty
Pinus resinosa Ait.	red pine, Norway pine	amerikansk rödtall	punamänty, amerikanpunamänty
Pinus roxburghii Sarg.	Chir pine, Imodi pine	-	-
Pinus sibirica Du Tour	Siberian stone, Siberian pine, Siberian cedar	sibirisk cembratall	siperiansempra, siperianmänty
Pinus strobus L.	Eastern white pine, white pine, Weymouth pine	Weymouthtall	Weymouthmänty
Pinus sylvestris L.	Scots pine	tall, pelartall	mänty
Pinus taeda L.	loblolly pine	loblolly-tall	loblollymänty
Pinus wallichiana A.B. Jacks.	Himalaya(n white) pine, Buthan pine	Himalayatall	kyynelmänty
Picea			
Picea abies (L.) H. Karst.	Norway spruce	gran, rödgran	kuusi
Picea glauca (Moench) Voss	white spruce, cat spruce	vitgran	valkokuusi
Picea koraiensis Nakai	Korean spruce	-	koreankuusi
Picea mariana (Mill.) B.S.P.	black spruce, bog spruce, swamp spruce	svartgran, amerikansk svartgran	mustakuusi
Picea omorika (Pančić) Purkyne	Serbian spruce	serbisk gran, omorikagran	serbiankuusi
Picea pungens Engelm.	Colorado spruce, blue spruce	blågran, stickgran, pungensgran	okakuusi
Picea sitchensis (Bong.) Carr.	Sitka spruce, tideland spruce	Sitkagran	Sitkakuusi

Latin	English	Swedish	Finnish
Abies			
Abies alba Mill.	silver fir	silvergran	saksanpihta
Abies amabilis (Dougl.) J.Forbes	Pacific silver fir, amabilis fir	purpurgran	purppurapihta
Abies balsamea (L.) Mill.	balsam fir	balsamgran	palsamipihta
Abies concolor (Gord. & Glend.) Hildebr.	white fir	Coloradogran	harmaapihta
Abies lasiocarpa (Hook.) Nutt.	subalpine fir, alpine fir	berggran	lännenpihta
Abies pindrow (Royle ex D. Don) Royle	pindrow fir, west Himalayan fir	pindrowgran	pindrowinpihta
Abies sachalinensis (F. Schmidt) Mast.	Sachalin fir	Sachalingran	Sahalininpihta
Abies sibirica Ledeb.	Siberian fir	pichtagran, sibirisk ädelgran	siperianpihta
Abies veitchii Lindl.	Veitchi's silver fir	Fujigran	japaninpihta
Larix			
Larix decidua Mill.	European larch	europeisk lärk	euroopanlehtikuusi
Larix gmelinii (Rupr.) Kuzeneva	Dahurian larch	dahurlärk	dahurianlehtikuusi
Larix gmelinii var. *japonica* (Maxim. et Regel) Pilg.	Kurile larch	kurilerlärk	kurilienlehtikuusi
Larix gmelinii var. *olgensis* (Henry) Ostenf & Syrach-Larsen	Olga Bay larch	koreansk lärk, ussurilärk	olganlehtikuusi
Larix kaempferi (Lamb.) Carr.	Japanese larch	japansk lärk	japaninlehtikuusi
Larix lariciana (Du Roi) K. Koch	tamarack, hackmatack, Eastern larch, Alaska larch	kanadalärk	kanadanlehtikuusi
Larix sibirica Ledeb.	Siberian larch	sibirisk lärk	siperianlehtikuusi
Other			
Pseudotsuga menziensii (Mirb.) Franco	Douglas-fir	douglasgran	douglaskuusi
Tsuga canadiensis (L.) Carr.	Eastern hemlock	hemlock	kanadanhemlokki
Tsuga heterophylla (Raf.) Sarg.	Western hemlock	västamerikansk hemlock, jättehemlock	lännenhemlokki
Tsuga mertensiana (Bong.) Carr.	mountain hemlock	berghemlock	vuorihemlokki

A2 Sample information

Species	Growth location	Sampling date	Age years		
			T 1	T 2	T 3
Pinus					
Pinus banksiana	Blandin Land, Itasca Co, MN, USA	July 2001	50	52	-
Pinus contorta	Sävar, Sweden	Sept 2000	22	22	-
Pinus elliottii	Southlands Forest, Decatur Co, GA, USA	Feb 2006	20	20	-
Pinus gerardiana	Pakistan	Autumn 2005		n.k.	
Pinus nigra	Sauviat-sur-vige, France	May 2003	36	36	36
Pinus pinaster	La Roche-Posay, France	May 2003	20	20	20
Pinus radiata [1]	Colunga, Asturias, Spain	May 2002	10	n.k.	-
Pinus resinosa	Blandin Land, Itasca Co, MN, USA	July 2001	42	23	-
Pinus roxburghii	Pakistan	Autumn 2005		n.k.	
Pinus sibirica	St Petersburg region, Russia	Jan 2001	20	20	-
Pinus strobus	Cape Breton, Nova Scotia, Canada	Aug 2002	53	45	-
Pinus sylvestris	Ekenäs, Finland	May 2000	72	73	-
Pinus taeda	Southlands Forest, Decatur Co, GA, USA	Feb 2006	20	20	-
Pinus wallichiana	Pakistan	Autumn 2005		n.k.	
Picea					
Picea abies FI	Ekenäs, Finland	May 2000	66	71	-
Picea abies FR	Saint-Dié-des-Vosges, France	Jan 2001	35	-	-
Picea glauca	Blandin Land, Itasca Co, MN, USA	Feb 2001	31	26	-
Picea koraiensis [1]	Arboretum Mustila, Elimäki, Finland	May 2002	-	-	-
Picea mariana	Solböle, Bromarv, Finland	Nov 2001	63	63	-
Picea omorika [1]	Arboretum Mustila, Elimäki, Finland	May 2002	94	-	-
Picea pungens	Arboretum Mustila, Elimäki, Finland	May 2002	47	-	-
Picea sitchensis	Llandegla, North Wales, UK	Sept 2000	20	16	-
Abies					
Abies alba FR 1	Saint-Dié-des-Vosges, France	Jan 2001	31	-	-
Abies alba FR 2	Sauviat-sur-vige, France	May 2003	30–35	30–35	30–35
Abies amabilis [1]	Arboretum Mustila, Elimäki, Finland	May 2002	88	-	-
Abies balsamea [2]	Blandin Land, Itasca Co, MN, USA	Spring 2001	41	-	-
Abies concolor	Solböle, Bromarv, Finland	Nov 2001	n.k.	-	-
Abies lasiocarpa	Solböle, Bromarv, Finland	Nov 2001	58	59	-
Abies pindrow	Pakistan	Autumn 2005	n.k.		
Abies sachalinensis [1]	Arboretum Mustila, Elimäki, Finland	May 2002	78	-	-
Abies sibirica	St Petersburg region, Russia	Mar 2001	30	37	-
Abies veitchii [1]	Arboretum Mustila, Elimäki, Finland	May 2002	n.k.	-	-
Larix					
Larix decidua FI	Solböle, Bromarv, Finland	Nov 2001	61	62	-
Larix decidua FR	Sauviat-sur-vige, France	May 2003	43	43	43
Larix gmelinii var. *gmelinii*	Punkaharju, Finland	Dec 2005	70–80	70–80	-
Larix gmelinii var. *japonica*	Punkaharju, Finland	Dec 2005	70–80	70–80	-
Larix gmelinii var. *olgensis*	Punkaharju, Finland	Dec 2005	70–80	70–80	-
Larix kaempferi	Punkaharju, Finland	Dec 2005	70–80	70–80	70–80
Larix lariciana	Blandin Land, Itasca Co, MN, USA	Spring 2001	53	44	-
Larix sibirica RU 1	St Petersburg region, Russia	Nov 2000	49	50	-
Larix sibirica RU 2	Habarovsk, Eastern Siberia, Russia	Mar 2007	90–105	90–105	-
Larix sibirica RU 3	Baikal, Southern Siberia, Russia	Mar 2007	60–80	60–80	-
Other					
Pseudotsuga menziensii	Solböle, Bromarv, Finland	Nov 2001	55	54	-
Tsuga canadiensis	Cape Breton, Nova Scotia, Canada	Aug 2002	196	98	-
Tsuga heterophylla CA	Port Hardy, Vancouver Island, Canada	June 2002	80	80	-
Tsuga heterophylla FI	Solböle, Bromarv, Finland	May 2004	n.k.	-	-
Tsuga mertensiana	Solböle, Bromarv, Finland	May 2004	n.k.	-	-

[1] Bore samples.

[2] Stem wood divided into three parts: 3–8 y, 9–18 y and 18–39 y.

T 1 = tree number 1
T 2 = tree number 2
T 3 = tree number 3
n.k. = not known

Species	Number of trees	Number of knots					
		LK			DK		
		T 1	T 2	T 3	T 1	T 2	T 3
Pinus							
Pinus banksiana	2	-	4+1	-	1	-	-
Pinus contorta	2	2	2	-	-	-	-
Pinus elliottii	2	2	1	-	5	5	-
Pinus gerardiana	n.k.			300 g[3]			
Pinus nigra	3	2	3	3	3	3	3
Pinus pinaster	3	3	3	3	3	3	3
Pinus radiata[1]	2	1	1	-	-	1	-
Pinus resinosa	2	2	3	-	3+2	1	-
Pinus roxburghii	n.k.			300 g[3]			
Pinus sibirica	2	4	4	-	2	1	-
Pinus strobus	2	1	1	-	1	1	-
Pinus sylvestris	2	1	1	-	1	1	-
Pinus taeda	2	2	2	-	2	3	-
Pinus wallichiana	n.k.			300 g[3]			
Picea							
Picea abies FI	2	1	1	-	1	1	-
Picea abies FR	1	3	-	-	5	-	-
Picea glauca	2	3	2	-	2	3	-
Picea koraiensis[1]	1	1	-	-	1	-	-
Picea mariana	2	6	7	-	9	8	-
Picea omorika[1]	1	2	-	-	1	-	-
Picea pungens	1	5+6	-	-	9	-	-
Picea sitchensis	2	1	2	-	2	1	-
Abies							
Abies alba FR 1	1	2	-	-	3+1	-	-
Abies alba FR 2	3	3	3	3	3	3	3
Abies amabilis[1]	1	2	-	-	2	-	-
Abies balsamea[2]	1	2	-	-	4	-	-
Abies concolor	1	2	-	-	-	-	-
Abies lasiocarpa	2	9	7	-	7	8	-
Abies pindrow	n.k.			300 g[3]			
Abies sachalinensis[1]	1	2	-	-	1	-	-
Abies sibirica	2	3	3	-	1	2	-
Abies veitchii[1]	1	2	-	-	1	-	-
Larix							
Larix decidua FI	2	3	2	-	3	3	-
Larix decidua FR	3	1	1	3	3	3	3
Larix gmelinii var. *gmelinii*	2	1	1	-	1	1	-
Larix gmelinii var. *japonica*	2	1	1	-	1	2	-
Larix gmelinii var. *olgensis*	2	1	1	-	1	1	-
Larix kaempferi	3	4	3	2	8	7	7
Larix lariciana	2	1	1	-	1	2	-
Larix sibirica RU 1	2	1	-	-	1	1	-
Larix sibirica RU 2	2	-	-	-	2	2	-
Larix sibirica RU 3	2	-	-	-	2	2	-
Other							
Pseudotsuga menziensii	2	6	5	-	5	6	-
Tsuga canadiensis	2	1	1	-	1	1	-
Tsuga heterophylla CA	2	1	1	-	1	1	-
Tsuga heterophylla FI	1	-	-	-	1	-	-
Tsuga mertensiana	1	1	-	-	-	-	-

[1] Bore samples.

[2] Stem wood divided into three parts: 3–8 y, 9–18 y and 18–39 y.

[3] Only pooled knots were analysed, the number of trees sampled and the knot types are unknown.

Underlined = number of knots pooled and analysed together.

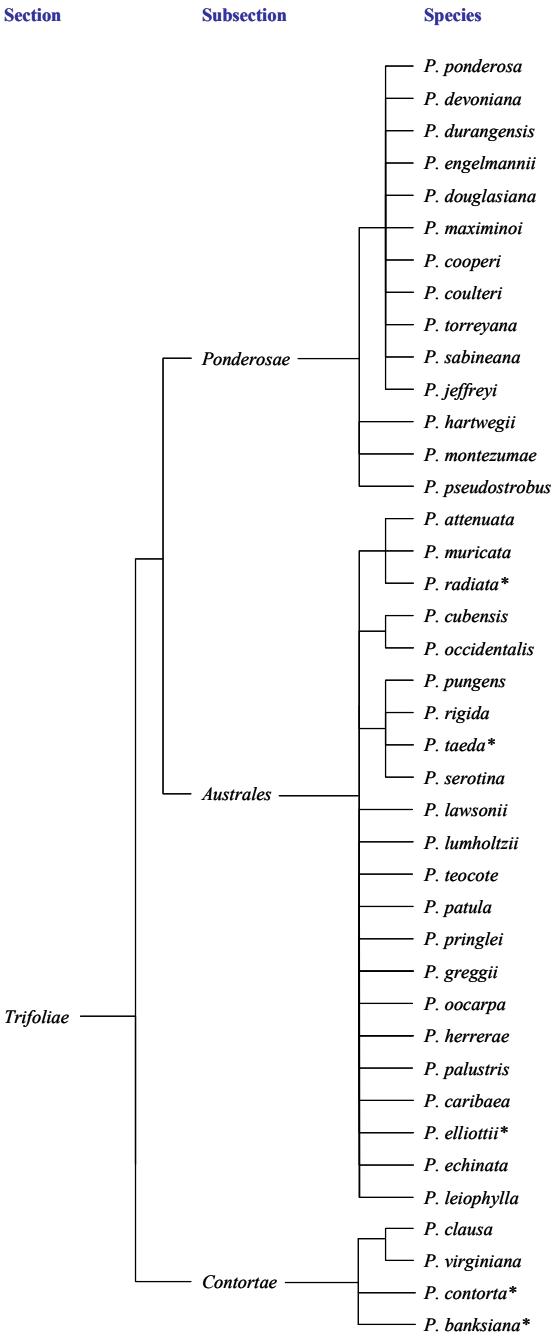
LK = living knot

DK = dead knot

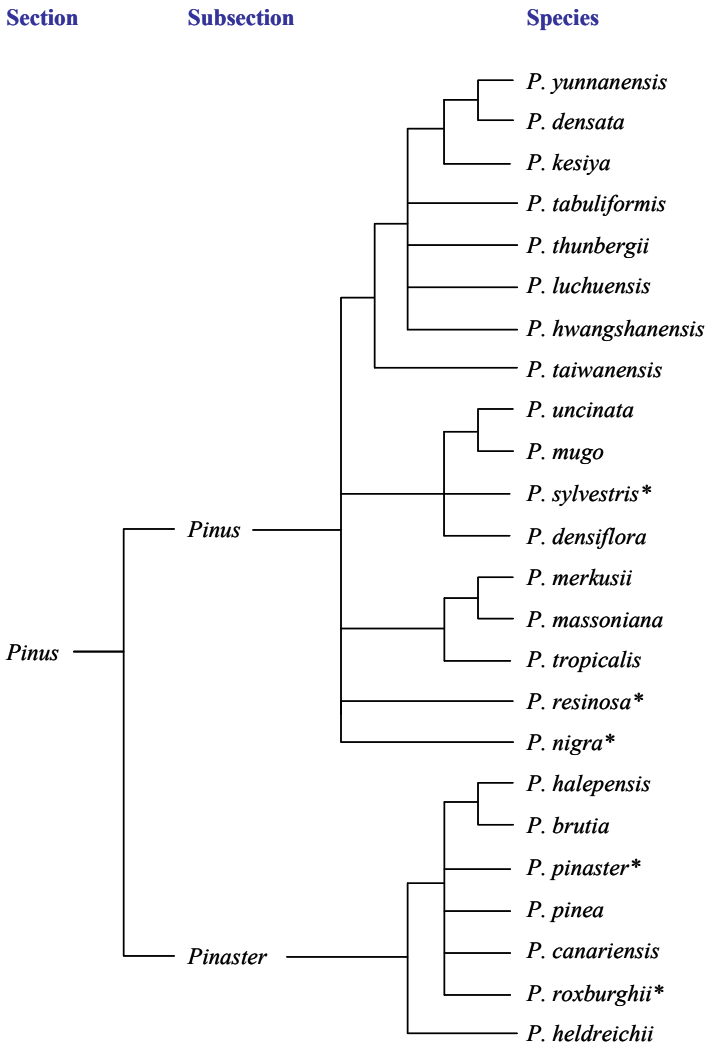
n.k. = not known

Appendix B Cladograms

B1 Pine section *Trifoliae* (modified from Gernandt et al. 2005)
Studied species marked with an asterisk (*)

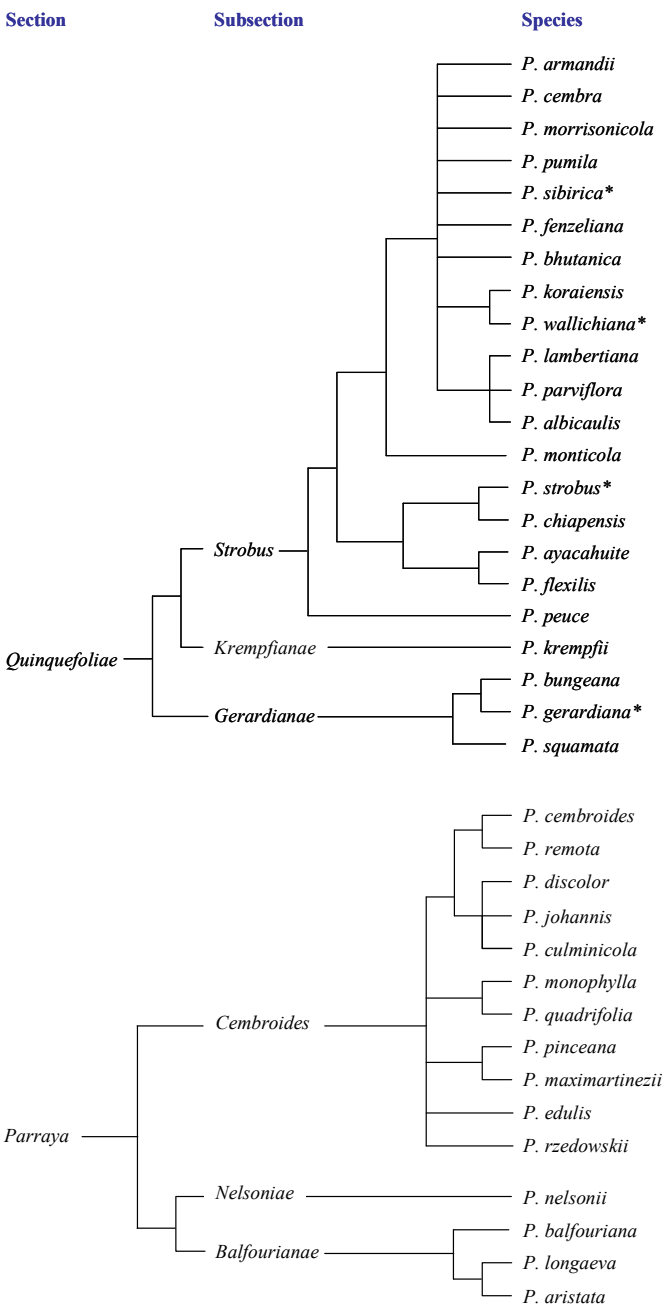


B2 Pine section *Pinus* (modified from Gernandt et al. 2005)
Studied species marked with an asterisk (*)

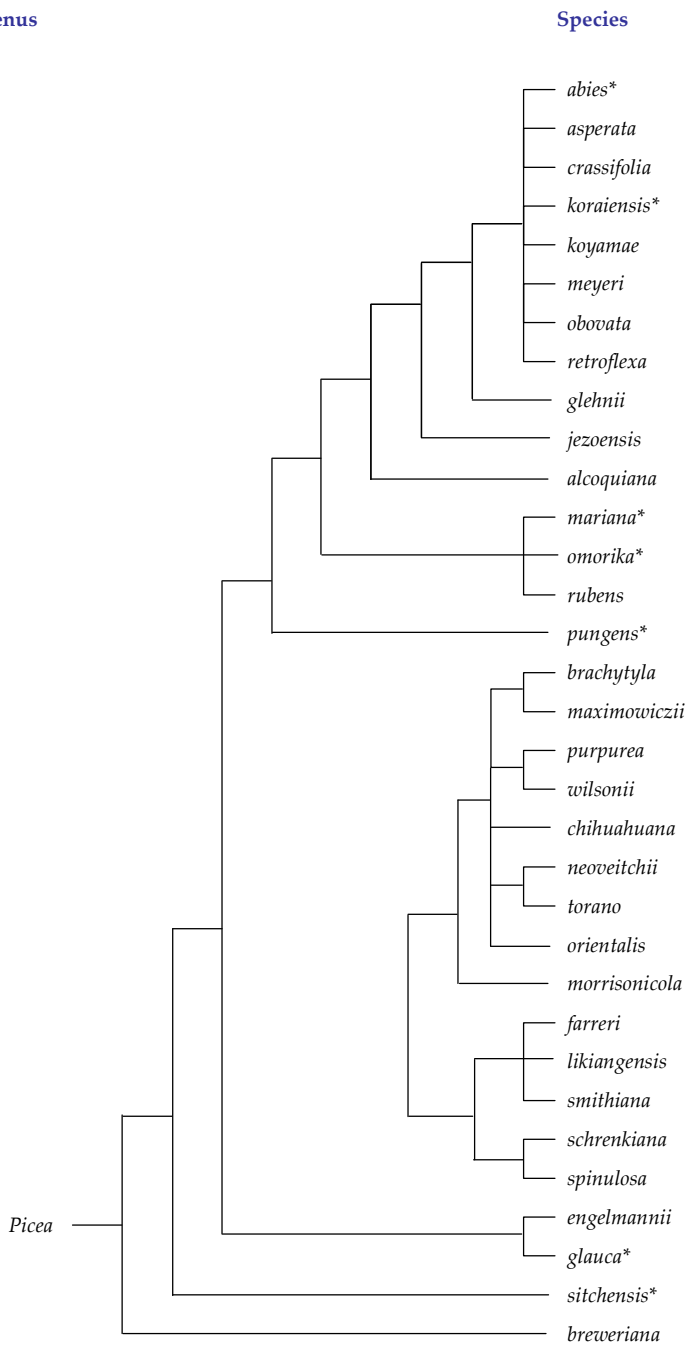


B3 Pine sections *Quinquefoliae* and *Parraya* (modified from Gernandt et al. 2005)

Studied species marked with an asterisk (*)

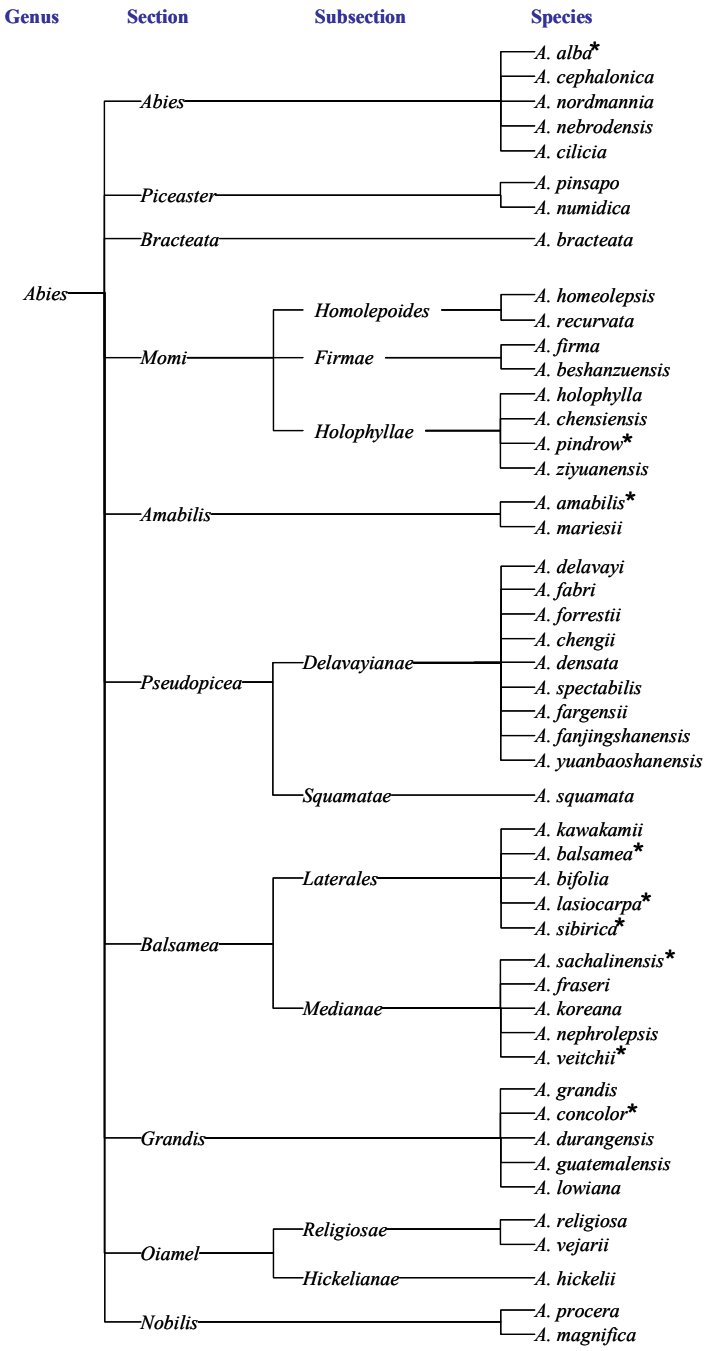


B4 Genus *Picea* (modified from Jin-Hua et al. 2006)
Studied species marked with an asterisk (*)



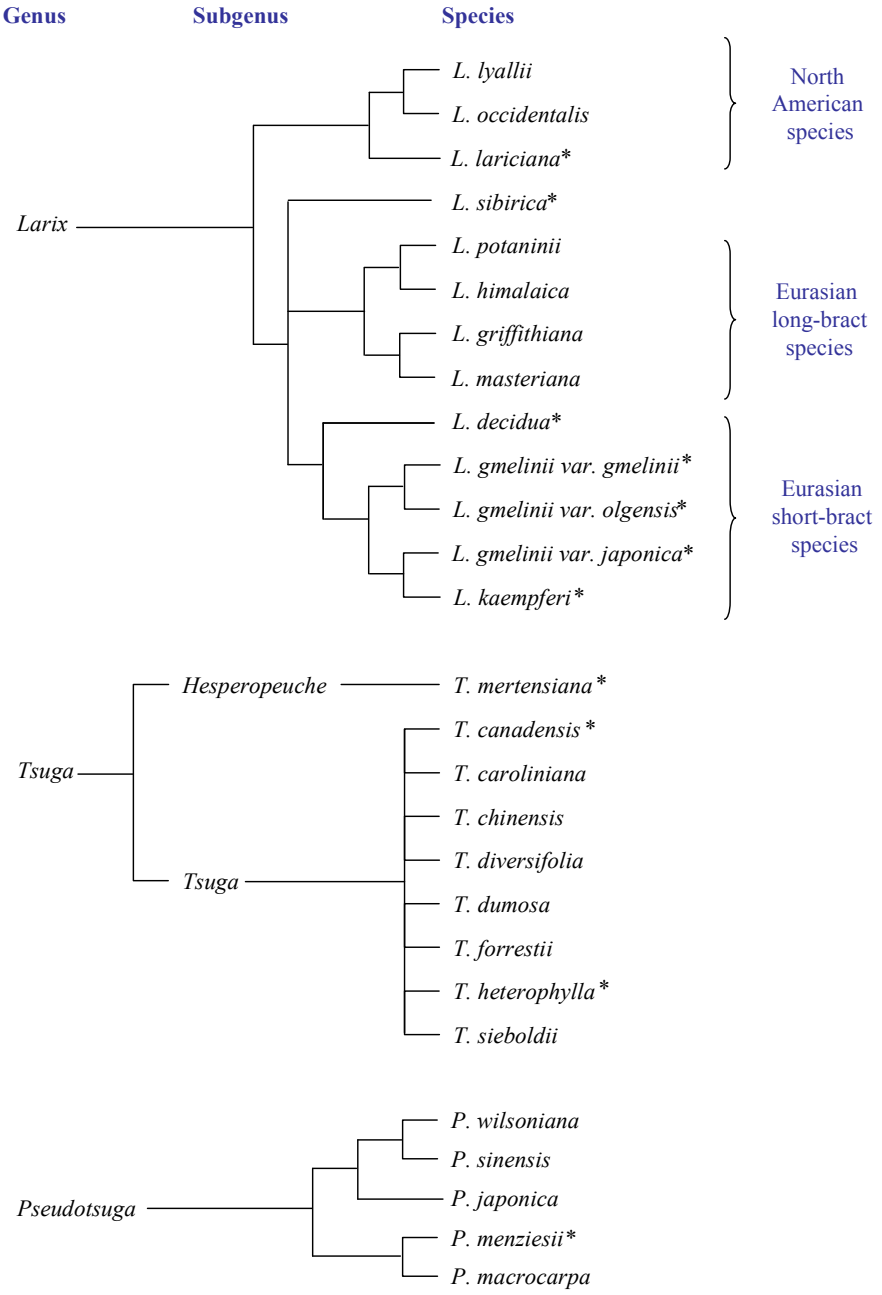
B5 Genus *Abies* (modified from Earle 2011a)

Studied species marked with an asterisk (*)



B6 Genera *Larix* (Earle 2011b), *Tsuga* (Earle 2011c) and *Pseudotsuga* (Gernandt 2005)

Studied species marked with an asterisk (*)

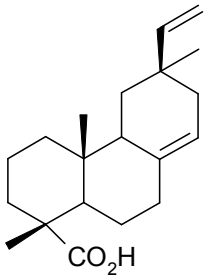


Appendix C Chemical structures

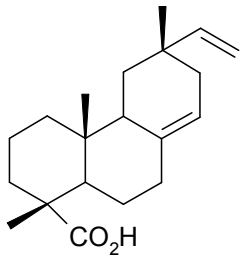
The H-atoms at chiral sites have been omitted for clarity and simplicity. If complete stereochemical structures are needed, they can be obtained by aid of the CAS numbers given below the structures in this appendix.

