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A literature review

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Summary

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Forest-based biomass is one of the main sources of energy and feedstock for industrial production of bio-materials, bio-chemicals, bio-fuels, and other novel bio-refinery products in Finland. Apart from its main chemical constituents (cellulose, hemicellulose and lignin), wood also contains a wide variety of low molecular mass compounds known as extractives. These compounds can be separated from insoluble wood constituents by simple solvent extraction using polar or non-polar solvents. The aim of enhancing efficiency in the utilization of feedstock through product diversification and improved recovery has led to an increased interest in studying individual chemical components of wood. In particular, extractive compounds provide potential functionalities for several types of industrial chemicals and well-being and health products for consumers.

The extractives content within a tree and between trees in the same stand is not uniform and may also vary according to the age of the trees, the season, the site and provenance. Differences in the amounts of extractives from one geographic location to the next can be found, but the differences between plots and parts of a single tree are clearer.

The effects of different factors (e.g. location, the part of the tree, age, the site type, time of harvesting, or storage time) on the quantity of extractives have been well studied, but no review summarizing the effects of the aforementioned parameters on individual extractive compounds exists. A comprehensive review (or a set of more detailed summaries) concerning the extractive compositions of the overall tree biomass (incl. not only the stem, but also the bark, foliage, and stump-root system) of most common Finnish industrial wood species has not been available until now. Often scientific articles are concentrated on studying certain parts of trees, while some examine the geographic origins or site, or they might focus on even more specific issues such as certain groups of compounds in certain parts of the tree. In addition, the study material in some studies is very limited. In this report the results of the studies on extractives of Norway spruce, Scots pine, and silver and white birch have been summarized to facilitate the identification of the best suitable biomass assortments for sourcing future biorefineries and their production lines.

Keywords: extractives, secondary metabolites, Norway spruce, Scots pine, silver birch, white birch, value added chemicals, forest industry, circular economy, biorefining/biorefinery

Tiivistelmä

Metsäbiomassa on yksi biomateriaalien, biokemikaalien ja muiden uusien biotuotteiden sekä bioenergian pääraaka-aineista. Pääosa metsäbiomassasta koostuu erilaisesta puuaineksesta. Puussa on sen pääkomponenttien (selluloosa, hemiselluloosa ja ligniini) lisäksi erilaisia pienimolekyylisiä uuteaineita, jotka voidaan nimensä mukaisesti erottaa puusta uutamalla. Nykyisin metsäbiomassan hyödyntämistä pyritään kasvattamaan ja käyttöä monipuolistamaan, minkä vuoksi yksittäisiin uuteaineyhdisteisiin kohdistuva kiinnostus lisääntyy. Näitä uuteaineyhdisteitä voidaan hyödyntää erityisesti lähtöaineina hyvinvointi- ja terveystuotteiden ja erilaisten teollisuuskemikaalien valmistuksessa.

Uuteaineiden koostumus ja määrä puun sisällä ja puuyksilöiden välillä vaihtelee runsaasti, ja lisäksi puun ikä, korjuuajankohta, geneettinen alkuperä ja kasvupaikka vaikuttavat uuteaineiden määrään. Uuteaineiden määrä vaihtelee maantieteellisen sijainnin mukaan, mutta erot ovat paljon selvemmät puun eri osien välillä ja yksittäisten metsikköjen välillä.

Eri tekijöiden vaikutusta uuteaineiden määrään on tutkittu paljon, mutta yhteenvetoa näiden tekijöiden vaikutuksesta ei ole tehty. Kattavia tai yksityiskohtaisia yhteenvetoja koskien uuteaineiden määrää puun eri osissa (ei vain runkopuussa, vaan myös kuoressa, lehvästössä, kantopuussa ja juurissa) ei ole tehty yleisimmillä suomalaisilla puulajeilla. Tieteelliset artikkelit ovat usein keskittyneet tiettyyn puun osaan, tai yhteen tiettyyn yhdisteryhmään tietyssä osassa puuta. Lisäksi tutkitut aineistot ovat olleet usein pieniä. Tämä raportti on yhteenveto kuusen, männyn ja koivun uuteaineiden tutkimustuloksista. Sen tulosten toivotaan edesauttavan biojalostukseen ja sen prosesseihin parhaiten soveltuvien biomassaositteiden tunnistamisessa.

Asiasanat: uuteaineet, kuusi, mänty, rauduskoivu, hieskoivu, arvokemikaalit, metsäteollisuus, kierto-talous, biojalostus/biojalostamo

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1. Introduction

The aim of forest management worldwide has changed over the years. In Finland and the other Nordic countries, the shift has been towards management practices aiming at producing both quality timber in addition to other forest products and services (Routa et al. 2013). The product palette is currently broadening to include novel biorefinery products, liquid biofuels, wild forest products and a multitude of forest related ecosystem services. This is obviously reflected in forest management schemes as well. One of the management options available is to implement pre-commercial and commercial forest thinnings to promote the volume growth and formation of high quality wood in the remaining trees before final harvesting of the trees. This practice combined with other management options, such as increased initial stand density and forest fertilization, increases the generation of forest biomass collectively including energy wood (logging residues, small diameter stem wood and stumps) (Alam et al. 2010). Trees from thinning operations have been used primarily as a raw material in the pulp, paper and paperboard industries. In addition, small-diameter logs for mechanical wood processing can be recovered as well as biomass for the production of wood energy for households, heating plants and combined heat and power plants.

Forest-based biomass is the largest single source of energy and a very potential feedstock for industrial production of different bio-materials, bio-chemicals, bio-fuels, and other novel bio-refinery products in Finland. Interest in studying the individual chemical components of wood with the aim of enhancing efficiency in feedstock utilization through product diversification and improved recovery has been increasing. Apart from its main chemical constituents (cellulose, hemicellulose, and lignin), wood also contains a wide variety of low molecular mass compounds known as extractives. These compounds can be separated from the insoluble wood constituents by simple solvent extraction using polar or non-polar solvents. In particular, wood extractives provide potential functionalities for several types of platform and specialty chemicals, such as pharmaceutical or nutritional products, cosmetics, beverages, wood adhesives, paints, wood protection agents, plant-protective products and detergents (Roitto et al. 2016). Valuable compounds can be obtained directly from different parts of standing trees (Mantau & Saal 2010), or as by-products of forest industries (Saal 2010). Specialty chemicals have a potentially high value in various raw materials and products for techno-chemical industries and a multitude of consumer products. The demand for nature-derived ingredients to replace synthetic chemicals is increasing and markets for natural health products are growing (Royer et al. 2012).

In addition to cellulose and lignin, the most important chemical factors affecting the quality of wood are extractives, since their presence affects the processing and use of wood. In use, either in the soil, above ground or immersed in water, wood is exposed to attack from a number of bacteria, fungi, insects and marine organisms (Zabel & Morrell 1992). The major contribution of extractives in the use of solid wood is in their natural resistance against fungi and insects they impart. The extractives also add to the density, geometric stability and some mechanical properties of wood (e.g. Hillis 1971, Zobel & van Buijtenen 1989, Hakkila and Verkasalo 2009).

The chemical composition of wood cannot be defined precisely for a given tree species or even for a single tree (Alen 2011). The wood chemical composition of an individual tree can be influenced by many factors and variations exist between tree part (bark, stem, or branch), the type of stemwood (sapwood or heartwood) and the growth conditions, among other factors (Alen 2000, 2011). In addition, the age of a tree has effects on the extractives of the tree; generally, old trees contain more extractives in their heartwood than young trees (Hillis 1962, Uprichard and Lloyd 1980). While differences in the chemical composition of major cell wall components of the three (cellulose, hemicelluloses and lignin) vary only sparingly between different tree species, there is a great diversity in the extractives throughout species (Umezawa 2000). The extractives content within an individual tree or and between trees in same stand is not uniform (Solhaug 1990, Bergström et al. 1999, Ekeberg et al. 2006) and it may considerably vary according to age, season, provenance and

site (Solhaug 1990, Toscano et al. 1991, Lindberg et al. 1992). Differences in the amounts of extractives in different geographic locations can also be found (Wilföör et al. 2003a, Kaakinen 2007, Piispanen 2008, Hakkila & Verkasalo 2009, Roitto et al 2016), but the differences between plots and parts of single trees are clearer. This has effects on the supply of raw materials, sampling and sorting if the aim is to procure raw materials containing specific extractives or to avoid certain extractives in the raw materials.

In pulping, the presence of extractives is detrimental (Martinez-Inigo et al. 1999, Pereira et al. 2003). Usually, the extractives affect the bleachability of pulps negatively, causing lower brightness and higher brightness reversion of kraft pulp or lead to increased consumption of bleaching chemicals (Jewell et al. 1991). On the other hand, tall oil and turpentine are commercially important side-products of softwood kraft pulping (Alén 2000). Tall oil has wide variety of uses in industry (see chapter 7). For example, fats are valuable resources for producing fuels such as biodiesel while resins are suitable for producing glues and inks (Demirbas 2011). Wood knots which contain more extractives than clear wood, are particularly detrimental to pulping processes and pulp quality; and they should preferably be separated before pulping (Wilföör et al. 2004).

The forest industries use substantial amounts of wood resources annually in Finland. In total 67 million m³ of wood were utilized in 2016 (Official Statistics of Finland 2017a). As a result of this utilization, there are significant amounts of side streams such as bark, branches and tree stumps. The consumption of bark in energy use in Finland was about 7.3 million m³ in 2016. Additionally, 2.5 million m³ of logging residues and 0.8 million m³ of tree stumps were used in energy production in 2016 (Official Statistics of Finland 2017b).

The aims of this report are 1) to identify the most interesting wood extractives for biorefining, 2) to assess the factors influencing the variation of their concentrations and 3) to summarize the data on concentrations. A number of selected experts were interviewed to identify the extractives with the highest utilization potential. A literature review was then carried out to determine the average concentrations of extractives and their variation due to a variety of factors. The main emphasis was on the industrially most important Finnish tree species, namely Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*), silver birch (*Betula pendula*) and white birch (*Betula pubescens*).

2. Expert interviews

A total of eight experts (listed in the Acknowledgements) representing both research and industry were interviewed to determine the most interesting extractives and other compounds now and in the future from the perspective of research and development activities and industrial utilization. The experts were asked whether it was possible for them to name some individual extractives that occur in forest biomass and which of the extractives would be interesting for industrial-scale utilization. They were also asked for specific information on how different factors (e.g. geographic location, part of tree, age, site type, time of harvesting, or storage time) affect the yield of extractives.

The experts emphasized some extractive groups, but also some interesting single compounds. Stilbenes, tannins, lignans and terpenes were mentioned in every interview. Additionally, pinosylvin, pinosylvin monomethyl ether (stilbens), hydroxymatairesinol (lignans), betulin (triterpenoid), α - β -pinene (monoterpenes), resin acids (diterpenoids) and fatty acids were all listed. In addition, galactoglucomannan (hemicellulose) and xylans (hemicellulose) were mentioned as interesting compounds, although they are not extractives.

The concern of chemical instability and decomposition of extractives during the storage of wood-based raw materials was also raised. Amounts of hydrophilic and lipophilic extractives decrease significantly during storage, as do lipophilic extractives. Therefore, it is important to plan supply chains taking storage losses into consideration.

The scale of operations was also mentioned as a risk factor. If extractives are utilized on a large scale in the secondary flow of a pulp mill, it does not mean much if the concentration is a little bit higher of some individual compounds of extractives from wood from some particular areas. However, on a small-scale use, when a company has specialized in selected valuable products, for example pharmaceutical or nutritional products, the choice of raw material sources is very important. According to one of the experts, it may be possible to separate selected extractives more accurately with special methods (e.g. hot water extraction was mentioned) retaining the original composition of the compounds. Furthermore, the experts emphasized the very large inter-tree variation in concentration and variation in spatial distribution of extractives.

3. Extractives

Extractives are numerous low molecular mass non-structural compounds present in wood that can be extracted using polar and non-polar solvents (Hillis 1971, Alen 2000, Taylor 2002). They include compounds such as alkaloids, waxes, fats, proteins, phenolics, gums, pectins, resins, terpenes, and essential oils (Nascimento et al. 2013).

Most of the extractives are secondary metabolites, which are compounds that play other roles in a tree than those involved in growth and cell development, namely protection of the tree against pathogens or other biotic attacks (Barnett and Jeronimidis 2003). Morphological sites and main functions of different wood extractives are shown in Table 1. The secondary metabolites are preferentially deposited in the inner part of the stem, in the heartwood. In the outer part of the stem, the sapwood includes recently divided cell layers, where molecules used in the metabolic synthesis of the cell wall are found as extractives. Some species have specialized defense structures to protect themselves from attack, either physical or biotic. For example, resin canals in softwoods are particularly developed in pines that produce resin, which is a mixture of terpenoid compounds which are also important extractives in the wood of these trees (Table 1). A high content of extractives and their nature may be involved in the defense strategy of trees against biotic and abiotic injuries. Extractives represent a small proportion of wood, typically less than 10% of the dry mass, with the exception of tropical woods, where the proportion can be higher.

There are considerable differences between extractives in softwoods and hardwoods, and also between tree species. Resin acids occur only in softwoods and the proportions between individual resin acids differ between tree species. The fatty acid composition also differs between softwoods and hardwoods and also between tree species (Holmbom 1999).

Table 1. Morphological sites and main functions of wood extractives (Holmbom 1999).

Location in wood	Major compound classes	Main function in the tree
Resin canals (oleoresin)	Resin acids, monoterpenoids, other terpenoids	Protection
Parenchyma cells	Fats, fatty acids, steryl esters, sterols	Physiological food reserve, cell membrane components
Heartwood	Phenolic substances	Protection
Cambium and growth zone	Glycosides, Sugars, starch, proteins	Biosynthesis, food reserve
Ascending water Sap	Inorganics	Photosynthesis, biosynthesis

Extractives of wood can be classified into the different groups as shown in Table 2, i.e. aliphatic and alicyclic compounds, phenolic compounds and other compounds. The composition of extractives varies widely from species to species, and the total amount of extractives in a given species depends on the growth conditions. For example, the typical content of extractives in Scots pine, Norway spruce and silver birch stem wood are, respectively, in the range of 2.5% to 4.5%, 1.0% to 2.0%, and 1.0% to 3.5%, of the wood on a dry basis (Alén 2011).

Table 2. Classification of organic extractives in wood (Alén 2011).

Aliphatic and alicyclic compounds	Phenolic compounds	Other compounds
Terpenes and terpenoids (including resin acids and steroids) Esters of fatty acids (fats and waxes) Fatty acids Alkanes	Simple phenols Stilbenes Lignans Isoflavones Flavonoids Condensed tannins Hydrolyzable tannins	Sugars Cyclitols Tropolones Amino acids Alkaloids Coumarins Quinones

However, many initial extractives suitable for potential applications are either rather volatile or chemically unstable. As it was mentioned in the expert interviews, the amount of many extractives starts to decrease immediately after tree felling and this degradation continues during storage (Ekman 2000, Lappi et al. 2014a). This also means that the chemical composition of the extractives-based fraction changes as a function of time (Lappi et al. 2014a, b, c, Alén 2000).

All chemical and biochemical reactions are largely influenced by the conditions prevailing during wood storage and they are markedly faster when the wood is stored in the form of chips instead of logs. The volatile extractives in the wood tissue of different tree species are unique and may be used for species identification (Wajs et al. 2007).

4. Variation of chemical composition

4.1. Different parts of the tree

4.1.1. Stem: Heartwood and sapwood

The formation of heartwood is strongly dependent on the age of the tree. Heartwood differs from sapwood in anatomical and physiological features. Heartwood is darker in color and denser and stiffer than sapwood in some species (Taylor et al. 2002, Spicer 2005), while heartwood contains more extractives than sapwood (Rydholm 1967, Yanchuk et al. 1988, Campbell et al. 1990).

Norway spruce sapwood contains more lipophilic extractives than heartwood (Ekman 1979, Bertaud and Holmbom 2004). This is mainly due to the larger quantity of triglycerides. The qualitative composition of volatile organic compounds (VOCs) is similar in spruce sapwood and heartwood in the study of Wajs et al. (2006).

Higher amounts of terpenes have been found in the heartwood than in the sapwood of southern pines while fatty acids and resin acids have been found more in the heartwood of radiata pine (Upprichard and Lloyd 1980, Ingram et al 2000). The total resin acid concentration in Scots pine heartwood is much higher than in the sapwood, but the composition of resin acids is similar (Martinex-Inigo 1999, Turtola 2002). In a study by Arshadi et al. (2013), Scots pine heartwood contained up to five times more extractives than sapwood. Furthermore, resin acids were mainly associated with heartwood, but fatty acids were found more in sapwood. Additionally, the quantity of stilbenes (e.g. pinosylvins and pinosylvin monomethyl ester) in Scots pine heartwood is higher than in the sapwood (Willför 2003b, Ekeberg et al 2006, Siwale 2015).

The total extractive content of birch stemwood is low but it seems to rise from the base toward the top (Roitto et al. 2016). Piispanen & Saranpää (2004) found that the concentration of fatty acids and steryl esters were highest in samples close to the pith.

The heartwood samples of goat willow (*Salix caprea*) stemwood contained 5–20 times more hydrophilic extractives (most abundant catechin) than the sapwood samples (Pohjamo et al. 2003).

The heartwood and sapwood samples of common aspen (*Populus tremula*) and quaking aspen (*Populus tremuloides*) contained similar amounts of extractives (Pietarinen et al. 2006a).

4.1.2. Knots

Internal knots (i.e. branch bases inside tree stems) of several tree species have a remarkably high amount of phenolic substances, being therefore a valuable source of bioactive compounds. Softwood knots contain extremely large amounts of phenolic extractives (Willför et al. 2002, Holmbom et al. 2003, Willför et al. 2003a, b, c). Norway spruce knots contain as much as 6–24% of lignans, with 7-hydroxymatairesinol (HMR) as the predominant (70–85%) compound (Holmbom et al. 2003, Willför et al. 2002, 2003a, Kebbi-Bendeker et al. 2015). Some other spruce species also contain HMR as the main lignan, but some spruce species also have other dominating lignans. The content of lignans in knot heartwood can be 30–500 times higher than in the stem heartwood. (Willför et al. 2003a). The variation in the amount of lignan is large from knot to knot, both in an individual tree and from tree to tree (Willför 2003 a). Lignans occur also in the knots of pines, although in lower amounts than in the knots of spruces or firs (Holmbom et al. 2003).

The concentration of extractives in the knotwood of Scots pines has been found to be higher than that in the stem heartwood (Erdtman and Rennerfelt 1944, Boutelje 1966, Willför et al. 2003a, Hovelstad et al. 2006), even up to four- to five-fold in a study by Karppanen et al. (2007). Scots pine knots have been found to contain 0.4–3% of lignans and 1–2.95% of stilbenes (Ekman et al. 2002,

Willför 2003b, Hovelstad et al. 2006). Furthermore, Scots pine knots also contain large amounts of lipophilic extractives (4.5–32%) mainly resin acids (Willför 2003b).

Lignans have also been identified in the knots of some hardwoods, although flavonoids are more abundant in hardwoods. The concentrations of hydrophilic extractives in willow have been found to be 2–10 times higher in the knots than in the stemwood (Pohjamo et al. 2003). Aspen (*Populus tremula*) knots have been found to be a rich source of bioactive flavonoids, and the quantity of hydrophilic extractives is larger in the knots than in the stemwood (Pietarinen et al. 2006a).

The lignan content gradually decreases in the radial direction from the knot pith towards the outer wood, finally reaching the same level as in the surrounding stemwood (Willför et al. 2003a). In the branches, the lignan content also decreases in the radial direction from the branch pith outwards, and approaches the same level as it is in the stemwood 20 cm outside the stem (Willför et al. 2005).

The fact that the knots contain considerable amounts of lignans, unlike the surrounding wood tissue can be of technical and industrial importance. The knots can be recovered in a pulp mill before pulping and the lignans can then be extracted and utilized as active ingredients in health-promoting foods or pharmaceuticals, or as natural antioxidants in various applications (Willför et al. 2005).

The HMR concentration is also the highest in the knots close to the starting point of the living crown and in knots that are in connection to living branches (Piispanen et al. 2008, Willför 2003a). Snow loading on the branches can also affect the lignan concentrations of the knots, causing mechanical loading in branch wood (Piispanen et al. 2008). Branches and thus knots seem to possess a chemical response to mechanical loads such as wind and snow, especially in the case of softwoods, which do not lose their leaves during winter.

The extractive content in the knots of broad-leaved species (hardwoods) is lower than in coniferous species (softwoods) (Pohjamo et al. 2003, Pietarinen et al. 2006 a, b). The knotwood of hardwoods contains mainly flavonoids, tannins and/or sugars (Kebbi-Bendeker et al. 2015).