C1 Resin acids

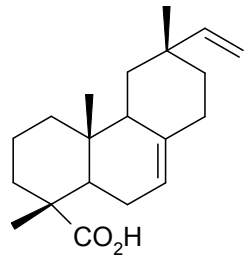
Pimarane type



Pimaric acid
Pi
127-27-5

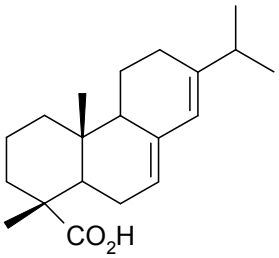


Sandaracopimaric acid
Sa
471-74-9

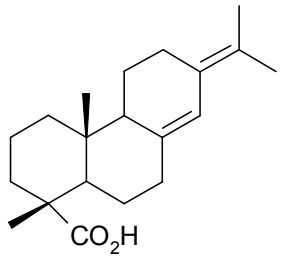


Isopimaric acid
iPi
5835-26-7

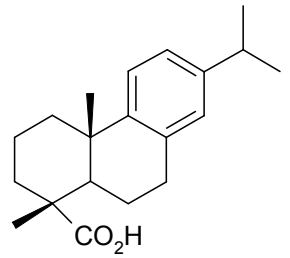
Abietane type



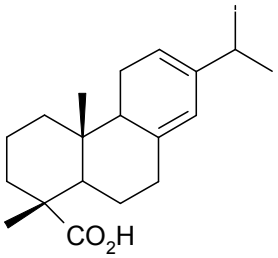
Abietic acid
Ab
514-10-3



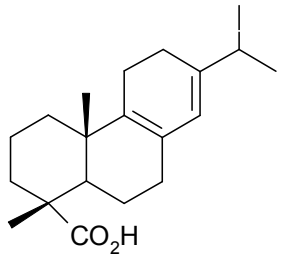
Neoabietic acid
Neo
471-77-2



Dehydroabietic asid
DeAb
1740-19-8

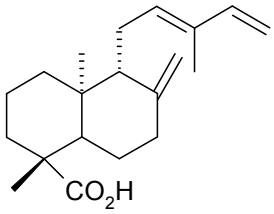


Levopimaric acid
Levo
79-54-9

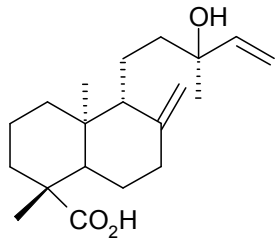


Palustric acid
Pal
1945-53-5

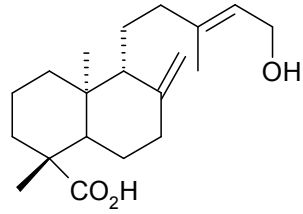
Labdane type



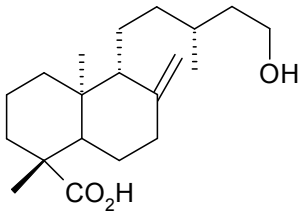
Communic acid
(Elliotinoic acid)
Com
2761-77-5



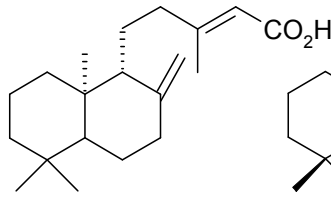
Cupressic acid
Cup
1909-90-6



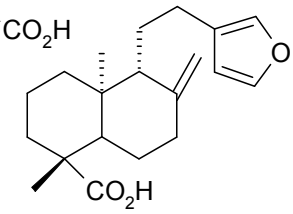
Isocupressic acid
iCup
1909-91-7



Imbricatolic acid
Im
6832-60-6

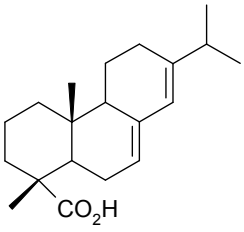


Anticopalic acid
An
24470-48-2

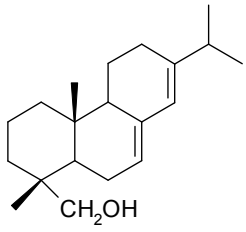


Lambertianic acid
(Antidaniellic acid)
Lam
4966-13-6

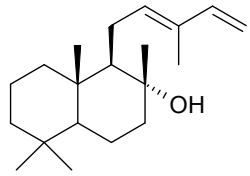
C2 Diterpenes and diterpenoids



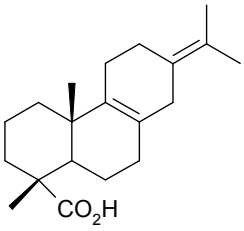
Abietic acid
514-10-3



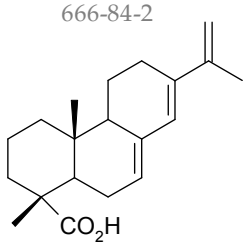
Abietol
(Abietinol)
666-84-2



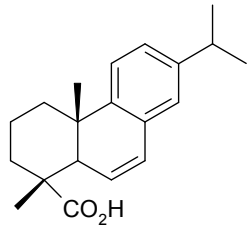
cis-Abienol
17990-16-8



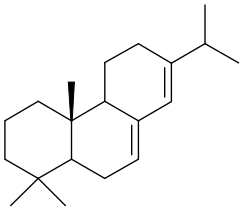
Abieta-8,13-dienoic acid
19402-33-6



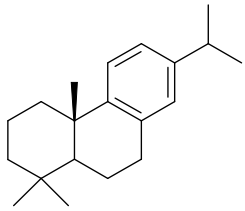
Abieta-7,13,15-trienoic acid
83905-82-2



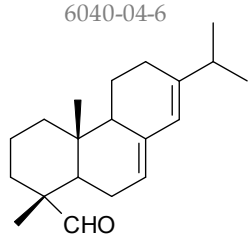
Abieta-6,8,11,13-tetra-
18-enoic acid
6040-04-6



Abieta-7,13-diene
35241-40-8

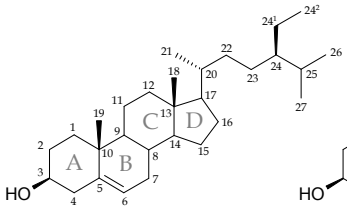


Abieta-8,11,13-triene
19407-28-4

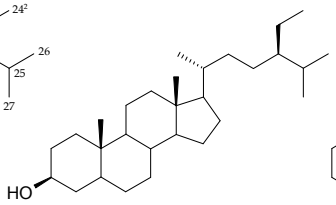


Abietal
(Abietinal)
6704-50-3

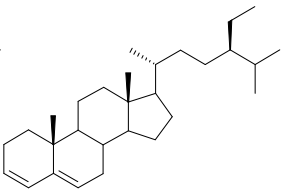
C3 Sterols and triterpenols



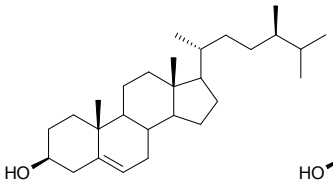
β-Sitosterol
(Stigmast-5-en-3-ol)
83-46-5



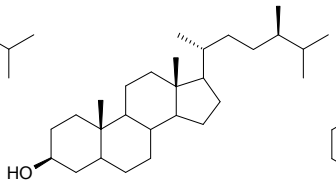
β-Sitostanol
(Fucostanol,
Stigmastan-3-ol)
83-45-4



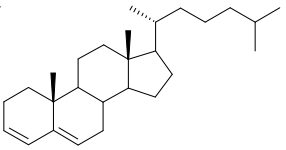
Stigmasta-3,5-diene
4970-37-0



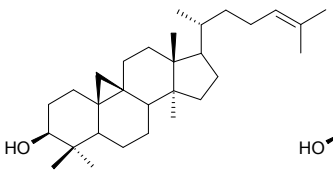
Campesterol
(Ergost-5-en-3-ol)
474-62-4



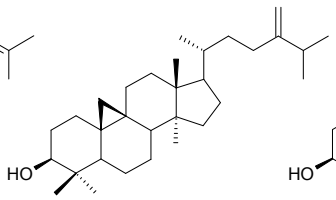
Campestanol
(Ergostan-3-ol)
474-60-2



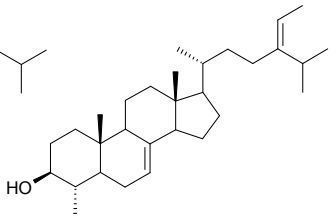
Cholesta-3,5-diene
747-90-0



Cycloartenol
(9,19-Cyclolanost-24-en-3-ol)
469-38-5

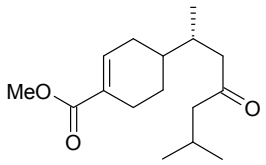


24-Methylenecycloartanol
(24-Methylene-9,19-
cyclolanostan-3-ol)
1449-09-8

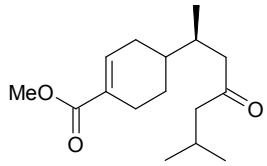


Citrostadienol
(α-Sitosterol)
474-40-8

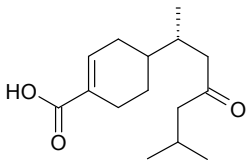
C4 Juvabiones



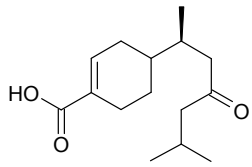
Juvabione
(Methyl todomatuate)
Juva, 17904-27-7



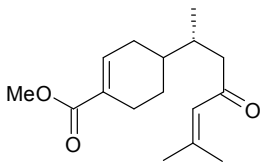
Epijuvabione
26575-87-1



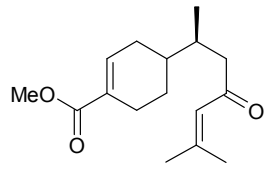
Todomatuic acid
TodoA, 6753-22-6



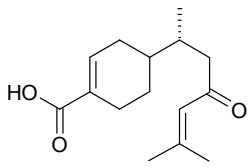
Epitodomatuic acid
26091-09-8



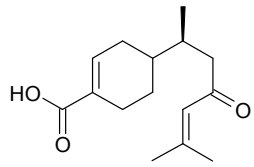
4′-Dehydrojuvabione
4′-DeJuva, 16060-78-9



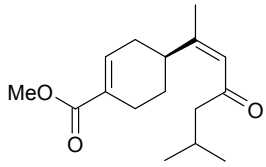
4′-Dehydroepijuvabione
65621-12-7



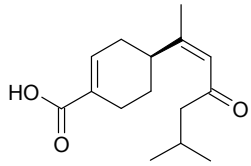
4′-Dehydrotodomatuic acid
4′-DeTodoA, 17904-28-8



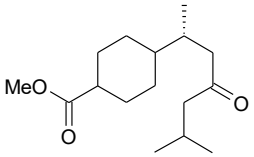
4′-Dehydroepitodomatuic acid
93888-57-4



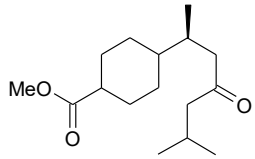
1′-Dehydrojuvabione
1′-DeJuva
64314-12-1 (*cis*), 64314-13-2 (*trans*)



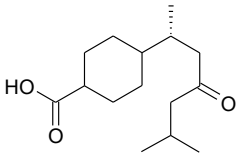
1′-Dehydrotodomatuic acid
93888-59-6



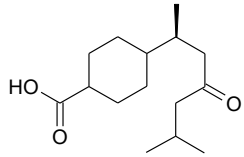
Dihydrojuvabione
(Methyl dihydrotodomatuate)
17904-29-9 (*cis*), 17909-96-5 (*trans*)



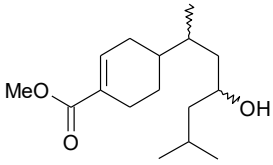
Dihydroepijuvabione
n.k.



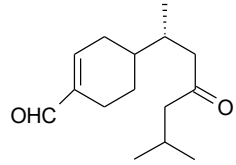
Dihydrotodomatuic acid
Dihydro-TodoA
38963-91-6 (*cis*)



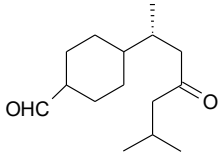
Dihydroepitodomatuic acid
n.k.



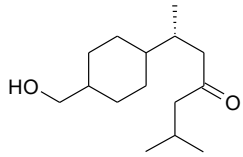
Juvabiol
JuvaOH, 60134-56-7



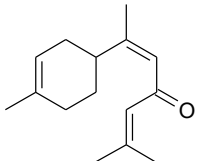
Pseudotsugonal
42719-55-1



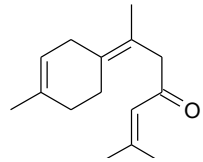
Dihydropseudotsugonal
52363-41-4



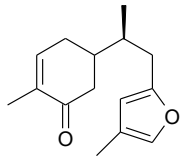
Dihydropseudotsugonol
52363-42-5



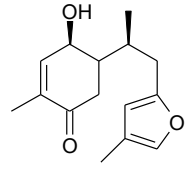
α-Atlantone
26294-59-7



γ-Atlantone
108549-47-9 (*trans*), 532-66-1 (racemate)

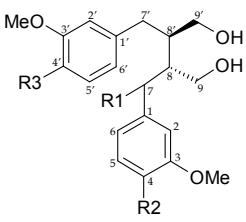


Lasiocarpenone
Lasio
55708-41-3

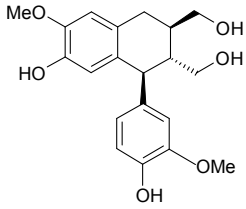


Lasiocarpenonol
LasioOH
125290-13-3

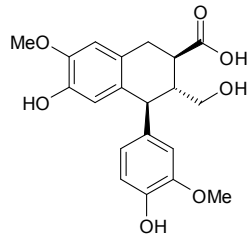
C5 Lignans



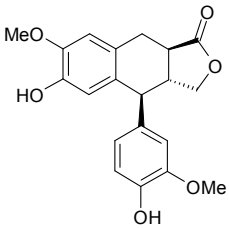
Secoisolariciresinol R1=H, R2=R3=OH
Seco, 29388-59-8
7-hydroxysecoisolariciresinol R1=R2=R3=OH
Hydroxy-Seco, n.k.
4-monomethylsecoisolariciresinol R1=H, R2=OMe, R3=OH
Seco MME, n.k.
4,4′-dimethylsecoisolariciresinol R1=H, R2=R3=OMe
Seco DME, n.k.



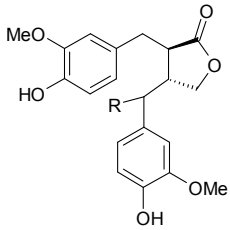
Cyclolariciresinol
cLari
548-29-8



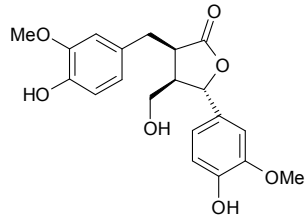
α-Conidendric acid
ConiA
11041-15-9



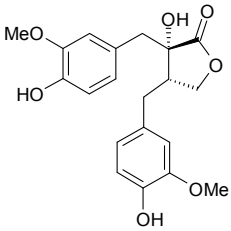
α-Conidendrin
Coni
518-55-8



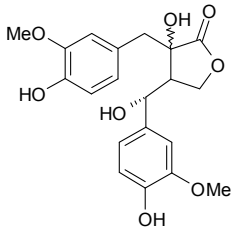
Mataiciresinol R=H
MR, 580-72-3
7-oxomatairesinol R=O
oxo-MR, n.k.
7-hydroxymatairesinol R=OH
HMR, 20268-71-7



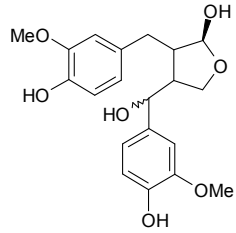
iso-Hydroxymatairesinol
iso-HMR
293744-18-0



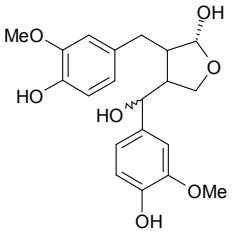
Nortrachelogenin
(Wikstromol,
Pinopalustrin)
NTG
34444-37-6



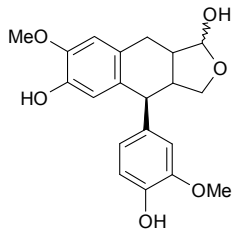
7′-hydroxynortrachelogenin
Hydroxy-NTG
n.k.



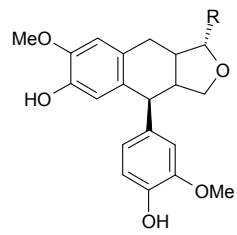
7-Isoliovil
iLi
n.k.



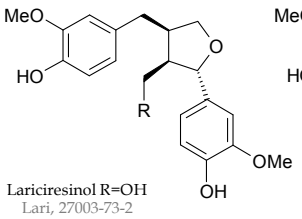
7-Todolactol A
Todo A
n.k.



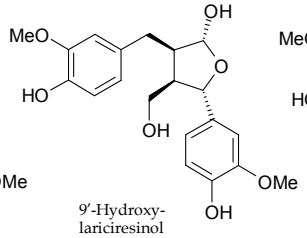
Todolactol B
Todo B
111956-89-9



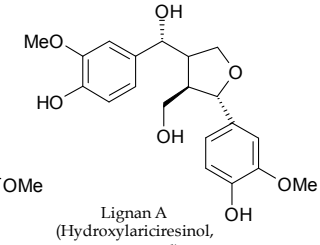
Todolactol C R=OMe
Todo C, 71724-99-7
Todolactol D R=OEt
Todo D, 114924-88-8



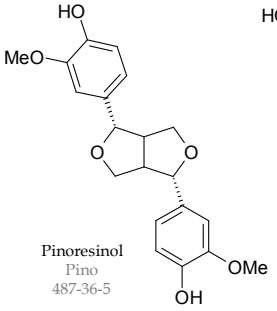
Lariciresinol R=OH
Lari, 27003-73-2
Lariciresinol-9-acetate R=Ac
Lari-Ac, 79114-77-5



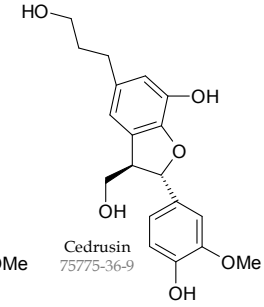
9′-Hydroxy-
lariciresinol
Hydroxy-Lari
n.k.



Lignan A
(Hydroxylariciresinol,
Picearesinol)
Lig A
n.k.



Pinoresinol
Pino
487-36-5



Cedrusin
75775-36-9

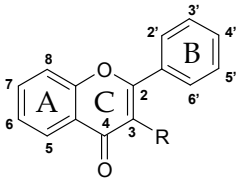
Definitions according to IUPAC (2000)

Lignans are phenylpropane units with β,β′ bonding
Neolignans are coupled in other positions than β−β
Cycolignans have an additional ring
Oxyneolignans contain an ether bindings instead of a carbon-carbon bond

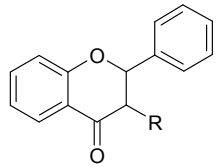
Sesquineolignans have 3 C_6C_3 units
Dineolignans have 4 C_6C_3 units
Sesterneolignans have 5 C_6C_3 units

The prefix **seco-** is used when a ring bond is cleaved and hydrogen atoms are added
The prefix **nor-** us used when one carbon atoms are lost from a lignan, neolignan or oxyneolignan.
Dinor- is used when two carbon atoms are lost etc.

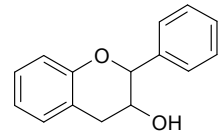
C6 Flavonoids



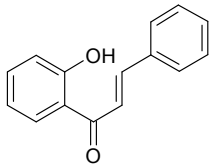
R=H in flavones
R=OH in flavonols



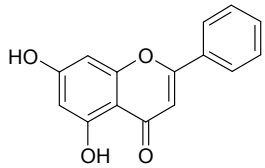
R=H in flavanones
R=OH in flavanonols



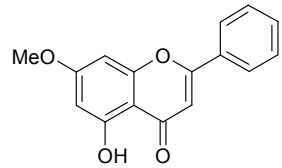
Flavan-3-ols



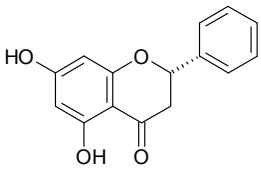
2′-Hydroxychalcone
1214-47-7



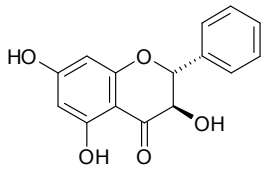
Chrysin
480-40-0



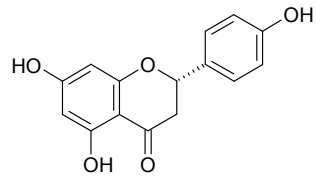
Tectochrysin
520-28-5



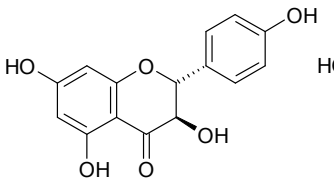
Pinocembrin
(Dihydrochrysin)
PC
480-39-7



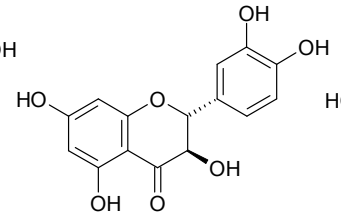
Pinobanksin
(Dihydrogalangin)
PB
548-82-3



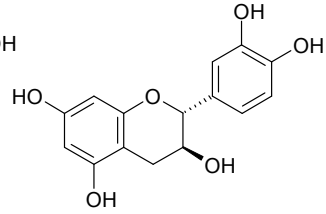
Naringenin
480-41-1



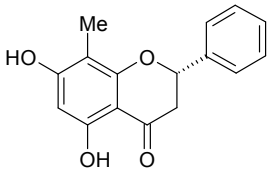
Dihydrokaempferol
(Aromadendrin,
Katuranin)
480-20-6



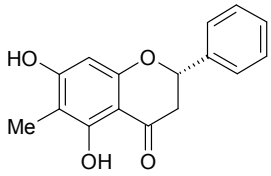
Taxifolin
(Dihydroquercetin,
Distylin)
480-18-2



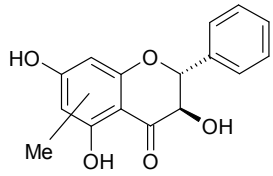
Catechin
(Catechol)
154-23-4



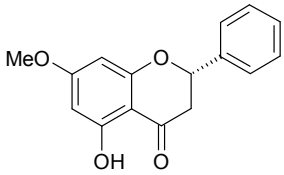
Cryptostrobin
55743-21-0



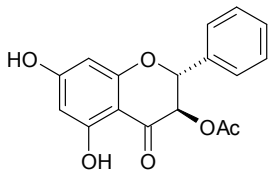
Strobopinin
11023-71-5



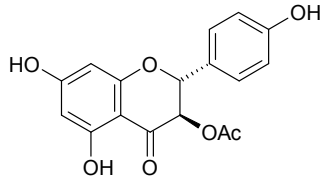
Strobobanksin
SB
n.k.



Pinostrobin
PSt
480-37-5

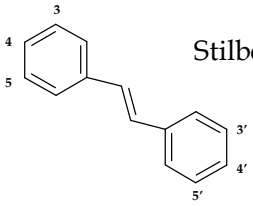


Pinobanksin 3-*O*-
acetate
PB-Ac
52117-69-8

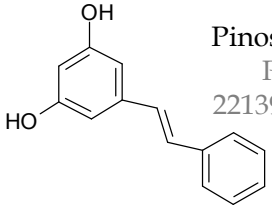


Dihydrokaempferol
3-acetate
n.k.

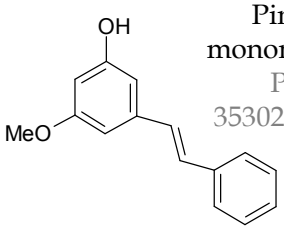
C7 Stilbenes



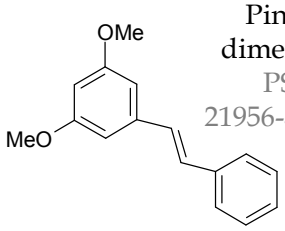
Stilbene



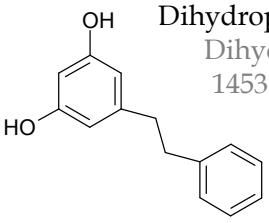
Pinosylvin
PS
22139-77-1



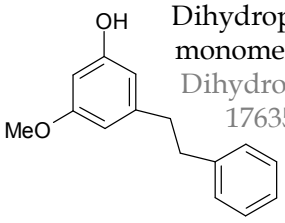
Pinosylvin
monomethyl ether
PSMME
35302-70-6 (*trans*)



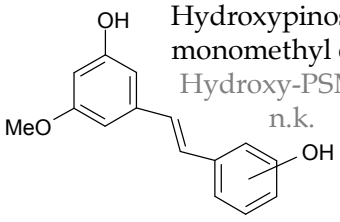
Pinosylvin
dimethyl ether
PSDME
21956-56-9 (*trans*)



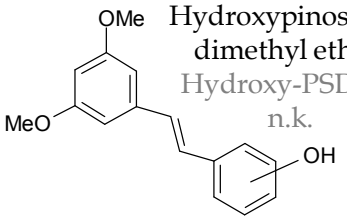
Dihydropinosylvin
Dihydro-PS
14531-52-3



Dihydropinosylvin
monomethyl ether
Dihydro-PSMME
17635-59-5



Hydroxypinosylvin
monomethyl ether[1]
Hydroxy-PSMME
n.k.



Hydroxypinosylvin
dimethyl ether[2]
Hydroxy-PSDME
n.k.

[1] Pinostilbene with –OH at 4′ was identified by Tyukavkina et al. 1972
[2] Pterostilbene with –OH at 4′ was identified by Ghisalberti et al. 1978

Appendix D Concentrations of compounds

D1 Resin acids

PINUS			Composition of resin acids																		
			Ab			Neo			Pal			Levo			DeAb			Pi		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of total resin acids in dry wood																		
P. banksiana	HW	2	21	22	23	13	14	14	17	17	17	12	17	23	12	16	19	4	4	5
	SW	2	10	10	10	11	12	13	14	14	15	33	35	37	14	15	17	3	4	4
	LK	2(5)	19	19	19	22	22	23	15	15	16	12	13	13	17	17	17	4	4	4
	DK	1		22			15			15			21			12			4	
P. contorta	HW	2	10	13	16	11	11	12	12	12	13	31	32	34	5	6	7	9	10	10
	SW	2	10	11	12	11	11	12	11	11	11	30	31	32	9	10	12	9	9	10
	LK	4	13	15	17	11	11	12	11	12	13	18	29	33	2	8	20	9	10	11
P. elliottii	HW	2	17	20	21	14	16	16	15	16	17	8	8	9	7	7	7	4	5	6
	SW	2	12	13	14	11	12	12	15	17	18	10	12	13	11	11	11	5	6	7
	LK	3	24	32	54	2	9	12	3	10	12	+	7	10	4	5	9	5	6	7
	DK	10	18	29	56	1	11	16	3	12	16	+	7	18	5	6	10	4	6	7
P. gerardiana	knots	300 g		43			11			14			+			6			-	
P. nigra	HW	3	28	29	30	6	9	12	2	9	13	4	5	6	23	28	37	6	8	11
	SW	3	15	19	25	11	7	11	14	10	14	19	9	19	20	33	48	11	9	11
	LK	8	17	19	38	14	15	19	4	16	18	+	8	23	5	23	32	4	10	11
	DK	9	20	25	34	14	16	19	3	16	19	+	10	23	4	15	24	6	8	10
P. pinaster	HW	3	20	23	27	4	9	12	1	9	13	4	12	18	21	28	40	10	11	13
	SW	3	16	17	18	1	8	11	2	8	10	2	14	19	10	34	56	11	11	77
	LK	9	16	18	24	12	15	17	10	11	14	14	30	37	10	14	25	8	8	11
	DK	9	17	19	22	15	15	16	10	12	15	10	25	29	8	13	29	8	9	10
P. radiata	HW	1		28			10			16			5			26			11	
	SW	1(2)		19			18			16			+			32			11	
	LK	2	22	21	21	10	13	14	17	16	15	-	+	+	39	37	36	8	9	9
	DK	1		18			19			19			+			28			10	
P. resinosa	HW	2	21	22	22	15	15	15	14	17	18	21	23	24	8	9	12	7	8	8
	SW	2	11	11	12	13	14	15	13	13	13	41	42	43	5	5	5	7	7	8
	LK	3(5)	32	33	36	17	18	19	13	17	19	9	10	13	5	8	9	6	7	8
	DK	3(6)	27	30	30	14	16	17	13	17	18	10	12	18	11	12	13	7	8	8
P. roxburghii	knots	300 g		33			6			4			4			20			9	
P. sibirica	HW	2	23	23	23	2	2	2	2	2	2	2	2	2	9	9	9		-	
	SW	2	22	23	23	3	4	4	2	2	2	5	6	6	3	4	4	+	+	+
	LK	2(8)	23	24	25	2	3	3	2	2	2	1	2	3	6	7	9	-	+	+
	DK	2(3)	24	26	27	4	4	5	3	3	3	3	5	7	3	4	5		-	
P. strobus	HW	2	19	24	28	13	15	18	8	10	11	3	4	4	1	2	2	+	+	+
	SW	2	23	25	27	12	13	13	9	10	11	3	3	4	2	3	4	+	+	+
	LK	2	33	36	39	12	12	12	9	10	11	+	+	+	1	2	2	+	+	+
	DK	2	21	24	27	12	12	12	8	9	10	1	1	1	3	3	3	+	+	+
P. sylvestris	HW	2	28	29	30	13	14	15	17	18	20	10	11	13	10	12	13	7	8	9
	SW	2	12	13	14	13	13	14	13	15	17	40	41	42	+	2	5	6	7	8
	LK	2	23	26	30	19	19	19	15	18	22	16	20	23	+	+	+	6	8	9
	DK	2	28	30	32	16	17	19	16	17	18	10	10	10	9	10	11	8	9	10
P. taeda	HW	1		32			16			23			6			14			6	
	SW	2	9	11	12	6	8	9	13	17	19	18	19	19	29	32	36	7	7	8
	LK	4	9	34	35	3	16	17	10	20	21	6	13	15	4	7	53	6	6	9
	DK	5	15	37	39	7	15	17	13	19	21	9	11	22	6	8	36	6	6	8
P. wallichiana	knots	300 g		35			4			7			+			3			-	

- not detected
+ less than 1%
n = number of analyses (number of knots)

Ab = Abietic acid
Neo = Neoabietic acid
Pal = Palustric acid
Levo = Levopimaric acid
DeAb = Dehydroabietic acid
Pi = Pimaric acid

Composition of resin acids (cont.)																						Concentration		
Sa			iPi			Com			iCup			Im			An			Lam			RAs total		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
% of total resin acids in dry wood																						mg/g dry wood		
1	2	2	8	8	9		-			-			-			-			-			9.9	12	14
2	2	2	7	7	8		-			-			-			-			-			1.2	1.4	1.7
1	1	1	8	8	9		-			-			-			-			-			210	215	219
	1			9			-			-			-			-			-				179	
2	2	2	10	11	11		-		3	3	3		-			-			-			26	28	31
1	1	1	10	11	12		-		4	4	4		-			-			-			1.3	1.7	2.0
1	1	1	10	10	10		-		3	4	5		-			-			-			92	136	179
2	2	2	16	16	17	8	9	10	+	+	+	2	2	2		-			-			18	24	30
2	2	2	+	11	21	6	17	27	+	+	+	+	+	1		-			-			6.2	6.3	6.4
2	2	2	15	18	23	+	9	12	+	1	2		-			-			-			39	71	102
2	2	3	11	15	22	+	11	17	+	1	2		-			-			-			44	95	133
	9			17			-			-			-			-			+				3.8	
2	2	2	8	10	11		-			-			-			-			-			5.6	6.0	6.5
3	3	3	8	10	11		-			-			-			-			-			1.7	2.0	2.5
2	2	2	6	6	10		-			-			-			-			-			12	60	132
2	2	2	6	7	9		-			-			-			-			-			48	86	118
2	2	3	3	5	7		-			-			-			-			-			6.0	7.4	8.2
2	3	7	2	3	5		-			-			-			-			-			<0.05	0.91	2.0
2	2	2	2	3	5		-			-			-			-			-			6.9	27	71
2	1	2	2	4	6		-			-			-			-			-			53	88	122
	1			3			-			-			-			-			-				4.0	
	1			4			-			-			-			-			-				8.5	
1	2	2	2	2	2		-			-			-			-			-			2.6	3.3	4.1
	2			3			-			-			-			-			-				52	
2	2	2	4	5	8		-			-			-			-			-			17	33	50
1	1	1	5	6	7		-			-			-			-			-			2.8	2.8	2.9
1	1	1	3	4	8		-			-			-			-			-			114	162	195
1	1	2	3	4	7		-			-			-			-			-			78	131	169
	2			21			-			-			-			-			+				3.4	
2	2	2	35	35	36		-			-			-			-		25	25	25		2.3	2.4	2.4
1	1	1	33	34	35		-			-			-			-		26	26	27		1.8	2.0	2.3
1	1	1	37	38	39		-			-			-			-		20	22	25		3.5	9.0	14
1	1	1	32	33	35		-			-			-			-		23	24	25		44	90	136
1	2	2	24	27	30		-			-			-		11	17	24		-			29	44	60
1	2	2	27	28	29		-			-			-		12	15	19		-			5.6	6.0	6.3
1	1	2	28	30	32		-			-			-		7	7	8		-			40	43	46
2	2	2	29	30	31		-			-			-		18	19	19		-			56	87	119
2	2	2	4	6	7		-			-			-			-			-			16	19	22
1	2	2	5	6	7		-			-			-			-			-			1.7	2.0	2.2
1	1	1	6	8	9		-			-			-			-			-			163	189	214
2	2	2	5	6	6		-			-			-			-			-			182	184	185
	2			2			-			-			-			-			-				24	
2	2	2	3	5	7		-			-			-			-			-			1.6	1.7	1.9
2	2	2	2	2	7		-		+	+	+		-			-			-			1.9	22	52
2	2	2	1	2	5		-		+	+	+		-			-			-			2.3	58	105
	1			27			-			+			-			-			20				14	

Sa = Sandaracopimaric acid
iPi = Isopimaric acid
Com = Communic acid
iCup = Isocupressic acid
Im = Imbricatolic acid
An = Anticopalic acid
Lam = Lambertianic acid
RAs = Resin acids

PICEA & PSEUDOTSUGA			Composition of resin acids											
			Ab			Neo			Pal			Levo		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of total resin acids in dry wood											
Picea abies FI	HW	2	10	10	11	6	7	8	13	16	19	5	10	14
	SW	2	7	7	8	10	10	10	12	15	17	14	20	27
	LK	2	5	6	6	2	3	4	7	10	14	3	6	8
	DK	2	4	8	12	2	4	7	8	11	14	2	7	12
Picea abies FR	HW	1		3			+			6			+	
	SW	1		6			6			19			17	
	LK	1(3)		6			4			12			8	
	DK	1(5)		12			7			18			17	
Picea glauca	HW	2	6	7	8	2	3	3	12	14	16	4	5	7
	SW	2	8	9	11	12	12	12	19	20	20	+	15	29
	LK	3(5)	7	8	9	3	4	4	11	11	12	7	9	11
	DK	2(5)	9	9	10	6	8	10	10	12	13	6	11	16
Picea koraiensis	HW	1		10			3			3			-	
	SW	1		18			6			12			9	
	LK	1		11			-			4			-	
	DK	1		10			1			5			2	
Picea mariana	HW	2	7	13	19	2	4	7	18	21	24	3	6	9
	SW	2	9	15	22	8	11	14	19	23	27	18	22	27
	LK	2(13)	11	14	18	5	7	9	20	21	22	14	15	16
	DK	2(17)	13	17	21	8	10	13	23	26	30	+	13	26
Picea omorika	HW	1		20			4			12			3	
	SW	1		27			10			16			11	
	LK	1(2)		13			11			18			22	
	DK	1		23			11			17			18	
Picea pungens	HW	2	8	10	11	2	6	9	18	18	18	3	10	17
	SW	2	9	9	9	10	10	11	23	24	24	22	22	22
	LK	7(11)	10	12	15	6	11	13	13	16	19	8	20	30
	DK	9	8	12	14	4	9	12	6	17	21	4	19	24
Picea sitchensis	HW	2	11	11	12	1	2	3	12	15	18	4	10	16
	SW	2	15	16	17	5	5	5	18	19	19	25	28	31
	LK	2(3)	8	9	9	3	4	5	12	17	19	7	15	21
	DK	2(3)	16	16	17	-	2	4	17	19	20	14	22	29
Pseudotsuga menziensii	HW	2	15	15	16	13	14	15	27	28	28	11	11	12
	SW	2	12	14	16	15	16	17	27	28	29	14	14	15
	LK	2(11)	11	14	17	8	12	16	21	25	28	11	13	16
	DK	2(11)	14	16	18	12	12	13	25	26	28	11	12	13

- not detected
+ less than 1%
n = number of analyses (number of knots)

Ab = Abietic acid
Neo = Neoabietic acid
Pal = Palustric acid
Levo = Levopimaric acid

Composition of resin acids (cont.)													Concentration		
DeAb			Pi			iPi			Sa				RAs total		
min	avg	max	min	avg	max	min	avg	max	min	avg	max		min	avg	max
% of total resin acids in dry wood													mg/g dry wood		
23	32	40	2	4	5	12	15	17	5	7	9		0.79	1.5	2.2
14	24	34	3	4	4	11	13	16	5	7	9		0.60	1.3	2.1
44	54	65	2	3	3	8	13	17	4	5	6		0.32	0.44	0.57
29	47	64	2	3	4	8	14	19	5	6	7		0.28	0.90	1.5
	66			5			10			9				0.48	
	30			4			10			7				1.6	
	53			3			10			5				0.20	
	22			4			16			5				4.5	
40	47	54	2	3	4	14	15	15	4	5	6		1.6	1.7	1.8
6	26	45	+	2	3	12	13	13	3	4	5		1.8	2.3	2.8
44	48	51	1	2	3	13	14	14	3	4	4		0.49	0.60	0.68
37	41	46	2	2	3	13	13	14	2	3	4		0.79	0.81	0.83
	61			2			17			5				1.9	
	32			1			17			5				2.9	
	58			-			14			13				0.85	
	53			+			18			10				1.8	
26	41	56	3	3	3	6	6	7	4	5	6		0.93	0.95	0.96
10	13	16	2	2	2	8	10	11	4	4	4		1.4	1.7	1.9
20	25	30	2	3	3	11	11	11	3	4	4		0.87	0.91	0.94
8	18	29	2	2	2	10	10	10	3	4	4		8.6	11	14
	42			+			13			6				1.8	
	21			+			10			4				1.0	
	16			+			17			4				25	
	13			+			14			3				5.8	
19	31	43	2	2	3	16	17	18	5	6	7		1.6	2.1	2.5
13	15	16	2	2	2	12	14	15	5	5	6		0.21	1.5	2.8
10	17	29	+	1	2	15	17	19	5	5	8		0.46	0.68	0.85
17	21	52	+	1	2	11	15	20	4	6	7		0.40	3.2	14
28	36	43	2	2	3	16	18	20	4	5	6		0.71	0.82	0.94
9	10	10	1	1	2	14	17	20	4	5	6		0.63	0.65	0.67
19	28	37	2	3	4	15	18	24	6	7	9		<0.05	0.13	0.26
10	16	22	2	4	5	15	17	18	4	5	6		<0.05	2.7	5.4
10	10	10		-		19	19	19	3	3	3		0.89	1.0	1.1
5	6	6		-		19	19	20	2	2	3		1.1	1.3	1.5
5	11	17		-		20	22	24	2	3	3		1.6	2.4	3.2
9	10	10		-		19	20	21	3	4	5		12	15	19