4.1.3. Bark

Bark represents typically 10–15% of total weight of tree stems (Fengel and Wegener 1984, Sipi 2006, Krogell et al. 2012). Large amounts of bark waste are produced in the pulp and paper industry and in sawmilling operations. Bark is currently used mainly for producing heat and power. The extraction of valuable components before combustion is an interesting option for better utilization of tree bark. Bark contains 2–6 times more extractives than stemwood does. The total content of both lipophilic and hydrophilic extractives usually corresponds to 20–40% of the dry weight of bark (Sjöström 1993). For this reason, bark can be considered a potential raw material for the production of a range of value-added products, e.g. platform and specialty chemicals, cosmetics, dietary supplements, biopolymers, bioplastics, foams/emulsions, coatings, pharmaceuticals (drugs or drug precursors).

Bark is both morphologically and chemically very heterogeneous, and also differs considerably between wood species; not only between hardwoods and softwoods, but also between individual hardwood and softwood species (Fengel and Wegener 1984, Sakai 2001). Bark is built up of two major parts: the inner bark and outer bark. The proportion of inner and outer bark varies between species and according to the age of the tree, and it depends also on the height of the tree. The overall composition of inner and outer tree bark differs considerably.

The quantity of lipophilic extractives has been found to be about two times larger in the outer bark of Norway spruce compared to the inner bark (Ånäs et al. 1983, Krogell et al. 2012). The overall compositions of inner and outer bark of Norway spruce differ significantly: the inner bark contains large amounts of hydrophilic extractives whereas the outer bark contains more lipophilic extractives (Krogell et al. 2012). Resin acids, fatty acids, sterol esters, diterpenoids and triglycerides are the dominant compounds in Norway spruce bark (Ånäs et al. 1983, Krogell 2012). Stilbene glucosides, isorhapontin, astringin and piceid may account for up to 7.2% of Norway spruce bark dry weight (Man-

nila and Talvitie 1992, Krogell et al. 2012, Jyske 2014). According to Latva-Mäenpää (2017) the average concentrations of major stilbenoid glucosides (isorhapontin and astringin) are mainly localized in the inner bark of stumps and roots, and the concentrations are 30–200 times higher in the inner bark compared to the outer bark. Unique component in bark that is not present in wood is the suberin (Krogell et al 2012). Another example regarding the common softwood species, *P. sylvestris* and *P. abies*, are the condensed tannins that are present in bark but not in wood (see table 6).

Resin acids and fatty acids are dominant compounds in Scots pine bark (Valentín et al. 2010). Bark extract have also been found to contain smaller amounts of other lipophilic compounds as well as some phenolic compounds such as stilbene glycosides, lignans and flavonoids (Pan and Lundgren 1996). The lipophilic compounds include fatty acids, fatty alcohols, oxidised resin acids, and sterols (Valentín et al. 2010, Belt 2013). Pine bark has also been found to be rich in condensed tannins (Karonen et al. 2004a, Matthews et al. 1997).

The highest concentrations of extractives in birch wood are found in bark (Roitto et al. 2016). The concentrations of individual compounds are quite low in birch bark (less than 1%) except for betulinol (up to 12.7%) (Roitto et al. 2016). Birch bark chemistry differs considerably from that of spruce and pine. For example, the outer bark of silver birch trees contains about 40% extractives, 45% suberin, 9% lignin, 4% hemicelluloses and 2% cellulose (Pinto et al. 2009). The extractives mainly comprise different triterpenoids, especially betulin and different betulin derivatives, accounting for as much as 30% of the dry weight (Ekman 1983). The birch outer bark contains only about 2 mg/g of phenolics, mainly comprising esterified hydroxycinnamic acids, whereas the inner bark has very high phenolics contents (Kähkönen 1999). Suberin itself is an interesting cross-linked co-polymer with polyaliphatic and polyaromatic domains, mainly made of the esterified long- and mid-chain hydroxy/epoxy fatty acids and fatty diacids as well as a few phenolic constituents (Pinto 2009). While bark triterpenes possess considerably pharmaceutical potential, suberinic fatty acids are interesting building blocks for novel biopolymers and coating materials (Alakurtti 2006, 2013, Dzubak 2006, Gandini 2006).

4.1.4. Stumps and roots

Stumps are an underutilized source of renewable forest biomass which are rich in chemical composition in comparison to stemwood. The roots and stumps of Norway spruce and Scots pine trees are a vast source of biomass potentially containing many bioactive polyphenolic extractives (Latva-Mäenpää 2017), but this biomass is currently used for low-value energy production only. With already existing harvesting techniques, roots and stumps of conifer trees could be used as a source of commercially valuable biochemicals (Latva-Mäenpää 2017).

The main extractives found in the root bark of Norway spruce are astringin and isorhapontin, as well as smaller amounts of piceid (Latva-Mäenpää et al. 2013, Mulat et al. 2014). The bark of fine roots of Norway spruce has been found to contain between 15% and 29% of extractives (Matthews et al. 1997, Richter et al. 2007). Latva-Mäenpää et al. (2013) found that root bark has a much higher extractive content than the wood of roots; the root zone nearest the stem had the highest amounts of extractives in the bark and the zone closest to the root tip had the highest amounts of extractives in the wood. While isorhapontin was the major stilbenoid found in the bark in all three of the root zones, astringin was the major compound found in the stump bark. Within the wood they mainly found saccharides, such as fructose, glucose and sucrose, as well as fatty acids and resin acids, such as pimaric acid, abietic acid and dehydroabietic acid (Latva-Mäenpää et al. 2013). Latva-Mäenpää et al. (2014) found relatively high concentrations of lignans in the root neck of Norway spruce (approximately 10% of total dry weight).

According to Hakkila (1989), the stump-root system of a 100-year-old pine showed larger concentrations of extractives than a 25-year-old pine. Accordingly, an order of magnitude regarding higher yields of extractions obtained with different solvents (methanol-benzene, acetone, ether,

water) was observed compared to younger trees. This in turn might indicate that there are differences in the relative compositions of extractive fractions of trees due to the different maturity. The concentration of acetone-extractives is highest in the stump and in the roots near the stump with high amounts of heartwood, and the concentration of extractives decreases towards the ends of the roots (Hakkila 1989). The composition of pine stump extractives is presented in Fig. 6 in Chapter 4.6.3.

Proportion of extractives in different parts of common Finnish wood species according to different studies are presented in table 3.

Table 3. Proportion of extractives in different parts of common Finnish wood species according to different studies, as dry mass percentages.

	<i>Picea abies</i>	<i>Pinus sylvestris</i>	<i>Betula pendula</i>	<i>Betula pubescens</i>
Stemwood	1.0-4.5 ¹⁻¹¹	1-6.8 ^{2,5,6,8,11,14}	0.8-5 ^{5,6,8,11,20}	0.8-6.7 ^{5,6,8,20}
Sapwood	1.7-2.7 ¹²⁻¹³	3.1 ^{12,14}		
Heartwood	1.1-1.8 ¹²⁻¹³	5.1-5.35 ^{12,14}		
Branchwood	6.8-13.7 ⁵⁻⁸	8.4-14.1 ^{5,6,8}	1.7-7.6 ^{5,6,8,20}	1.9-9.7 ^{5,6,8,20}
Knots		24.6 ¹⁸		
Stump	1.9-3.6 ^{6,16,17}	6.5-18.7 ^{6,17,19}	3.6 ⁶	5.8 ⁶
Rootwood	2.4-6.5 ^{6,16,17}	4.2-6.4 ^{6,17,19}	5.8-12.1 ^{5,6}	7.9 ⁶
All bark	23.5-28.3 ⁵⁻⁸	16-25.9 ^{5,6,8}	8-30.7 ^{5,6,8,20}	10.9-33 ^{5,6,8,20}
Inner bark	17.3-38.7 ^{5,6,8}	15.4-41.9 ^{5,6,8}	14.3-18.9 ^{5,6,8}	9.6-22.5 ^{5,6,8}
Outer bark	19.1-29.2 ^{5,6,8}	16.4-20.8 ^{5,6,8}	32.1-56.9 ^{5,6,8}	31.4-57.8 ^{5,6,8}
Foliage	37.8-43.3 ^{5,6}	38.6-40.6 ^{5,6}	28.8-33.4 ^{2,4}	32.4-32.5 ^{6,8}

¹Anttonen et al 2002, ²Holmbom and Ekman 1978, ³Kaakinen et al. 2007, ⁴Kaakinen et al. 2009, ⁵Nurmi 1993, ⁶Nurmi 1997, ⁷Rhen 2004, ⁸Voipio 1992, ⁹Kimland ¹⁰Fengel 11Alen 2000, ¹²Shain 1971, ¹³Hakkila and Verkasalo 2009, ¹⁴Kilpeläinen et al. 2003, ¹⁵Martinez-Inigo et al. 1999, ¹⁶Latva-Mäenpää et al. 2014, ¹⁷Hakkila 1975, ¹⁸Belt 2013, ¹⁹Latva-Mäenpää 2017, ²⁰Roitto 2016,

4.2. Effect of tree age

Tree age has an effect on the extractives content of wood biomass, as shown in Tables 4 and 5. The stemwood of a 100-year-old pine shows larger concentrations of extractives than a 25-year-old pine (Table 4). Additionally, the order of magnitude of the yields of extractions with different solvents was different than in a younger tree.

Table 4. The proportion of extractives in the stemwood of a 25- and 100-year-old *Pinus Sylvestris* when using different solvents in the extraction (Hakkila 1989).

	Average proportion of extractives (% w/w)				
	Solvent				
	Methanol-benzene	Acetone	Ether	Hot water	Cold water
25-year old tree	1.9	1.5	0.9	2.3	1.0
100-year old tree	3.5	2.9	2.1	3.4	2.1

Older trees contain more extractives in the heartwood than young trees (Hillis 1962, Uprichard and Lloyd 1980, Kasmani et al. 2011, Seyed Mohammadi et al. 2011). The formation of heartwood is strongly dependent of the age of tree, and heartwood contains more extractives than sapwood (Yanchuk et al. 1988, Rydholm 1967, Campbell et al. 1990). The stump center of a 100-year old pine is particularly rich in extractives (Table 5).

Table 5. The proportion of extractives in the stump-root system of a 25- and 100-year-old *Pinus sylvestris* when using different solvents in the extraction (Hakkila 1989).