DeAb = Dehydroabietic acid iPi = Isopimaric acid RAs = Resin acids
Pi = Pimaric acid Sa = Sandaracopimaric acid

ABIES & TSUGA			Composition of resin acids											
			Ab			Neo			Pal			Levo		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of total resin acids in dry wood											
A. alba	HW	4	37	60	79	-	+	1	-	4	11	-	6	12
	SW	4	11	22	34	-	13	33	-	7	12	7	24	54
	LK	11	-	22	42	-	4	9	-	4	12	-	9	25
	DK	11(13)	-	15	40	-	3	13	-	4	15	-	7	16
A. amabilis	HW	1		3			+			3			3	
	SW	1		30			1			7			25	
	LK	2	4	8	12	3	4	4	1	3	4	3	4	6
	DK	1(2)		8			+			+			6	
A. balsamea	Stem	3	16	42	58	3	6	8	8	28	65	-	+	3
	LK	1(2)		49			10			-			-	
	DK	1(4)		20			6			51			5	
A. concolor	HW	1		-			16			46			5	
	LK	1(2)		14			-			2			19	
A. lasiocarpa	HW	2	12	24	35	4	7	10	6	17	28	5	5	6
	SW	2	21	33	44	10	10	10	16	21	25	+	1	1
	LK	2(16)	18	21	23	4	5	6	5	12	19	-	3	7
	DK	2(15)	37	39	42	4	4	4	4	5	7	5	7	9
A. pindrow	Knots	300 g		40			3			7			1	
A. sachalinensis	HW	1		12			4			+			5	
	SW	1		22			5			4			8	
	LK	1(2)		27			4			6			5	
	DK	1		2			6			3			11	
A. sibirica	HW	2	29	32	35	11	15	19	20	20	20	1	2	2
	SW	2	49	53	57	8	9	10	6	7	8	8	16	23
	LK	2(6)	10	26	43	+	+	1	-	8	15	3	15	27
	DK	2(3)	52	53	53	7	7	7	1	2	2	5	6	8
A. veitchii	HW	1		6			5			9			8	
	SW	1		22			7			6			8	
	LK	1(2)		17			7			4			5	
	DK	1		9			3			2			4	
T. canadensis	HW	2	55	64	74		-			-			-	
	SW	2	52	58	65	-	13	26		-			-	
	LK	2	44	54	64	17	21	24		-			-	
	DK	2	43	50	58	-	22	45		-		-	1	2
T. heterophylla CA	HW	2	-	18	36		-		37	51	64		-	
	SW	2	15	40	65		-		-	8	16		-	
	LK	2	11	14	17		-		69	73	77		-	
	DK	2	14	19	24		-		60	63	65		-	
T. heterophylla FI	Dead branch	1		22			-			-			11	
	DK	1		4			9			+			11	
T. mertensiana	LK	1		2			-			+			2	
	HW of branch	1		10			-			14			6	
	SW of branch	1		16			31			29			1	

- not detected
+ less than 1%
n = number of analyses (number of knots)

Ab = Abietic acid
Neo = Neoabietic acid

Pal = Palustric acid
Levo = Levopimaric acid

Composition of resin acids (cont.)													Concentration		
DeAb			Pi			iPi			Sa				RAs total		
min	avg	max	min	avg	max	min	avg	max	min	avg	max		min	avg	max
% of total resin acids in dry wood													mg/g dry wood		
-	6	24	-	1	5	-	1	4	7	21	40		<0.05	<0.05	<0.05
-	19	47	-	3	6	-	3	6	3	9	17		<0.05	<0.05	<0.05
-	15	41	-	15	38	-	4	8	-	17	58		-	<0.05	0.07
-	9	25	-	19	45	-	17	65	-	17	32		-	0.16	0.87
	81			2			+			7				0.13	
	23			+			6			8				0.05	
27	34	42	2	4	6	8	14	21	15	29	43		<0.05	0.28	0.53
	44			2			18			20				0.09	
7	13	15	-	3	6	+	2	4	2	6	9		<0.05	0.07	0.13
	8			-			25			9				<0.05	
	4			+			11			3				0.09	
	1			-			25			7				0.11	
	18			-			42			5				<0.05	
20	25	31	7	8	10	11	14	17		-			0.06	0.07	0.07
8	10	12	6	13	21	9	12	15		-			0.07	0.07	0.08
2	15	27	7	7	7	24	37	50		-			0.10	0.40	0.71
7	9	10	+	2	3	30	34	37		-			1.1	1.2	1.3
	13			3			30			4				1.0	
	38			1			1			38				0.06	
	25			+			11			25				<0.05	
	25			1			14			17				0.12	
	57			3			13			6				0.35	
19	20	21		-			-		10	12	14		<0.05	<0.05	<0.05
10	13	17		-			-		2	3	3		<0.05	<0.05	<0.05
12	12	13		-			-		17	38	58		0.05	0.06	0.08
4	4	5		-			-		28	28	28		0.20	0.22	0.24
	51			6			3			12				<0.05	
	31			+			6			20				<0.05	
	23			2			5			37				0.17	
	35			2			3			42				0.68	
26	36	45		-			-			-			<0.05	<0.05	<0.05
9	29	48		-			-			-			<0.05	<0.05	<0.05
19	25	32		-			-			-			<0.05	<0.05	<0.05
4	23	42		-			-		-	3	6		<0.05	0.09	0.17
-	31	63		-			-			-			<0.05	<0.05	<0.05
-	28	55	8	21	35	-	3	6		-			<0.05	<0.05	<0.05
6	9	12	-	4	8		-			-			<0.05	<0.05	<0.05
6	8	10	5	6	6	3	5	6		-			<0.05	<0.05	<0.05
	2			20			30			16				<0.05	
	8			18			42			8				0.06	
	-			52			33			10				0.09	
	33			19			11			7				<0.05	
	-			4			5			14				<0.05	

DeAb = Dehydroabietic acid
Pi = Pimaric acid
iPi = Isopimaric acid
Sa = Sandaracopimaric acid
RAs = Resin acids

LARIX			Composition of resin acids											
			Ab			Neo			Pal			Levo		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of total resin acids in dry wood											
L. decidua	HW	5	10	12	14	7	9	13	10	20	30	-	2	3
	SW	5	7	12	16	2	9	14	10	20	30	+	1	3
	LK	7(10)	12	19	30	4	6	7	11	14	19	-	3	6
	DK	11(15)	12	23	38	5	7	9	12	15	19	-	3	6
L. gmelinii	HW	2	8	9	10	10	10	10	23	24	25	+	+	1
var. *gmelinii*	SW	2	7	7	7	3	4	4	13	13	14	-	+	+
	LK	2	10	14	19	5	6	7	11	15	18	1	2	2
	DK	2	14	19	25	5	5	5	11	12	12	3	4	5
L. gmelinii	HW	2	10	13	15	9	10	11	21	21	21	+	+	1
var. *japonica*	SW	2	11	13	16	11	11	12	21	21	21	+	+	+
	LK	2	10	11	12	3	4	4	10	13	16	+	1	2
	DK	3	14	16	17	6	8	11	16	17	18	1	2	3
L. gmelinii	HW	2	9	9	9	4	6	9	18	22	25	+	+	+
var. *olgensis*	SW	2	9	10	10	6	7	9	20	22	24	+	+	+
	LK	2	8	9	9	3	5	7	17	20	22	+	+	+
	DK	2	14	15	16	4	4	4	13	15	18	1	2	3
L. kaempferi	HW	3	9	12	15	4	7	9	19	22	24	2	2	2
	SW	3	+	7	12	4	7	9	20	23	25	+	1	2
	LK	9	4	12	22	3	5	6	18	19	20	2	2	3
	DK	22	1	10	16	3	5	7	16	18	19	1	1	2
L. lariciana	HW	2	9	11	12	6	7	9	13	13	14	+	+	1
	SW	2	10	10	11	10	12	13	17	18	18	+	+	1
	LK	2	13	14	16	5	5	5	4	8	12	-	+	+
	DK	2(3)	13	14	15	4	4	5	5	8	12	+	2	3
L. sibirica	HW	6	8	17	21	2	8	10	10	18	22	-	+	2
	SW	6	5	13	19	+	6	11	10	15	19	-	+	+
	LK	1		29			4			9			6	
	DK	10	10	22	32	+	5	15	5	12	16	-	1	4

- not detected
+ less than 1%
n = number of analyses (number of knots)
Ab = Abietic acid
Neo = Neoabietic acid
Pal = Palustric acid
Levo = Levopimaric acid

Composition of resin acids (cont.)																Concentration		
DeAb			iPi			Sa			Com			Cup			RAs total		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
% of total resin acids in dry wood															mg/g dry wood		
4	5	9	37	38	40	2	2	2	+	11	20		-		0.76	1.3	1.8
2	6	14	36	38	40	2	2	2	+	12	24		-		0.80	1.8	3.2
6	8	10	30	36	40	1	2	2	3	12	20		-		0.22	0.87	2.2
2	6	8	30	33	38	2	2	2	2	12	21		-		0.39	3.7	13
4	4	4	45	46	46	5	5	5	1	2	2		-		1.0	1.1	1.1
19	19	20	49	51	54	1	4	7	+	1	2		-		0.69	0.81	0.93
11	11	11	32	35	39	5	6	6	8	11	15		-		1.1	1.8	2.4
8	9	10	25	34	44	5	6	7	5	11	17		-		0.32	0.97	1.6
4	5	6	44	47	50	2	3	3	1	1	2		-		0.47	1.1	1.7
4	5	5	42	46	49	2	2	2	+	1	2		-		0.79	1.7	2.5
15	18	21	46	48	49	3	3	3	2	2	2		-		0.22	0.40	0.58
5	7	9	30	35	45	3	3	3	5	13	18		-		0.29	1.8	3.3
3	5	6	48	53	58	3	3	3	1	1	2		-		1.4	1.4	1.5
3	4	4	47	53	58	3	3	3	+	2	3		-		1.1	1.7	2.3
4	6	8	40	47	54	3	4	4	5	9	13		-		0.34	0.97	1.6
4	5	6	40	42	45	3	4	4	10	12	14		-		1.8	2.4	3.1
5	5	6	31	36	42	3	3	3	1	10	18	+	3	4	1.5	1.9	2.4
4	5	6	34	39	46	2	2	3	1	11	21	+	3	5	1.4	1.5	1.7
7	8	9	35	37	38	3	3	4	1	11	19	+	3	5	0.56	0.74	1.1
5	6	7	37	44	48	2	3	3	1	10	17	+	2	3	2.5	4.4	5.7
9	9	10	40	41	41	6	6	6	4	6	7	6	7	7	0.62	0.75	0.88
2	2	2	37	39	42	4	5	5	6	9	13	4	4	4	1.5	2.2	3.0
12	20	27	34	39	44	6	6	6	3	3	3	4	5	5	0.18	0.25	0.32
7	13	20	39	41	43	5	6	6	5	8	11	3	3	4	0.36	0.93	1.5
3	7	17	29	36	44	2	3	7	4	11	15		-		0.88	1.7	2.7
2	9	22	32	41	56	1	3	4	2	13	22		-		1.0	2.1	3.2
	4			37			3			8			-			4.1	
3	11	31	24	34	42	2	3	5	6	11	25		-		0.26	1.0	2.7

DeAb = Dehydroabietic acid
iPi = Isopimaric acid
Sa = Sandaracopimaric acid
Com = Communic acid
Cup = Cupressic acid
RAs = Resin acids

D2 Fatty acids and acylglycerols

PINUS			Composition of FAs																		
			16:0			17:0ai			18:0			20:0			22:0			24:0			9-18:1		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of free fatty acids																			
P. banksiana	HW	2	3	3	3	2	2	3	1	1	1	+	1	2	1	1	2	1	1	1	23	23	23
	SW	2	5	5	5	2	2	2	1	1	2	+	+	+	+	+	+	+	+	+	28	31	34
	LK	2(5)	4	4	4	+	1	2	25	26	27	15	15	15	+	+	1	1	2	2	11	11	11
	DK	1		4			1			8			8			1			2			21	
P. contorta	HW	2	5	6	7	3	4	4	+	1	1	3	4	5	+	+	+		-		20	21	23
	SW	2	8	11	13	3	3	3	-	+	+	1	1	1	+	+	+	-	+	+	25	29	34
	LK	4	7	9	11	2	2	3	2	2	3	10	12	13		-		-	+	+	20	22	24
P. elliottii	HW	2	4	5	5	4	5	6	-	+	+	+	+	1	-	+	1	1	2	2	23	25	26
	SW	2	8	8	9	7	7	7	2	2	2	5	5	6	2	2	3	+	+	2	18	18	18
	LK	3	5	8	11	-	9	17	27	28	29	+	3	7	4	9	14	+	+	1	11	12	13
	DK	10	4	7	13	-	3	16	8	29	42	4	13	27	4	9	18	-	1	4	+	10	24
P. gerardiana	knots	300 g		82			-			-			-			-			-			6	
P. nigra	HW	3	3	4	5		-		2	2	3		-		1	3	5	+	9	24	28	35	39
	SW	3	5	5	5	-	+	+	2	2	2	+	+	+	+	+	+	+	+	+	55	58	62
	LK	8	4	6	11		-		-	5	9	+	6	10	-	2	2	-	1	2	46	55	72
	DK	9	5	7	13		-		-	10	15	+	5	20	-	2	3	-	2	2	43	48	55
P. pinaster	HW	3	4	6	6	+	1	2	1	2	2	2	3	3	1	2	3	+	1	2	34	38	41
	SW	3	+	6	10	+	+	1	1	10	25	+	6	14	+	3	8	-	+	+	17	49	75
	LK	9	5	8	12	+	2	3	2	6	11	-	1	4	-	-	-	+	2	5	22	36	47
	DK	9	+	9	13	+	2	4	-	10	17	-	+	+	-	-	-	-	1	2	21	39	78
P. radiata	HW	1		17			+			2			+			2			+			36	
	SW	1(2)		22			3			3			1			3			+			27	
	LK	2	29	29	30	+	+	+	+	+	+	+	+	+	+	1	1	+	+	+	27	29	32
	DK	1		19			6			5			+			+			+			29	
P. resinosa	HW	2	+	1	1	+	+	+		-		-	+	+	+	+	+	+	+	+	22	23	24
	SW	2	7	9	12	3	3	3	2	2	3		-		1	1	1	2	2	2	34	35	35
	LK	3(5)	4	5	6	-	+	+		-		2	4	6	-	+	1	-	+	2	20	22	24
	DK	3(6)	5	6	7		-			-		3	4	5	+	+	1	-	+	1	23	24	25
P. roxburghii	knots	300 g		17			-			-			-			-			-			59	
P. sibirica	HW	2	3	3	3	3	3	3	+	+	+	1	1	1		-		1	1	1	20	20	20
	SW	2	7	7	7	2	2	3	4	5	6	+	1	1		-		2	3	3	21	21	22
	LK	2(8)	6	6	7	1	2	2		-		-	+	+		-		2	3	3	24	24	24
	DK	2(3)	8	8	9	2	2	3		-			-			-		1	2	2	25	26	26
P. strobus	HW	2	5	6	7	1	1	1	-	+	1	+	+	+	+	+	+	+	+	+	20	24	27
	SW	2	11	18	25	1	2	2	3	4	5	3	5	6	2	3	4	1	2	2	22	22	22
	LK	2	15	15	16	+	1	2		-		1	1	1	+	1	1	-	+	+	22	26	30
	DK	2	15	16	18	1	2	2		-		2	2	3	2	2	+	+	+	+	24	25	26
P. sylvestris	HW	2	2	2	2	+	+	1	-	+	+	+	+	1	+	+	+	+	+	+	25	26	27
	SW	2	9	9	9	-	+	+	-	1	2	1	1	2	1	2	2	+	+	+	30	32	33
	LK	2	5	5	5	-	+	+		-		3	4	4	+	+	+	-	+	+	32	32	32
	DK	2	4	4	4	+	+	+		-		7	8	9	1	1	1	1	2	2	30	30	30
P. taeda	HW	1		5			4			10			7			-			+			22	
	SW	2	14	15	16	2	2	3	7	9	11	3	3	4		-		1	2	3	24	27	29
	LK	4	4	8	13	2	11	20	-	2	3	+	+	1	+	1	2	+	+	+	18	24	30
	DK	5	4	7	10	+	11	22	-	2	5	+	1	4	+	1	2	+	+	2	19	26	35
P. wallichiana	knots	300 g		73			-			-			-			-			-			7	

- not detected
+ less than 1%
n = number of analyses (number of knots)
FAs = Fatty acids
DGs = Diacylglycerols
TGs = Triacylglycerols

Composition of FAs (cont.)															Concentration								
11-18:1[1]			9,12-18:2			5,9,12-18:3			5,11,14-20:3			Other FAs			Free FAs			DGs			TGs		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
% of free fatty acids															mg/g dry wood								
2	2	2	36	36	37	18	19	21	7	8	8	1	1	1	3.3	3.3	3.3	0.69	0.72	0.75	0.56	1.3	2.1
+	+	1	31	32	34	19	20	22	5	5	5	+	1	1	2.9	2.9	2.9	0.69	0.91	1.1	6.7	7.9	9.1
10	10	10	16	17	17	7	8	9	4	4	4	1	1	1	7.4	7.9	8.4	2.0	2.2	2.3	1.8	1.9	2.0
	9			25			13			5			2			6.9			4.6			1.6	
1	2	2	34	36	38	15	16	17	6	6	6	4	4	5	6.0	8.5	11	0.25	0.50	0.75	1.0	1.2	1.4
+	+	1	31	34	37	11	14	17	4	5	6	2	3	3	2.3	2.6	2.8	0.52	0.59	0.66	8.6	11	13
3	3	4	27	27	28	10	11	12	3	3	3	6	7	8	12	16	21	0.38	0.81	1.5	1.5	2.1	2.4
1	1	2	35	38	40	9	11	14	7	7	8	4	5	7	1.8	1.9	2.0	0.89	0.92	0.94	1.7	2.0	2.3
3	3	3	32	32	32	10	10	10	1	1	5	12	12	12	0.29	0.29	0.29	0.28	0.31	0.34	8.6	9.3	10
+	+	2	11	15	20	5	8	11	+	2	3	1	4	7	1.2	1.6	2.0	0.64	1.4	2.1	0.72	4.0	7.4
-	1	3	7	15	23	-	2	12	+	4	7	2	4	8	0.89	1.8	4.8	0.65	1.9	5.9	0.18	1.6	6.4
	-			12			-			-			-			0.07			0.07			+	
-	+	1	27	38	43		-		7	7	7	2	2	3	2.2	3.6	4.3	0.33	0.59	1.0	0.41	1.1	2.3
+	+	1	22	28	31	+	+	+	3	3	4	+	1	2	3.9	4.2	4.4	0.67	0.98	1.3	3.8	8.4	13
6	17	41	-	1	3		-		-	4	7	+	3	9	1.0	2.8	5.3	0.54	1.1	3.1	0.50	12	30
11	19	42	-	+	+		-		-	4	7	+	3	7	1.6	2.9	4.1	0.42	1.0	2.4	+	6.6	16
1	1	1	35	38	43	+	+	1	5	6	7	1	2	2	1.7	2.7	4.0	0.16	0.29	0.49	0.06	0.60	1.4
-	-	-	4	14	29	-	+	+	+	9	23	1	3	5	+	4.8	8.9	+	0.16	0.39	+	0.70	2.0
-	+	1	17	25	36	-	1	3	3	4	7	4	14	31	0.82	1.9	3.1	-	0.36	1.1	0.10	1.6	2.7
-	-	-	10	18	25	-	5	12	-	2	5	-	15	20	1.4	2.0	3.0	-	0.54	1.3	+	0.22	0.85
	17			25			1			+			-			4.6			0.14			0.38	
	14			25			2			+			-			0.86			0.07			6.3	
17	20	22	17	18	18	+	1	1	+	+	+		-		2.6	2.9	3.3	0.14	0.19	0.24	5.7	6.9	8.2
	20			18			1			+			-			13			0.50			2.2	
+	1	2	48	49	49	17	18	19	6	6	7	+	+	+	11	12	13	0.57	0.58	0.59	1.8	3.4	5.0
4	5	5	26	29	32	6	7	8	4	4	4	2	2	3	0.27	0.29	0.30	0.46	0.52	0.59	21	22	22
6	10	18	34	37	39	8	14	18	4	5	6	+	1	2	3.7	4.4	5.0	1.1	1.8	2.1	3.7	7.2	13
8	9	10	34	36	37	11	13	15	5	6	6	+	+	1	2.2	3.7	4.5	1.2	1.8	2.3	3.1	8.6	19
	-			23			-			-			-			0.23			0.10			0.17	
+	+	+	38	38	39	17	17	17	8	8	8	7	7	7	2.9	2.9	2.9	0.15	0.19	0.23	1.3	1.4	1.4
-	+	1	25	27	29	14	15	15	4	6	8	11	13	15	0.15	0.18	0.21	0.15	0.16	0.17	12	12	12
-	+	1	36	36	37	18	19	19	6	7	7	3	3	3	3.4	3.9	4.5	0.13	0.14	0.14	2.2	2.5	2.8
-	+	+	31	32	33	17	19	22	7	7	7	3	3	3	4.5	5.7	6.9	0.11	0.16	0.20	0.85	0.88	0.90
3	4	5	38	39	39	18	19	19	+	4	8	1	2	2	14	16	18	0.96	1.2	1.5	1.1	1.2	1.4
7	14	22	15	16	18	7	8	8	-	1	3	1	5	9	0.45	0.62	0.79	1.6	1.6	1.7	22	25	28
3	4	5	17	22	28	8	9	10	-	12	24	7	8	8	11	12	14	2.5	2.8	3.0	5.5	7.0	8.5
9	9	9	22	24	25	9	9	9	3	3	3	6	7	8	7.3	8.4	9.5	2.4	2.6	2.8	2.7	3.1	3.6
1	1	2	43	44	46	16	17	17	7	7	7	+	+	+	5.4	7.4	9.4	0.43	0.61	0.79	0.17	0.21	0.26
4	5	6	29	31	32	10	11	12	5	5	5	2	2	3	0.18	0.20	0.22	0.28	0.30	0.31	8.4	12	16
12	14	16	31	31	31	11	11	11	2	2	2	-	+	+	4.7	5.3	5.9	0.77	0.87	0.98	3.0	3.0	3.1
9	9	9	30	32	33	11	11	12	1	2	2	+	+	+	6.6	6.6	6.6	1.5	1.7	2.0	0.52	0.81	1.1
	2			29			10			4			8			0.91			1.1			4.0	
+	+	+	23	26	28	+	2	3	3	4	5	9	10	10	0.17	0.20	0.23	0.26	0.28	0.29	8.7	8.8	9.0
+	1	2	37	40	43	2	4	5	4	5	5	2	4	4	0.67	1.3	2.1	0.43	0.48	0.52	5.4	8.6	11
+	1	2	35	39	43	3	4	5	+	2	4	3	4	6	1.3	2.3	3.7	0.52	0.79	1.1	2.6	5.8	9.7
	-			20			-			-			-			0.19			0.06			+	

[1] Overlap with traces of isopimarol.

PICEA			Composition of FAs																				
			16:0			17:0ai			18:0			20:0			22:0			24:0			9-18:1		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of free fatty acids																				
P. abies FI	HW	2	2	3	3	3	3	4	1	2	2	1	1	1	2	2	2	2	2	2	7	9	11
	SW	2	5	6	7	3	4	5	3	6	9	2	3	5	3	4	5	3	4	5	9	10	11
	LK	2	7	9	11	3	4	5	4	5	5	+	+	+	2	2	2	+	1	2	13	14	15
	DK	2	9	9	9	4	4	4	5	5	6	+	+	1	2	2	2	+	1	2	11	12	13
P. abies FR	HW	1		11			4			10			3			12			12			9	
	SW	1		8			3			15			1			8			9			5	
	LK	1(3)		22			1			23			+			4			+			10	
	DK	1(5)		20			+			29			+			7			2			10	
P. glauca	HW	2	4	4	4	4	4	4	3	3	3	1	2	2	3	3	4	6	7	8	15	16	18
	SW	2	5	6	7	+	1	1	15	17	20	-	+	+	4	4	4	10	10	10	10	11	11
	LK	3(5)	8	9	9	6	6	6	3	4	4	+	+	1	2	3	4	3	5	6	10	11	11
	DK	2(5)	7	8	9	4	4	5	4	5	5	+	+	+	2	4	6	3	6	9	9	11	12
P. koraiensis	HW	1		5			2			2			-			2			3			18	
	SW	1		10			2			13			-			7			8			18	
	LK	1		7			3			3			-			5			7			14	
	DK	1		9			3			4			-			5			6			16	
P. mariana	HW	2	5	5	5	+	+	+	3	3	4	1	2	3	3	6	8	4	7	9	13	15	17
	SW	2	6	7	8	+	2	3	4	4	4	2	2	2	2	2	2	2	2	3	12	14	15
	LK	2(13)	6	7	7	1	1	2	3	4	5	1	1	2	3	5	7	6	7	8	11	11	12
	DK	2(17)	5	6	6	+	1	2	12	15	17	2	3	3	5	6	7	6	7	7	12	12	12
P. omorika	HW	1		15			4			3			5			5			6			17	
	SW	1		9			+			6			3			4			7			16	
	LK	1(2)		19			2			+			5			3			5			27	
	DK	1		20			3			+			-			2			3			26	
P. pungens	HW	2	8	11	13	18	21	24	3	4	4	+	+	+	6	6	6	8	11	13	9	11	13
	SW	2	8	15	22	-	15	29	5	6	7	+	+	+	2	2	3	4	5	6	14	19	23
	LK	7(11)	7	11	16	2	11	31	1	3	5	+	+	+	2	3	4	2	4	5	7	13	16
	DK	9	7	12	18	10	19	38	4	6	10	+	+	+	2	4	6	5	9	14	9	14	19
P. sitchensis	HW	2	15	16	18	5	6	6	4	4	4	6	9	11	12	13	14	7	11	14	9	10	12
	SW	2	18	20	22	7	8	9	3	3	3	4	6	9	2	3	4	2	3	5	8	12	16
	LK	2(3)	19	20	20	7	8	11	4	6	7	1	2	3	4	7	11	4	6	7	11	12	12
	DK	2(3)	23	23	24	9	10	10	2	4	6	+	3	6	3	3	4	3	3	3	13	15	17

- not detected
+ less than 1%
n = number of analyses (number of knots)
FAs = Fatty acids
DGs = Diacylglycerols
TGs = Triacylglycerols

Composition of FAs (cont.)															Concentration								
11-18:1[1]			9,12-18:2			5,9,12-18:3			5,11,14-20:3			Other FAs			Free FAs			DGs			TGs		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
% of free fatty acids															mg/g dry wood								
3	4	4	40	41	43	22	26	29	5	5	5	2	3	3	1.2	1.4	1.7	0.34	0.35	0.37	0.48	0.66	0.84
5	8	11	27	27	27	9	12	15	3	4	5	7	11	15	0.14	0.19	0.23	0.18	0.27	0.37	4.3	4.9	5.5
4	5	6	33	34	35	17	19	21	2	2	2	4	5	7	2.1	2.4	2.7	0.06	0.14	0.23	0.31	0.56	0.82
4	4	4	34	34	35	18	19	20	2	3	3	5	6	7	1.9	2.4	2.9	0.20	0.21	0.23	0.59	0.90	1.2
	4			17			8			5			6			0.25			0.24			0.10	
	+			31			2			7			10			0.10			0.12			2.1	
	1			22			7			+			8			0.92			0.07			0.17	
	1			21			-			-			9			1.0			0.08			0.19	
3	3	3	33	34	35	15	17	18	3	3	3	4	4	4	0.46	0.55	0.65	0.19	0.20	0.22	1.6	1.6	1.6
-	+	+	25	30	34	4	5	6	4	4	4	11	11	11	0.12	0.15	0.18	0.12	0.16	0.20	4.4	4.6	4.7
4	5	5	27	29	33	19	21	23	3	4	4	3	3	4	0.78	0.92	1.2	0.12	0.14	0.16	0.91	1.1	1.2
4	4	4	27	31	35	16	20	24	3	3	4	2	3	3	1.3	1.4	1.4	0.12	0.13	0.15	0.39	0.47	0.54
	6			36			22			2			2			3.8			0.95			1.4	
	6			24			4			2			5			0.51			0.61			5.1	
	4			29			22			3			3			6.0			0.40			0.30	
	4			29			19			3			3			6.1			0.68			0.83	
3	4	4	29	31	34	17	19	22	5	5	5	3	3	4	0.29	0.51	0.72	0.19	0.24	0.30	0.43	0.53	0.64
4	5	6	28	28	28	15	18	20	4	5	6	12	12	13	0.26	0.42	0.57	0.23	0.23	0.24	1.8	3.0	4.2
3	4	5	28	30	32	19	21	23	5	5	5	4	5	6	0.60	0.73	0.86	0.27	0.29	0.31	0.81	1.1	1.3
10	11	12	22	22	22	8	11	13	4	4	5	2	2	3	0.81	0.84	0.86	0.33	0.34	0.36	0.36	0.45	0.54
	5			25			7			4			5			0.85			0.25			0.16	
	5			27			11			5			7			0.52			0.49			2.2	
	9			23			2			2			2			3.5			0.66			1.0	
	6			27			8			3			1			2.4			0.75			0.56	
3	4	5	9	17	24	9	13	16	+	1	2	1	1	1	1.1	1.1	1.1	0.51	0.59	0.67	0.58	0.59	0.61
6	9	12	21	24	28	-	-	-	2	2	3	+	2	2	0.32	0.48	0.64	0.54	0.57	0.59	4.1	4.2	4.4
3	5	6	11	29	39	11	18	22	2	2	3	+	1	3	1.2	3.4	9.4	0.50	1.1	1.6	2.3	2.8	3.0
2	4	6	14	18	20	8	11	14	+	2	2	1	2	3	0.66	2.4	5.4	0.20	0.45	1.5	-	0.32	0.50
3	4	4	14	15	17	4	4	4	3	4	5	3	4	5	0.10	0.10	0.11	0.20	0.24	0.27	0.06	0.07	0.08
4	4	5	23	24	26	5	6	6	2	3	3	6	7	9	0.10	0.14	0.17	0.10	0.12	0.14	0.72	0.73	0.74
+	2	3	20	22	27	6	7	7	6	7	7	2	2	2	0.26	0.27	0.30	0.10	0.11	0.12	0.06	0.20	0.49
3	4	4	23	24	25	5	6	8	+	4	7	1	1	1	0.32	0.36	0.41	0.06	0.07	0.09	+	0.06	0.10

[1] Overlap with traces of isopimarol.

ABIES			Composition of FAs																				
			16:0[1]			17:0ai			18:0			20:0			22:0			24:0			9-18:1		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of free fatty acids																				
A. alba	HW	4	12	16	22	15	17	22	2	3	4	1	3	5	4	5	6	3	5	6	10	15	21
	SW	4	9	13	16	9	12	14	3	4	5	1	2	3	7	10	16	9	14	18	7	8	9
	LK	11	11	27	38	8	13	20	2	6	18	-	1	2	1	3	4	-	3	4	4	9	18
	DK	11(13)	4	30	49	2	8	14	+	3	4	-	+	2	+	3	6	-	3	5	6	12	23
A. amabilis	HW	1		16			15			5			2			6			3			11	
	SW	1		21			12			5			1			2			2			6	
	LK	2		24			11			7			3			5			6			8	
	DK	1(2)		17			20			4			2			4			2			12	
A. balsamea	Stem	3	16	17	18	7	7	8	2	2	3	1	1	1	4	5	5	3	4	5	8	8	9
	LK	1(2)		29			2			1			2			9			10			9	
	DK	1(4)		33			2			1			1			7			4			12	
A. concolor	HW	1		15			15			2			2			6			3			11	
	LK	1(2)		15			14			3			2			4			2			10	
A. lasiocarpa	HW	2	55	56	56	11	11	11	2	2	2	+	+	+	3	3	4	2	2	2	4	5	5
	SW	2	18	18	18	8	9	9	3	5	6	-	1	2	3	4	5	2	2	2	11	12	13
	LK	2(16)	54	62	70	7	12	17	2	2	2	-	-	-	1	1	2	+	+	1	4	4	5
	DK	2(15)	67	68	69	8	10	12	1	2	2	+	+	+	1	1	1	+	+	1	3	4	5
A. pindrow	Knots	300 g		37			4			10			+			3			4			17	
A. sachalinensis	HW	1		+			16			9			4			10			11			18	
	SW	1		+			13			4			3			12			14			17	
	LK	1(2)		+			9			6			4			8			21			36	
	DK	1		+			12			8			1			7			18			35	
A. sibirica	HW	2	15	18	20	15	15	16	3	3	3	2	2	2	6	7	8	6	8	11	11	11	11
	SW	2	11	11	11	5	5	6	4	4	4	+	+	+	7	8	9	14	15	16	13	14	14
	LK	2(6)	31	36	41	5	6	8	2	3	3	+	1	1	3	3	4	3	4	5	6	7	8
	DK	2(3)	30	32	33	5	6	6	4	5	5	1	1	2	6	6	6	8	8	8	7	7	7
A. veitchii	HW	1		28			9			8			4			14			21			10	
	SW	1		18			19			5			2			7			7			12	
	LK	1(2)		26			10			7			2			5			14			13	
	DK	1		24			5			9			4			7			15			16	

- not detected

+ less than 1%

n = number of analyses (number of knots)

FAs = Fatty acids

DGs = Diacylglycerols

TGs = Triacylglycerols

[1] Overlap with juvabiol in *A. lasiocarpa, A. pindrow, A. sachalinensis, A. sibirica* and *A. veitchii.*

Composition of FAs (cont.)																Concentration								
11-18:1[2]			9,12-18:2			5,9,12-18:3			5,11,14-20:3			Other FAs				Free FAs			DGs			TGs		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max		min	avg	max	min	avg	max	min	avg	max
% of free fatty acids																mg/g dry wood								
11	15	19	4	6	10	1	2	2	1	2	3	8	10	11		0.75	0.95	1.3	0.09	0.15	0.29	+	+	0.07
5	6	8	8	11	15	2	3	4	2	3	4	11	14	15		0.10	0.16	0.22	+	0.09	0.20	+	0.07	0.15
7	9	14	5	10	13	3	11	27	3	5	6	2	4	8		1.4	2.0	2.4	+	0.09	0.16	+	0.39	0.75
5	8	15	4	11	20	3	14	39	2	4	8	1	3	9		1.4	3.0	5.4	+	0.10	0.17	0.06	0.22	0.46
	11			12			4			4			9				1.0			0.08			0.07	
	8			20			6			5			11				1.6			0.36			0.39	
	8			13			5			5			5				1.2			0.18			0.17	
	11			12			5			4			7				2.3			+			0.10	
4	4	5	30	31	34	9	10	11	4	6	7	2	4	6		1.0	1.3	1.6	0.08	0.10	0.14	+	0.07	0.13
	2			24			4			2			6				0.80			+			0.07	
	2			26			4			3			5				0.69			+			0.06	
	16			13			4			5			8				2.1			0.24			0.09	
	11			17			7			8			8				3.2			0.09			0.48	
3	3	4	10	10	10	3	3	4	2	2	3	2	2	2		1.3	1.4	1.6	0.15	0.19	0.23	0.09	0.13	0.18
7	9	12	17	18	20	7	7	7	8	10	11	5	5	5		0.18	0.42	0.67	0.14	0.15	0.16	1.9	2.0	2.1
1	2	3	6	7	9	4	6	7	2	2	2	1	1	1		2.1	2.4	2.7	0.26	0.29	0.32	0.73	0.81	0.89
1	2	2	5	6	6	4	4	5	1	2	2	+	1	2		3.4	3.8	4.2	0.28	0.40	0.51	0.21	0.42	0.62
	7			10			3			4			+				2.1			-			0.44	
	12			20			-			-			-				0.73			0.13			0.48	
	12			25			-			-			-				0.71			0.19			0.17	
	16			-			-			-			-				1.5			0.47			1.3	
	18			-			-			-			-				3.9			0.47			0.57	
5	5	5	15	15	16	6	6	6	4	4	5	5	5	5		1.1	1.1	1.2	0.08	0.17	0.26	+	0.06	0.08
4	4	4	21	21	22	6	6	6	5	5	5	5	6	7		0.15	0.15	0.16	0.05	0.09	0.13	1.4	1.6	1.7
3	4	4	21	22	23	5	6	8	4	4	4	3	3	3		1.8	1.9	2.1	0.05	0.06	0.08	0.29	0.35	0.42
4	4	4	20	20	21	2	2	3	4	4	5	4	4	5		2.5	2.6	2.7	+	+	0.06	0.09	0.12	0.15
	2			4			-			+			-				0.26			0.08			0.08	
	10			16			-			4			-				0.32			0.13			0.25	
	8			12			-			3			-				2.0			0.23			0.14	
	4			15			-			2			-				2.4			0.42			0.54	

[1] Overlap with traces of isopimarol.

LARIX, PSEUDOTSUGA & TSUGA			Composition of FAs																				
			16:0			17:0ai			18:0			20:0			22:0			24:0			9-18:1		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	% of free fatty acids																				
L. decidua	HW	5	6	11	19	1	5	7	3	5	8	-	+	1	+	4	8	+	4	11	11	16	21
	SW	5	4	7	11	1	5	8	3	7	16	+	1	2	+	+	+	+	+	2	7	13	16
	LK	7(10)	7	16	27	3	12	33	3	5	10	+	1	2	+	4	9	+	5	14	5	13	19
	DK	11(15)	6	13	25	1	17	45	3	6	18	+	1	2	+	3	7	+	4	9	4	13	19
L. gmelinii	HW	2	5	6	6	5	6	6	2	3	3	+	+	+	2	3	3	2	2	3	16	16	16
var. *gmelinii*	SW	2	15	15	16	9	9	9	6	7	8	4	4	5	2	2	2	3	3	3	21	22	22
	LK	2	11	13	15	6	7	7	11	11	11	3	3	3	3	4	5	3	5	7	8	9	11
	DK	2	12	15	18	6	9	12	9	15	20	1	1	1	2	3	4	2	3	4	1	2	2
L. gmelinii	HW	2	5	5	6	3	4	4	2	3	5	+	1	2	+	3	5	+	4	6	10	16	21
var. *japonica*	SW	2	5	8	11	+	2	2	12	14	15	3	5	7	2	2	2	2	3	3	5	9	13
	LK	2	28	34	40	5	17	29	3	5	6	+	2	3	2	3	5	2	4	5	7	8	9
	DK	3	11	14	15	3	5	10	3	16	25	+	3	5	2	3	5	2	3	4	4	7	11
L. gmelinii	HW	2	4	4	4	4	4	4	2	3	3	+	+	+	1	1	1	+	+	1	11	12	13
var. *olgensis*	SW	2	3	5	6	+	2	3	8	9	9	+	1	1	+	+	1	+	1	2	1	4	6
	LK	2	9	9	10	4	5	7	3	6	10	1	2	3	1	1	2	+	1	1	7	11	15
	DK	2	10	13	15	5	10	16	10	15	19	+	+	+	2	2	2	1	2	2	6	8	10
L. kaempferi	HW	3	6	7	9	1	2	3	2	3	5		-		3	4	5	3	5	6	20	21	22
	SW	3	6	9	21	+	7	14	2	18	34		-		+	2	4	+	3	5	9	14	35
	LK	9	8	13	17	+	2	3	2	3	4	-	+	2	1	4	9	2	3	6	19	22	30
	DK	22	6	12	23	-	4	12	+	3	9	-	3	8	-	3	8	-	3	7	15	20	25
L. lariciana	HW	2	4	4	5	4	5	5	3	3	4	+	+	+	1	3	4	2	4	6	13	13	14
	SW	2	7	7	7	4	6	8	34	38	42		-		2	3	3	5	6	6	9	10	10
	LK	2	5	5	5	5	5	6	2	2	3	+	+	+	2	2	3	3	4	5	11	11	12
	DK	2(3)	4	5	6	3	4	6	3	10	16	+	+	+	2	2	2	3	4	5	10	10	11
L. sibirica	HW	6	3	4	6	3	4	5	+	1	2	+	+	+	+	+	1	+	2	3	14	16	19
	SW	6	8	11	19	1	4	6	+	10	32	+	4	13	+	1	5	+	3	8	7	21	39
	LK	1		8			3			10			2			2			2			10	
	DK	10	4	7	10	1	4	7	+	2	7	+	+	1	+	+	2	1	2	4	11	14	20
P. menziensii	HW	2	-	9	17	6	8	11	6	8	10	2	2	3	5	6	6	1	2	3	40	42	44
	SW	2	-	+	+	15	15	15	5	7	8	2	3	3	7	9	11	4	6	9	21	25	29
	LK	2(11)	1	30	58	9	10	11	2	5	8	+	+	+	2	3	3	2	2	2	16	28	40
	DK	2(11)	+	24	46	7	7	7	2	4	6	+	+	1	3	3	4	1	1	1	17	27	38
T. canadensis	HW	2	7	9	11	11	11	12	4	4	5	4	6	8	4	8	11	6	11	16	8	8	8
	SW	2	14	17	20	10	11	13	2	3	3	3	4	4	3	3	4	3	4	4	11	13	15
	LK	2	11	12	12	9	9	10	7	8	8	4	5	5	4	4	4	3	3	4	9	9	10
	DK	2	10	14	19	7	8	9	7	7	7	3	3	4	3	3	4	3	3	3	15	16	17
T. heterophylla CA	HW	2	6	9	11	3	6	9	2	2	2	7	8	8	25	31	36	13	20	27	8	11	14
	SW	2	13	18	23	13	14	16	2	2	2	1	2	3	2	6	10	1	4	8	8	9	10
	LK	2	10	13	16	13	13	14	5	6	7	4	6	7	8	10	13	2	4	6	10	10	11
	DK	2	7	9	10	10	11	12	6	7	8	6	7	8	9	12	14	2	4	6	8	10	12
T. heterophylla FI	Dead branch	1		10			10			4			4			8			3			15	
	DK	1		17			9			7			5			7			6			14	
T. mertensiana	LK	1		18			11			6			3			8			5			21	
	HW of branch	1		17			16			5			4			8			4			23	
	SW of branch	1		24			14			3			2			1			+			20	

- not detected
+ less than 1%
n = number of analyses (number of knots)
FAs = Fatty acids
DGs = Diacylglycerols
TGs = Triacylglycerols

Composition of FAs (cont.)													Concentration								
11-18:1[1]			9,12-18:2			5,9,12-18:3			5,11,14-20:3			Other FAs			Free FAs			DGs			TGs		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
% of free fatty acids															mg/g dry wood								
1	2	3	18	28	36	17	20	25	3	5	7	+	+	2	0.55	0.73	1.0	0.07	0.15	0.24	0.07	0.31	0.51
+	2	3	5	23	35	19	33	54	3	4	5	+	3	7	0.34	0.66	1.1	0.06	0.18	0.35	0.41	1.6	3.0
+	3	6	14	24	34	6	12	21	2	4	6	+	+	+	0.17	0.83	2.1	0.10	0.18	0.31	0.31	0.59	1.3
+	3	5	8	23	33	8	13	33	+	4	7	+	+	+	0.23	1.1	2.5	0.07	0.19	0.31	0.16	0.32	0.53
2	2	2	32	33	34	24	24	24	5	5	5		-		1.6	1.6	1.7	0.08	0.16	0.23	0.11	0.24	0.37
3	3	3	16	17	18	13	16	18	2	3	4		-		0.32	0.36	0.40	0.09	0.18	0.27	0.59	1.2	1.8
1	1	1	22	25	29	19	21	23	+	1	1		-		1.4	2.1	2.9	0.11	0.18	0.25	0.05	1.1	2.1
2	2	3	25	27	30	16	22	27	+	+	1		-		0.60	0.63	0.65	+	+	+	+	+	+
2	2	2	36	36	36	23	23	23	3	4	5		-		1.2	2.2	3.2	0.07	0.20	0.33	0.10	0.23	0.36
-	+	2	24	32	39	23	23	24	2	2	3		-		0.17	0.26	0.35	+	0.06	0.11	2.2	3.0	3.8
2	2	2	15	16	16	8	9	10	+	+	+		-		0.50	0.58	0.66	0.13	0.14	0.16	0.25	0.27	0.29
1	2	3	17	24	34	19	22	27	+	+	1		-		0.63	0.68	0.77	0.08	0.11	0.17	0.07	0.10	0.15
+	+	+	39	40	42	26	28	30	4	4	4		-		1.9	2.4	2.9	0.06	0.07	0.08	0.12	0.13	0.13
-	+	+	35	40	45	37	37	38	+	+	+		-		0.35	0.52	0.69	0.06	0.07	0.08	5.4	5.5	5.7
+	1	1	25	31	38	24	31	38	+	+	+		-		0.56	0.66	0.76	0.06	0.09	0.13	0.19	0.27	0.35
+	+	1	17	23	30	26	26	26	+	+	+		-		1.4	1.4	1.4	0.08	0.12	0.16	0.05	0.19	0.33
3	4	5	35	37	39	16	17	19	+	+	+		-		0.39	0.63	0.82		-		0.34	0.69	0.95
2	6	10	20	26	36	2	8	16	-	+	2	+	6	13	0.11	0.30	1.3	0.21	0.21	0.23	4.5	5.5	6.3
2	3	5	30	36	41	9	13	16		-		-	+	2	0.25	0.41	0.88	0.11	0.16	0.22	0.40	2.1	5.1
2	16	31	13	26	39	4	9	14	-	+	2	-	+	5	0.37	1.1	2.9	0.07	0.11	0.17	0.14	0.23	0.35
+	+	1	33	36	40	18	19	21	5	5	6	5	5	6	0.58	1.0	1.4	0.16	0.19	0.23	0.68	0.90	1.1
1	2	3	15	17	19	3	3	4	3	4	4	4	5	5	0.21	0.23	0.25	0.17	0.19	0.21	5.7	6.0	6.2
+	1	2	35	38	40	21	21	22	4	5	6	4	5	5	1.1	1.1	1.2	0.11	0.15	0.19	0.65	0.88	1.1
+	1	2	33	35	36	18	20	21	4	5	6	3	4	5	1.6	1.6	1.7	0.18	0.22	0.25	0.34	0.66	0.98
1	2	2	35	36	37	23	31	37	+	1	4	+	2	5	2.0	3.0	4.2	0.07	0.10	0.13	0.15	0.36	0.71
+	2	3	7	19	31	2	20	35	+	+	2	+	4	13	0.50	1.0	1.4	0.11	0.12	0.13	1.3	3.2	5.1
	1			26			24			3			9			5.8			0.11			0.40	
1	3	6	30	39	44	18	24	30	+	+	2	+	3	8	1.0	2.8	5.2	0.08	0.12	0.16	0.07	0.24	0.43
3	5	6	10	12	15	1	2	3	3	4	5		-		0.39	0.49	0.59	0.10	0.12	0.15	0.26	0.37	0.48
5	5	6	15	17	19	5	5	5	8	8	8		-		0.06	0.10	0.13	+	0.07	0.09	1.1	1.5	1.8
4	4	5	4	16	27	+	2	3	1	2	2		-		2.4	2.8	3.2	0.12	0.14	0.16	0.25	0.33	0.41
3	4	5	14	23	31	3	3	4	2	2	2		-		2.3	3.2	4.0	0.16	0.18	0.21	0.28	0.28	0.28
2	2	2	22	27	32	6	7	8	4	5	6	2	2	3	0.35	0.40	0.45	0.10	0.11	0.12	0.05	0.06	0.07
3	3	3	29	30	32	5	6	8	4	4	4	2	2	2	0.16	0.19	0.22	0.14	0.17	0.21	0.93	0.93	0.93
2	2	2	32	33	34	7	8	8	5	6	6	1	2	2	0.27	0.31	0.34	0.07	0.09	0.12	0.10	0.10	0.10
4	8	12	26	26	26	6	7	8	4	4	4	+	+	1	0.49	0.53	0.57	0.12	0.13	0.14	0.09	0.09	0.10
1	2	2	4	6	9	+	2	3	1	2	3	3	3	3	0.17	0.17	0.17	0.15	0.15	0.15	+	+	+
+	1	2	27	28	30	5	5	5	5	6	6	4	4	4	0.10	0.11	0.12	0.07	0.09	0.10	0.18	0.19	0.21
2	3	4	20	22	25	3	4	5	3	4	5	4	4	4	0.18	0.20	0.22	+	+	+	+	0.18	0.33
1	3	5	24	26	29	3	3	3	4	4	5	3	4	4	0.21	0.28	0.35	+	+	+	0.06	0.06	0.06
	4			23			5			5			8			0.14			+			0.08	
	2			12			-			2			19			0.10			+			0.06	
	3			13			3			3			6			0.16			+			0.07	
	3			9			3			2			5			0.12			+			+	
	3			23			4			3			3			0.38			0.13			0.14	

[1] Overlap with traces of isopimarol.

D3 Sterols, triterpenols and their esters

PINUS			Concentration of sterols											
			Sitosterol			Sitostanol			Campesterol			Campestanol		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
P. banksiana[1]	HW	2	0.16	0.16	0.17	+	+	+	+	+	+	+	+	+
	SW	2	0.06	0.06	0.07	+	+	+	+	+	+	-	+	+
	LK	2(5)	0.16	0.16	0.17	+	+	+	+	+	+	+	+	+
	DK	1		0.28			+			+			+	
P. contorta	HW	2	0.12	0.13	0.15	+	+	+	+	+	+	-	+	+
	SW	2	0.07	0.08	0.08	+	+	+	+	+	+	+	+	+
	LK	4	0.09	0.11	0.13		-			-			-	
P. elliottii	HW	2	0.10	0.14	0.18	+	+	+	+	+	+	+	+	+
	SW	2	0.05	0.06	0.06	+	+	+	+	+	+	+	+	+
	LK	3	0.08	0.09	0.09	+	+	+	+	+	+	-	+	+
	DK	10	+	0.12	0.27	-	+	+	+	+	0.05	-	+	0.07
P. gerardiana	knots	300 g		-			-			-			-	
P. nigra	HW	3	0.09	0.15	0.18	+	+	+	+	+	+		-	
	SW	3	0.06	0.07	0.09	-	+	+	+	+	+		-	
	LK	8	+	0.12	0.16	-	0.06	0.17	-	+	0.07		-	
	DK	9	+	0.09	0.13	+	0.05	0.09	-	+	+		-	
P. pinaster	HW	3	0.07	0.09	0.10	+	+	+	+	+	+		-	
	SW	3	+	+	0.07	-	+	0.07	+	+	+		-	
	LK	9	+	0.06	0.10		-		-	+	+	-	+	+
	DK	9	+	0.07	0.09		-		-	+	+		-	
P. radiata	HW	1		0.09			-			-			-	
	SW	1(2)		0.06			-			-			-	
	LK	2	0.05	0.06	0.08		-			-			-	
	DK	1		-			-			-			-	
P. resinosa	HW	2	0.15	0.18	0.21	+	+	+	+	+	+	-	+	+
	SW	2	0.09	0.10	0.11	+	+	+	+	+	+	+	+	+
	LK	3(5)	0.09	0.13	0.16		-		-	+	+	-	+	+
	DK	3(6)	0.13	0.15	0.19	-	+	+	+	+	+	-	+	+
P. roxburghii	knots	300 g		-			-			-			-	
P. sibirica	HW	2	0.25	0.26	0.26	+	+	+	+	+	+	+	+	+
	SW	2	0.09	0.10	0.10	+	+	+	+	+	+	+	+	+
	LK	2(8)	0.17	0.18	0.18	-	+	+	-	+	+	-	+	+
	DK	2(3)	0.19	0.21	0.23		-		-	+	+	+	0.14	0.26
P. strobus	HW	2	0.14	0.14	0.15	-	+	+		-			-	
	SW	2	0.11	0.12	0.12	+	+	+	+	+	+		-	
	LK	2	0.10	0.11	0.12	-	0.05	0.11		-			-	
	DK	2	0.16	0.18	0.19	0.08	0.09	0.09		-			-	
P. sylvestris	HW	2	0.16	0.17	0.19	+	+	+	+	+	+	+	+	+
	SW	2	0.07	0.09	0.10	+	+	+	+	+	+	+	+	+
	LK	2	0.14	0.15	0.16	-	+	+	+	+	0.06	+	+	+
	DK	2	0.20	0.22	0.25	+	+	+	+	+	0.09	+	+	+
P. taeda	HW	1		0.12			+			+			+	
	SW	2	+	0.05	0.06	+	+	+	+	+	+	+	+	+
	LK	4	0.08	0.09	0.10	+	0.06	0.12	+	+	+	+	+	+
	DK	5	0.07	0.11	0.21	+	0.07	0.15	+	+	0.05	+	+	+
P. wallichiana	knots	300 g		-			-			-			-	

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

No sterols were detected in knots of *P. gerardiana, P. roxburghii* or *P. wallichiana.*

[1] All samples contained traces of hydroxysitosterol, stigmasta-3,5-diene and cholesta-3,5-diene.

Concentration of sterols (cont.)															
Cycloartenol			Me-cycloartanol			Citrostadienol			Sterols total			Steryl esters			
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	
mg/g dry wood															
+	+	+	+	+	+	+	+	+	0.22	0.22	0.23	1.3	1.5	1.7	
+	+	+	+	+	+	+	+	+	0.09	0.10	0.11	1.6	1.8	1.9	
+	+	+	+	+	+	+	+	+	0.25	0.27	0.29	2.0	2.3	2.5	
	+			+			+			0.42			2.0		
	-			-			-		0.14	0.16	0.18	1.5	1.6	1.6	
+	+	+	+	+	+		-		0.09	0.10	0.10	1.7	1.8	1.8	
-	+	+		-			-		0.09	0.11	0.13	1.8	1.8	1.9	
+	+	+	+	+	+	+	+	+	0.13	0.19	0.24	1.3	1.4	1.5	
+	+	+	+	+	+	+	+	+	0.06	0.07	0.07	1.1	1.2	1.3	
+	+	+	+	+	+	+	+	+	0.13	0.14	0.14	1.2	1.3	1.4	
-	+	+	+	+	+	-	+	+	0.08	0.19	0.34	0.81	1.1	1.5	
	-			-			-			-			0.11		
-	+	+		-			-		0.11	0.19	0.23	0.83	1.0	1.2	
-	+	+		-			-		0.07	0.08	0.09	0.58	0.60	0.62	
	-			-		+	0.11	0.34	0.06	0.32	0.66	1.1	1.4	1.9	
	-			-		-	0.10	0.26	+	0.26	0.42	0.92	1.4	2.1	
	-			-			-		0.09	0.11	0.13	0.85	0.87	0.89	
-	+	+	-	+	+		-		+	0.06	0.10	+	0.33	0.89	
	-			-			-		0.05	0.07	0.10	1.3	1.5	2.0	
-	+	+		-		-	+	+	+	0.09	0.17	1.0	1.4	1.9	
	-			-			-			0.09			0.77		
	-			-			-			0.06			0.98		
	-			-			-		0.05	0.06	0.08	1.1	1.2	1.4	
	-			-			-			-			0.88		
+	+	+	+	+	+	+	+	+	0.19	0.23	0.26	2.4	2.5	2.7	
+	+	+	+	+	+	+	+	+	0.10	0.12	0.13	0.89	2.1	2.1	
-	+	+	-	+	+	+	+	+	0.11	0.18	0.22	2.4	2.7	3.0	
+	+	+	-	+	+	+	+	+	0.20	0.21	0.22	3.1	3.5	4.2	
	-			-			-			-			0.06		
+	+	+	+	+	+	+	+	+	0.33	0.34	0.35	1.8	1.8	1.9	
+	+	+	+	+	+	+	+	+	0.11	0.12	0.13	2.1	2.1	2.2	
-	+	+		-		+	0.06	0.07	0.25	0.25	0.26	1.4	1.4	1.5	
+	+	+		-		-	+	+	0.22	0.40	0.58	1.3	1.4	1.5	
	-			-			-		0.15	0.15	0.16	2.8	2.9	2.9	
	-			-			-		0.13	0.13	0.14	2.3	2.5	2.7	
	-		-	+	0.08		-		0.10	0.16	0.23	3.8	4.5	5.3	
	-		-	+	0.06	-	+	0.05	0.24	0.29	0.33	2.8	3.3	3.8	
+	+	+	+	+	+		-		0.20	0.23	0.25	-	0.66	1.3	
-	+	+	+	+	+		-		0.08	0.10	0.11	1.2	1.6	1.9	
+	+	+	+	+	+		-		0.19	0.24	0.29	2.2	2.3	2.4	
+	+	+	+	+	+		-		0.27	0.34	0.41	1.3	1.4	1.5	
	+			+			+			0.17			1.4		
+	+	+	+	+	+	+	+	+	0.06	0.07	0.07	0.97	0.97	0.97	
+	+	+	+	+	+	+	+	+	0.10	0.18	0.24	1.5	1.5	1.6	
+	+	+	+	+	+	+	+	+	0.09	0.18	0.43	1.0	1.4	1.6	
	-			-			-			-			0.33		

PICEA			Concentration of sterols											
			Sitosterol			Sitostanol			Campesterol			Campestanol		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
P. abies FI	HW	2	0.13	0.14	0.15	+	+	+	0.05	0.06	0.07	+	+	+
	SW	2	0.07	0.07	0.07	+	+	+	+	+	+	+	+	+
	LK	2	0.20	0.38	0.56	+	+	+	0.13	0.14	0.15	+	0.17	0.34
	DK	2	0.21	0.37	0.52	+	+	+	0.13	0.15	0.17	0.15	0.18	0.20
P. abies FR	HW	1		0.23			+			0.07			+	
	SW	1		0.09			+			+			+	
	LK	1(3)		1.0			+			0.16			0.34	
	DK	1(5)		0.70			+			0.09			0.17	
P. glauca	HW	2	0.17	0.19	0.22	+	+	+	0.07	0.08	0.08	+	+	+
	SW	2	0.07	0.09	0.10	+	+	+	+	+	+	+	+	+
	LK	3(5)	0.16	0.26	0.42	+	+	+	0.05	0.08	0.11	+	+	+
	DK	2(5)	0.23	0.34	0.44	+	+	+	0.06	0.06	0.06	+	+	+
P. koraiensis	HW	1		0.39			0.07			0.21			+	
	SW	1		0.13			+			0.07			+	
	LK	1		0.25			0.06			0.20			+	
	DK	1		0.26			+			0.19			-	
P. mariana[1]	HW	2	0.07	0.10	0.13	+	+	+	+	0.06	0.06	+	+	+
	SW	2	0.06	0.07	0.08	+	+	+	+	+	+	-	+	+
	LK	2(13)	0.10	0.18	0.27	+	+	+	0.07	0.11	0.15		-	
	DK	2(17)	0.11	0.13	0.15	+	+	+	0.06	0.06	0.06	-	+	+
P. omorika	HW	1		0.19			+			0.05			+	
	SW	1		0.09			+			+			+	
	LK	1(2)		0.16			0.09			0.07			0.06	
	DK	1		0.19			0.05			0.07			0.06	
P. pungens	HW	2	0.23	0.25	0.26	+	+	0.05	0.08	0.08	0.08		-	
	SW	2	+	0.07	0.09	+	+	+	+	+	+		-	
	LK	7(11)	0.08	0.09	0.11	+	+	+	0.06	0.06	0.08		-	
	DK	9	0.10	0.14	0.16	+	+	+	0.07	0.08	0.11		-	
P. sitchensis	HW	2	0.12	0.14	0.15	+	+	+	+	+	+	+	+	+
	SW	2	0.05	0.05	0.06	+	+	+	+	+	+	+	+	+
	LK	2(3)	0.06	0.06	0.06	+	+	+	+	+	+	+	+	+
	DK	2(3)	0.06	0.07	0.08	+	+	+	+	+	+	+	+	+

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

[1] The heartwood and sapwood of *P. mariana* contained traces of sitostadien-7-one.

Concentration of sterols (cont.)															
Cycloartenol			Me-cycloartanol			Citrostadienol			Sterols total			Steryl esters			
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	
mg/g dry wood															
+	+	+	+	+	+		-		0.23	0.24	0.25	1.2	1.3	1.3	
+	+	+	+	+	+		-		0.11	0.11	0.12	1.7	1.8	1.9	
+	+	+	+	+	+		-		0.70	0.72	0.73	0.78	1.2	1.7	
+	+	+	+	+	+		-		0.52	0.72	0.92	1.9	2.0	2.2	
	+			+			-			0.36			0.69		
	+			+			+			0.13			1.3		
	0.10			+			+			1.7			0.58		
	+			+			+			1.0			0.41		
+	+	+	+	+	+	+	+	+	0.27	0.31	0.35	1.5	1.6	1.8	
+	+	+	+	+	+	+	+	+	0.12	0.15	0.18	1.9	2.0	2.2	
+	+	+	+	+	+	+	+	+	0.23	0.37	0.53	1.7	1.8	1.9	
+	+	+	+	+	+	+	+	+	0.34	0.44	0.53	1.6	1.6	1.6	
	-			-			-			0.68			1.8		
	-			-			-			0.25			1.8		
	-			-			-			0.55			1.5		
	-			-			-			0.47			1.8		
+	+	+	+	+	+	+	+	+	0.19	0.20	0.22	1.2	1.2	1.3	
+	+	+	+	+	+	-	+	+	0.09	0.11	0.13	2.0	2.1	2.2	
+	+	+	+	+	+	+	+	+	0.20	0.32	0.44	1.9	2.5	3.1	
+	+	+	+	+	+	+	+	+	0.22	0.23	0.24	1.6	1.9	2.2	
	-			-			-			0.30			0.63		
	-			-			-			0.15			2.0		
	-			-			-			0.38			1.7		
	-			-			-			0.36			1.7		
	-			-			-		0.37	0.37	0.38	1.6	1.8	2.0	
	-			-			-		0.05	0.10	0.14	2.0	2.1	2.3	
	-			-			-		0.15	0.17	0.19	2.8	3.2	3.4	
	-			-			-		0.20	0.24	0.30	0.95	1.4	2.5	
-	+	+	+	+	+		-		0.18	0.21	0.23	0.64	0.70	0.77	
+	+	+	-	+	+		-		0.08	0.08	0.08	0.98	1.0	1.0	
-	+	+	+	+	+		-		0.08	0.08	0.09	0.62	0.72	0.90	
	-		-	+	+		-		0.08	0.09	0.11	0.60	0.61	0.62	

ABIES			Concentration of sterols											
			Sitosterol			Sitostanol			Campesterol			Campestanol		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
A. alba	HW	4	0.12	0.16	0.19	+	0.06	0.08	0.07	0.08	0.09	+	+	0.05
	SW	4	0.06	0.10	0.14	+	+	0.05	+	+	0.07	+	+	+
	LK[1]	11	+	0.06	0.10	+	+	+	+	+	+	-	+	0.13
	DK[1]	11(13)	+	0.10	0.24	+	+	+	+	+	0.12	-	+	0.17
A. amabilis	HW	1		0.12			+			+			+	
	SW	1		0.23			0.08			0.10			+	
	LK	2	0.14	0.19	0.24	+	+	+	0.06	0.08	0.10	+	+	+
	DK	1(2)		0.18			0.06			0.08			+	
A. balsamea	Stem	3	0.21	0.24	0.27	+	0.05	0.06	0.08	0.08	0.09	+	+	+
	LK	1(2)		0.38			+			0.06			+	
	DK	1(4)		0.37			+			+			+	
A. concolor	HW	1		0.21			0.05			0.13			0.06	
	LK	1(2)		0.16			+			0.21			+	
A. lasiocarpa	HW	2	0.19	0.20	0.21	+	0.06	0.06	0.09	0.10	0.11	+	+	+
	SW	2	0.06	0.07	0.08	+	+	+	+	+	0.06	+	+	+
	LK	2(16)	0.12	0.13	0.13	+	+	+	0.07	0.07	0.08	+	+	+
	DK	2(15)	0.16	0.16	0.16	+	+	+	0.09	0.09	0.09	+	0.08	0.12
A. pindrow	Knots	300 g		0.15			+			0.17			0.14	
A. sachalinensis	HW	1		0.13			0.05			0.06			-	
	SW	1		0.18			0.07			0.07			-	
	LK	1(2)		0.19			+			0.17			-	
	DK	1		0.31			0.17			0.17			-	
A. sibirica	HW	2	0.22	0.23	0.25	0.08	0.08	0.08	0.13	0.15	0.16	+	+	+
	SW	2	0.07	0.07	0.08	+	+	+	+	+	0.05	+	+	+
	LK	2(6)	0.19	0.19	0.19	+	+	+	0.05	0.06	0.06	+	+	0.06
	DK	2(3)	0.29	0.30	0.32	+	+	+	0.06	0.06	0.07	0.06	0.10	0.14
A. veitchii	HW	1		0.22			0.11			0.05			+	
	SW	1		0.15			0.06			0.06			+	
	LK	1(2)		0.17			0.06			0.19			0.07	
	DK	1		0.22			0.14			0.17			+	

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

[1] The knots from Sauviat sur vige contained traces of stigmastadiene.

Concentration of sterols (cont.)															
Cycloartenol			Me-cycloartanol			Citrostadienol			Sterols total			Steryl esters			
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	
mg/g dry wood															
+	+	+	-	+	+	+	+	+	0.31	0.34	0.43	0.12	0.22	0.35	
+	+	+	+	+	+	-	+	+	0.11	0.20	0.29	0.17	0.32	0.64	
-	+	+	-	+	+	-	+	+	0.07	0.11	0.26	0.41	0.62	0.87	
-	+	+	-	+	+	-	+	+	0.08	0.19	0.41	0.32	0.51	0.82	
	-			-			-			0.24			0.13		
	-			-			-			0.44			0.62		
	-			-			-		0.27	0.30	0.33		0.19		
	-			-			-			0.33			0.17		
+	+	+		-		-	+	+	0.36	0.40	0.44	0.57	0.66	0.72	
	+			+			+			0.46			0.88		
	+			+			-			0.43			0.75		
	+			+			+			0.46			0.42		
	+			+			-			0.42			0.50		
+	+	+	+	+	+		-		0.37	0.38	0.39	0.36	0.38	0.39	
-	+	+		-		-	+	+	0.11	0.13	0.16	1.1	1.1	1.1	
-	+	+		-			-		0.21	0.24	0.28	0.93	1.1	1.2	
+	+	+	+	+	+		-		0.34	0.38	0.43	0.68	0.86	1.0	
	-			-			-			0.46			0.28		
	-			-			-			0.24			0.37		
	-			-			-			0.32			0.15		
	-			-			-			0.40			0.67		
	-			-			-			0.65			0.51		
+	+	+	+	+	+	+	+	+	0.50	0.52	0.53	0.28	0.31	0.34	
+	+	+	+	+	+	-	+	+	0.14	0.16	0.18	0.90	1.0	1.1	
+	+	+	+	+	+	-	+	+	0.30	0.32	0.34	0.86	0.96	1.1	
+	+	+	+	+	+		-		0.46	0.50	0.54	0.42	0.50	0.59	
	-			-			-			0.41			0.10		
	-			-			-			0.30			0.34		
	-			-			-			0.49			0.39		
	-			-			-			0.55			0.17		

LARIX, PSEUDOTSUGA & TSUGA		n	Concentration of sterols											
			Sitosterol			Sitostanol			Campesterol			Campestanol		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
			mg/g dry wood											
L. decidua [1]	HW	5	0.05	0.06	0.07	+	+	+	+	+	+	+	+	+
	SW	5	+	+	0.06	+	+	+	+	+	+	-	+	+
	LK	7(10)	+	+	0.07	+	+	+	+	+	+	-	+	+
	DK	11(15)	+	+	0.08	+	+	+	+	+	+	-	+	+
L. gmelinii	HW	2	0.06	0.07	0.08	+	+	+	+	+	+	+	+	+
var. *gmelinii*	SW	2	+	+	+	+	+	+	+	+	+	-	+	+
	LK	2	0.43	0.80	1.2	+	+	+	+	0.10	0.15	-	+	+
	DK	2	1.1	1.2	1.2	+	+	+	0.18	0.31	0.45	+	+	+
L. gmelinii	HW	2	+	0.05	0.07	+	+	+	+	+	+	+	+	+
var. *japonica*	SW	2	+	+	+	+	+	+	+	+	+	+	+	+
	LK	2	0.69	0.92	1.2	+	+	+	+	0.15	0.25	+	+	0.08
	DK	3	0.69	1.0	1.2	+	+	+	0.30	0.32	0.35	+	+	+
L. gmelinii	HW	2	+	+	+	+	+	+	0.08	0.11	0.13	+	+	+
var. *olgensis*	SW	2	+	+	+	+	+	+	+	+	+	+	+	+
	LK	2	0.43	0.67	0.90	+	+	+	0.21	0.22	0.22	-	+	+
	DK	2	0.98	1.2	1.4		-		0.12	0.20	0.28	-	+	+
L. kaempferi [2]	HW	3	+	0.06	0.07	+	+	+	+	+	+	-	+	+
	SW	3	+	+	+	+	+	+	+	+	+	-	+	+
	LK	9	+	0.06	0.09	+	+	0.07	+	+	+		-	
	DK	22	+	0.08	0.21	-	+	+	-	+	+		-	
L. lariciana	HW	2	0.09	0.11	0.13	+	+	+	+	+	+	+	+	+
	SW	2	0.05	0.05	0.05	+	+	+	+	+	+	+	+	+
	LK	2	0.08	0.10	0.11	+	+	+	0.08	0.09	0.10	+	+	+
	DK	2(3)	0.12	0.12	0.13	+	+	+	0.11	0.12	0.14	+	+	+
L. sibirica	HW	6	+	0.06	0.07	+	+	+	-	+	+	+	+	+
	SW	6	+	+	0.05	+	+	+	-	+	+	+	+	+
	LK	1		0.08			+			0.08			+	
	DK	10	+	0.08	0.15	+	0.11	0.39	-	+	0.14	+	+	+
P. menziensii	HW	2	+	0.06	0.08	+	+	+	+	+	+	+	+	+
	SW	2	+	+	+	+	+	+	+	+	+	+	+	+
	LK	2(11)	0.26	0.40	0.54	+	+	+	+	+	+	+	+	+
	DK	2(11)	0.15	0.39	0.63	+	+	+	+	+	+	+	+	+
T. canadensis	HW	2	0.12	0.14	0.15	+	+	+	0.05	0.07	0.09	+	+	+
	SW	2	0.06	0.08	0.09	+	+	+	+	+	+	+	+	+
	LK	2	+	+	+	+	+	+	+	+	+	+	+	+
	DK	2	+	+	0.06	+	+	+	+	+	+	+	+	+
T. heterophylla CA	HW	2	0.18	0.21	0.25	+	0.05	0.06	0.08	0.09	0.10	+	+	+
	SW	2	+	+	+	+	+	+	+	+	+	+	+	+
	LK	2	+	0.11	0.18	+	+	+	+	0.06	0.08	+	+	+
	DK	2	+	0.06	0.08	+	+	+	+	0.06	0.09	+	+	+
T. heterophylla FI	Dead branch	1		0.16			+			0.06			+	
	DK	1		0.10			+			0.05			+	
T. mertensiana	LK	1		0.17			+			0.06			+	
	HW of branch	1		0.14			+			0.06			+	
	SW of branch	1		0.08			+			0.07			+	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)

[1] Other = Cholestadiene and stigmasta-3,5-diene.