	Proportion of extractives (%)				
	Solvent				
	Methanol-benzene	Acetone	Ether	Hot water	Cold water
25-year old tree					
Root collar		1.7		2.4	1.6
Stump center	2.0	1.4	1.5	2.1	1.1
Taproot		1.3	1.0	1.4	0.8
Large laterals	1.9	1.6	1.4	2.0	1.0
Average	2.0	1.6	1.3	2.0	1.1
100-year old tree					
Root collar	6.6	5.9	4.9	3.6	1.5
Stump center	9.7	9.1	8.2	5.2	2.5
Taproot	6.9	6.6	4.7	2.7	0.9
Large laterals	2.8	2.0	1.6	2.2	1.2
Average	6.5	5.9	4.8	3.4	1.5

The proportion of extractives in the inner and outer bark varies between species and according to the age of the tree, and depends also on the height and position in a tree (Paszatory et al 2016). For example, older trees have higher average amounts of stilbene glucosides than younger trees in the bark of Norway spruce trees (Jyske et al 2014). The flavonoid composition of Scots pine trees seems also strongly dependent on the age of the tree (Oleszek et al. 2002). This applies also to the resin acid and total phenolics content of the needles. It has also been found that mature needles have higher concentrations of extractives compared to young needles for the afore-mentioned compounds (Nerg et al. 1994).

4.3. The effect of latitude

Willför (2003a) found lignan concentrations in spruce knotwood to be higher in northern Finland than in southern Finland. This is natural because the growth conditions are generally more unfavorable for Norway spruce close to the Arctic tree line than in more southern sites. It seems that these unfavorable environmental conditions could cause higher lignan production in spruce trees, which might be useful for the trees during occasional periods of environmental stresses, such as when the trees could be under microbial attack (Piispanen et al. 2008). Spruce trees in northern Finland have been observed to contain more than twice as many lignans in their knots than in southern Finland (Holmbom 2011). Kaakinen et al. (2007) confirmed this by finding that the stemwood of Norway spruce had 54% higher concentrations of extractives in a northern site than in a southern site.

Hakkila and Verkasalo (2009) reported higher amounts of acetone extractives in pine and spruce stem heartwood and sapwood in northern Finland than in southern Finland. Hakkila (1968) also found a higher total quantity of extractives in pine and spruce stemwood in northern Finland.

Siwale (2015) indicated strongly that the formation of vanillic acid in both young and mature Scots pine stem woods is affected by different climatic conditions due to the geographic location, and concluded that poor conditions favor the formation of vanillic acid. The mean concentration of vanillic acid in samples from first-thinning harvests increased from southern Finland (0.0069 µg/mg) to northern Lapland (0.01 µg/mg) and a significant difference was found between these two extreme locations. The concentrations of pinosylvin and pinosylvin monomethyl ester were also significantly affected by geographic location, and samples from middle Finland clearly had the lowest concentrations with the means being significantly lower than those in the samples from other locations.

Roitto et al. (2016) found considerable north-south differences in the concentrations of individual extractive compounds of birch in different climatic regions. They observed that gallocatechins and neolignans were generally more abundant in the north while (+) catechin and some lignans were more abundant in the central or southern regions (Figure 1). According to Oleszek et al. (2002) the relationship between the flavonoid level in pine needles and the latitude of the population origin is very evident. This can be explained by the protecting function of flavonoids against UV radiation. Thus, at higher latitudes the lower light intensity does not force the plants to produce metabolically costly protective flavonoids. Additionally, the taxifolin content of needles has been detected to vary according to the elevation (Nerg et al. 1994). It has also been found that the resin acid concentration of sun-exposed needles is significantly higher than in shaded needles. According to a study by Nerg et al. (1994) the concentrations of total monoterpenes and total phenolics in seedlings of *Pinus sylvestris* were the lowest in the most northern sampling locations.

Siwale (2015) showed for Scots pine that in southern Finland site soil fertility has a significant effect on the concentrations of pinosylvin, its glycoside and one of the neolignans, but the exact effect was not the same for all compounds. Site soil fertility affected the concentration of some phenolic compounds in Scots pine stemwood, but the exact effect was inconsistent.

Latva-Mäenpää et al. (2013) compared stilbene glucosides in Norway spruce roots and stumps grown on either peatland or mineral soil sites, observing that the isorhapontin concentration was especially higher in extracts obtained from the mineral soil than in those from peatland.

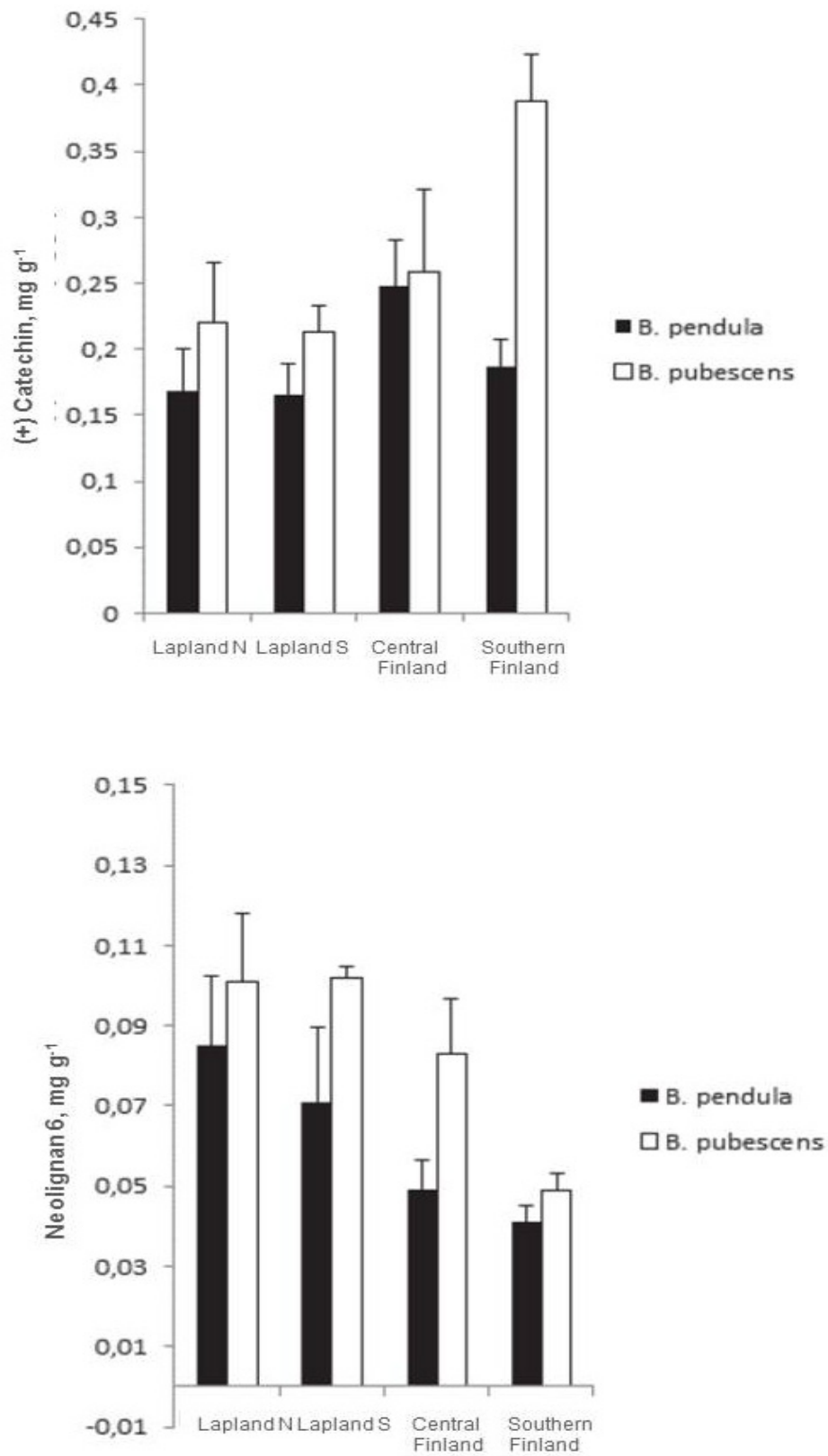


Figure 1. Examples of variation in the concentration of individual phenolic compounds: (+) catechin and an unidentified neolignan 6 in outer part of stemwood in *Betula pendula* and *B. pubescens* by geographic region in Finland. The values are the mean values obtained from multiple trees (Roitto et al. 2016).

However, the amounts of extractives display high between-tree variation, although the studies have often been made with very limited data, consisting of only few sample trees. For this reason, more studies are required to confirm conclusions about the effects of geographic location. Although there are not many studies of tree species in Finland, the effect of latitude has been studied more thoroughly on berries. Recent studies have shown that bilberry populations growing at northern latitudes contain significantly higher amounts of flavonoids, in particular anthocyanins, in comparison to the southern populations (Lätti et al. 2008, Uleberg et al 2009, Åkerström et al. 2010). Moreover, higher amounts of anthocyanins were found in bilberry fruits grown in controlled conditions in a phytotrone in 24 h natural daylight, mimicking the light conditions of Arctic summers (Uleberg et al. 2012).

4.4. Effect of fertilization

Fertilization treatment (for both macro and micro nutrients) has not been found to have any statistically significant effect on the total concentration of terpenes in Norway spruce stem wood (Anttonen et al. 2002). However, concentrations of acetone soluble extractives (mainly fatty acids, resin acids, non-structural carbohydrates and phenolics) were significantly higher in fertilized plots than control plots in their study. Production of secondary metabolites predominates in nutrient limiting situations, and has been shown in several studies where low nitrogen availability has resulted in the accumulation of phenolics in needles (Muzika 1993, Holopainen et al. 1995, Kainulainen et al. 1996). In Norway spruce knotwood, nitrogen fertilization was not found to cause any significant change in lignan concentration (Piispanen et al. 2008) (Figure 2).

The effects of nitrogen fertilization on wood chemistry in Norway spruce were mild and they differed between locations in a study by Kaakinen et al. (2007). However, the amounts of extractives in stemwood were higher in fertilized plots than in control plots. In contrast, Kostianen et al. (2004) found no changes in Norway spruce wood in the concentrations of extractives caused by fertilization (macro and micro nutrients).

In a study by Viiri et al. (2001), nitrogen fertilization resulted in lower concentrations of terpenes and stilbene aglycones in Norway spruce, but phosphorus fertilization led to a minor reduction in the concentration of total terpenes. The combination of nitrogen, phosphorus and potassium fertilization increased the total amount of terpenes.

In a study by Turtola et al. (2002) on Scots pines, nitrogen fertilization did not have any significant effect on the concentrations of resin acids in the heartwood, but in the sapwood the concentrations of individual resin acids, such as abietic and dehydroabietic acids decreased significantly in one of the locations. Nitrogen fertilization did not cause any significant changes in xylem monoterpene or heartwood resin acid concentrations of Scots pine (Thorin and Nommik 1974, Turtola et al. 2002).

Heijari et al. (2005) studied the resistance of Scots pine wood to brown-rot fungi after forest fertilization (nitrogen, calcium, phosphorus) and found that fertilization generally increased the concentration of extractives in the wood. They noted, however, that while in some cases fertilization increased the wood resistance to brown-rot fungi, in other cases it decreased.