[2] Other = stigmastadiene.

Concentration of sterols (cont.)																		
Cycloartenol			Me-cycloartanol			Citrostadienol			Other sterols			Sterols total			Steryl esters			
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	
mg/g dry wood																		
+	+	+	-	+	+	-	+	+	-	0.16	0.31	0.13	0.27	0.41	0.73	1.0	1.4	
+	+	+		-		-	+	+	-	+	+	0.05	0.07	0.09	0.63	0.98	1.4	
+	+	+	-	+	+	-	+	+	-	+	+	0.06	0.08	0.11	0.91	1.4	1.7	
+	+	+	+	+	+	-	+	+	-	+	+	0.06	0.09	0.16	0.79	1.0	1.4	
+	+	+		-			-			-		0.12	0.15	0.17	0.83	0.96	1.1	
+	+	+		-			-			-		+	0.06	0.08	0.53	0.70	0.87	
+	+	+	+	+	+		-			-		0.61	0.94	1.3	0.69	1.1	1.6	
+	+	+	+	+	+		-			-		1.3	1.5	1.7	0.66	0.69	0.72	
+	+	+		-			-			-		0.12	0.13	0.14	1.4	1.5	1.6	
+	+	+		-			-			-		0.05	0.06	0.06	1.2	1.3	1.3	
+	+	+	-	+	+		-			-		0.96	1.1	1.3	0.78	1.2	1.6	
+	+	0.06	-	+	+		-			-		1.1	1.4	1.5	0.71	1.1	1.3	
+	+	+	-	+	+		-			-		0.15	0.18	0.21	1.1	1.3	1.5	
+	+	+		-			-			-		0.06	0.06	0.07	1.4	1.6	1.8	
+	+	+	+	+	+		-			-		0.69	0.91	1.1	1.1	1.4	1.7	
+	+	+		-			-			-		1.1	1.4	1.7	0.87	1.5	2.0	
+	+	+		-			-			-		0.10	0.13	0.15	1.5	1.7	1.9	
+	+	+		-			-			-		+	0.06	0.07	1.3	1.5	1.7	
	-			-			-		+	+	+	0.07	0.10	0.13	0.66	1.5	2.2	
	-			-			-		+	+	+	0.12	0.13	0.14	0.35	0.82	1.2	
+	+	+	+	+	+	+	+	+		-		0.16	0.19	0.22	1.1	1.1	1.2	
+	+	+	+	+	+	-	+	+		-		0.09	0.09	0.10	1.2	1.4	1.6	
+	+	+	+	+	+	+	+	+		-		0.18	0.21	0.25	1.4	1.6	1.7	
+	+	+	+	+	+	+	+	+		-		0.26	0.28	0.31	1.4	1.6	1.8	
+	+	+	+	+	+	-	+	+		-		0.11	0.12	0.13	1.3	1.5	1.6	
+	+	+	-	+	+	-	+	+		-		0.07	0.07	0.08	0.71	1.2	1.8	
	+			-			-			-			0.22			1.7		
+	+	+	+	+	+	-	+	+		-		0.08	0.25	0.59	0.79	1.4	1.9	
-	+	+	+	+	+	+	+	+		-		0.08	0.11	0.13	2.4	2.4	2.4	
	-			-		-	+	+		-		+	+	+	1.9	2.0	2.0	
-	+	+	+	+	+	+	+	+		-		0.33	0.46	0.60	4.4	4.5	4.6	
	-		+	+	+	+	+	+		-		0.22	0.47	0.73	3.5	3.5	3.6	
+	+	+	-	+	+	-	+	+		-		0.24	0.28	0.31	0.25	0.28	0.32	
+	+	+		-		-	+	+		-		0.12	0.15	0.18	0.47	0.50	0.54	
+	+	+		-			-			-		0.07	0.07	0.07	0.38	0.42	0.46	
	-			-			-			-		0.07	0.08	0.10	0.35	0.35	0.36	
+	+	+		-		-	+	+		-		0.32	0.38	0.43	0.19	0.28	0.36	
+	+	+	+	+	+	-	+	+		-		0.08	0.08	0.09	0.08	0.08	0.09	
+	+	+	+	+	+	-	+	+		-		0.12	0.22	0.31	5.1	5.1	6.5	
+	+	+	+	+	0.06	-	+	+		-		0.13	0.19	0.26	8.3	8.9	9.5	
	+			+			+			-			0.26			0.35		
	+			+			+			-			0.18			0.09		
	+			+			-			-			0.25			0.38		
	+			+			+			-			0.22			0.15		
	+			+			-			-			0.18			0.47		

D4 Juvabiones

ABIES			Concentrations of juvabiones and sesquiterpenoids											
			Juva			TodoA			4'-DeJuva			4'-DeTodoA		
			mg/g dry wood											
		n	min	avg	max	min	avg	max	min	avg	max	min	avg	max
A. alba	HW	4	-	+	+	-	+	+	-	+	+	+	+	+
	SW	4	-	+	+	-	+	+	-	+	+	+	+	+
	LK	11	-	0.28	0.55	-	0.15	0.33	0.41	2.1	7.5	+	0.41	1.7
	DK	11(13)	-	0.66	2.5	-	1.7	5.6	0.18	3.1	8.6	0.23	1.7	3.5
A. amabilis	HW	1		+			+			-			+	
	SW	1		0.12			+			-			+	
	LK	2	+	+	+	+	+	+		-		+	+	+
	DK	1(2)		+			+			-			+	
A. balsamea	Stem	3	2.0	2.3	2.9	0.55	0.62	0.72	0.25	0.50	0.63		-	
	LK	1(2)		1.0			0.83			0.09			-	
	DK	1(4)		1.3			0.88			0.12			-	
A. concolor	HW	1		-			+			-			+	
	LK	1(2)		-			0.81			-			0.21	
A. lasiocarpa	HW	2	3.2	3.4	3.5	0.52	0.53	0.53		-		0.11	0.11	0.12
	SW	2	+	0.33	0.64	+	0.06	0.11		-		-	+	+
	LK	2(16)	7.5	10	13	0.77	1.5	2.1		-		0.66	0.89	1.1
	DK	2(15)	8.1	8.7	9.3	1.7	2.4	3.1		-		1.7	2.0	2.3
A. pindrow	Knots	300 g		0.34			1.0			0.37			0.71	
A. sachalinensis	HW	1		2.5			0.49			0.11			0.09	
	SW	1		3.0			0.71			0.13			0.07	
	LK	1(2)		17			3.7			1.9			4.5	
	DK	1		9.2			2.9			1.3			3.8	
Abies sibirica	HW	2	0.45	0.67	0.89	0.22	0.22	0.23	+	+	+	+	+	+
	SW	2	+	+	+	+	+	+	-	+	+		-	
	LK	2(6)	2.2	2.6	3.0	0.83	1.4	1.9	1.2	3.0	4.9	0.41	1.7	3.0
	DK	2(3)	1.5	2.1	2.6	0.86	1.5	2.0	2.1	4.6	7.1	0.96	2.7	4.5
A. veitchii	HW	1		0.12			+			+			+	
	SW	1		1.3			0.23			+			+	
	LK	1(2)		1.9			1.5			1.8			5.8	
	DK	1		1.7			1.2			1.5			5.9	

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

Juva = Juvabione

TodoA = Todomatuic acid

4'-DeJuva = 4'-Dehydrojuvabione

4'-DeTodoA = 4'-Dehydrotodomatuic acid

1'-DeJuva = 1'-Dehydrojuvabione

Lasio = Lasiocarpenonone

LasioOH = Lasiocarpenonol

Concentrations of juvabiones and sesquiterpenoids (cont.)

1'-DeJuva			JuvaOH			Lasio			LasioOH			α-Atlantone[1]			Juvabiones total		
mg/g dry wood																	
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
	-		+	+	+		-			-		-	+	+	+	+	0.09
	-		-	+	+		-			-		-	+	+	+	+	+
	-		+	0.14	0.56		-			-		-	+	0.06	0.86	3.0	9.9
	-		0.19	0.37	0.57		-			-		-	+	0.13	0.81	7.6	18
	-			-			-			-			-			+	
	-			-			-			-			-			0.13	
	-			-			-			-			-		+	0.07	0.09
	-			-			-			-			-			0.06	
0.07	0.10	0.12	0.25	0.34	0.43	+	+	0.05		-		+	0.05	0.07	3.3	4.0	4.9
	0.29			0.79			+			-			+			3.0	
	0.35			0.74			+			-			+			3.4	
	-			-			-			-			-			+	
	-			-			-			-			-			1.0	
0.37	1.1	1.7	2.7	3.4	4.2	0.58	1.2	1.7	0.06	0.12	0.19	1.6	1.8	2.1	9.1	12	14
+	0.22	0.42	-	0.35	0.69	-	0.71	1.4	+	0.15	0.27	0.07	0.13	0.20	0.11	2.0	3.8
1.0	5.3	9.6	-	12	16	15	20	25	3.0	6.5	10	3.3	4.3	5.3	32	61	82
1.3	2.8	4.3	8.9	9.1	9.3	18	20	21	1.9	4.3	6.7	1.9	2.3	2.8	46	51	57
	-			-			-			-			-			2.4	
	-			1.0			-			-			0.06			4.3	
	-			1.3			-			-			0.06			5.2	
	-			9.9			0.46			0.26			0.31			37	
	-			6.7			0.57			0.48			0.20			25	
0.29	0.38	0.48	0.19	0.27	0.35	+	+	+	0.08	0.10	0.13	0.05	0.06	0.06	1.3	1.8	2.2
+	+	+	+	+	+	+	+	+		-		+	+	+	+	+	+
2.7	2.8	2.9	1.9	2.5	3.2	0.64	1.4	2.2	0.59	0.85	1.1	0.12	0.22	0.32	11	16	22
1.6	1.9	2.3	1.3	1.8	2.3	0.78	1.2	1.7	0.34	0.34	0.34	0.09	0.21	0.32	9.5	16	23
	-			+			+			-			-			0.12	
	-			0.46			+			-			-			2.0	
	-			2.0			-			-			-			13	
	-			1.7			0.06			0.06			-			12	

[1] Sum of α- and γ-atlantone for *A. balsamea* and *A. sibirica,* for others only α-atlantone.

PINUS & PICEA			Concentrations of juvabiones											
			Juva			TodoA			4'-DeJuva			Juvabiones total		
			mg/g dry wood											
		n	min	avg	max	min	avg	max	min	avg	max	min	avg	max
Pinus banksiana	HW	2		-		0.06	0.07	0.08		-		0.06	0.07	0.08
	SW	2		-		+	+	+		-		+	+	+
	LK	2(5)		-		13	13	13		-		13	13	13
	DK	1		-			2.6			-			2.6	
Pinus elliottii	HW	2	+	+	+	+	+	+		-		+	+	+
	SW	2	+	+	+	+	+	+		-		+	+	+
	LK	3	+	0.14	0.25	0.70	4.5	8.4	-	0.87	1.7	0.73	5.6	10
	DK	10	+	0.09	0.14	1.3	3.7	6.1	0.24	1.5	2.8	1.8	5.3	9.0
Pinus nigra	HW	3	-	+	+		-			-		-	+	+
	SW	3	-	+	+		-			-		-	+	+
	LK	8	-	+	+		-			-		-	+	+
	DK	9	-	+	+		-			-		-	+	+
Pinus pinaster	HW	3	-	+	+	+	+	+	-	+	+	+	+	+
	SW	3		-		+	+	+	-	+	+	+	+	+
	LK	9	-	0.08	0.21	6.1	11	23	-	+	+	6.2	11	23
	DK	9	-	0.11	0.17	7.8	17	26		-		8.0	17	26
Pinus roxburghii	knots	300 g		-			0.40			-			0.43	
Pinus taeda	HW	1		+			0.37			-			0.38	
	SW	2	+	+	+	+	+	+		-		+	+	+
	LK	4	+	0.14	0.33	+	3.5	9.3		-		+	3.6	9.6
	DK	5	+	0.20	0.41	0.05	4.6	10		-		0.06	4.8	11
Picea koraiensis	HW	1		+			-			-			+	
	SW	1		0.05			-			-			0.05	
	LK	1		+			-			-			+	
	DK	1		+			-			-			+	
Picea mariana	HW	2		-			-			-		+	+	+
	SW	2		-			-			-		+	+	+
	LK	2(13)		-			-			-		+	+	+
	DK	2(17)		-			-			-		+	+	+

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

Juva = Juvabione

TodoA = Todomatuic acid

4'-DeJuva = 4'-Dehydrojuvabione

Traces of 4'-dehydrotodomatuic acid in some sapwood samples of *Pinus nigra*

Traces of dihydrotodomatuic acid in knots of *Pinus roxburghii.*

Traces of α-Atlantone in all samples of *Picea mariana.*

No juvabiones were detected in *Pinus contorta* , *P. gerardiana* , *P. radiata* , *P. resinosa* , *P. sibirica* , *P. strobus* , *P. sylvestris* , *P. wallichiana* , *Picea abies* , *P. glauca* , *P. omorika* , *P. pungens* , or *P. sitchensis.*

LARIX, PSEUDOTSUGA & TSUGA		n	Concentrations of juvabiones: Juva (min)	Juva (avg)	Juva (max)	TodoA (min)	TodoA (avg)	TodoA (max)	Dihydro-TodoA (min)	Dihydro-TodoA (avg)	Dihydro-TodoA (max)	4'-DeJuva (min)	4'-DeJuva (avg)	4'-DeJuva (max)	4'-DeTodoA (min)	4'-DeTodoA (avg)	4'-DeTodoA (max)	Juvabiones total (min)	Juvabiones total (avg)	Juvabiones total (max)
			mg/g dry wood																	
L. decidua	HW	5	-	+	+	-	+	+		-			-			-		-	+	+
	SW	5	-	+	+	-	+	+		-			-			-		-	+	+
	LK	7(10)	-	+	+	-	+	+		-			-			-		-	+	+
	DK	11(15)	-	+	+	-	+	+		-		-	+	+		-		-	+	+
L. gmelinii	HW	2		-		+	+	+		-			-		-	+	+	+	+	+
var. *gmelinii*	SW	2	+	+	+	+	+	+		-		-	+	+		-		+	+	+
	LK	2	+	+	+	0.26	0.37	0.48		-		+	+	+	+	+	0.08	0.38	0.43	0.49
	DK	2	+	+	+	0.30	0.32	0.35		-			-			-		0.33	0.34	0.35
L. gmelinii	HW	2		-		+	+	+		-			-		-	+	+	+	+	+
var. *japonica*	SW	2	-	+	+	+	+	+		-			-			-		+	+	+
	LK	2	+	+	+	0.56	0.68	0.79		-			-		0.19	0.28	0.37	0.76	0.96	1.2
	DK	3	+	+	+	0.26	0.41	0.60		-			-		0.10	0.19	0.31	0.38	0.62	0.92
L. gmelinii	HW	2	-	+	+	+	+	+		-			-			-		+	+	+
var. *olgensis*	SW	2	-	+	+	+	+	+		-			-			-		+	+	+
	LK	2	+	+	+	0.08	0.16	0.24		-			-		+	0.05	0.05	0.17	0.24	0.32
	DK	2	+	+	+	0.25	0.42	0.58		-			-		0.06	0.08	0.09	0.33	0.50	0.68
L. sibirica	HW	6		-		-	+	+		-			-			-		-	+	+
	SW	6		-		-	+	+		-			-			-		-	+	+
	LK	1		-			-			-			-			-			-	
	DK	10		-		-	0.06	0.27		-			-			-		-	0.06	0.27
P. menziensii	HW	2		-			-		0.31	0.38	0.46		-			-		0.31	0.38	0.46
	SW	2		-			-		+	+	+		-			-		+	+	+
	LK	2(11)		-			-		5.1	5.2	5.4		-			-		5.1	5.2	5.4
	DK	2(11)		-			-		3.4	4.2	5.0		-			-		3.4	4.2	5.0
T. heterophylla FI	Dead branch	1		+			+			-			-			-			+	
	DK	1		+			+			-			+			+			+	
T. mertensiana	LK	1		+			+			-			-			+			+	
	HW of branch	1		+			+			-			-			-			0.06	
	SW of branch	1		+			+			-			+			-			+	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)
Juva = Juvabione
TodoA = Todomatuic acid
Dihydro-TodoA = Dihydrotodomatuic acid
4'-DeJuva = 4'-Dehydrojuvabione
4'-DeTodoA = 4'-Dehydrotodomatuic acid
No juvabiones were detected in *Larix kaempferi, L. lariciana, Tsuga canadensis* or *T. heterophylla* CA.

D5 Other lipophilic compounds

PINUS			Concentration of other lipophilic compounds											
			Thunbergol			Thunbergene			Manoyl oxide			Squalene		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
P. banksiana	HW	2		-			-			-		+	+	+
	SW	2		-			-			-		+	+	+
	LK	2(5)		-			-			-		0.10	0.11	0.11
	DK	1		-			-			-			0.13	
P. contorta	HW	2		-			-			-		+	+	+
	SW	2		-			-			-		+	+	+
	LK	4		-			-			-		0.14	0.17	0.22
P. elliottii	HW	2	+	+	+	+	+	+		-		+	+	+
	SW	2	+	+	+	+	+	+		-		+	+	+
	LK	3		-			-			-		+	+	+
	DK	10		-			-			-		-	+	+
P. gerardiana	knots	300 g		-			-			-			-	
P. nigra	HW	3	0.42	1.0	1.5	+	0.07	0.12	+	+	+	+	+	+
	SW	3	0.21	0.48	0.67	+	+	+	-	+	+	+	+	+
	LK	8	0.86	17	37	+	0.64	1.3	+	0.07	0.16	-	+	+
	DK	9	5.7	20	30	0.21	1.1	2.0	0.06	0.10	0.16	-	+	+
P. pinaster	HW	3		-		+	+	+	+	+	+	+	+	+
	SW	3		-			-		-	+	+	+	+	+
	LK	9		-		+	+	+	+	0.06	0.15	+	+	0.06
	DK	9		-		+	+	+	-	0.13	0.26	+	+	0.06
P. radiata	HW	1		-			-			-			+	
	SW	1(2)		-			-			-			-	
	LK	2		-			-			-		-	+	+
	DK	1		-			-			-			-	
P. resinosa	HW	2		-			-			-		+	+	+
	SW	2		-			-			-		+	+	+
	LK	3(5)		-			-			-		0.07	0.12	0.15
	DK	3(6)		-			-			-		0.09	0.12	0.15
P. roxburghii	knots	300 g		+			-			-				
P. sibirica	HW	2	+	0.05	0.05		-			-		+	+	+
	SW	2	0.06	0.06	0.07		-			-		+	+	+
	LK	2(8)	0.13	0.22	0.31		-			-		+	+	+
	DK	2(3)	0.78	2.4	4.0		-			-		+	+	+
P. strobus	HW	2		-			-			-		+	+	0.06
	SW	2		-			-			-		+	+	+
	LK	2		-			-			-			-	
	DK	2		-			-			-		-	+	0.07
P. sylvestris	HW	2	+	+	+		-			-		+	+	+
	SW	2	-	+	+		-			-		+	+	+
	LK	2		-			-			-		+	+	+
	DK	2	+	+	+		-			-		+	+	+
P. taeda	HW	1		+			+			-			+	
	SW	2	+	+	+	+	+	+		-		+	+	+
	LK	4		-			-			-		+	+	+
	DK	5		-			-			-		+	+	+
P. wallichiana	knots	300 g		0.32			0.38			-			-	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)

PICEA			Concentration of other lipophilic compounds											
			Thunbergol			Manool			Manoyl oxide			Squalene		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
P. abies FI[1]	HW	2	+	+	+	+	+	+		-		+	+	+
	SW	2	+	+	+	+	+	+		-		+	+	+
	LK	2	+	+	+	+	+	+		+		+	+	+
	DK	2	+	+	0.07	+	+	0.06		+		+	+	+
P. abies FR	HW	1		+			-			-			+	
	SW	1		+			-			-			+	
	LK	1(3)		+			-			-			+	
	DK	1(5)		0.16			-			-			+	
P. glauca	HW	2	-	+	+	+	+	+		-		+	+	+
	SW	2		-		+	+	+		-		+	+	+
	LK	3(5)	-	+	+	+	+	+		-		+	+	+
	DK	2(5)	-	+	+	+	0.06	0.09		-		+	+	+
P. koraiensis	HW	1		-			-		+	+	+	+	+	+
	SW	1		-			-		+	+	+	+	0.06	0.08
	LK	1		-			-			-			+	
	DK	1		-			-			+			+	
P. mariana	HW	2		-		+	0.05	0.06	+	+	+	+	+	+
	SW	2		-		+	0.05	0.09	+	+	+	+	+	+
	LK	2(13)		-		0.16	0.22	0.28	+	+	+	+	0.09	0.17
	DK[2]	2(17)		-		1.8	2.3	2.9	0.08	0.10	0.12	+	+	0.07
P. omorika	HW	1		-		+	+	+		-		-	+	+
	SW	1		+			0.13			-			+	
	LK	1(2)		-			5.3			-			-	
	DK	1		-			0.45			-			+	
P. pungens	HW	2	-	0.08	0.23		-		+	+	+	+	+	+
	SW	2	+	0.19	0.36		-		+	+	+	+	+	+
	LK	7(11)		-			-		+	+	+	-	+	+
	DK	9		-			-		+	+	+	+	+	+
P. sitchensis	HW	2		-		+	0.06	0.10		-		+	+	+
	SW	2		-		+	+	0.06		-		+	+	+
	LK	2(3)		-		+	+	0.05		-		+	+	+
	DK	2(3)		-		+	0.48	0.94		-		+	+	+

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

[1] Traces of thunbergene in LK and traces of epimanoyloxide in both LK and DK.

[2] Manool overlaps with abienol in DK.

ABIES			Concentration of other lipophilic compounds											
			Thunbergol			Manool			Manoyl oxide			Squalene		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
A. alba	HW	4	-	+	+	-	+	+		+	+	+	+	+
	SW	4	-	+	+	+	+	+		+	+	+	+	+
	LK	11	-	+	+	+	+	+	-	+	+	-	+	+
	DK	11(13)	-	+	+	+	1.7	7.8	-	+	+	+	+	+
A. amabilis	HW	1		-			+			+			+	
	SW	1		-			0.07			+			+	
	LK	2		-		+	+	+	+	+	+	+	+	+
	DK	1(2)		-			+			+			+	
A. balsamea	Stem	3	+	+	+		-			-		+	+	+
	LK	1(2)		+			-			-			+	
	DK	1(4)		+			-			-			+	
A. concolor	HW	1		-			-			-			+	
	LK	1(2)		-			-			-			+	
A. lasiocarpa	HW	2		-			-			-		+	+	+
	SW	2		-			-			-		+	+	+
	LK	2(16)		-			-			-		+	+	+
	DK	2(15)		-			-			-		+	+	+
A. pindrow [1]	Knots	300 g		-			0.62			0.05			+	
A. sachalinensis	HW	1		-			-			-			+	
	SW	1		-			-			-			+	
	LK	1(2)		-			-			-			+	
	DK	1		-			-			-			+	
A. sibirica	HW	2	-	+	+	+	+	+		-		+	+	+
	SW	2	-	+	+		-			-		+	+	+
	LK	2(6)	-	+	+	0.07	0.07	0.07		-		+	+	+
	DK	2(3)	+	+	+	1.1	1.6	2.1		-		+	+	+
A. veitchii	HW	1		-			+			+			+	
	SW	1		-			+			+			+	
	LK	1(2)		-			+			+			+	
	DK	1		-			1.1			0.80			+	

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

[1] Traces of thunbergene in the knots.

LARIX, PSEUDOTSUGA & TSUGA		n	Concentration of other lipophilic compounds																	
			Thunbergol			Manool			Manoyl oxide			Larixol			Larixyl acetate			Squalene		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
			mg/g dry wood																	
L. decidua [1]	HW	5	-	+	+	+	0.08	0.12	-	+	+		-		-	0.14	0.75	+	+	+
	SW	5	-	+	+	+	0.17	0.33		-			-		-	0.37	2.0	-	+	+
	LK	7(10)	-	+	+	+	0.28	1.1	-	+	+		-		-	0.14	1.3	+	+	+
	DK	11(15)	-	+	0.15	+	0.55	4.4	-	+	+		-		-	0.25	5.9	+	+	+
L. gmelinii	HW	2		-		0.14	0.16	0.19	-	+	+	+	0.06	0.08	0.74	0.83	0.93	+	+	+
var. *gmelinii*	SW	2		-		0.10	0.17	0.24	-	+	+	0.05	0.07	0.09	0.56	0.84	1.1	+	+	+
	LK	2		-		0.56	0.77	0.97	+	+	+	0.72	0.94	1.1	0.87	1.4	1.8	+	+	+
	DK	2		-		0.22	0.70	1.2	+	+	+	0.34	1.0	1.7	0.18	0.54	0.91	+	+	+
L. gmelinii	HW	2		-		0.07	0.23	0.38	-	+	+	+	0.08	0.12	0.29	0.70	1.1	+	+	+
var. *japonica*	SW	2		-		0.10	0.28	0.45	+	+	+	+	0.07	0.10	0.39	0.91	1.4	+	+	+
	LK	2		-		0.38	0.48	0.58	+	+	+	0.13	0.24	0.35	0.17	0.35	0.53	+	+	+
	DK	3		-		0.28	1.1	1.9	+	+	+	0.15	1.2	1.8	0.19	0.92	1.8	+	+	+
L. gmelinii	HW	2		-		0.40	0.46	0.52	+	+	+	0.19	0.21	0.22	1.0	1.0	1.1	+	+	+
var. *olgensis*	SW	2		-		0.26	0.59	0.92	+	+	+	0.09	0.15	0.22	0.72	1.2	1.7	+	+	+
	LK	2		+		0.13	0.32	0.50	+	+	+	0.08	0.24	0.40	0.26	0.68	1.1	+	+	+
	DK	2		-		2.2	3.6	5.0	+	0.09	0.13	2.1	4.4	6.7	0.92	1.0	1.1	+	+	+
L. kaempferi	HW	3	0.32	0.42	0.47	0.31	0.40	0.57		-		+	+	0.06	+	0.29	0.52	+	+	+
	SW	3	0.31	0.33	0.35	0.23	0.27	0.31		-		+	+	0.11	+	0.28	0.42	+	+	+
	LK	9	0.06	0.22	0.38	0.12	0.42	0.72		-		+	0.08	0.38	+	0.13	0.39	+	+	+
	DK	22	0.22	3.9	18	-	6.3	30		-		-	0.55	4.6	-	0.70	3.9	-	+	0.16
L. lariciana	HW	2	+	+	+	+	+	+	+	+	+		-		+	0.05	0.05	+	+	+
	SW	2	+	+	+	+	0.06	0.06	+	+	+		-		+	0.07	0.07	+	+	+
	LK	2	+	+	+	+	+	+	+	+	+		-		+	+	+	+	+	+
	DK	2(3)	+	+	+	0.05	0.43	0.81	+	+	+		-		0.06	0.27	0.49	+	+	+
L. sibirica [2]	HW	6	-	0.11	0.36	-	0.08	0.22	-	+	+	-	+	0.24	+	0.30	0.92	-	+	0.07
	SW	6	-	0.17	0.53	-	0.07	0.15	-	+	+	-	+	0.10	+	0.22	0.66	-	+	0.06
	LK	1		3.2			0.23			0.12			-			0.26			0.10	
	DK	10	-	0.27	2.7	-	+	0.38	-	+	0.07	-	+	0.63	+	+	0.45	-	+	0.08
P. menziensii	HW	2	+	+	+		-			-			-			-		+	+	+
	SW	2	+	+	+		-			-			-			-		+	+	+
	LK	2(11)	+	0.06	0.06		-			-			-			-		+	+	+
	DK	2(11)	0.58	0.79	1.0		-			-			-			-		+	+	+

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

Traces of thunbergene in all samples of *L kaempferi,* and in all samples of *L. sibirica* where thunbergol was detected.

Traces of squalene in all samples of *T. canadensis* and *T. heterophylla* CA.

Traces of thunbergol and squalene in all samples of *T. heterophylla* FI.

Traces of thunbergol in all samples, and of squalene in the living knot of *T. mertensiana.*

[1] Three unidentified diterpene alcohols in trees from France.

[2] No thunbergol in trees from Habarovsk.

D6 Stilbenes

PINUS			Concentration of stilbenes											
			PS[1]			PSMME[1]			PSDME			Dihydro-PS		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
P. banksiana	HW	2	1.0	1.8	2.6	4.8	5.0	5.2		-			-	
	SW	2	+	+	+	+	+	+		-			-	
	LK	2(5)	2.1	2.4	2.7	16	16	17		-			-	
	DK	1		1.7			9.2			-			-	
P. contorta	HW	2	1.7	1.8	1.9	2.1	2.2	2.3	+	0.06	0.08		-	
	SW	2	+	+	+	+	+	0.06	+	+	+		-	
	LK	4	1.0	2.0	3.1	1.8	3.1	4.5	0.15	0.28	0.43		-	
P. elliottii	HW	2	1.3	2.3	3.3	6.2	9.8	13	0.79	1.8	2.7	+	+	+
	SW	2	+	+	+	+	+	+	+	+	0.07	+	+	+
	LK	3	0.93	4.6	7.5	2.0	9.8	15	0.47	0.54	0.61		-	
	DK	10	1.2	4.2	8.8	2.8	10	17	0.33	0.79	1.5		-	
P. gerardiana	knots	300 g		0.39			6.0			0.20			0.05	
P. nigra	HW	3	3.3	8.1	13	8.8	17	27	0.10	0.34	0.79		-	
	SW	3	+	+	0.06	+	+	+	+	+	+		-	
	LK	8	1.7	14	33	3.5	18	40	0.08	0.24	0.47	-	+	+
	DK	9	6.6	16	24	14	23	32	0.28	0.60	0.95	-	+	+
P. pinaster	HW	3	0.07	0.09	0.11	0.80	0.95	1.2		-			-	
	SW	3	-	+	+	-	+	+		-			-	
	LK	9	0.80	1.7	2.7	1.4	2.4	4.0		-			-	
	DK	9	1.6	2.5	4.0	3.5	4.4	5.7		-			-	
P. radiata[2]	HW	1		1.0			3.6			-			-	
	SW	1(2)		-			+			-			-	
	DK	1		1.9			3.7			-			-	
P. resinosa	HW	2	3.8	5.1	6.5	12	15	17		-			-	
	SW	2	+	+	+	+	+	+		-			-	
	LK	3(5)	8.7	11	14	23	35	42		-			-	
	DK	3(6)	8.3	12	14	23	37	45		-			-	
P. roxburghii	knots	300 g		0.10			+			-			+	
P. sibirica	HW	2	0.45	0.46	0.46	5.7	5.9	6.1	0.06	0.06	0.07	0.13	0.13	0.14
	SW	2	+	+	+	+	+	+	+	+	+		-	
	LK	2(8)	4.0	4.7	5.4	56	63	70	0.40	0.50	0.60	2.6	3.1	3.6
	DK	2(3)	4.0	4.3	4.5	44	47	51	0.30	0.31	0.31	3.0	3.2	3.4
P. strobus	HW	2	-	2.3	4.6	5.5	10	15		-		-	+	+
	SW	2	-	0.27	0.54	+	+	+		-			-	
	LK	2	12	16	20	88	109	130		-		1.2	3.3	5.4
	DK	2	4.3	5.7	7.2	43	56	69		-		1.1	1.5	1.8
P. sylvestris	HW	2	4.2	4.6	5.0	6.1	6.7	7.4	+	+	+		-	
	SW	2	+	+	+	+	+	+	+	+	+		-	
	LK	2	13	16	19	37	40	43	0.11	0.14	0.17		-	
	DK	2	3.8	6.7	9.6	14	19	23	+	0.09	0.18		-	
P. taeda	HW	1		2.5			17			1.9			-	
	SW	2	+	+	+	+	+	+	+	+	+		-	
	LK	4	+	2.4	5.9	0.08	9.2	23	+	0.57	1.2		-	
	DK	5	+	3.9	8.1	0.17	16	32	+	1.0	2.0		-	
P. wallichiana	knots	300 g		1.1			8.2			0.14			0.67	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)
[1] Sum of two isomers.
[2] No stilbenes detected in the living knots of *P. radiata*.