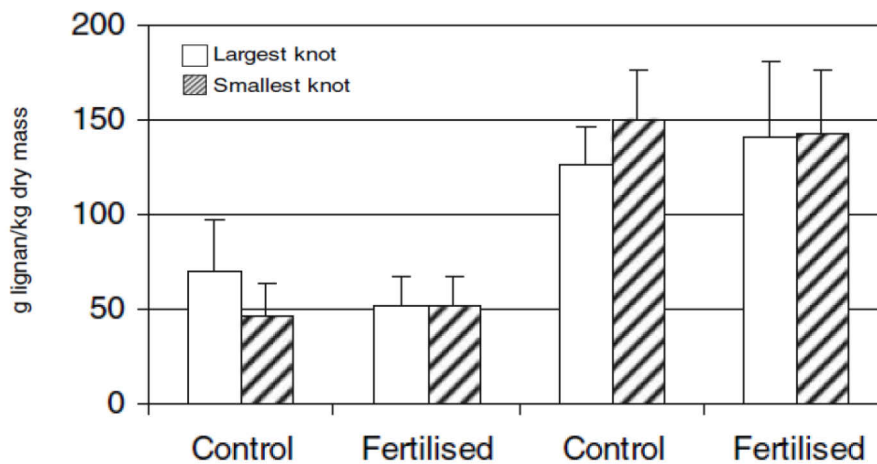


Figure 2. Concentrations of knotwood lignans according to the size of knot in two experimental sites with two treatments of fertilization (control and N-fertilized) (Piispanen et al. 2008).

4.5. Seasonal variation

The products of photosynthesis of trees are stored as reserves in living cells, and the sugar content is typically high in the winter and low in the summer, whereas the starch content is high in the spring and in the autumn and low throughout the rest of the year (Höll 1985).

Large seasonal variation in the amounts of soluble sugar and starch were detected in the secondary xylem of young silver birch trees (Piispanen & Saranpää 2001, Höll 1981). In a study by Piispanen & Saranpää (2001) the amount of sucrose decreased gradually during the spring until July, while it stayed near the minimum level in September and increased dramatically in November.

In coniferous trees (e.g. Scots pines in Fischer and Höll 1992) the changes in soluble sugars are less pronounced than in silver birch. Hoch et al. (2003) found no significant seasonal variation in storage lipids in the sapwood of several coniferous and deciduous trees. Additionally, in a study by Piispanen & Saranpää (2004) the seasonal variation of storage lipids was low in silver birch trees.

Free fatty acid concentrations in silver birch trees have been found to be the highest during mid-summer and September, and they increase during the spring (Piispanen & Saranpää 2004). The triacylglycerol concentration of silver birch have been found to be slightly but not significantly higher during the dormant period in November and in March than during summer and spring.

The concentration and fatty acid composition of triacylglycerols have been found to remain stable in Scots pine sapwood throughout the year (Saranpää & Nyberg 1987, Fischer & Höll 1992). No seasonal trend in the distribution pattern or concentration of pinosylvin in Scots pine trees was found in a study by Berström et al 1999. In contrast, Höll & Priebe (1985) reported marked seasonal variation in triacylglycerols in the wood of elm trees (*Tilia cordata*).

According to Höll (1985) Norway spruce stem wood contains higher concentrations of soluble sugars in the cold period than in the spring and summer months. According to Solhaug (1990) stilbene glucoside concentrations in Norway spruce bark tend to increase during the summer and early autumn. The free sugars in spruce bark are at their maximum level after the growing season and at their lowest in May/June (Weissman, 1984).

In their study on young seedlings of Scots pine trees, Nerg et al. (1994) detected remarkable seasonal variation of terpene, resin acid and total phenolic concentrations. The overall phenolic concentration was higher in the spring than in the autumn, whereas concentrations of some individual resin acids (levopimaric and dehydroabietic acids) were higher in the autumn. The total monoterpene concentration was higher in the spring.

4.6. Effect of storage

Many initial extractives suitable for potential raw material applications are either rather volatile or chemically unstable. The extractives content starts to decrease immediately after tree felling and this degradation continues during storage (Alén 2000, Assarsson et al. 1963, Jirjis & Theander 1990, Ekman 2000, Lappi et al. 2014a). This also means that the chemical composition of the extractives-based fraction changes gradually.

The major chemical changes in the resin during wood storage can be divided into three types: (1) rapid hydrolysis of triglycerides accompanied by slower hydrolysis of waxes, especially steryl esters, (2) oxidation/degradation/polymerization of resin acids, unsaturated fatty acids and to some extent other unsaturated compounds, and (3) evaporation of volatile terpenoids, mainly monoterpenes (Ekman 2000). The rate of all these reactions increases with increasing temperature.

It has to be pointed out that not only storage, but also other phases of the wood handling process affect the extractives content of the biomass material, as well as the composition of the extractives fraction. Several factors determine the nature and rate of change in the properties of wood resin (Ekman 2000, Rupar & Sanati 2005). These factors include the particular types of harvesting, transportation, storage and the inventory-control systems of the wood used at the mill. They also depend on the tree species, type of material, age of the material, time in storage, physical form of the wood, and the weather and other environmental conditions in all phases of the wood-handling process.

The parallel effects of different factors related to the storage of wood-based biomass on the chemical compounds and their concentration is summarized as follows:

Weather and other environmental conditions: High temperatures generally facilitate chemical reactions (Ekman 2000). Transition metal ions and light generally accelerate auto-oxidation reactions (Alén 2000). For example, according to Zahri et al. (2007), UV light induces the degradation of phenolic compounds present in oak extract. It is known that stilbenes are sensitive to daylight. The photo-induced chemical reactions of compounds belonging to this compound group have been studied, e.g., by Zhang and Gellerstedt (1994). The key step in these reactions seems to be an electron-proton transfer reaction leading to the formation of a stilbene phenoxyl radical. Increasing ventilation and thereby increasing the access of air and oxygen in the chip pile further speeds up evaporation and oxidation reactions (Ekman 2000). Some extractives are water soluble (hydrophilic), which means that both rainfall and water-debarking at the mill will leach some compounds of extractives from the biomass. Different tree species contain varying concentrations and types of water-soluble compounds in their wood and their leaching rates vary as well (Hedmark and Scholz 2008). The compounds of extractives that are generally found in woodyard runoff include phenolic compounds, resin acids and short chain fatty acids. According to Rupar and Sanati (2005), there seems to be correlation between the amount of precipitation and the emission levels of terpenes into the air. They also concluded that this phenomenon is more obvious for bark or wood chips than for forest residues, because bark and wood chips are more sensitive to precipitation owing to the smaller particle size of the material, and for bark, owing to the porosity of the material.

Tree species: different tree species have different extractives contents (see chapters 4.6.1-4.6.3) and the composition of this fraction which affects the chemical decomposition reactions during storage

Harvesting: the time of the year, environmental conditions and whether it is the first-thinning or final felling (for the effect of tree age on the composition of wood extractives, see chapter 4.2) have an effect on chemical reactions occurring after the tree is felled.

Transportation: If an open carriage is used during train or truck transport it leaves the material vulnerable to weather conditions, or generally to environmental conditions during the transport. When transportation in water is used, the situation is totally different as water protects wood from damage caused by fungi or insects (Kinnari 2002). Additionally, the chemical reactions in water are

different (see the text related to the storage below). Average delivery times from the logging site to the sawmill or pulp mill in Finland are approximately 2–3 weeks for sawn wood, 4 weeks for spruce pulpwood and 8–13 weeks for pine and birch pulp wood (Lukkari et al. 2004). Road transportation takes only hours or days, whereas transportation in ships or barges takes approximately one week.

Storage: Outside or inside storage and seasoning in water are all utilized when supplying wood to the mills. Environmental storage conditions (e.g., temperature and precipitation) and the duration of storage after harvesting the wood are important factors determining the amount and composition of wood resins after the storage period. It is well known that the hydrolysis of glycerides leading to free fatty acids and glycerol proceeds faster when the conditions for wood storage are wet instead of dry (Alén 2000). On the other hand, water and a high moisture content of wood protect it from damage caused by fungi or insects (Kinnari 2002). This is particularly important during the storage of wood logs in water in the summer (Alén 2000). During seasoning there is an increase in the amount of fatty acids and a reduction in neutral resin components (i.e., hydrocarbons, waxes, glycerides and higher alcohols) which is ascribed mostly to the saponifiable substances (Assarsson & Åkerlund 1967). Unsaponifiables have shown only a small decrease. The only chemical reaction taking place when wood is seasoned under water is the hydrolysis of glycerides to fatty acids. No changes indicative of metabolism or autoxidation have been observed (Assarsson & Åkerlund 1966).

Type of biomass material: As it was mentioned before, the porosity of material among other factors might have effects on the chemical reactions of extractives, because evaporation of volatile terpenes is faster for more porous material (Rupar & Sanati 2005). Not only the tree species, but also different parts of the wood have different extractives contents and the compositions of extractive fractions (see chapters 4.6.1–4.6.3). This affects the chemical decomposition reactions of extractives during storage and wood handling as described above.

Physical form of the wood: Chemical reactions are markedly faster when the wood is stored in the form of chips instead of logs (Alén 2000). Promberger et al. (2004) concluded that the faster deterioration of compounds in wood chips is due to the larger surface area that makes substances more easily accessible. As an example, it has been reported that the degree of hydrolysis of triglycerides after eight weeks of outdoor chip storage was about the same as round-wood storage for one year (Ekman 2000). Living cells, which are contained in the bark, foliage, and wood, remain viable for some time when the tree is cut (Fuller 1985). These cells remain viable for long periods of time when the wood is stored in log form. When wood is chipped and placed in a pile, the living parenchyma cells respire in an attempt to heal the tree. Oxygen is consumed and heat is released. This heat generation provides good growth conditions for bacteria which feed on the extractives in the wood. After a period of 7–14 days, it is not unusual that the temperature in a chip pile has reached about 50 °C (Nurmi 1999). The rate of heating is influenced by the rate of the pile construction and the freshness of the wood. Additionally, the tree species and season of the year affect the temperature build-up. Pulpwood chip storage piles contain a myriad of microorganisms that develop in the wood one after another (Ekman 2000). The predominant microorganisms in chip piles are thermal-tolerant fungi and bacteria. Instead, chip piles rarely experience attacks by brown-rot fungi which are common in piles of round-wood. Microorganisms in round-wood stored under continuous sprays of water are very different from those in dry piles. Every change in wood storage and handling technology (e.g. flotted and irrigated wood vs. dry wood, or storing stem wood vs. storing chips) will result in new substrate and environmental conditions for the development of wood-attacking microorganisms.