PS = Pinosylvin
PSMME = Pinosylvin monomethyl ether
PSDME = Pinosylvin dimethyl ether
Dihydro-PS = Dihydropinosylvin

Concentration of stilbenes (cont.)												
Dihydro-PSMME[1]			Hydroxy-PSMME[1]			Hydroxy-PSDME[1]			Stilbenes total		
min	avg	max	min	avg	max	min	avg	max	min	avg	max
mg/g dry wood											
	-			-			-		6.2	6.8	7.5
	-			-			-		+	+	+
	-			-			-		18	19	20
	-			-			-			11	
	-		+	+	+		-		4.0	4.1	4.1
	-		+	+	+		-		+	0.05	0.07
	-		+	0.07	0.13		-		3.0	5.4	8.0
+	+	+	0.07	0.12	0.16	+	0.23	0.42	8.5	14	20
+	+	+	+	+	+	+	+	+	+	0.08	0.12
	-		0.07	0.34	0.60	0.14	1.4	2.5	3.6	17	26
	-		0.18	0.41	0.69	0.36	1.4	2.5	4.8	17	29
	0.27			0.17			0.14			7.2	
	-		-	0.14	0.22	0.53	0.72	0.86	13	26	37
	-		-	+	+	+	+	+	0.07	0.09	0.11
	-		+	0.05	0.14	0.19	0.92	2.1	5.4	34	76
	-		+	0.06	0.09	0.36	1.3	2.0	23	42	55
	-			-			-		0.89	1.0	1.3
	-			-			-		+	+	0.05
	-		-	+	+	+	0.14	0.44	2.3	4.2	7.1
	-		-	+	+	0.14	0.22	0.28	5.3	7.1	7.9
	-			-			-			4.6	
	-			-			-			+	
	-			-			-			5.6	
	-		0.23	0.24	0.25	0.43	0.45	0.48	16	20	24
	-		+	+	+	+	+	+	+	+	+
	-		0.62	1.2	1.4	1.3	2.0	2.6	32	47	54
	-		1.4	1.6	1.7	2.0	2.4	2.7	32	49	58
	+			-			-			0.18	
1.6	1.7	1.8		-			-		8.0	8.2	8.5
+	+	+		-			-		+	+	+
48	49	51		-			-		110	120	130
22	32	43		-			-		74	88	101
0.50	0.86	1.2		-			-		11	13	16
+	+	+		-			-		+	0.29	0.56
8.5	18	28		-			-		110	147	184
9.7	11	13		-			-		58	75	91
	-		0.09	0.11	0.13	0.08	0.12	0.16	11	11	12
	-		+	+	+	+	+	+	+	+	+
	-		0.60	1.1	1.6	1.7	2.0	2.3	51	57	63
	-		0.51	0.83	1.2	0.69	1.1	1.5	18	25	32
	+			-			0.08			21	
+	+	+		-			-		+	+	+
	-		+	+	0.06	+	0.16	0.46	0.14	12	31
	-		+	0.09	0.30	+	0.29	0.61	0.22	21	43
	3.3			+			-			13	

Dihydro-PSMME = Dihydropinosylvin monomethyl ether
Hydroxy-PSMME = Hydroxypinosylvin monomethyl ether
Hydroxy-PSDME = Hydroxypinosylvin dimethyl ether
[1] Sum of two isomers.

D7 Lignans and oligolignans

N.B. Tables continue on several pages!

PINUS			Concentration of lignans															
			Coni			ConiA			HMR[1]			cLari			Lari		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood															
P. banksiana	HW	2	-	+	+		-		+	+	+	0.10	0.10	0.10	+	+	+
	SW	2	+	+	+		-		+	+	+	+	+	+	+	+	+
	LK	2(5)	0.05	0.06	0.06		-		0.35	0.36	0.38	0.51	0.53	0.55	+	+	+
	DK	1		+			-			+			0.16			+	
P. contorta	HW	2		-			-			-			-			-	
	SW	2		-			-			-			-			-	
	LK	4		-			-			-			-			-	
P. elliottii	HW	2	+	+	+		-		+	0.06	0.12	0.12	0.14	0.15	+	+	+
	SW	2	+	+	+		-		+	+	+	+	+	+	+	+	+
	LK	3	+	+	+	0.59	1.1	1.6	+	+	+	0.09	0.15	0.20	0.09	0.15	0.20
	DK	10	+	+	0.09	0.29	0.68	1.3	+	0.06	0.36	-	0.63	4.2	0.10	0.38	0.74
P. gerardiana	knots	300 g		-			-			-			1.6			0.24	
P. nigra	HW	3		-			-			-		-	0.08	0.15	-	0.06	0.09
	SW	3		-			-			-		-	+	+	+	+	0.06
	LK	8	-	+	+	+	0.07	0.20	0.07	0.35	0.94	+	0.08	0.20	+	0.16	0.44
	DK	9	-	0.06	0.13	+	0.08	0.14	0.08	0.20	0.37	+	0.11	0.20	+	0.10	0.19
P. pinaster	HW	3		-			-			-		0.15	0.21	0.27		-	
	SW	3		-			-		-	+	+	+	+	+		-	
	LK	9	0.09	0.21	0.35		-		0.29	0.45	0.72	0.10	0.37	0.69	+	0.70	1.7
	DK	9	0.13	0.16	0.21		-		0.34	0.54	0.74	0.40	0.81	1.2	0.18	0.76	1.7
P. radiata	HW	1		-			-			-			-			-	
	SW	1(2)		-			-			+			+			-	
	LK	2		-			-			-		-	+	+		-	
	DK	1		-			-			-			0.12			0.11	
P. resinosa	HW	2		-			-		+	+	+	+	+	+	+	+	+
	SW	2	+	+	+		-		+	+	+	+	+	+	+	+	+
	LK	3(5)		-			-		0.08	0.53	0.77	0.08	0.22	0.30	0.06	0.08	0.10
	DK	3(6)	-	+	+		-		0.09	0.62	0.91	+	0.24	0.37	+	0.10	0.13
P. roxburghii	knots	300 g		-			-			-			+			+	
P. sibirica	HW	2	+	+	+	+	+	0.05	0.11	0.12	0.12	0.34	0.35	0.36	0.41	0.48	0.56
	SW	2	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	LK	2(8)	-	+	+	+	+	+	1.2	1.3	1.4	4.3	4.6	4.9	37	38	38
	DK	2(3)		-		0.05	0.13	0.20	0.54	0.94	1.3	2.8	4.0	5.3	16	23	29
P. strobus	HW	2		-			-			-		0.09	0.15	0.22	-	+	+
	SW	2		-			-			-			-		+	+	+
	LK	2		-			-			-		0.99	1.8	2.5	5.7	7.9	10
	DK	2		-			-			-		3.9	4.5	5.1	0.99	1.4	1.7
P. sylvestris	HW	2		-			-		+	+	+	+	+	0.05	+	+	+
	SW	2		-			-		+	+	+	+	+	+	+	+	+
	LK	2		-			-		+	+	+	0.11	0.17	0.23	-	+	+
	DK	2		-			-		+	+	+	0.16	0.18	0.21	+	+	+
P. taeda	HW	1		+			0.14			+			0.06			+	
	SW	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	LK	4	+	+	0.06	+	0.26	0.63	+	+	+	+	+	0.14	+	0.06	0.15
	DK	5	+	+	+	+	0.39	0.60	+	+	+	+	0.11	0.20	+	0.09	0.17
P. wallichiana	knots	300 g		-			-			-			1.9			0.47	

\- not detected

\+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

Traces of seco DME in some HW and DK samples of *P. nigra* and in some DK samples of *P. pinaster*.

[1] Sum of two isomers.

Coni = α-Conidendrin

ConiA = α-Conidendric acid

HMR = 7-Hydroxymatairesinol

cLari = Cyclolariciresinol

Lari = Lariciresinol

Concentration of lignans (cont.)																					
Hydroxy-Lari			Lig A			MR			NTG			Pino			Seco			Seco MME		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
mg/g dry wood																				
	-			-			+		+	+		+	0.07	0.09	0.10	0.17	0.17	0.17		-	
	-			-			+		+	+		+	0.07	0.10	0.13	+	+	+		-	
	-			-			0.51	0.60	0.70	15	16	17	0.10	0.10	0.10	0.67	0.79	0.91		-	
	-			-				1.2			4.4			0.07			0.52			-	
	-			-				-		+	+	+	+	+	+	+	0.08	0.13		-	
	-			-				-		+	+	+	+	+	+	+	+	+		-	
	-			-				-		0.61	1.2	2.1	+	0.10	0.19	0.12	0.21	0.27		-	
	-			-			+	+	+	0.09	0.22	0.35	+	+	+	+	0.06	0.07		-	
	-			-			+	+	+	+	+	+	+	+	+	+	+	+		-	
	-			-			1.2	10	20	1.7	4.3	7.0	+	0.06	0.10	0.23	1.8	3.3		-	
	-			-			0.12	14	33	1.7	18	60	+	0.11	0.24	+	2.2	5.9		-	
	-			-				-			-			0.08			+			-	
	-			-				-		-	0.20	0.46		-		-	0.20	0.29		-	
	-			-				-		-	+	+		-			-			-	
	-			-			0.11	11	31	3.3	27	74	0.08	0.31	0.67	0.17	0.65	1.5	-	+	+
	-			-			0.39	9.7	26	8.3	22	39	+	0.17	0.29	0.33	0.86	1.3	-	0.05	0.07
	-			-				-		+	0.25	0.40	-	+	0.10		-			-	
	-			-			-	+	+	-	+	+	+	+	+	+	+	+		-	
	-		0.11	0.34	0.58	0.20	0.38	0.64	11	27	50	0.12	1.8	5.8	0.48	0.82	1.3	-	+	+
	-		0.42	0.49	0.61	+	0.34	0.68	30	40	47	0.39	2.3	6.4	0.58	1.0	1.9	-	+	0.09
	-			-				-			-			-			-			-	
	-			-				-			-			-			-			-	
	-			-				-			-			-			-			-	
	-			-				-			0.59			+			0.21			-	
-	+	+		-			+	0.06	0.11		-		+	+	+	+	+	+		-	
-	+	+		-			+	+	+		-		+	+	+	+	+	+		-	
0.36	0.39	0.41		-			1.0	5.0	12	-	0.57	1.7	0.11	0.27	0.47	0.42	0.51	0.56		-	
0.22	0.28	0.35		-			1.4	6.8	17	-	0.44	1.3	0.08	0.32	0.54	0.49	0.62	0.75		-	
	-			-				-			2.4			+			0.17			-	
	-			-			+	+	+		-		0.08	0.09	0.11	0.15	0.16	0.17		-	
	-			-			-	+	+		-		+	+	+	+	+	+		-	
	-			-			1.3	1.4	1.4		-		0.87	0.91	0.95	3.4	3.8	4.3		-	
	-			-			0.38	1.3	2.3		-		0.58	0.76	0.93	0.63	2.5	4.3		-	
	-			-				-			-			-			-			-	
	-			-				-			-			-			-			-	
	-			-				-			-			-			-			-	
	-			-				-			-			-			-			-	
	-			-				-		+	+	+	+	+	+	+	+	+		-	
	-			-				-		+	+	+	+	+	+	+	+	+		-	
	-			-				-		12	22	32	+	0.06	0.10	0.16	0.49	0.82		-	
	-			-				-		5.9	16	25	+	0.09	0.13	0.06	0.29	0.52		-	
	-			-				+			0.96			+			+			-	
	-			-			+	+	+	+	+	+	+	+	+	+	+	+		-	
	-			-			-	+	+	0.09	16	46	+	0.07	0.17	+	0.31	0.85		-	
	-			-			-	+	+	0.16	23	46	+	0.10	0.20	+	0.39	0.77		-	
	-			-				-			-			0.08			0.17			-	

Hydroxy-Lari = Hydroxylariciresinol
Lig A = Lignan A
MR = Matairesinol
NTG = Nortrachelogenin
Pino = Pinoresinol
Seco = Secoisolariciresinol
Seco MME = 4-Monomethylsecoisolariciresinol

Continues on next page!

PINUS			Concentration of lignans (cont.)									Concentration of oligolignans								
			Todo A			Unknown			Lignans total			Sesquilignans			Dilignans			Sesterlignans		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood																	
P. banksiana	HW	2	0.14	0.21	0.28		-		0.59	0.65	0.72	0.52	0.63	0.74	0.10	0.12	0.13	0.08	0.10	0.11
	SW	2	+	+	0.06		-		0.14	0.20	0.27	-	+	0.10	-	+	+	-	+	0.09
	LK	2(5)	0.34	0.68	1.0		-		19	19	20	2.0	2.1	2.1	1.4	1.4	1.4	0.32	0.33	0.34
	DK	1		0.15			-			6.5			0.80			0.41			0.17	
P. contorta	HW	2	0.09	0.12	0.14		-		0.25	0.27	0.29	0.07	0.10	0.12	0.13	0.14	0.15		-	
	SW	2	+	+	+		-		+	+	+	0.06	0.06	0.07	+	+	+	0.17	0.18	0.19
	LK	4	0.13	0.52	1.0		-		0.98	2.0	3.5	0.16	0.25	0.34	0.14	0.26	0.38	-	+	0.17
P. elliottii	HW	2	0.15	0.28	0.42		-		0.46	0.80	1.1	0.47	0.73	0.99	0.05	0.16	0.28	0.09	0.16	0.23
	SW	2	+	+	+		-		+	+	+	0.08	0.08	0.09	+	+	+	0.17	0.18	0.19
	LK	3	0.14	0.76	1.9		-		9.5	19	28	0.72	1.7	2.7	0.26	0.98	1.7	0.50	0.70	0.91
	DK	10	0.12	0.35	1.6		-		8.0	37	69	0.89	2.7	4.0	0.25	0.62	1.3	+	0.37	1.3
P. gerardiana	knots	300 g		-			-			2.0			0.47			0.29			0.15	
P. nigra	HW	3	0.19	0.26	0.34	+	+	0.05	0.59	0.83	1.1	0.70	0.90	1.1	0.12	0.42	0.75	+	0.46	0.88
	SW	3	+	+	+	+	+	+	+	0.07	0.10	0.06	0.20	0.29	+	+	+	+	0.07	0.09
	LK	8	0.07	0.25	0.48	-	+	0.05	4.2	40	109	0.66	3.0	7.0	0.25	1.0	2.0	0.34	1.1	2.6
	DK	9	0.08	0.39	0.93	-	0.11	0.20	11	34	66	1.6	3.6	5.7	0.81	1.3	1.9	0.45	1.0	1.5
P. pinaster	HW	3	0.20	0.31	0.48		-		0.41	0.81	1.1	0.58	0.76	1.0	0.06	0.10	0.14	+	+	+
	SW	3	+	+	0.06	-	+	+	+	0.07	0.12	0.09	0.28	0.46	+	0.07	0.15	+	0.05	0.08
	LK	9	0.15	0.30	0.47		-		13	32	56	2.1	3.7	5.7	0.44	0.64	0.90	0.08	0.11	0.13
	DK	9	0.19	0.25	0.36		-		37	46	53	3.6	4.9	6.5	0.67	0.94	1.4	0.10	0.22	0.51
P. radiata	HW	1		-			+			+			1.1			0.42			0.50	
	SW	1(2)		-			+			+			0.24			0.28			1.7	
	LK	2		-			-		-	+	+	0.36	0.75	1.1	0.34	0.36	0.38	1.6	1.7	1.8
	DK	1		0.19			0.15			1.4			0.42			0.25			0.45	
P. resinosa	HW	2	0.21	0.22	0.24	+	0.07	0.13	0.35	0.45	0.54	0.20	0.25	0.30	0.08	0.10	0.11	0.19	0.23	0.26
	SW	2	+	+	+	+	+	+	0.06	0.08	0.09	0.07	0.08	0.20	+	+	0.11	0.10	0.11	0.26
	LK	3(5)	0.33	2.7	3.9	-	0.82	1.5	7.1	10	15	0.86	2.6	3.6	0.43	1.0	1.5	0.27	0.50	0.70
	DK	3(6)	0.52	3.6	5.3	-	0.73	1.2	8.7	13	20	0.93	3.0	4.0	0.56	1.2	1.5	0.64	0.69	0.74
P. roxburghii	knots	300 g		-			-			2.6			0.43			0.09			+	
P. sibirica	HW	2	0.60	0.62	0.64	0.09	0.11	0.12	1.9	2.0	2.1	0.45	0.48	0.51	0.28	0.29	0.30		-	
	SW	2	+	+	+	+	+	+	0.07	0.07	0.07	+	+	+	0.07	0.07	0.07	0.38	0.39	0.39
	LK	2(8)	0.39	0.40	0.40		-		50	50	50	5.4	5.8	6.1	1.6	1.8	2.0	0.42	0.93	1.4
	DK	2(3)	0.17	0.32	0.47		-		21	33	44	2.6	3.5	4.3	0.82	1.3	1.9	-	0.25	0.51
P. strobus	HW	2		-			-		0.09	0.17	0.26	0.55	0.72	0.88	0.39	0.42	0.44	0.42	0.50	0.57
	SW	2		-			-		+	+	+	0.10	0.14	0.18	0.06	0.07	0.08	0.16	0.17	0.19
	LK	2		-			-		6.7	9.7	13	2.0	2.9	3.9	1.7	1.9	2.1	2.4	2.5	2.6
	DK	2		-			-		4.9	5.9	6.8	2.1	2.7	3.3	0.97	1.2	1.4	1.6	1.7	1.7
P. sylvestris	HW	2	+	0.07	0.09	0.20	0.21	0.23	0.38	0.40	0.42	0.33	0.34	0.35	+	+	+	0.07	0.07	0.07
	SW	2	+	+	+	+	+	+	+	0.06	0.07	0.05	0.07	0.09	+	+	+	0.17	0.22	0.26
	LK	2	0.38	0.41	0.44	0.67	1.0	1.3	14	25	35	0.86	1.5	2.1	1.1	1.7	2.2	-	0.34	0.67
	DK	2	0.08	0.09	0.10	0.70	1.1	1.4	7.0	17	28	1.3	2.1	2.9	0.32	0.89	1.5		-	
P. taeda	HW	1		0.26			-			1.5			-			-			-	
	SW	2	+	+	+		-		+	+	0.06		-			-			-	
	LK	4	+	0.10	0.22		-		0.17	17	48		-			-			-	
	DK	5	+	0.14	0.26		-		0.23	24	49		-			-			-	
P. wallichiana	knots	300 g		-			-			2.6			0.32			0.24			0.07	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)
Todo A = 7-Todolactol A

PICEA, PSEUDOTSUGA & TSUGA			Concentration of lignans													
			Coni			ConiA			HMR[1]			cLari			Lari		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood														
Picea abies FI	HW	2	+	+	+	+	+	+	0.06	0.23	0.39	+	+	+	+	+	0.06
	SW	2	+	+	+	+	+	+	+	0.15	0.28	+	+	+	+	+	+
	LK	2	4.9	5.4	5.9	1.2	1.4	1.7	77	81	84	0.42	0.46	0.51	1.7	2.4	3.1
	DK	2	3.2	4.3	5.4	0.97	1.2	1.5	70	75	79	0.39	0.44	0.48	1.7	1.8	1.8
Picea abies FR	HW	1		0.55			0.34			9.8			0.11			0.44	
	SW	1		-			+			+			+			+	
	LK	1(3)		4.2			2.1			105			0.16			1.6	
	DK	1(5)		3.1			1.1			50			+			1.2	
Picea glauca	HW	2	-	+	+	+	+	+	+	+	0.06	+	+	+	+	+	+
	SW	2		-		+	+	+	+	+	+		-		+	+	+
	LK	3(5)	1.7	2.0	2.6	0.40	0.70	1.1	37	47	55	-	0.09	0.23	0.54	0.63	0.73
	DK	2(5)	3.6	3.8	3.9	0.69	0.86	1.0	70	74	77	+	0.15	0.26	0.83	0.91	1.00
Picea koraiensis	HW	1		0.40			0.08			2.7			0.13			0.09	
	SW	1		+			+			+			+			+	
	LK	1		14			3.0			89			0.61			3.2	
	DK	1		16			2.9			75			0.75			2.4	
Picea mariana	HW	2	-	0.06	0.13		-		0.18	0.59	0.99	0.13	0.17	0.21	0.09	0.11	0.13
	SW	2	+	+	+		-		+	0.06	0.10	+	+	+	+	+	+
	LK	2(13)	1.1	2.4	3.7		-		14	31	48	0.23	0.28	0.34	0.62	0.89	1.2
	DK	2(17)	2.1	2.7	3.2		-		11	17	23	0.50	0.89	1.3	0.43	0.62	0.81
Picea omorika	HW	1		0.11			+			0.63			0.15			+	
	SW	1		+			+			0.05			+			+	
	LK	1(2)		2.6			1.0			15			0.24			0.43	
	DK	1		2.0			0.49			11			0.31			0.48	
Picea pungens	HW	2		-			-		+	0.21	0.40	+	0.06	0.09	0.14	0.21	0.29
	SW	2		-			-		+	+	+	+	+	+	+	+	+
	LK	7(11)		-			-		0.81	1.4	1.9	-	0.10	0.13	0.28	0.32	0.36
	DK	9		-			-		0.78	1.6	2.1	0.06	0.15	0.23	0.31	0.67	1.1
Picea sitchensis	HW	2		-			-		0.10	0.32	0.55	0.06	0.12	0.18	0.17	0.30	0.43
	SW	2		-			-		+	+	+	+	+	+	+	+	+
	LK	2(3)		-			-		2.0	2.8	3.7	0.13	0.23	0.31	0.13	0.28	0.36
	DK	2(3)		-			-		2.2	2.4	2.6	0.25	0.31	0.37	0.21	0.31	0.41
Pseudotsuga menziesii	HW	2	+	+	+		-		+	+	+	1.9	1.9	1.9	+	0.05	0.07
	SW	2	-	+	+		-		+	+	+	+	+	+	+	+	0.08
	LK	2(11)	+	+	+		-		0.18	1.1	2.0	2.9	29	55	0.12	2.5	4.9
	DK	2(11)	-	+	+		-		0.13	0.99	1.8	2.4	24	46	0.09	1.5	3.0
T. canadensis	HW	2	0.10	0.28	0.47		-		0.13	0.41	0.68		-		+	0.09	0.14
	SW	2		-			-		+	+	+	-	+	+	+	+	+
	LK	2	5.8	7.0	8.1		-		112	117	122	1.4	1.7	2.0	3.1	3.3	3.4
	DK	2	5.4	9.8	14		-		68	78	88	1.3	1.8	2.2	0.90	1.7	2.4
T. heterophylla CA	HW	2	0.66	1.1	1.5		-		4.5	5.0	5.6		-		0.10	0.16	0.23
	SW	2		-			-		+	+	+		-		-	+	+
	LK	2	0.92	1.7	2.4		-		63	73	83		-		0.39	0.40	0.41
	DK	2	1.2	3.0	4.8		-		99	105	112		-		0.53	0.58	0.63
T. heterophylla FI	Dead branch	1		4.1			-			14			0.37			0.52	
	DK	1		0.99			-			0.90			0.10			0.09	
T. mertensiana	LK	1		7.1			-			75			0.31			2.3	
	HW of branch	1		3.3			-			35			+			1.1	
	SW of branch	1		0.18			-			2.3			+			0.08	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)
Traces of Seco DME in SW of branch of *T. mertensiana*.
[1] Sum of two isomers.

Coni = α-Conidendrin
ConiA = α-Conidendric acid
HMR = 7-Hydroxymatairesinol
cLari = Cyclolariciresinol
Lari = Lariciresinol

Continues on next page!

PICEA, PSEUDOTSUGA & TSUGA			Concentration of lignans (cont.)																
			Hydroxy-Lari			Lig A			Lig B			MR			oxo-MR			NTG		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood																
Picea abies FI	HW	2		-		+	+	+		-		+	+	+		-			-	
	SW	2		-		+	+	+		-		+	+	+		-			-	
	LK	2		-		0.70	0.85	1.0		-		3.9	3.9	3.9		-			-	
	DK	2		-		0.96	1.5	2.0		-		2.1	2.7	3.4		-			-	
Picea abies FR	HW	1		-			0.06			-			0.62			-			-	
	SW	1		-			+			-			+			-			-	
	LK	1(3)		-			0.30			-			6.7			-			-	
	DK	1(5)		-			0.69			-			3.1			-			-	
Picea glauca	HW	2		-			-			-		+	+	+		-			-	
	SW	2		-			-			-		+	+	+		-		+	+	+
	LK	3(5)		-			-			-		1.2	1.8	2.8		-		1.2	1.7	2.4
	DK	2(5)		-			-			-		2.3	2.5	2.7		-		2.7	2.8	3.0
Picea koraiensis	HW	1		-			+			-			0.15			-			-	
	SW	1		-			-			-			+			-			-	
	LK	1		-			+			-			4.0			-			-	
	DK	1		-			+			-			3.9			-			-	
Picea mariana	HW	2		-		-	+	+		-		+	0.06	0.11		-		+	0.06	0.09
	SW	2		-		-	+	+		-		+	+	+		-		+	+	+
	LK	2(13)		-		0.16	0.41	0.65		-		0.21	0.37	0.53		-		1.1	1.8	2.4
	DK	2(17)		-		0.24	0.50	0.77		-		0.32	0.35	0.38		-		0.95	1.4	1.9
Picea omorika	HW	1		-			-			-			+			+			+	
	SW	1		-			-			-			+			+			+	
	LK	1(2)		-			-			-			0.96			0.11			0.73	
	DK	1		-			-			-			0.78			0.11			0.46	
Picea pungens	HW	2	+	0.15	0.28	+	0.07	0.12	-	+	+		-			-		+	+	0.07
	SW	2	+	0.14	0.28	+	0.06	0.10		-			-			-		+	+	+
	LK	7(11)	+	0.89	2.0	0.33	0.58	0.76	0.08	0.10	0.12		-			-		0.19	0.28	0.37
	DK	9	0.46	1.2	1.5	0.36	0.92	1.3	0.07	0.14	0.17		-			-		0.24	0.49	0.89
Picea sitchensis	HW	2	0.28	0.49	0.71		-			-			-			-		+	0.11	0.18
	SW	2	+	+	+		-			-			-			-			-	
	LK	2(3)	0.82	1.3	1.9		-			-			-			-		0.66	0.83	1.1
	DK	2(3)	0.94	1.6	2.2		-			-			-			-		0.78	0.83	0.88
Pseudotsuga menziesii	HW	2		-			-			-		0.14	0.17	0.19		-		+	+	+
	SW	2		-			-			-		+	+	+		-		+	+	+
	LK	2(11)		-			-			-		+	0.06	0.11		-		0.75	3.4	6.0
	DK	2(11)		-			-			-		-	0.11	0.22		-		1.2	2.3	3.4
T. canadensis	HW	2		-			-			-		0.15	0.21	0.28		-		0.14	0.25	0.36
	SW	2		-			-			-			-			-		-	+	+
	LK	2		-			-			-		1.6	2.9	4.3	+	+	+	3.7	4.2	4.7
	DK	2		-			-			-		0.79	5.2	9.6	+	+	+	2.6	3.0	3.4
T. heterophylla CA	HW	2	0.40	0.66	0.93	0.30	0.31	0.33		-			-			-			-	
	SW	2	-	+	+	+	+	+		-			-			-			-	
	LK	2	1.1	1.5	1.9	1.3	2.8	4.4		-			-			-			-	
	DK	2	1.8	2.1	2.5	4.0	4.8	5.6		-			-			-			-	
T. heterophylla FI	Dead branch	1		-			0.46			-			0.62			0.31			0.51	
	DK	1		-			0.06			-			0.14			0.10			0.06	
T. mertensiana	LK	1		-			1.9			-			+			0.90			0.95	
	HW of branch	1		-			1.0			-			1.7			0.51			0.60	
	SW of branch	1		-			0.06			-			0.08			+			+	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)

Hydroxy-Lari = Hydroxylariciresinol
Lig A = Lignan A
Lig B = Lignan B
MR = Matairesinol
oxo-MR = 7-Oxomatairesinol
NTG = Nortrachelogenin

Concentration of lignans (cont.)																				
Hydroxy-NTG			Pino			Seco			Todo A			iLi			Unknown			Lignans total		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
mg/g dry wood																				
	-		+	+	+	+	+	+	+	+	0.07		-		0.37	0.40	0.43	0.57	0.87	1.2
	-		+	+	+	+	+	+	+	+	0.07		-		0.10	0.16	0.21	0.22	0.45	0.69
	-		+	+	+	5.7	6.2	6.7	3.3	4.2	5.0		-		14	15	17	119	121	122
	-		+	+	0.06	4.1	6.2	8.2	3.0	4.0	5.1		-		13	15	16	110	112	113
	-			+			0.44			2.3			-			0.12			15	
	-			+			+			+			-			+			0.11	
	-			0.16			4.6			7.3			-			0.95			133	
	-			0.17			1.7			3.7			-			0.50			65	
	-		+	+	+	+	+	+	+	+	+		-		+	+	+	0.13	0.15	0.17
	-		+	+	+	+	+	+	+	+	+		-		+	+	+	0.06	0.07	0.08
	-		+	+	+	0.66	2.9	6.8	1.8	2.3	2.7		-			-		45	59	67
	-		0.10	0.10	0.10	3.5	6.6	9.7	3.1	3.2	3.2		-			-		94	95	95
	-			-			0.08			0.21			-			-			3.9	
	-			-			-			+			-			-			0.14	
	-			-			4.1			4.3			-			-			122	
	-			-			2.4			3.7			-			-			107	
	-		+	+	+	+	0.06	0.09	0.08	0.09	0.10		-		+	0.06	0.09	0.70	1.3	1.9
	-		+	+	+	+	+	+	+	+	0.07		-		+	+	0.06	0.07	0.19	0.32
	-		0.15	0.17	0.19	1.1	4.3	7.4	3.7	5.1	6.6		-		1.8	2.0	2.2	24	48	72
	-		0.45	0.48	0.50	1.4	3.1	4.8	2.0	2.0	2.1		-		1.2	2.0	2.7	20	31	41
	-			+			0.15			0.11			-			-			1.3	
	-			+			+			+			-			-			0.22	
	-			-			4.6			2.3			-			-			28	
	-			0.36			4.1			1.5			-			-			22	
	-		+	+	0.05	0.08	0.35	0.62	0.26	0.81	1.4		-		+	0.08	0.15	0.60	1.9	3.1
	-		+	+	+	+	+	+	+	0.05	0.07		-		+	+	+	0.13	0.18	0.24
	-		+	+	+	5.4	8.0	10	3.0	5.3	7.5		-		0.30	0.49	0.59	10	17	22
	-		0.18	0.63	2.2	3.3	7.7	11	2.0	4.4	7.9		-		0.30	0.56	0.87	7.6	17	28
0.06	0.19	0.32	+	+	+	+	0.06	0.08	0.61	1.5	2.5	0.06	0.10	0.15	0.30	0.55	0.81	1.4	3.2	5.0
	-		+	+	+	+	+	+	+	+	+	-	-	-	+	+	+	+	0.05	0.07
0.44	0.58	0.75	0.06	0.08	0.11	0.51	0.85	1.2	3.1	4.3	5.0	0.21	0.33	0.42	4.1	4.7	5.4	12	15	16
0.49	0.64	0.79	0.06	0.10	0.13	0.55	1.3	2.0	3.4	4.8	6.2	0.21	0.39	0.56	4.5	4.7	4.8	13	15	18
	-		+	+	+	0.06	0.09	0.11	0.16	0.17	0.19		-			-		2.4	2.4	2.5
	-		+	+	+	+	+	+	+	+	+		-			-		0.12	0.15	0.19
	-		+	+	+	0.82	8.4	16	1.1	1.6	2.0		-			-		11	46	81
	-		+	0.05	0.07	0.57	7.3	14	0.45	1.6	2.7		-			-		7.2	38	69
	-		+	+	+	0.10	0.15	0.20	0.85	2.0	3.2		-		0.12	0.50	0.88	1.7	3.9	6.1
	-		+	+	+	+	+	+	+	0.15	0.29		-		0.45	0.49	0.54	0.49	0.71	0.93
	-		0.46	0.49	0.52	3.4	4.0	4.5	4.9	5.0	5.2		-		0.63	0.72	0.81	137	146	156
	-		0.52	0.53	0.53	2.9	3.5	4.1	3.3	3.4	3.5		-		0.36	0.47	0.58	107	107	108
	-		+	+	0.05		-		1.9	3.4	4.9	0.64	0.87	1.1	0.99	1.7	2.4	10	12	13
	-		-	+	+		-		+	+	+	-	+	+	+	+	+	+	+	0.05
	-		0.23	0.25	0.27		-		0.70	1.5	2.3	1.1	2.3	3.5	-	0.25	0.50	72	83	95
	-		0.48	0.52	0.56		-		0.33	0.42	0.52	2.7	3.8	4.8	-	+	+	114	121	127
	-			0.41			1.2			2.1			0.24			+			25	
	-			0.09			0.20			0.32			+			0.14			3.2	
	-			3.7			8.5			6.8			-			1.0			109	
	-			1.5			2.8			3.8			-			+			52	
	-			0.08			0.06			0.33			-			0.06			3.3	

Hydroxy-NTG = 7'-Hydroxynortrachelogenin
Pino = Pinoresinol
Seco = Secoisolariciresinol
Todo A = 7-Todolactol A
iLi = 7-Isoliovil

Continues on next page!