4.6.1. Birch

Stemwood

In birch round-wood storage, the dominating reaction is hydrolysis of triglycerides, resulting in the formation of free fatty acids (Ekman 2000), while steryl esters and unsaponifiables are generally sta-

ble. Assarsson et al (1963) observed that the amount of free, unmodified fatty acids increased strongly at the beginning and reached a maximum level after 3–4 months in experiments with birch logs. After that period, the rate of reactions modifying free fatty acids (mostly oxidation) was greater than the ester hydrolysis, and, hence, the amount of unmodified free fatty acids in the resin decreased. Assarsson et al (1963) found also that the rate of hydrolysis slowed down after 5–6 months storage of birch logs, after which period the amount of esterified fatty acids constituted less than 10% of the resin; in the beginning this fraction amounted about 70% of the resin. During chip storage the triglyceride hydrolysis is fast during the first couple of weeks (Ekman 2000). With longer storage times, the total amount of resin decreases as the fatty acids and steryl esters are degraded.

Bark

The total amount of birch bark extractives decreases notably and the chemical composition of this fraction changes during 24 weeks of storage (Figures 3 and 4) (Lappi et al. 2014a, b). Not only the amount of tri- and diglycerides but also the amount of betulin and other bioactive triterpenoids decrease significantly during the storage of birch bark.

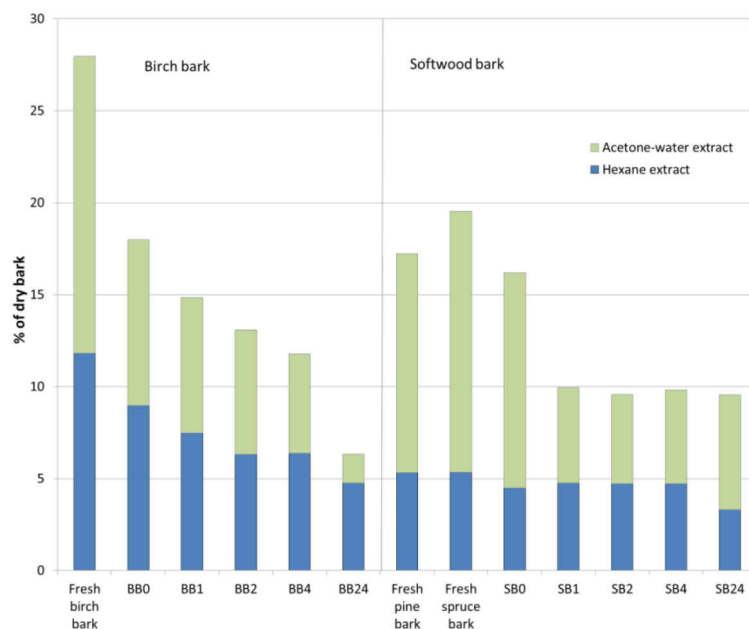


Figure 3. Gravimetric amounts of extractives (Lappi et al. 2014c). Key: BB0 = birch bark sample taken before storage, BB1 = after 1 week, BB2 = after 2 weeks, BB4 = after 4 weeks, and BB24 = after 24 weeks. Similarly, SB0 = softwood bark sample taken before storage, SB1 = after 1 week, SB2 = after 2 weeks, SB4 = after 4 weeks, and SB24 = after 24 weeks. Fresh birch, pine, and spruce bark samples were used as references to determine the amount of losses of extractives before and during the pulp mill wet debarking.

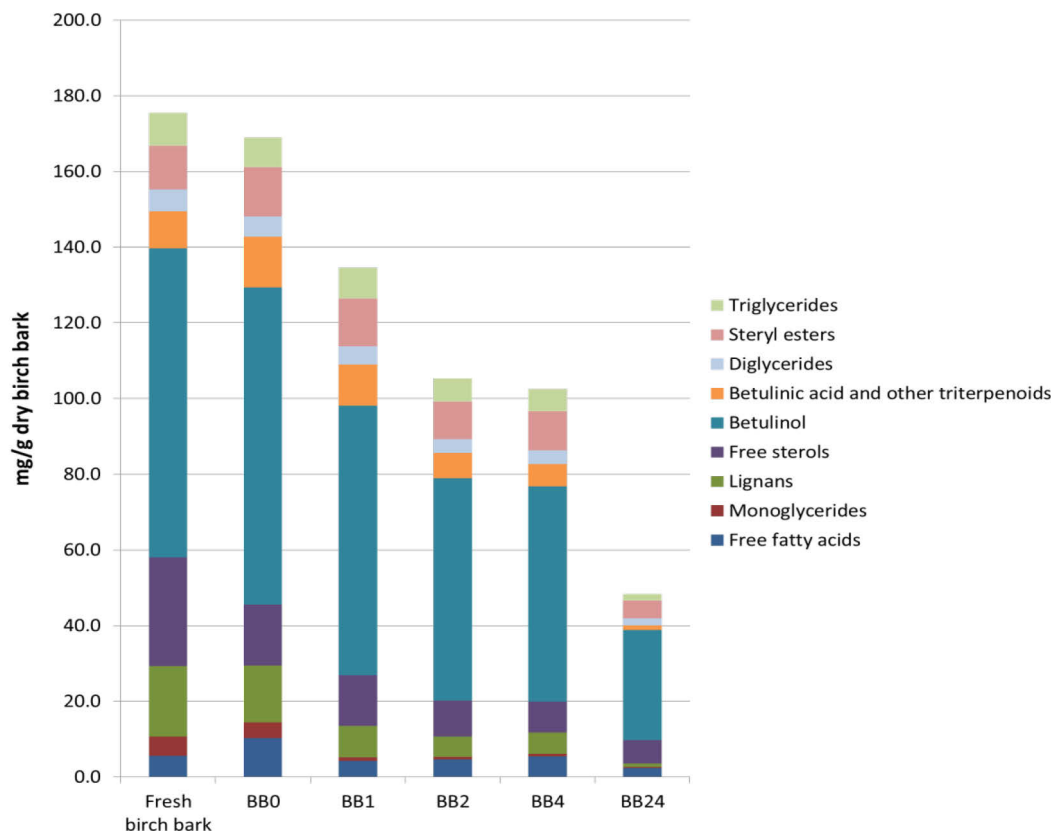


Figure 4. Results of extractive group analysis for birch bark. Key: BB0 = birch bark sample taken before storage, BB1 = after 1 week, BB2 = after 2 weeks, BB4 = after 4 weeks, and BB24 = after 24 weeks (Lappi et al. 2014c).

4.6.2. Spruce

Stemwood

According Assarsson et al. (1963), the total resin content in chipped spruce wood was almost constant for two weeks. Thereafter the resin content decreased. After four weeks the rate of hydrolysis reaction slowed down. In spruce wood chip seasoning, the amounts of triglycerides decreased by 90% and the amounts of waxes decreased by 70% in 3 months (Assarsson & Åkerlund 1967). The remaining esters might have been sterol esters to a large extent, as these are more difficult to hydrolyze than glycerol esters.

The amounts of free fatty acids increased strongly at the beginning and reached a maximum level after one week in a spruce chip pile (Assarsson et al 1963). After that period, the rate of free fatty acid oxidation became greater than that of ester hydrolysis, hence, the amount of free fatty acids started to decrease.

Assarsson et al (1963) also found that in a spruce chip pile, resin acids were not affected until after two to four weeks seasoning. In a later study the amounts of resin acids had decreased by 60% after 3 months seasoning (Assarsson & Åkerlund 1967). The unsaponifiable compounds seemed to have remained fairly constant during the first eight weeks in the chip pile, whereafter a decrease was discernible. In the log storage of spruce wood, the unsaponifiable fraction was found to be almost unaffected (Assarsson et al 1963).

Ekman (2000) studied the changes in the resin content of heartwood and sapwood of spruce during log storage. He detected that no triglyceride hydrolysis or other changes occurred in the heartwood, in contrast to sapwood. The resin content rapidly decreased in the sapwood but remained constant in the heartwood.

Spruce wood samples taken from round-wood piles in a pulp mill woodyard on land in southwestern Finland were analyzed (Ekman 2000). The resin content in logs that had been sprayed with water to avoid drying showed a very similar pattern of change as logs stored in water. As in the case of birch the most dominant chemical reaction was triglyceride hydrolysis, while total resin content decreased only slightly. In contrast, dry round-wood from piles without spraying with water showed a considerable decrease in the total amount of the wood resin. There was a decrease especially in the concentration of unsaturated fatty acids.

Bark

The amounts of extractives in the bark material which consisted of mixed softwoods (Norway spruce and Scots pine) decreased significantly during storage on land, roughly halving during the first four weeks (Lappi et al. 2014a, b, c). The total amounts of extractives decreased notably and the chemical composition of this fraction changed as well (Figs. 3 and 5) (Lappi et al. 2014a, b). Not only the amount of tri- and diglycerides decreased but so did the amounts of lignans.