PICEA, PSEUDOTSUGA & TSUGA			Concentration of oligolignans								
			Sesquilignans			Dilignans			Sesterlignans		
			min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood								
Picea abies FI	HW	2	0.27	0.29	0.31	0.12	0.15	0.18	+	0.09	0.15
	SW	2	0.06	0.11	0.16	+	+	+	0.07	0.07	0.07
	LK	2	12	13	14	8.2	8.6	9.1	1.5	2.8	4.1
	DK	2	9.9	10	11	9.4	11	12	3.4	3.6	3.7
Picea abies FR	HW	1		1.5			1.2			0.16	
	SW	1		+			+			0.09	
	LK	1(3)		12			17			3.0	
	DK	1(5)		5.3			15			2.6	
Picea glauca	HW	2	+	+	0.05	+	+	+	+	+	0.06
	SW	2	+	+	+	+	+	0.05	0.09	0.12	0.14
	LK	3(5)	1.7	2.5	3.6	3.1	4.1	4.7	0.72	0.98	1.3
	DK	2(5)	4.1	4.2	4.3	7.4	8.6	9.7	1.4	1.5	1.5
Picea koraiensis	HW	1		1.5			0.79			0.62	
	SW	1		0.27			0.43			1.8	
	LK	1		21			16			8.5	
	DK	1		20			7.6			19	
Picea mariana	HW	2	0.31	0.33	0.35	0.10	0.12	0.13	+	+	0.07
	SW	2	0.08	0.12	0.16	+	0.06	0.09	+	0.06	0.09
	LK	2(13)	3.6	5.7	7.7	5.5	8.2	11	1.5	2.1	2.7
	DK	2(17)	3.7	4.0	4.3	5.9	6.7	7.4	1.9	2.4	2.8
Picea omorika	HW	1		0.66			0.32			0.35	
	SW	1		0.23			0.19			0.46	
	LK	1(2)		4.8			5.1			3.5	
	DK	1		3.1			3.5			2.3	
Picea pungens	HW	2	0.37	0.90	1.4	0.23	0.74	1.3	0.23	0.53	0.83
	SW	2	0.10	0.13	0.15	0.11	0.17	0.23	0.21	0.44	0.68
	LK	7(11)	3.4	5.3	7.1	2.9	5.9	6.9	-	2.8	9.9
	DK	9	6.5	12	18	7.3	12	17	-	8.4	18
Picea sitchensis	HW	2	0.37	0.73	1.1	0.31	0.52	0.72	0.11	0.16	0.21
	SW	2	0.07	0.08	0.09	0.05	0.05	0.05	0.06	0.07	0.08
	LK	2(3)	2.6	3.2	3.8	3.7	4.1	4.6	2.5	2.6	2.8
	DK	2(3)	3.2	3.4	3.5	4.4	4.4	4.5	2.2	2.6	3.1
Pseudotsuga menziesii	HW	2	1.0	1.2	1.4	0.37	0.37	0.38	+	0.13	0.24
	SW	2	0.95	1.1	1.3	0.07	0.09	0.10	0.14	0.17	0.19
	LK	2(11)	2.1	3.9	5.7	3.2	3.5	3.8	0.28	0.51	0.74
	DK	2(11)	2.3	3.2	4.2	1.4	2.4	3.3	0.24	0.41	0.57
T. canadensis	HW	2	1.2	1.6	2.1	0.44	0.61	0.78	0.27	0.30	0.34
	SW	2	0.36	0.50	0.65	0.12	0.13	0.13	0.08	0.09	0.11
	LK	2	8.8	8.9	8.9	13	14	16	2.3	2.5	2.7
	DK	2	6.1	6.4	6.6	11	16	20	1.1	1.9	2.8
T. heterophylla CA	HW	2	0.15	0.15	0.15	+	0.07	0.09	+	+	+
	SW	2	0.07	0.09	0.10	0.36	0.38	0.40	0.18	0.19	0.21
	LK	2	0.64	0.68	0.71	5.0	5.2	5.4	+	0.18	0.33
	DK	2	0.66	0.69	0.73	3.6	4.7	5.7	0.06	0.06	0.06
T. heterophylla FI	Dead branch	1		1.1			5.2			+	
	DK	1		1.8			3.2			4.3	
T. mertensiana	LK	1		15			9.1			+	
	HW of branch	1		7.2			9.2			0.37	
	SW of branch	1		2.6			0.63			0.18	

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

ABIES			Concentration of lignans														
			Coni			ConiA			HMR[1]			cLari			Lari		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood														
A. alba	HW	4	+	0.16	0.26	-	0.07	0.27	0.18	0.31	0.39	0.06	0.12	0.19	+	0.12	0.22
	SW	4	+	+	+		-		-	+	+	+	+	+	+	0.06	0.09
	LK	11	-	+	+		-		0.54	2.5	8.5	0.16	0.30	0.48	0.30	2.6	6.4
	DK	11(13)	-	+	+		-		2.3	8.4	17	2.6	7.4	15	9.5	25	55
A. amabilis	HW	1		1.8			0.37			3.4			0.11			0.19	
	SW	1		+			+			+			+			0.05	
	LK	2	0.37	2.3	4.2	2.4	2.5	2.6	51	51	51	0.53	0.72	0.90	1.9	2.1	2.3
	DK	1(2)		1.0			1.0			8.0			-			0.61	
A. balsamea	Stem	3		-		+	+	+	0.06	0.09	0.12	+	+	0.07	0.08	0.10	0.11
	LK	1(2)		-			+			3.2			3.6			25	
	DK	1(4)		-			0.12			2.9			3.1			21	
A. concolor	HW	1		-			-			0.96			0.16			+	
	LK	1(2)		-			-			19			0.69			0.56	
A. lasiocarpa	HW	2	+	+	+		-		+	0.07	0.11	+	+	0.06	0.07	0.07	0.07
	SW	2	+	+	+		-		+	+	+	+	+	+	+	+	+
	LK	2(16)		-			-		0.36	1.8	3.3	+	0.10	0.19	0.28	0.54	0.80
	DK	2(15)		-			-		0.93	2.1	3.2	0.49	0.55	0.62	1.5	1.6	1.6
A. pindrow	Knots	300 g		1.5			-			29			1.8			9.1	
A. sachalinensis	HW	1		+			+			0.07			+			0.10	
	SW	1		+			0.05			+			+			0.11	
	LK	1(2)		0.11			0.15			0.55			1.1			1.7	
	DK	1		0.21			0.15			0.73			0.40			1.8	
A. sibirica	HW	2		-		+	+	+	+	+	+	+	+	+	0.10	0.13	0.16
	SW	2		-		+	+	+	+	+	+	+	+	+	+	+	+
	LK	2(6)	0.18	0.21	0.24	0.15	0.17	0.19	3.0	3.0	3.0	0.40	0.49	0.58	2.8	5.4	7.9
	DK	2(3)	0.20	0.29	0.37	0.20	0.25	0.31	3.8	4.5	5.2	0.68	0.92	1.2	5.4	10	15
A. veitchii	HW	1		+			+			+			+			+	
	SW	1		0.07			0.05			0.08			+			0.05	
	LK	1(2)		0.15			0.30			1.8			1.4			6.5	
	DK	1		0.21			0.35			2.9			0.54			5.4	

- not detected
+ less than 0.05 mg/g dry wood
n = nr of analyses (nr of knots)
[1] Sum of two isomers.

Coni = α-Conidendrin
ConiA = α-Conidendric acid
HMR = 7-Hydroxymatairesinol
cLari = Cyclolariciresinol
Lari = Lariciresinol

Continues on next page!

ABIES			Concentration of lignans (cont.)																	
			Lig A			MR[2]			NTG			Pino			Seco			Seco MME		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood																	
A. alba	HW	4	-	0.34	0.58	-	0.08	0.30		-		+	+	0.08	0.08	0.14	0.21	+	+	+
	SW	4	-	+	+	+	+	+		-		+	+	+	-	+	+	+	+	+
	LK	11	-	0.67	1.1	+	0.57	3.1		-		0.11	0.24	0.52	8.9	18	36	0.60	0.94	1.1
	DK	11(13)	-	3.4	5.2	+	0.60	3.2		-		0.54	1.4	2.9	31	45	64	2.4	4.5	6.6
A. amabilis	HW	1		0.08			0.59			0.10			+			0.58			-	
	SW	1		-			0.07			+			+			0.05			-	
	LK	2	+	0.22	0.42	+	+	+	3.7	4.6	5.4	+	0.13	0.22	58	61	64		-	
	DK	1(2)		0.09			1.1			0.67			0.08			6.6			-	
A. balsamea	Stem	3	+	+	+	0.18	0.27	0.35		-		+	+	+	+	0.07	0.12		-	
	LK	1(2)		-			3.7			-			1.5			45			-	
	DK	1(4)		-			3.1			-			1.3			42			-	
A. concolor	HW	1		+			0.77			-			0.05			0.52			0.06	
	LK	1(2)		0.56			5.4[2]			-			0.35			30			0.37	
A. lasiocarpa	HW	2	0.06	0.09	0.12	+	+	+		-		+	0.06	0.07	+	+	+		-	
	SW	2	-	+	+	+	+	+		-		+	+	+	+	+	+		-	
	LK	2(16)	0.23	0.54	0.85	0.15	0.46	0.78		-		0.07	0.19	0.32	1.0	5.2	9.3		-	
	DK	2(15)	0.38	0.53	0.68	0.38	0.79	1.2		-		0.26	0.31	0.36	5.1	8.2	11		-	
A. pindrow	Knots	300 g		5.2			1.3			-			1.7			60			1.7	
A. sachalinensis	HW	1		-			0.14			-			+			-			-	
	SW	1		0.09			+			-			+			-			-	
	LK	1(2)		1.1			+			-			0.33			26			-	
	DK	1		1.2			0.07			-			0.29			19			-	
A. sibirica	HW	2	+	+	+	0.09	0.09	0.10		-		+	0.05	0.07	+	+	+		-	
	SW	2	+	+	+	+	+	+		-		+	+	+	+	+	+		-	
	LK	2(6)	-	+	+	2.2	2.3	2.3		-		0.20	0.32	0.43	23	25	27		-	
	DK	2(3)	+	+	0.05	3.2	3.3	3.5		-		0.58	0.80	1.0	39	42	45		-	
A. veitchii	HW	1		+			-			-			+			+			-	
	SW	1		0.15			-			-			+			0.27			-	
	LK	1(2)		1.9			-			-			0.29			27			-	
	DK	1		2.0			-			-			0.50			26			-	

- not detected
+ less than 0.05 mg/g dry wood
n = nr of analyses (nr of knots)

[2] MR overlapped with traces of 7-methoxy matairesinol.

Lig A = Lignan A
MR = Matairesinol
NTG = Nortrachelogenin
Pino = Pinoresinol
Seco = Secoisolariciresinol
Seco MME = 4-Monomethylsecoisolariciresinol

Concentration of lignans (cont.)															Concentration of oligolignans								
Seco DME			Hydroxy-Seco			Todo A			Unknown			Lignans total			Sesquilignans			Dilignans			Sesterlignans		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
mg/g dry wood																							
-	+	+		-		1.9	3.1	5.2	+	0.42	0.93	3.1	4.9	7.9	0.51	1.6	2.6	0.18	0.57	1.1	0.06	0.14	0.33
-	+	+		-		-	+	0.06	-	+	+	0.05	0.14	0.24	0.24	0.71	1.7	+	0.10	0.24	+	0.09	0.19
+	0.17	0.74		-		0.82	2.1	7.1	-	0.15	0.25	13	28	66	4.7	8.0	14	2.3	4.7	14	0.21	0.72	2.8
+	0.16	0.71		-		4.5	7.6	11	-	1.4	2.3	74	105	135	16	34	45	11	16	19	0.85	1.8	3.1
	-			-			1.3			-			8.6			2.8			2.2			1.2	
	-			-			+			-			0.28			0.46			0.25			0.23	
	-		+	0.37	0.72	3.5	4.7	5.8		-		121	129	137		23*			28*			9.3*	
	-			0.38			2.3			-			22			3.9			6.3			2.4	
	-			-		0.40	1.0	1.6	0.16	0.49	0.80	1.0	1.7	2.2	0.47	0.56	0.60	0.10	0.14	0.16	-	0.13	0.21
	-			-			8.4			0.12			90			8.4			25			4.4	
	-			-			5.3			0.08			79			7.1			24			5.5	
	-			-			4.7			0.91			8.1			3.5			2.1			0.72	
	-			-			4.4			0.55			62			15			15			4.0	
	-			-		0.31	0.37	0.43		-		0.56	0.74	0.91	1.7	1.8	1.9	0.33	0.56	0.79	0.25	0.38	0.50
	-			-		+	+	0.09		-		+	0.13	0.22	0.95	1.0	1.1	-	0.06	0.13	0.24	0.26	0.27
	-			-		0.92	1.7	2.5		-		3.1	11	18	1.8	3.6	5.4	2.5	6.2	9.9	1.4	2.1	2.8
	-			-		0.95	1.2	1.5		-		10	15	20	4.4	5.2	6.0	6.5	8.3	10	2.2	2.6	2.9
	-			-			4.7			2.1			118			-			24			8.1	
	-			-			0.57			-			0.98			1.5			0.46			0.85	
	-			-			0.35			-			0.72			1.2			0.51			1.2	
	-			-			1.6			-			33			16			10			6.1	
	-			-			2.1			-			26			17			11			11	
	-			-		0.20	0.22	0.24	0.12	0.14	0.16	0.66	0.76	0.86	0.59	0.64	0.69	0.12	0.13	0.13	-	0.06	0.12
	-			-		+	+	+	+	+	+	0.09	0.10	0.10	0.34	0.37	0.39	+	+	0.05	0.11	0.14	0.16
	-			-		1.3	1.4	1.6	0.28	0.41	0.53	38	39	40	6.1	7.6	9.0	22	30	39	3.9	4.4	4.9
	-			-		1.4	1.6	1.9	0.19	0.28	0.37	55	64	73	9.0	12	14	35	43	51	5.4	6.2	7.1
	-			-			0.08			-			0.21			0.55			0.06			+	
	-			-			0.27			-			0.99			1.9			0.66			0.56	
	-			-			4.1			-			43			16			17			5.5	
	-			-			4.0			-			42			19			20			9.4	

Seco DME = 4,4'-Dimethylsecoisolariciresinol
Hydroxy-Seco = Hydroxysecoisolariciresinol
Todo A = 7-Todolactol A

* Only one sample analysed

LARIX			Concentration of lignans															
			Coni			ConiA			HMR[1]			cLari			Lari			Lari-Ac		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood																	
L. decidua	HW	5	-	+	+		-		-	+	0.05	+	0.25	0.67	-	+	+		-	
	SW	5	-	+	+		-		-	+	+	-	+	+	-	+	+		-	
	LK	7(10)	-	+	+		-		-	0.50	1.3	-	4.0	13	0.54	5.0	16		-	
	DK	11(15)	-	+	+		-		+	0.19	0.48	-	2.4	8.7	0.37	3.8	11		-	
L. gmelinii	HW	2		-			-		+	+	+	0.15	0.22	0.29	+	+	+		-	
var. *gmelinii*	SW	2	+	+	+		-		+	+	+	+	+	+	+	+	+		-	
	LK	2	0.40	0.58	0.75		-		0.51	1.2	1.8	2.2	2.9	3.6	4.5	10	15	+	0.10	0.21
	DK	2	0.32	0.51	0.69		-		0.54	1.0	1.5	8.7	9.0	9.3	24	27	29	+	0.07	0.09
L. gmelinii	HW	2		-			-		-	+	0.06	0.06	0.26	0.47	+	+	+		-	
var. *japonica*	SW	2	-	+	+		-		+	+	+	-	+	+	+	+	+		-	
	LK	2	0.78	0.98	1.2		-		2.0	2.5	2.9	1.4	1.6	1.8	13	14	15	+	2.4	4.9
	DK	3	0.06	0.23	0.50		-		1.8	2.0	2.4	3.7	8.5	14	11	15	21	0.05	2.4	3.9
L. gmelinii	HW	2	-	+	+		-		+	+	+	0.79	0.97	1.2	0.05	0.06	0.06		-	
var. *olgensis*	SW	2		-			-		+	+	+	-	+	+	-	+	+		-	
	LK	2	0.19	0.33	0.47		-		0.38	0.54	0.71	4.3	9.7	15	5.1	6.4	7.6	0.09	0.16	0.22
	DK	2	0.58	0.79	1.0		-		0.79	0.81	0.84	9.8	19	28	7.1	12	18	0.14	0.21	0.29
L. kaempferi	HW	3		-			-			-		0.62	0.65	0.67		-			-	
	SW	3		-			-			-		+	+	+		-			-	
	LK	9	-	+	+		-		0.70	1.5	2.9	3.2	11	22	+	19	34		-	
	DK	22	-	+	+		-		0.14	0.69	1.9	6.5	24	61	+	3.4	18		-	
L. lariciana	HW	2	-	+	+	+	+	+	+	+	0.06	0.11	0.13	0.14	0.09	0.10	0.11		-	
	SW	2		-			-		+	+	+	+	+	+	-	+	+		-	
	LK	2		-		+	+	+	0.16	0.17	0.17	0.68	0.89	1.1	0.27	0.62	0.96		-	
	DK	2(3)		-		-	+	+	0.19	0.31	0.44	0.92	1.1	1.3	0.55	1.1	1.7		-	
L. sibirica	HW	6	-	+	+	+	0.07	0.11	+	+	+	-	0.16	0.39	+	+	0.12		-	
	SW	6	-	+	+	-	+	+	+	+	+	+	+	+	+	+	+		-	
	LK	1		-			0.22			0.61			0.89			4.0			-	
	DK	10	-	+	0.09	0.18	0.52	0.81	0.30	0.68	1.5	0.19	3.0	7.0	0.30	4.5	10		-	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)
[1] Sum of two isomers.

Coni = α-Conidendrin
ConiA = α-Conidendric acid
HMR = 7-Hydroxymatairesinol
cLari = Cyclolariciresinol
Lari = Lariciresinol
Lari-Ac = Lariciresinol-9-acetate

Concentration of lignans (cont.)																				
Lig A			Lig B			MR			NTG			Pino			Seco			Seco DME		
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
mg/g dry wood																				
	-			-		-	+	+	-	+	+	+	+	+	+	0.06	0.14	-	+	+
	-			-		-	+	+	-	+	+	-	+	+	-	+	+	-	+	+
-	+	0.11		-		+	0.41	1.0	2.7	8.5	20	+	0.24	0.66	27	50	80	-	+	+
-	+	0.10		-		+	0.14	0.38	1.2	8.2	21	+	0.15	0.61	12	42	69	-	+	+
+	+	+		-		+	+	+	-	+	+	+	+	+	+	0.10	0.14	-	+	+
+	+	+		-		+	+	+	-	+	+	+	0.08	0.13	+	+	+	+	+	+
0.42	1.7	2.9		-		0.07	0.19	0.30	1.9	2.1	2.2	0.22	0.43	0.65	17	55	93	-	+	+
1.1	1.7	2.3		-		0.26	0.31	0.36	2.7	2.7	2.7	0.46	0.58	0.70	44	70	96	+	+	+
+	+	+		-			-			-		-	+	+	0.05	0.07	0.08		-	
	-			-		+	+	+		-		+	+	+	+	+	+		-	
1.9	2.2	2.4		-		0.25	0.29	0.33	1.2	1.6	2.0	0.29	0.38	0.47	33	53	72	+	+	+
1.1	1.1	1.1		-		0.22	0.30	0.36	0.82	1.2	1.8	0.37	0.48	0.62	23	43	61	+	+	+
+	+	+		-		-	+	+	+	+	+	+	+	+	0.12	0.15	0.18	-	+	+
	-			-		+	+	+		-		+	+	+	+	+	+	-	+	+
0.89	1.1	1.3		-		0.13	0.14	0.16	3.0	4.6	6.1	0.26	0.33	0.40	28	37	46	-	+	+
1.2	1.9	2.6		-		0.22	0.29	0.37	4.0	8.2	12	1.1	1.2	1.4	76	77	77	-	+	+
	-			-			-			-		0.08	0.08	0.08		-			-	
	-			-			-			-		+	0.06	0.09		-			-	
	-		0.93	2.2	4.5	+	0.08	0.20	1.9	9.5	17	0.38	0.79	1.4	15	68	142		-	
	-		0.54	1.6	3.1	+	0.07	0.13	1.2	6.3	14	0.38	0.88	2.3	4.6	40	102		-	
	-			-		+	+	0.05		-		+	+	+	0.18	0.20	0.21		-	
	-			-			-			-		+	+	+	+	+	+		-	
	-			-		0.13	0.14	0.15		-		+	+	+	2.3	3.2	4.0		-	
	-			-		0.11	0.24	0.37		-		+	+	+	5.6	15	24		-	
-	+	+		-		-	+	+	+	+	+	+	+	+	0.07	0.16	0.28		-	
-	+	+		-		-	+	+	+	+	+	+	+	0.08	+	+	0.13		-	
	-			-			0.52			1.1			0.35			14			-	
-	+	+		-		+	0.19	1.2	0.14	1.5	3.0	0.06	0.17	0.31	7.2	26	50		-	

Lig A = Lignan A
Lig B = Lignan B
MR = Matairesinol
NTG = Nortrachelogenin
Pino = Pinoresinol
Seco = Secoisolariciresinol
Seco DME = 4,4'-Dimethylsecoisolariciresinol

Continues on next page!

LARIX			Concentration of lignans (cont.)									Concentration of oligolignans								
			Todo A			Unknown			Lignans total			Sesquilignans			Dilignans			Sesterlignans		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood																	
L. decidua	HW	5	-	+	0.09		-		0.06	0.41	1.1	0.57	1.7	3.4	0.30	0.47	0.72	0.24	4.8	9.9
	SW	5	-	+	+		-		+	+	0.10	0.22	0.38	0.64	0.05	0.09	0.15	0.13	0.20	0.35
	LK	7(10)	-	0.33	1.1	-	+	+	32	69	97	4.3	7.6	14	4.7	12	22	2.6	3.2	4.2
	DK	11(15)	-	0.11	0.28	-	+	+	19	57	90	2.7	7.1	13	9.1	10	12	0.88	1.9	2.7
L. gmelinii	HW	2	0.05	0.09	0.13	+	+	+	0.71	0.75	0.79	+	0.06	0.11	+	+	+	+	+	+
var. *gmelinii*	SW	2	+	+	+	-	+	+	0.22	0.23	0.23	0.36	0.41	0.45	0.13	0.16	0.20	0.17	0.20	0.24
	LK	2	1.7	2.5	3.4	0.33	0.33	0.33	31	77	123	3.3	6.2	9.0	4.1	12	20	-	+	+
	DK	2	0.53	1.6	2.7	0.28	0.74	1.2	85	115	145	9.2	11	13	9.1	15	22	+	1.4	2.7
L. gmelinii	HW	2	0.06	0.07	0.07		-		0.24	0.63	1.0	0.33	0.33	0.33	0.06	0.11	0.17	+	+	+
var. *japonica*	SW	2	+	+	+		-		0.06	0.09	0.12	0.57	0.61	0.66	0.17	0.18	0.19	0.38	0.46	0.54
	LK	2	5.5	7.8	10	0.55	0.96	1.4	65	87	108	6.4	7.5	8.7	7.9	10	13	+	0.54	1.0
	DK	3	0.88	2.1	4.3	-	0.24	0.60	51	76	91	4.5	6.4	8.4	7.7	15	23	-	0.75	2.2
L. gmelinii	HW	2	0.05	0.16	0.27	-	+	+	1.7	1.9	2.1	0.18	0.29	0.39	0.08	0.15	0.22	+	+	+
var. *olgensis*	SW	2	+	+	+		-		0.05	0.05	0.06	0.78	1.4	2.0	0.36	0.42	0.48	1.5	1.7	1.8
	LK	2	0.13	0.95	1.8	0.13	0.32	0.52	50	61	73	7.2	7.9	8.6	7.8	9.7	12	+	0.13	0.23
	DK	2	0.17	0.27	0.37	0.62	0.87	1.1	121	123	124	14	16	17	14	15	16	0.76	1.0	1.3
L. kaempferi	HW	3		-			-		0.70	0.73	0.76		-		0.27	0.37	0.45	0.26	0.57	1.2
	SW	3	+	0.06	0.08		-		0.10	0.14	0.19		-		+	+	+	0.19	0.20	0.22
	LK	9	1.0	1.9	2.6	+	0.39	0.53	27	110	220	4.8	17	28	1.0	6.2	11	-	1.5	7.3
	DK	22	0.41	0.48	0.52	-	0.05	0.25	16	76	171	2.9	13	32	1.3	5.3	13	-	1.7	6.1
L. lariciana	HW	2	0.31	0.34	0.37	0.15	0.17	0.19	1.0	1.1	1.1	0.23	0.28	0.33	0.10	0.10	0.11	0.05	0.05	0.06
	SW	2	+	+	+	+	+	+	0.08	0.08	0.09	+	+	+	0.10	0.11	0.12	0.23	0.24	0.25
	LK	2	0.66	0.69	0.72	0.29	0.29	0.30	4.6	6.0	7.4	0.63	0.67	0.72	1.1	1.1	1.2	0.76	0.77	0.79
	DK	2(3)	0.62	0.87	1.1	0.23	0.37	0.50	8.2	19	29	0.87	1.4	1.8	1.7	2.7	3.6	0.93	1.1	1.2
L. sibirica	HW	6	0.08	0.20	0.35		-		0.47	0.73	0.99	-	0.06	0.17	0.10	0.14	0.18	0.06	0.12	0.18
	SW	6	+	+	+		-		0.09	0.16	0.19	-	+	0.06	+	0.06	0.10	0.06	0.15	0.26
	LK	1		1.6			-			23			2.8			8.0			1.7	
	DK	10	0.55	1.2	2.6		-		10	38	64	-	0.49	2.6	1.8	4.4	7.7	-	1.9	3.3

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

Todo A = 7-Todolactol A

D8 Flavonoids

LARIX, PSEUDOTSUGA & TSUGA			Concentration of flavonoids													
			Catechin[1]			Dihydro-kaempferol			Naringenin			Taxifolin[1]			Flavonoids total		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood														
L. decidua	HW	5	0.24	0.30	0.35	2.0	4.7	9.0		-		6.5	20	34	15	25	36
	SW	5	0.06	0.11	0.17	+	+	+		-		+	+	+	+	0.09	0.18
	LK	7(10)		-		1.4	3.7	11		-		13	29	36	24	33	39
	DK	11(15)		-		2.1	3.2	10		-		10	27	35	13	30	38
L. gmelinii	HW	2		-		0.23	0.35	0.46		-		1.6	2.5	3.4	2.1	2.8	3.6
var. *gmelinii*	SW	2	+	+	+		-			-			-		+	+	+
	LK	2		-		0.23	0.25	0.26		-		2.9	3.5	4.1	3.1	3.8	4.4
	DK	2		-		0.56	0.58	0.61		-		5.9	14	22	6.5	14	22
L. gmelinii	HW	2		-		0.10	0.31	0.71		-		0.39	1.9	4.7	0.49	2.2	5.4
var. *japonica*	SW	2		-			-			-			-			-	
	LK	2		-		0.37	0.41	0.45		-		6.5	10	14	7.0	11	15
	DK	3		-		0.41	0.46	0.49		-		7.9	9.3	11	8.3	9.8	12
L. gmelinii	HW	2		-		0.36	0.38	0.41		-		7.2	11	14	7.7	11	14
var. *olgensis*	SW	2		-			-			-			-			-	
	LK	2		-		1.1	1.4	1.7		-		24	25	27	25	27	28
	DK	2		-		0.12	1.2	2.2		-		13	15	17	15	16	17
L. kaempferi	HW	3		-		1.1	1.4	1.5		-		9.5	12	17	11	13	19
	SW	3	+	+	0.08		-			-			-		+	+	0.08
	LK	9		-		0.80	2.7	5.6		-		3.0	11	19	3.9	13	24
	DK	22		-		0.88	2.0	3.1		-		4.4	10	20	5.3	12	23
L. lariciana	HW	2		-		0.07	0.08	0.09	+	+	+	0.51	0.57	0.64	0.59	0.68	0.77
	SW	2		-		-	+	+		-		+	+	+	+	+	+
	LK	2		-		0.07	0.10	0.12	+	+	0.05	3.8	4.5	5.1	4.0	4.6	5.2
	DK	2(3)		-		0.07	0.10	0.13	0.06	0.07	0.07	3.7	3.9	4.1	3.9	4.1	4.2
L. sibirica	HW	6		-		+	0.05	0.10		-		0.10	0.56	1.2	0.11	0.62	1.3
	SW	6	-	+	0.06	-	+	+		-		-	+	0.07	+	0.06	0.14
	LK	1		-			0.34			-			2.7			3.0	
	DK	10		-		0.08	0.21	0.46		-		0.91	5.7	8.9	1.0	5.9	9.1
P. menziensii	HW	2		-		1.2	1.5	1.9		-		25	28	30	26	29	32
	SW	2		-		+	+	+		-		+	+	+	+	+	+
	LK	2(11)		-		0.33	0.38	0.43		-		0.95	21	41	1.4	22	42
	DK	2(11)		-		0.50	0.53	0.56		-		3.9	18	31	4.5	18	32
T. canadensis	HW	2	+	+	+		-			-			-		+	+	+
	SW	2	+	+	+		-			-			-		+	+	+
	LK	2		-			-			-			-		-	+	+
	DK	2		-			-			-			-			-	
T. heterophylla CA	HW	2	+	+	+		-			-			-		+	+	+
	SW	2	0.10	0.11	0.12		-			-			-		0.10	0.11	0.12
	LK	2	0.98	1.1	1.2		-			-			-		0.98	1.1	1.2
	DK	2	1.7	1.7	1.7		-			-			-		1.7	1.7	1.7
T. heterophylla FI	Dead branch	1		-			-			-			+			+	
	DK	1		-			-			-			+			+	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)
Traces of pinobanksin in LK of *Tsuga canadensis*
[1] Two isomers in *Larix*.

PINUS			Concentration of flavonoids											
			PC[1]			PB[1]			PB-Ac			Dihydro-kaempferol		
			min	avg	max	min	avg	max	min	avg	max	min	avg	max
		n	mg/g dry wood											
P. banksiana	HW	2	4.5	6.2	7.9	3.0	4.0	5.1	0.19	0.56	0.93	0.31	0.35	0.39
	SW	2	+	+	+	+	+	+	+	+	+	+	+	+
	LK	2(5)	9.9	11	11	6.1	6.4	6.6	0.95	1.1	1.3	0.34	0.37	0.40
	DK	1		3.3			3.6			0.33			0.25	
P. contorta	HW	2	6.4	7.4	8.4	0.82	1.6	2.4	0.44	0.81	1.2	0.43	0.55	0.67
	SW	2	+	+	+	-	-	-	+	+	+	-	-	-
	LK	4	3.8	5.6	7.4	0.78	1.6	2.8	0.24	0.51	0.79	0.31	0.55	0.83
P. elliottii	HW	2	10	15	20	7.8	9.0	10	1.7	6.3	11	0.77	1.0	1.2
	SW	2	0.15	0.15	0.15	+	+	+	+	+	+	+	+	+
	LK	3	0.91	4.7	9.4	0.97	3.7	5.7	2.9	6.7	11	0.14	0.56	0.80
	DK	10	1.3	8.9	13	1.4	5.5	8.8	3.7	7.8	11	0.20	0.66	1.2
P. gerardiana	knots	300 g		0.12			0.33			+			-	
P. nigra	HW	3	0.62	0.68	0.79		-			-		+	+	0.05
	SW	3	0.12	0.24	0.46		-			-		+	+	+
	LK	8	0.49	2.0	4.3		-			-		+	0.16	0.40
	DK	9	1.1	2.2	3.0		-			-		+	0.15	0.34
P. pinaster	HW	3	4.7	6.7	10	1.7	2.0	2.4	+	+	+	0.26	0.43	0.54
	SW	3	+	0.05	0.09		-			-			-	
	LK	9	2.9	4.2	6.6	0.15	0.30	0.46	0.14	0.26	0.56	0.08	0.13	0.22
	DK	9	7.0	9.5	12	0.42	0.89	1.4	0.27	0.53	0.80	0.21	0.25	0.33
P. radiata	HW	1		5.5			5.1			0.23			0.19	
	SW	1(2)		0.11			+			-			-	
	LK	2	+	+	+		-			-			-	
	DK	1		3.2			1.7			0.54			0.09	
P. roxburghii	knots	300 g		0.23			0.18			0.08			-	
P. sibirica	HW	2	0.84	0.87	0.90	0.12	0.12	0.12	+	+	+	+	+	+
	SW	2	+	+	+	+	+	+	+	+	+	+	+	+
	LK	2(8)	11	12	13	1.5	1.7	1.9	1.5	1.7	2.0	0.73	0.75	0.76
	DK	2(3)	6.2	9.1	12	1.2	1.9	2.6	0.17	0.92	1.7	0.39	0.64	0.89
P. strobus	HW	2	0.31	0.61	0.91	0.15	0.87	1.6	-	+	0.09		-	
	SW	2	+	+	0.06		-			-			-	
	LK	2	5.5	6.3	7.1	8.9	9.6	10	3.7	5.9	8.1		-	
	DK	2	3.2	3.5	3.8	5.4	5.6	5.8	0.34	0.66	0.97		-	
P. sylvestris	HW	2		-			-			-		+	+	+
	SW	2		-			-			-		-	+	+
	LK	2		-			-			-		+	+	+
	DK	2		-			-			-		+	+	+
P. taeda	HW	1		7.7			6.9			8.8			0.18	
	SW	2	+	+	+	+	+	+	+	+	+	+	+	+
	LK	4	0.19	4.3	7.5	+	2.5	6.6	+	3.1	7.7	+	0.10	0.25
	DK	5	0.15	6.1	10	+	5.1	10	+	5.1	10	+	0.14	0.28
P. wallichiana	knots	300 g		1.8			0.87			0.41			-	

- not detected
+ less than 0.05 mg/g dry wood
n = number of analyses (number of knots)
No flavonoids detected in *Pinus resinosa.*
[1] Two isomers.

PC = Pinocembrin
PB = Pinobanksin
PB-Ac = Pinobanksin-3-acetate

Concentration of flavonoids (cont.)															
PSt			SB			Chrysin			Other flavonoids[2]			Flavonoids total			
min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	
mg/g dry wood															
	-			-			-			-		8.1	11	14	
	-			-			-			-		+	0.07	0.10	
	-			-			-			-		17	19	20	
	-			-			-			-			7.5		
	-			-			-			-		8.1	10	13	
	-			-			-			-		+	+	+	
	-			-			-			-		5.2	8.3	12	
	-			-			-		0.17	0.26	0.36	20	32	43	
	-			-			-		+	+	+	0.17	0.18	0.19	
	-			-			-		+	0.07	0.12	5.0	16	21	
	-			-			-		+	0.17	0.40	6.6	23	32	
	-			0.97			-			0.08			1.5		
	-			-			-			-		0.66	0.72	0.84	
	-			-			-			-		0.12	0.25	0.46	
	-			-			-			+		0.51	2.1	4.7	
	-			-			-			-		1.1	2.3	3.3	
	-			-			-		+	+	+	7.1	9.1	13	
	-			-			-		+	0.11	0.19	0.12	0.16	0.20	
	-			-			-		+	0.05	0.07	3.4	4.9	7.6	
	-			-			-		+	0.07	0.09	8.0	11	15	
	-			-			-			-			11		
	-			-			-			-			0.15		
	-			-			-			-		+	+	+	
	-			-			-			-			5.5		
	-			+			+			+			0.54		
0.21	0.21	0.22		-		0.11	0.14	0.18	0.07	0.08	0.09	2.6	2.6	2.6	
0.06	0.06	0.06		-			-		+	+	+	0.17	0.18	0.19	
4.2	4.6	5.0		-		1.7	2.7	3.8	0.51	0.80	1.1	39	41	43	
2.8	3.6	4.4		-		1.2	1.2	1.2	0.27	0.37	0.47	21	30	39	
0.35	0.73	1.1	1.4	3.0	4.5	-	+	0.07	2.0	3.4	4.8	4.2	8.7	13	
	-		-	+	+	+	+	+	+	0.08	0.13	0.07	0.13	0.20	
3.2	3.2	3.2	1.7	3.2	4.6	0.65	1.2	1.7	8.0	10	12	39	40	40	
2.0	2.1	2.2	2.4	4.1	5.8	0.58	0.95	1.3	5.0	7.0	9.0	20	24	28	
	-			-			-		+	+	+	+	+	+	
	-			-			-		+	+	+	+	+	+	
	-			-			-			-		+	+	+	
	-			-			-		+	+	+	+	+	+	
	-			-			-			-			24		
	-			-			-			-		+	+	+	
	-			-			-			-		0.23	9.9	22	
	-			-			-			-		0.23	16	30	
	-			+			0.29			0.07			3.5		

PSt = Pinostrobin
SB = Strobobanksin
[2] Sum of cryptostrobin, strobopinin, tectochrysin, catechin, dihydrokaempferol-3-acetate, taxifolin and three unknown flavonoids.