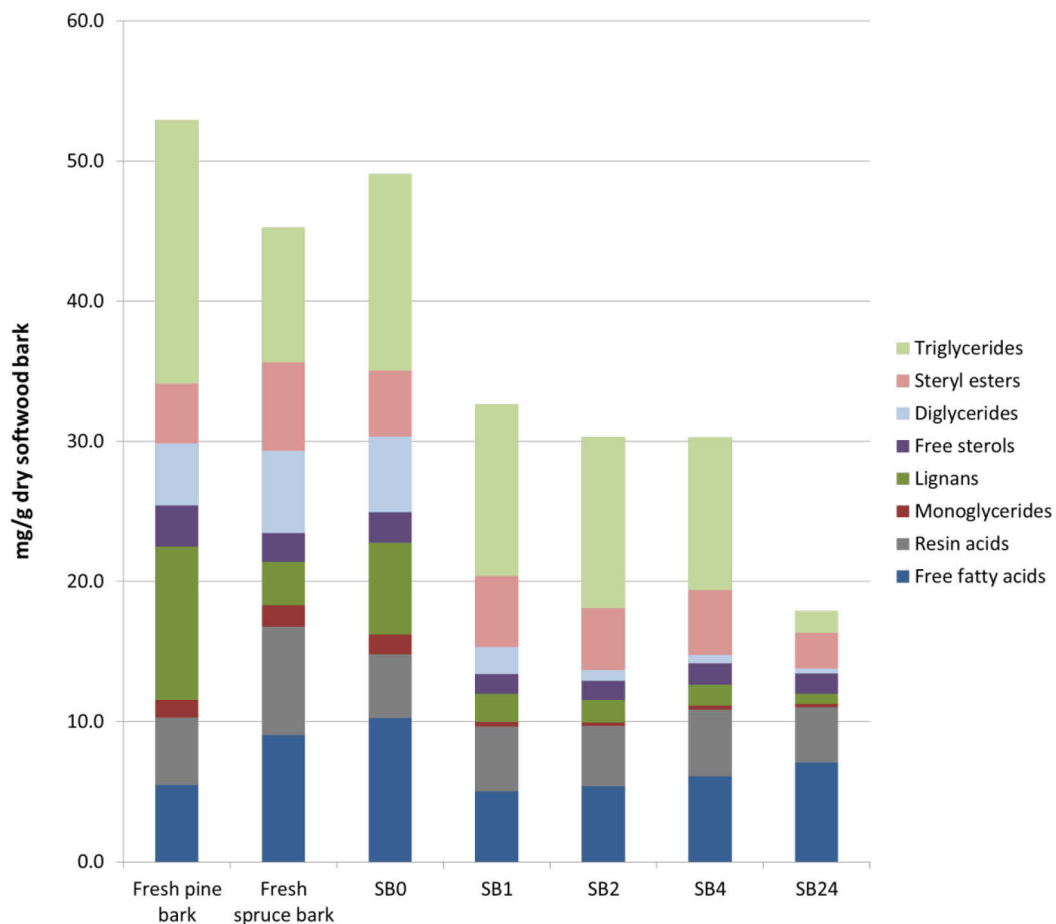


Figure 5. Results of extractives group analysis for softwood bark. Key: SB0= sample taken before storage, SB1= after 1 week, SB2= after 2 weeks, SB4= after 4 weeks, SB24=after 24 weeks (Lappi et al. 2014c).

Lappi et al. (2014c) did not analyze stilbenes in the aforementioned study. However, it is known that the spruce bark stilbenes are sensitive to degradation (Holmbom 2011). Industrial bark at mill sites usually contains only 1–2% of stilbenes, sometimes even less. During debarking at the mills much of the stilbenes which are still left after storage are dissolved in the debarking process waters (Holmbom 2011).

4.6.3. Pine

Stemwood

A drawback of seasoning Scots pine wood chips is that microbial degradation and oxidation reactions of fatty and resin acids directly decrease the yield of tall oil and turpentine which are by-products of kraft pulping (Ekman 2000). Fatty acids are oxidized much faster than resin acids during chip storage and at a faster rate than the amount of resin acids. Tall oil from fresh pine yields approximately equal amounts of fatty and resin acids. After four months storage, only 25% of the fatty acids remain, while 56% of the resin acids are retained. A few weeks of storing pine wood chips can lower the turpentine yield by about 50%. The losses are due to evaporation of volatile terpenes that are carried away in the convection of moist air currents that normally occur in the pile. Obviously, during round-wood storage, the turpentine components of the wood resin, especially the most volatile monoterpenes also evaporate, but at a much slower rate. According to one earlier study on radiata pine, if logs or chips remain wet during storage, triglyceride hydrolysis and other changes of the resin components occur primarily in the sapwood due to biological reactions (Ekman 2000).

Stumps

In stump wood of Scots pine trees, the changes in the chemical composition of the extractives fraction are more remarkable than the changes in the gravimetric extractives amount (Lappi et al.2014b). In a study by Lappi et. al (2014b), stump material consisted of pine (*Pinus sylvestris*) stumps. The stumps were lifted and crushed and a storage pile (150 m³) built at UPM Pietarsaari Mill. The sampling frequency was initiated after 1, 2, 4, and 24 weeks of storage. Four different samples were taken at each sampling time, representing all areas of the pile. The average result based on the analysis of these samples is presented in Fig. 6. The total amount of stump-derived extractives decreased slightly during 24 weeks of storage, from 4.1% of dry solids to 3.6% of dry solids in the case of fresh stumps (Lappi et al.2014b). It has to be taken into account that although multiple samples were taken at each sampling time, some variation in the sample composition still may exist. However, it was concluded so that general trends on the behavior of extractives compounds of stumps could be noted based on these results.

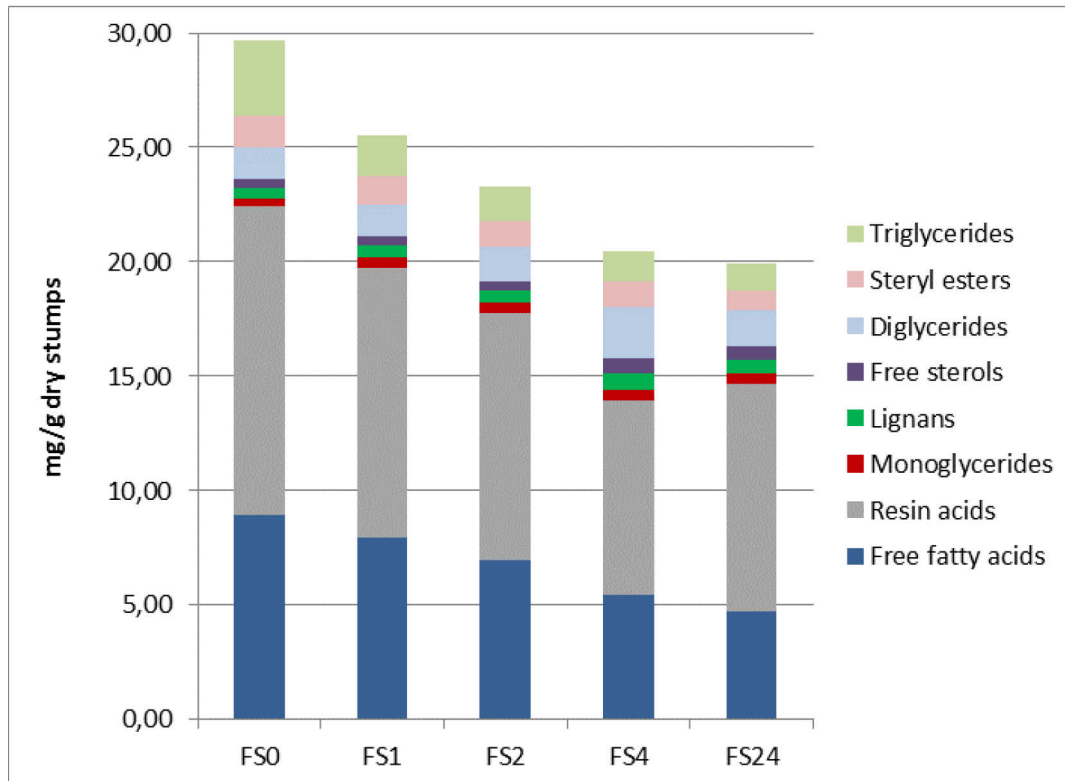


Figure 6. Results of an extractives group analysis for fresh stump and root biomass of Scots pine trees. Key: FS0 = fresh stump sample taken before storage, FS1 = after 1 week, FS2 = after 2 weeks, FS4 = after 4 weeks, and FS24 = after 24 weeks (Lappi et al. 2014b).

5. Distribution and content of extractives in tree biomass

In this chapter the results from the studies on extractives of Norway spruce, Scots pine and silver and white birch trees have been summarized. It is rather challenging to compile data about the contents of individual extractives compounds in different parts of the tree. This is partly because the yields of extractives strongly depend on the extraction method and solvent (Co et al. 2012). The solvent used for extraction and the extraction method itself affect the gravimetric amount of the extractives fraction as well as its composition to some extent. Furthermore, the analysis techniques have some limitations, meaning that, for example, not all chemical compounds are detected by gas chromatography (GC). This might concern very low- or high-molecular weight compounds due to the restrictions caused by GC-column dimensions and/or GC-oven temperature program, or due to the retention of some compounds or part of them in a GC-column stationary phase. Thus, the true amounts of gravimetric extractives differ from the amount determined by gas chromatography (GC). In addition, different analysis methods (e.g., GC, HPLC and NMR) may result in differences in the analysis results. Thus, the amounts of extractives given in the following text cannot strictly be compared with each other, unless they are from the same references. However, they do provide general trends in the extractives contents of the different tree parts and information on the composition of those extracts.

In Table 6, the variation in the amounts of different groups of extractives has been collated and reported regardless of the solvent used or the analytical method applied. The solubility of extractives varies greatly from one solvent to another. Extractives are typically removed from wood by solvent extraction, and the choice of solvent is a critical factor that determines the chemical composition and yield of the extract. Although significant differences can exist between specific extractives, hydrophilic extractives (phenolics) generally have better solubility in more polar solvents, while lipophilic extractives (terpenoids and aliphatic compounds) have better solubility in less polar solvents. Acetone is an exception in this rule, as it is known to dissolve both hydrophilic and lipophilic extractives with great efficiency (Harkin & Rowe 1971, Holmbom 1999). As for inorganic solvents, aqueous alkali is highly effective at dissolving otherwise insoluble components, mainly some phenolic acids and the insoluble fraction of condensed tannins, while water is a moderately effective solvent for most phenolics (Harkin & Rowe 1971, Fengel & Wegener 1989, Conde et al. 2013).

Table 6. Range of variation of different groups of extractives (% w/w) in Norway spruce, Scots pine and Finnish birch species in stem heartwood, stem sapwood, knots, bark and tree stumps. Values have been reported regardless of solvent or method used. This information can be found in the literature.