PICEA & ABIES			Concentration of flavonoids															
			Catechin			Dihydro-kaempferol			PC			Taxifolin			Flavonoids total			
			min	avg	max	min	avg	max	min	avg	max	min	avg	max	min	avg	max	
		n	mg/g dry wood															
P. abies FR	HW	1		-			+			-			+			+		
	SW	1		-			+			-			+			+		
	LK	1(3)		-			+			-			0.17			0.17		
	DK	1(5)		-			-			-			0.05			0.05		
P. glauca	HW	2		-		+	+	+		-		+	+	+	+	+	+	
	SW	2		-		+	+	+		-		+	+	+	+	+	+	
	LK	3(5)		-		-	+	+		-		+	+	0.07	+	+	0.07	
	DK	2(5)		-		+	+	+		-		+	+	+	+	+	+	
P. mariana	HW	2	+	+	+		-			-			-		+	+	+	
	SW	2	-	+	+		-			-			-		-	+	+	
	LK	2(13)	0.07	0.07	0.08		-			-			-		0.07	0.07	0.08	
	DK	2(17)	+	+	+		-			-			-		+	+	+	
P. sitchensis	HW	2	-	+	+	0.11	0.15	0.19	+	+	+	0.05	0.20	0.34	0.21	0.38	0.56	
	SW	2	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
	LK	2(3)	+	+	0.08	0.05	0.07	0.09	+	+	+	0.11	0.18	0.22	0.19	0.30	0.35	
	DK	2(3)	-	+	+	0.11	0.11	0.12	+	+	+	0.17	0.24	0.32	0.34	0.40	0.46	
A. alba	HW	4	-	0.11	0.41		-						-		-	0.11	0.41	
	SW	4	-	0.10	0.20		-						-		+	0.10	0.20	
	LK	11		-			-						-			-		
	DK	11(13)		-			-						-			-		
A. balsamea	Stem	3		-			+					+	+	+	+	+	+	
	LK	1(2)		-			-						+			+		
	DK	1(4)		-			-						+			+		

- not detected

+ less than 0.05 mg/g dry wood

n = number of analyses (number of knots)

PC = Pinocembrin

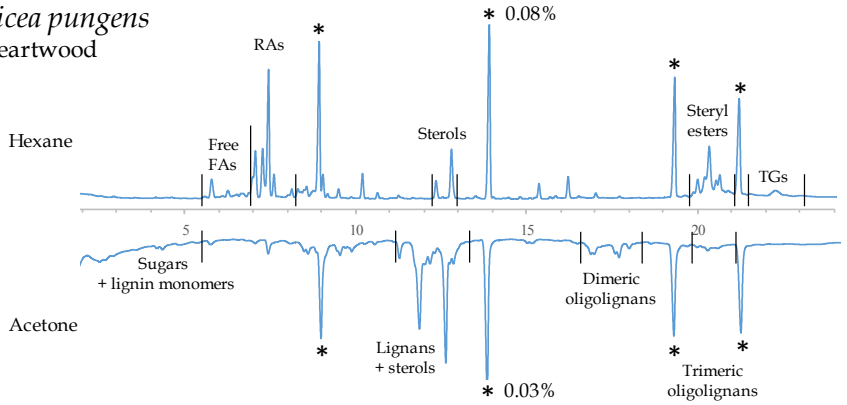
No flavonoids were detected in *Picea abies* FI, *P. koraiensis, P. pungens, P. omorika, Abies amabilis, A. concolor, A. lasiocarpa, A. pindrow, A. sachalinensis, A. sibirica* or *A. veitchii.*

Appendix E Chromatograms

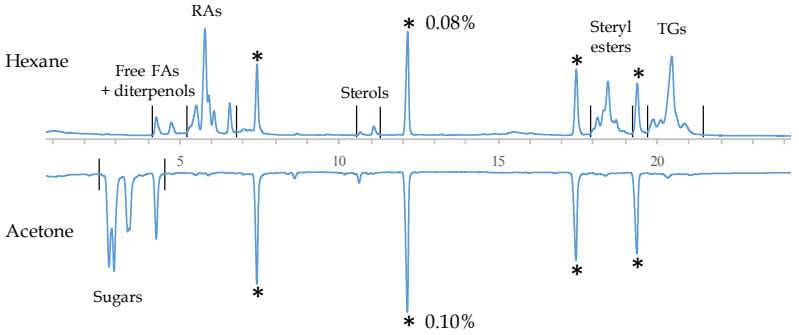
E1 Short-column GC

Standard peaks are marked with asterisks (*).

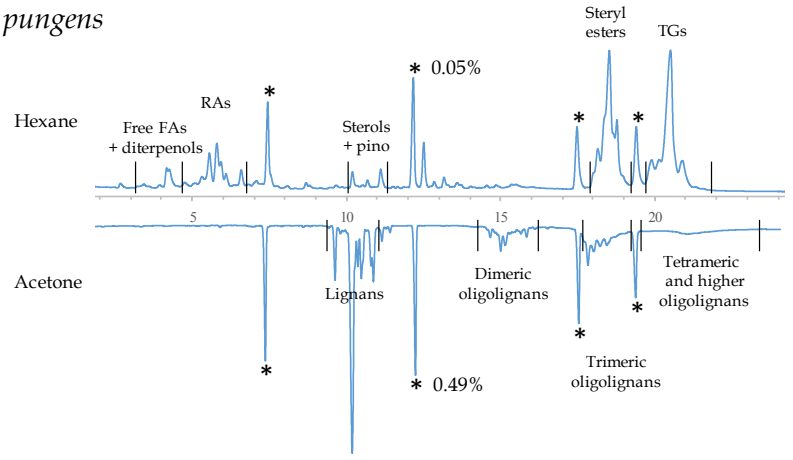
Picea pungens
Heartwood



Picea pungens
Sapwood

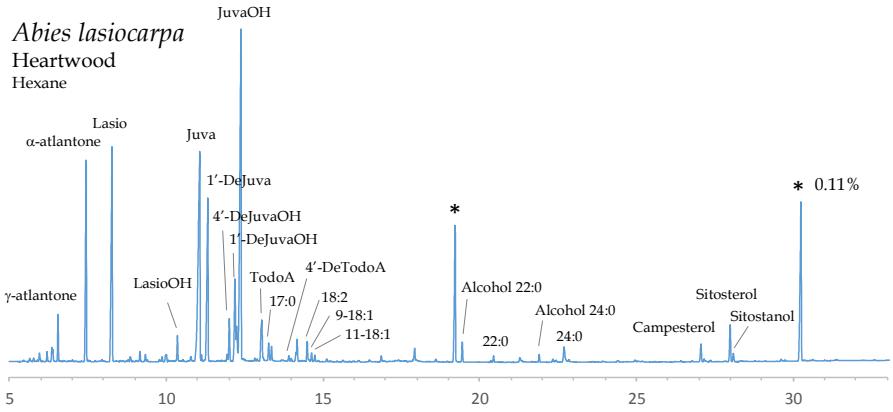


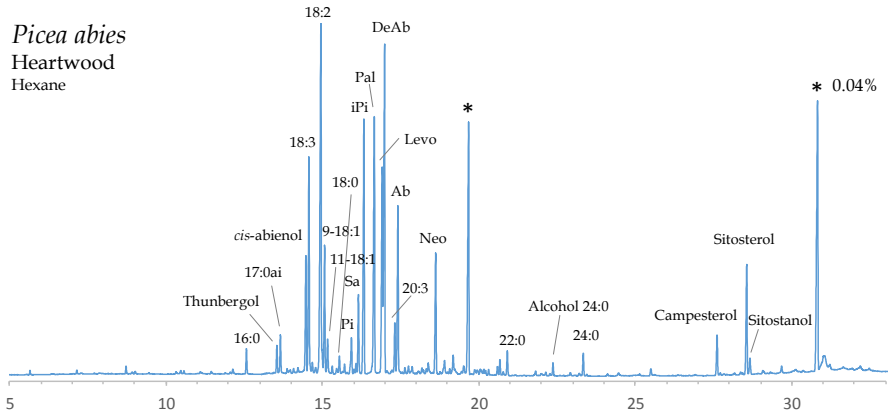
Picea pungens
Knots

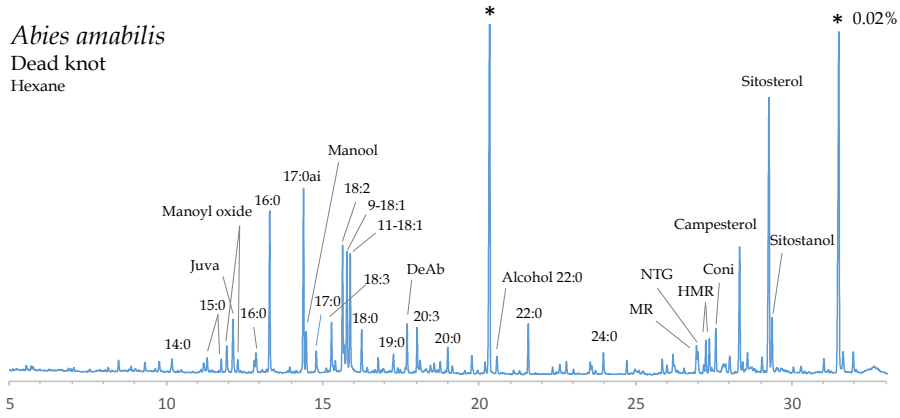


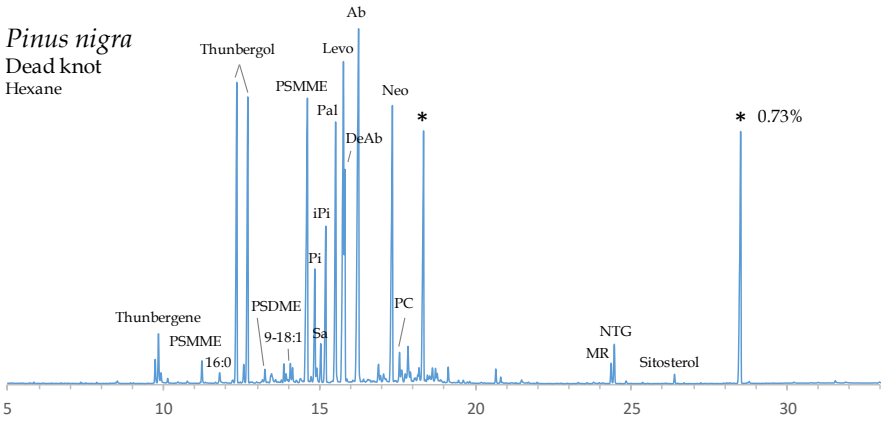
E2 Long-column GC

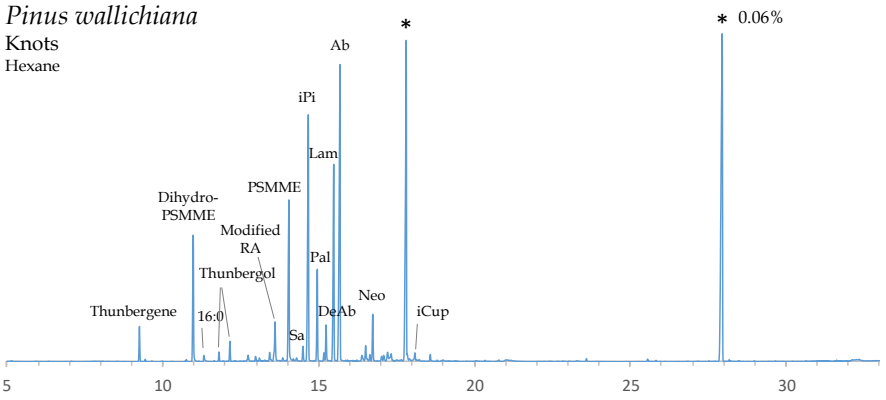
Standard peaks are marked with asterisks (*).

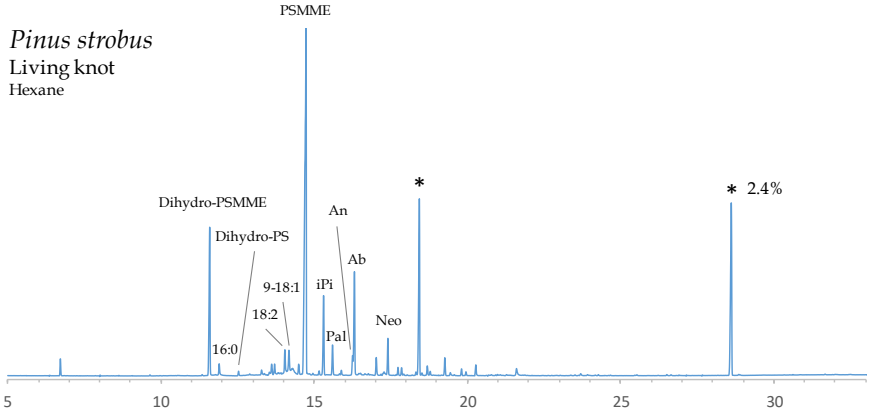


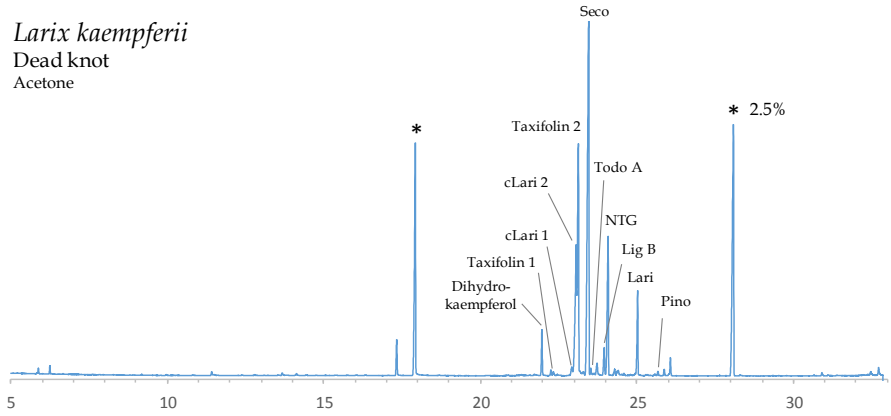


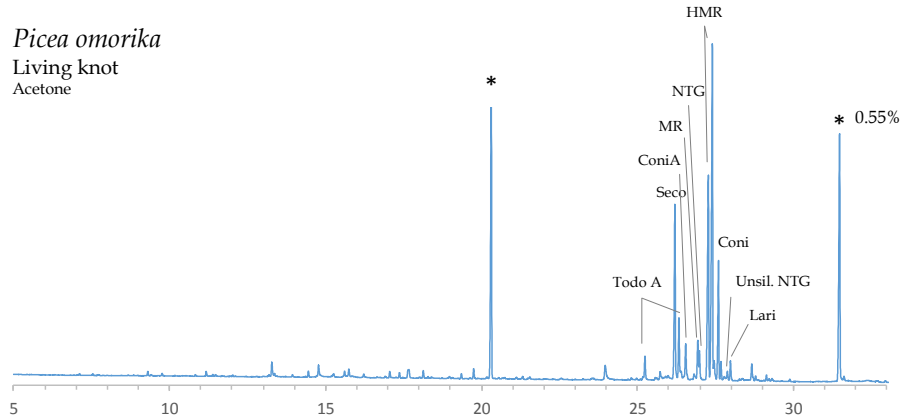



Pinus nigra
Dead knot
Hexane
Ab
Thunbergol
Levo
PSMME
Neo
Pal
*
DeAb
* 0.73%
iPi
Pi
PSDME
PC
Thunbergene
PSMME
9-18:1
Sa
NTG
MR
16:0
Sitosterol
5
10
15
20
25
30


Pinus wallichiana
Knots
Hexane
*
* 0.06%
Ab
iPi
Lam
PSMME
Dihydro-
PSMME
Modified
RA
Pal
Thunbergol
Neo
Thunbergene
16:0
DeAb
iCup
Sa
5
10
15
20
25
30


Pinus strobus
Living knot
Hexane
PSMME
*
* 2.4%
Dihydro-PSMME
An
Dihydro-PS
Ab
9-18:1
iPi
18:2
Neo
Pal
16:0
5
10
15
20
25
30


Larix kaempferii
Dead knot
Acetone
Seco
Taxifolin 2
Todo A
cLari 2
NTG
cLari 1
Lig B
Taxifolin 1
Lari
Dihydro-
kaempferol
Pino
* 2.5%
5
10
15
20
25
30


Picea omorika
Living knot
Acetone
HMR
NTG
MR
ConiA
Seco
Coni
Todo A
Unsil. NTG
Lari
* 0.55%
5
10
15
20
25
30

Appendix F Plant synonyms

F Plant synonyms

Taxa used in this thesis in bold. The list is extracted from Farjon (1998) and synonyms in rank of variety or subspecies are omitted.

Abies

***Abies alba* Mill. 1768**

***Abies amabilis* (Dougl.) J. Forbes 1839**

Abies argentea Chambray, see *Abies alba* Mill.

Abies baldensis (Zuccagni) Nyman, see *Abies alba* Mill. 1768

***Abies balsamea* (L.) Mill. 1768**

Abies bifolia A. E. Murray, see *Abies lasiocarpa* (Hook.) Nutt.

Abies californica Hort ex Steud, see *Pseudotsuga menziesii* (Mirb.) Franco

Abies canadensis Mill., see *Picea glauca* (Moench) Voss

Abies candicans Fisch. ex Endl., see *Abies alba* Mill. 1768

Abies chlorocarpa Purk. ex Nyman, see *Abies alba* Mill. 1768

Abies commutata (Parl.) Gordon var. *glauca* Chargueraud, see *Picea pungens* Engelm.

***Abies concolor* (Gord. & Glend.) Lindl. ex Hildebr. 1861**

Abies denticulata Michx., see *Picea mariana* (Mill.) B.S.P.

Abies eichleri Lauche 1882, see *Abies veichii* Lindl.

Abies excelsa Link, see *Abies alba* Mill.

Abies falcata Raf., see *Picea sitchensis* (Bong.) Carr.

Abies gmelinii Rupr., see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Abies grandis (Dougl. ex D. Don) Lindl. var. *concolor* A. Murray bis 1875, see *Abies concolor* (Gord. & Glend.) Hildebr. 1861

Abies grandis A.E. Murray, see *Abies amabilis*

Abies grandis Franco, see *Abies amabilis*

Abies grandis Hook., see *Abies amabilis*

Abies heterophylla Raf. 1832 (Taylor 1993)., see *Tsuga heterophylla* (Raf.) Sarg.

***Abies lasiocarpa* (Hook.) Nutt. 1849**

Abies ledebourii Rupr. (Dallim. et al. 1967)., see *Larix sibirica* Ledeb.

Abies ledebourii Rupr., see *Larix sibirica* Ledeb.

Abies leptolepis Sieb. et Zucc., (1842), see *Larix kaempferi* (Lamb.) Carr. 1856

Abies mariana Mill. 1768, see *Picea mariana* (Mill.) B.S.P.

Abies mayriana Miyabe & Kudo, see *Abies sachalinensis* (F.Schmidt) Mast.

Abies menziesii (Dougl. ex D. Don) Lindl. 1835, see *Picea sitchensis* (Bong.) Carr.

Abies menziesii Engelm., see *Picea pungens* Engelm.

Abies menziesii Lindl. var. *parryana* André, see *Picea pungens* Engelm

Abies menziesii Mirb. 1825, see *Pseudotsuga menziensii* (Mirb.) Franco

Abies mucronata Raf., see *Pseudotsuga menziensii* (Mirb.) Franco

Abies nigra (Aiton) Poir., see *Picea mariana* (Mill.) B.S.P.

Abies nigra Du Roi, see *Picea mariana* (Mill.) B.S.P.

Abies nobilis A.Dietr., see *Abies alba* Mill. 1768
Abies omorica (Pančić) Nyman, see *Picea omorika* (Pančić) Purkyne 1877
Abies pardei Gaussen (Silba 1986), see *Abies alba* Mill. 1768
Abies pattoniana Jeffrey ex Balf., see *Tsuga mertensiana* (Bong.) Carr.
Abies pectinata (Lam.) D.C. 1768, see *Abies aba* Mill. 1768
Abies picea (L.) Lindl., see *Abies alba* Mill.
***Abies pindrow* (Royle ex D. Don) Royle 1836**
***Abies sachalinensis* (F. Schmidt) Mast. 1879**
***Abies sibirica* Ledeb. 1833**
Abies sitchensis Lindl. & Gordon, see *Picea sitchensis* (Bong.) Carrière
Abies subalpina Engelm., see *Abies lasiocarpa* (Hook.) Nutt.
Abies taxifolia Desf., see *Abies alba* Mill. 1768
Abies taxifolia Poir. 1805, see *Pseudotsuga menziensii* (Mirb.) Franco
Abies trigona Raf., see *Picea sitchensis* (Bong.) Carrière
***Abies veichii* Lindl. 1861**
Abies vulgaris Poir., see *Abies alba* Mill. 1768
Abies webbiana Lindl. var. *pindrow* (Royle) Brandis, see *Abies pindrow* (D.Don) Royle

Larix
Larix alaskensis W. Wight, see *Larix lariciana* (Du Roi) K. Koch
Larix amurensis Beissn., see *Larix gmelinii* (Rupr.) Kuzeneva 1920
Larix archangelica Lawson, see *Larix sibirica* Ledeb.
Larix cajanderi Mayr, see *Larix gmelinii* (Rupr.) Kuzeneva 1920
Larix dahurica Turcz. ex Trautv. var. *cajanderi* (Mayr) Szafer, see *Larix gmelinii* (Rupr.) Kuzen.
Larix dahurica Turcz. ex Trautv. var. *japonica* Maxim. ex Regel,
see *Larix gmelinii* (Rupr.) Kuzen. var. *japonica* (Maxim. ex Regel) Pilg.
Larix dahurica Turcz. ex Trautv., see *Larix gmelinii* (Rupr.) Kuzeneva 1920
Larix dahurica Turcz. var. *pubescens* Patscke, see *Larix gmelinii* (Rupr.) Kuzen.
Larix dahurica Turcz., see *Larix gmelinii* (Rupr.) Kuzen.
Larix dahurica var. *prostata* Reg., see *Larix gmelinii* (Rupr.) Kuzeneva 1920
Larix dahurica var. *pubescens* Patschke, see *Larix gmelinii* (Rupr.) Kuzeneva 1920
***Larix decidua* Mill. 1768**
Larix decidua Mill. ssp. *sibirica* (Ledeb.) Domin, *see Larix sibirica* Ledeb.
Larix decidua Mill. var. *sibirica* (Ledeb.) Regel, see *Larix sibirica* Ledeb.
Larix decidua var. *russica* Henk. and Hochst., see *Larix sibirica* Ledeb.
Larix decidua var. *sibirica* (Ledeb.) Reg., see *Larix sibirica* Ledeb.
Larix europaea DC. var. *rossica* (Henkel & Hochst) Beissn., see *Larix sibirica* Ledeb.
Larix europaea DC. var. *sibirica* (Fisch.) Loud., see *Larix sibirica* Ledeb.
Larix europaea Lam. & DC., see *Larix decidua* Mill.
Larix europaea Middend., see *Larix sibirica* Ledeb.
***Larix gmelinii* (Rupr.) Kuzeneva 1920**
Larix gmelinii var. *hsinganica* Yang & Chou, see *Larix gmelinii* (Rupr.) Kuzeneva 1920
***Larix gmelinii* var. *japonica* (Maxim. et Regel) Pilg.**

***Larix gmelinii* var. *olgensis* (Henry) Ostenf & Syrach**

Larix heilingensis Yang & Chou. , see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Larix intermedia Fisch. ex. Turcz., see *Larix sibirica* Ledeb.

Larix intermedia K.Koch, see *Larix gmelinii* (Rupr.) Kuzen.

Larix japonica A. Murray bis 1863 non Carr. 1855, see *Larix kaempferi* (Lamb.) Carr. 1856

Larix japonica Carr., see *Larix kaempferi* (Lamb.) Carr.

Larix japonica hort. ex Carr. 1855, see *Larix kaempferi* (Lamb.) Carr. 1856

***Larix kaempferi* (Lamb.) Carr. 1856**

Larix kamtschatica (Endl.) Carr., see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Larix komarovii Kolesn., see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Larix kurilensis Mayr, see *Larix gmelinii* (Rupr.) Kuzen.

Larix kurilensis Mayr, see *Larix gmelinii* var. *japonica* (Regel) Pilg.

***Larix lariciana* (Du Roi) K. Koch 1873**

Larix ledebourii (Rupr.) Cinovskis, see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Larix leptolepis (Sieb. & Zucc.) Gordon, see *Larix kaempferi* (Lamb.) Carr.

Larix leptolepis (Sieb. et Zucc.) Gord. (1858), see *Larix kaempferi* (Lamb.) Carr. 1856

Larix leptolepis var. *louchanensis* Ferré et M.T. Augère 1943., see *Larix kaempferi* (Lamb.) Carr. 1856

Larix middendorfii Kolesn., see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Larix ochotensis Kolesn., see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Larix olgensis A.Henry, see *Larix gmelinii* (Rupr.) Kuzen. var. *olgensis* (A.Henry) Ostenf. & Syrach

Larix russica (Endl.) Sabine ex Trautv. 1884, see *Larix sibirica* Ledeb.

***Larix sibirica* Ledeb. 1833**

Larix sibirica Maxim., see *Larix gmelinii* (Rupr.) Kuzeneva 1920

Larix sibirica Sabine ex Lindl., see *Larix sibirica* Ledeb.

Larix sudetica Domin (Farjon 1990), see *Larix decidua* Mill.

Larix sukachevii Djil., see *Larix sibirica* Ledeb.

Larix sukaczewii (Dylis) 1981 (W.C.Cheng & L.K.Fu 1978), see *Larix sibirica* Ledeb.

Picea

***Picea abies* (L.) H. Karst. 1881**

Picea alba (Aiton) Link, see *Picea glauca* (Moench) Voss

Picea albertiana S.Br., see *Picea glauca* (Moench) Voss

Picea brevifolia Peck, see *Picea mariana* (Mill.) B.S.P.

Picea canadensis (Mill.) B.S.P., see *Picea glauca* (Moench) Voss

Picea concolor Gord. 1858, see *Abies concolor* (Gord. & Glend.) Hildebr. 1861

Picea excelsa (Lam.) Link, see *Picea abies* (L.) H. Karst.

Picea excelsa Wender., see *Abies alba* Mill.

Picea falcata (Raf.) Suringar, see *Picea sitchensis* (Bong.) Carr.

***Picea glauca* (Moench) Voss 1907**

Picea intercedens Nakai, see *Picea koraiensis* Nakai

***Picea koraiensis* Nakai 1919**

***Picea mariana* (Mill.) B.S.P. 1888**

Picea menziesii (D.Don) Carriére var. *crispa* (Ant.) Carriére, see *Picea sitchensis* (Bong.) Carrière

Picea menziesii (Dougl. ex D. Don) Carr., see *Picea sitchensis* (Bong.) Carr.
Picea menziesii (Engelm.) Engelm., see *Picea pungens* Engelm.
Picea montana Schur, see *Picea abies* (L.) H. Karst.
Picea nigra (Aiton) Link var. *brevifolia* (Peck) Rehder ex L.H.Bailey, see *Picea mariana* (Mill.) B.S.P.
Picea nigra (Aiton) Link, see *Picea mariana* (Mill.) B.S.P.
Picea omorica, see *Picea omorika* (Pančić) Purk. 1877
***Picea omorika* (Pančić) Purk. 1877**
Picea parryana Sarg., see *Picea pungens* Engelm.
Picea pectinata (Lam.) Loudon, see *Abies alba* Mill.
***Picea pungens* Engelm. 1877**
Picea rubra A. Dietr., see *Picea abies* (L.) H. Karst.
***Picea sitchensis* (Bong.) Carr. 1855**
Picea sitchensis Trautv. & Mey. see *Picea sitchensis* (Bong.) Carrière
Picea tonaiensis Nakai, see *Picea koraiensis* Nakai
Picea veitchii (Lindl.) Gord. 1862, see *Abies veichii* Lindl.
Picea vulgaris Link, see *Picea abies* (L.) H. Karst.

Pinus
Pinus abies Du Roi var. *leioclada* Steven ex Endl., see *Abies alba* Mill.
Pinus abies L. var. *mariana* (Mill.) Mänchh., see *Picea mariana* (Mill.) B.S.P.
Pinus abies L. var. *pectinata* (Lam.) H. Christ, see *Abies alba* Mill.
Pinus abies L., see *Picea abies* (L.) H. Karst.
Pinus alba Aiton (Taylor 1993)., see *Picea glauca* (Moench) Voss
Pinus alba Aiton var. *canadensis* Prov., see *Pinus strobus* L.
Pinus baldensis Zuccagni, see *Abies alba* Mill.
Pinus balsamea L. 1753 (Hunt 1993)., see *Abies balsamea* (L.) Mill.
***Pinus banksiana* Lamb. 1803**
Pinus canadensis L. 1763 (Taylor 1993)., see *Tsuga canadiensis* (L.) Carr.
Pinus cembra L. ssp. *sibirica* (Du Tour) Krylov, see *Pinus sibirica* Du Tour
Pinus cembra L. var. *sibirica* (Du Tour), see *Pinus sibirica* Du Tour
Pinus chylla Lodd, see *Pinus wallichiana* A.B. Jacks.
Pinus concolor (Gord.) Parl. in D.C. 1868, see *Abies concolor* (Gord. & Glend.) Hildebr. 1861
***Pinus contorta* Dougl. 1883**
Pinus coronans Litv. 1913, see *Pinus sibirica* Du Tour
Pinus denticulata (Michx.) Muhl., see *Picea mariana* (Mill.) B.S.P.
Pinus divaricata (Aiton) Dum.Cours., see *Pinus banksiana* Lamb.
Pinus divaricata (Aiton) Sudworth, see *Pinus banksiana*
***Pinus elliottii* Engelm. 1880**
Pinus escarena Risso 1826, see *Pinus pinaster* Aiton
Pinus excelsa Wall. ex. D. Don, see *Pinus wallichiana* A.B. Jacks.
***Pinus gerardiana* Wall. 1832**
Pinus gerardii J.Forbes 1833, see *Pinus gerardiana* Wall.
Pinus glomerata Salisb. 1796, see *Pinus pinaster* Aiton

Pinus griffithii McClelland 1854 non Parl., see *Pinus wallichiana* A.B. Jacks.
Pinus hamiltonii Ten. 1845, see *Pinus pinaster* Aiton
Pinus heterophylla (Elliott) Sudworth 1893, not K. Koch 1849, see *Pinus elliottii* Engelm.
Pinus hingganensis H.J. Zhang 1985, see *Pinus sibirica* Du Tour
Pinus hudsonica Poir., see *Pinus banksiana* Lamb.
Pinus insignis Dougl. ex Loud. (Kral 1993, Millar 1986), see *Pinus radiata* D. Don
Pinus intermedia (Fisch.) Turcz., see *Larix sibirica* Ledeb.
Pinus kaempferi Lamb. (1824), see *Larix kaempferi* (Lamb.) Carr. 1856
Pinus laricina Du Roi 1771, see *Larix lariciana* (Du Roi) K. Koch
Pinus laricio Poir., see *Pinus nigra* Arnold
Pinus laricio Savi 1798, see *Pinus pinaster* Aiton
Pinus larix L. 1753, see *Larix decidua* Mill.
Pinus larix Thunb., see *Larix kaempferi* (Lamb.) Carr. 1856
Pinus larix var. *russica* Endl., see *Larix sibirica* Ledeb.
Pinus lasiocarpa Hooker 1838., see *Abies lasiocarpa* (Hook.) Nutt.
Pinus ledebouri (Rupr.) Endl., see *Larix sibirica* Ledeb.
Pinus leptolepis (Sieb. et Zucc.) Endl. 1847, see *Larix kaempferi* (Lamb.) Carr. 1856
Pinus longifolia Roxb. ex Lamb. 1803 non Salisb. 1796, see *Pinus roxburghii* Sarg.
Pinus lucida Salisb., see *Abies alba* Mill.
Pinus lutea Walter, see *Pinus taeda* L.
Pinus mariana (Mill.) Du Roi, see *Picea mariana* (Mill.) B.S.P.
Pinus maritima Poir., see *Pinus pinaster* Aiton
Pinus menziesii Dougl. ex D. Don (Taylor 1993)., see *Picea sitchensis* (Bong.) Carr.
Pinus menziesii Douglas ex D.Don var. *crispa* Ant., see *Picea sitchensis* (Bong.) Carrière
Pinus mertensiana Bong. 1832, see *Tsuga mertensiana* (Bong.) Carr.
Pinus mesogeensis Fieschi & Gaussen 1932, see *Pinus pinaster* Aiton
Pinus montereyensis Rauch, see *Pinus radiata* D.Don
Pinus nepalensis De Chambey, see *Pinus wallichiana* A.B. Jacks.
Pinus nigra Aiton (Taylor 1993), see *Picea mariana* (Mill.) B.S.P.
***Pinus nigra* Arnold. 1785**
Pinus omorika Pančić, see *Picea omorika* (Pančić) Purkyne 1877
Pinus parryana Ehrh. ex Voss, see *Picea pungens* Engelm.
Pinus pattoniana (Balf.) Parl., see *Tsuga mertensiana* (Bong.) Carr.
Pinus pectinata Lam., see *Abies alba* Mill.
Pinus picea L., see *Abies alba* Mill.
***Pinus pinaster* Aiton 1789**
Pinus pindrow (Royle) D.Don, see *Abies pindrow* (D.Don) Royle
***Pinus radiata* D. Don 1836**
***Pinus resinosa* Aiton 1789**
***Pinus roxburghii* Sarg. 1897**
Pinus rubra Michx., see *Pinus resinosa* Aiton
Pinus rupestris F. Michx., see *Pinus banksiana* Lamb.

Pinus selenolepis Parl. 1868, see *Abies veichii* Lindl.

Pinus sibirica (Loudon) Mayr, see *Pinus sibirica* Du Tour

***Pinus sibirica* Du Tour 1803**

Pinus silvestris L. 1753, see *Pinus sylvestris* L. 1753

Pinus sitchensis Bong. 1832, see *Picea sitchensis* (Bong.) Carr.

***Pinus strobus* L. 1753**

Pinus sylvestris L. var. *divaricata* Aiton, see *Pinus banksiana* Lamb.

***Pinus sylvestris* L.1753**

***Pinus taeda* L. 1753**

Pinus takahasii Nakai, see *Pinus sylvestris* L.

Pinus taxifolia Lamb. 1803, not Salisb. 1796, see *Pseudotsuga menziensii* (Mirb.) Franco

Pinus tuberculata D. Don, see *Pinus radiata* D. Don

Pinus veitchii (Lindl.) McNab 1876 non Roezl, see *Abies veichii* Lindl.

***Pinus wallichiana* A.B. Jacks. 1938**

Other

Hesperopeuce mertensiana (Bong.) Rydb., see *Tsuga mertensiana* (Bong.) Carr.

Hesperopeuce pattoniana (Balf.) Lemm. (Taylor 1993), see *Tsuga mertensiana* (Bong.) Carr.

Leucopitys strobus (L.) Nieuwl., see *Pinus strobus* L.

Peuce abies (DuRoi) Rich., see *Abies alba* Mill. 1768

Pseudotsuga douglasii (Lindl.) Carr., see *Pseudotsuga menziensii* (Mirb.) Franco

Pseudotsuga douglasii Carrière var. *caesia* Schwer., see *Pseudotsuga menziesii* (Mirb.) Franco

***Pseudotsuga menziensii* (Mirb.) Franco 1950**

Pseudotsuga mucronata (Raf.) Sudw., see *Pseudotsuga menziensii* (Mirb.) Franco

Pseudotsuga taxifolia (Lamb.) Britt. (Lipscomb 1993)., see *Pseudotsuga menziensii* (Mirb.) Franco

Strobus weymouthiana Opiz, see *Pinus strobus* L.

***Tsuga canadiensis* (L.) Carr. 1855**

Tsuga crassifolia Flous, see *Tsuga mertensiana* (Bong.) Carr.

***Tsuga heterophylla* (Raf.) Sarg. 1898**

***Tsuga mertensiana* (Bong.) Carr. 1867**

Tsuga pattoniana (Balf.) Sénéclause, see *Tsuga mertensiana* (Bong.) Carr.

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