Norway spruce								
Extractive	Heartwood	Sapwood	Stem	Knotwood	Bark : 1) Inner bark 2) Outer bark	Stumps	Roots	Study
Triglycerides	0.07	0.45	0.25		0.37- 0.96			Ånäs 1983, Anttonen et al. 2002, Bertaud and Holmbom 2004, Krogell et al. 2012, Lappi et al. 2014,
Diglycerides					0.06- 0.59			Krogell et al. 2012

Monoglycerides					0.15			Lappi et al. 2014
Fatty acids	0.11-0.17	0.06-0.74	0.01	0.25	0.05-0.91			Ånäs 1983, Anttonen et al. 2002, Willför et al. 2003, Bertaud & Holmbom 2004, Krogell et al. 2012, Lappi et al. 2014
Steryl esters	0.11	0.14	0.16		0.10-0.63			Anttonen et al. 2002, Bertaud & Holmbom 2004, Lappi et al. 2014, Krogell et al. 2012, Anäs 1983
Sterols	0.02-0.09	0.01-0.11	0.01	0.10	0.02-0.29			Ånäs 1983, Anttonen et al. 2002, Willför et al. 2003, Bertaud & Holmbom 2004, Krogell et al. 2012, Lappi et al. 2014
Resin acids	0.18-0.19	0.17-0.22	0.28	0.04-0.24	0.02-0.29 ¹⁾ 0.03-0.29 ²⁾	2	0.47	Ånäs 1983, Anttonen et al. 2002, Willför et al. 2003, Bertaud & Holmbom 2004, Hovelstad et al. 2006, Krogell et al. 2012, Latva-Mäenpää 2013 et al., Lappi et al. 2014
Stilbenes					0.07-0.27			Hammerbacher et al. 2011, Krogell et al. 2012
Stilbene glucosides					2.4-5.5			Krogell et al. 2012, Jyske et al. 2014
Lignans	0.05-1.2	0.04-0.05	0.06	7.9-12.3	0.31			Holmbom et al. 2003, Willför et al. 2003, 2004, 2005, Piispanen et al. 2008, Lappi et al. 2014
Oliolignans	0.02	0.05		2.5-2.87				Willför et al. 2003, 2004
Flavanoids					0.14			Krogell et al. 2012
Tannins					10.7			Kemppainen et al. 2014
Condensed tannins					1.7-1.9 ¹⁾ 7.9-8.0 ²⁾			Holmbom et al. 2007
Terpenes			0.03					Anttonen et al. 2002
Sesquiterpenes	0.00	0.02						Wajs et al. 2006
Diterpenoids	0.05	0.53			0.005-0.7 ¹⁾ 0.005- 0.32 ²⁾			Willför et al. 2005, Krogell et al. 2012
Aliphatic alcohols					0.04			Krogell et al. 2012

Scots pine							
Extractive	Heart-wood	Sapwood	Stem	Knotwood	Bark : 1) Inner bark 2) Outer bark	Stumps	Study
Triglycerides	0.03-0.1	0.73-1.22	0.62	0.27	0.17 ¹⁾ 3.34 ²⁾ 1.88	0.32	Ånäs 1983, Martinez-Inigo et al. 1999, Willför et al. 2003, Lappi et al. 2014
Diglycerides					0.44	0.14	Lappi et al. 2014
Mono and diglycerides					0.23 ¹⁾ 0.55 ²⁾		Ånäs 1983
Monoglycerides					0.12	0.03	Lappi et al. 2014
Free Fatty acids	0.22-1.8	0.03-0.4	0.11-0.94	0.42	0.06 ¹⁾ 0.17 ²⁾ 0.55	0.90	Ånäs 1983, Martinez-Inigo et al. 1999, Fries et al. 2000, Piispanen & Saranpää 2002, Willför et al. 2003, Ekeberg et al. 2006, Karppanen et al. 2008, Tiitta et al. 2009, Arshadi et al. 2013, Lappi et al. 2014
Steryl esters	0.05-0.14	0.07-0.17	0.15	0.25	0.09-0.43	0.14	Ånäs 1983
Sterols	0.01				0.45 ¹⁾ 0.3 ²⁾ 0.29	0.03	Fries et al. 2000, Lappi et al. 2014, Ånäs 1983
Resin acids	0.21-6.34	0.26-0.89	0.85-1.8	7.97-20.2	0.72 ¹⁾ 0.24 ²⁾ 0.49	1.35	Ånäs 1983, Martinez-Inigo et al. 1999, Fries et al. 2000, Turtola et al. 2002, Harju et al. 2002, Willför et al. 2003, Ekeberg et al. 2006, Hovelstad et al. 2006, Karppanen et al. 2007, 2008, Leinonen et al. 2008, Tiitta et al. 2009, Arshadi et al. 2013, Lappi et al. 2014
Stilbenes	0.14-1.67			4.59-5.21			Fries et al. 2000, Hovelstad et al. 2006, Karppanen et al. 2007, 2008, Partanen et al. 2011
Lignans	0.01	0.01	0.01	1.33	1.09	0.05	Lappi et al. 2014, Willför et al. 2013
Oligolignans	0.08	0.03	0.06	0.39			Willför et al. 2003
Condensed tannins					3.21-8.51		Steinshamn 2014
Diterpenoids	0.05	0.53			0.0005-0.2		Willför et al. 2005, Krogell et al. 2012
Aliphatic alcohols					0.04		Krogell et al. 2012
Soluble sugars	0.02-0.03						Karppanen et al. 2008, Tiitta et al. 2009

Silver birch					
	Stemwood	Branches	Bark	Roots	Study
Triacylglycerols	0.2-0.68	0.4	0.8-1		Piispanen & Saranpää 2004, Lappi et al. 2014, Roitto et al 2016
Diglycerides			0.57		Lappi et al. 2014
Monoglycerides			0.51		Lappi et al. 2014
Fatty acids	0.03-0.25	0.38	0.48-0.57		Piispanen & Saranpää 2004, Lappi et al. 2014, Roitto et al 2016
Steryl esters	0.18-0.50	0.41-0.42	0.78-1.16		Piispanen & Saranpää 2004, Lappi et al. 2014, Roitto et al 2016
Free sterols			3		Lappi et al. 2014
Sterols		0.10-0.11	0.5-0.7		Roitto et al. 2016
Lignans	0.06	0.18	0.29-1.86		Lappi et al. 2014, Roitto et al. 2016
Flavonoids	0.55-1.43			1.14	Sutela et al. 2009, 2014
Phenolic glycosides	1.68-2.84				Sutela 2009, 2014
Procyanidin	0.005				Roitto et al. 2016
Betulin and other triterpenoids			0.98		Lappi et al. 2014
Condensed tannins	10.8			13.05	Sutela et al.2009
Total Cinnamic acids	0.17				Sutela et al. 2014

6. Valuable bioactive extractives in common Finnish wood species and their properties

Bioactive molecules are readily available through eco-friendly extraction processes using mild organic or aqueous solvents (Royer et al. 2012). Controlled and optimized isolation of extractives, e.g., from wood or forest residues prior to their use as combustible material represents an essential path leading to added intrinsic value. Extracts may be used in various applications, e.g., pharmaceuticals, agri-food additives, cosmeceuticals, and nutraceuticals. Worldwide demand for bioactive molecules of natural origin has increased sharply in recent years. The natural health products (NHP) market has shown remarkable growth in developed countries. In Figure 7 routes to obtaining valuable bioactive extractives are summarized. More about the replacement of fossil fuel based chemicals and chemicals from edible oils with, e.g., tall oil based compounds are discussed in Chapter 7.

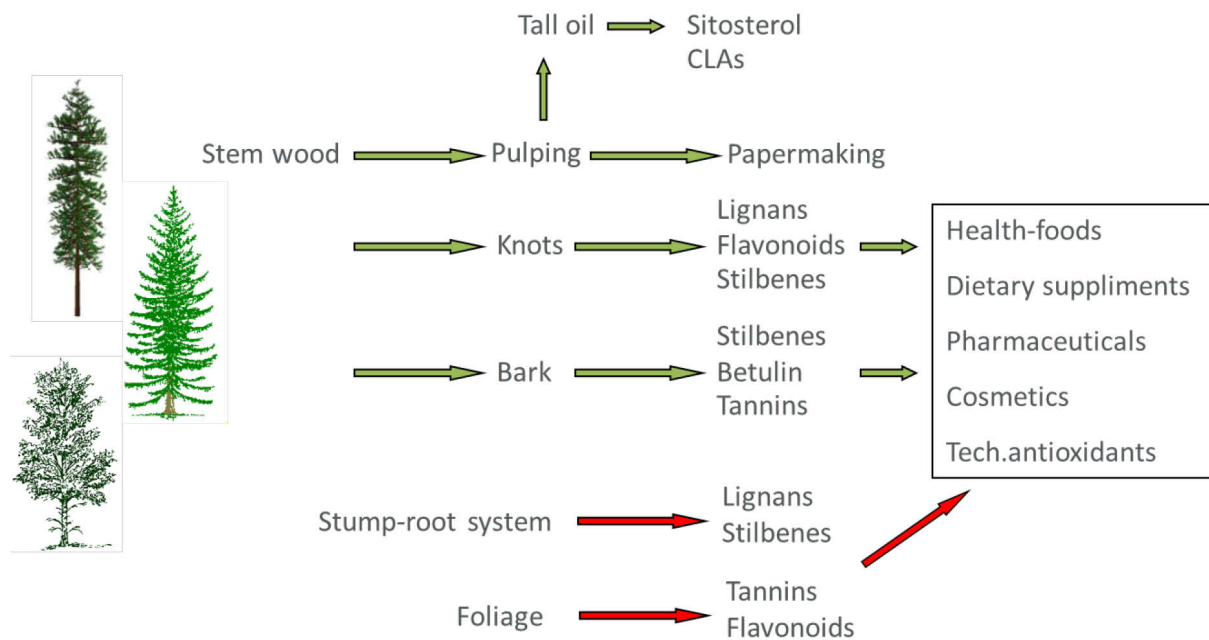


Figure 7. Routes to obtaining valuable bioactive extractives. Currently utilized routes are illustrated with green arrows (modified from Holmbom 2010). Red arrows are used for the routes that currently are not commercially utilized. However, some research related to these routes is ongoing.

Residues like bark represent attractive sources of bioactive molecules (Royer et al. 2012). Bark is a low-value by-product which is a readily available renewable resource, amounting generally to 7–13% of the total volume of the tree (Xavier et al. 2012). Bark generally contains a high concentration of extractives, a number of which possess unique biological and therapeutic properties (Royer et al. 2012). Bark contains, for example, polyphenols which have beneficial properties such as antioxidant, anticancer, bactericidal, fungicidal, antispasmodic, sedative, analgesic and anti-inflammatory qualities.

Both bioactivities of pure extractives (Pietarinen et al. 2006a), knotwood extracts (Välilä et al. 2007, Pietarinen et al. 2006a, b, Metsämuuronen & Siren 2014) and bark extracts (Pietarinen et al. 2006a) have been studied. Various bark extracts have been used in traditional medicine, such as Chi-

nese and Indian medicine, for the treatment of many diseases (Holmbom 2011). Resins scraped from the bark of old Norway spruce trees have been used as a resin salve in Northern Sweden and Finland for centuries. Recently this old invention was rediscovered in Finland and a commercial resin salve possessing antifungal and antibacterial properties was developed and introduced to the market. This is effective against pressure ulcers, burns and wound infections.

In the following a number of extractives from wood biomass which have been found interesting due to their bioactivity potential are presented. However, not all such extractives have been listed and new ones can be found.

6.1. Phenolic extractives

Plant phenolics have been suggested to provide multiple advantageous health and well-being effects, including maintenance of health and protection from diseases such as cancer and coronary heart disease (Karonen et al. 2004b). It is also possible to use them as natural food additives, since they influence the quality and stability of foods by acting as flavourants, colourants and antioxidants.

A large variety of low-molecular phenolic compounds are found in trees, especially in the heartwood, bark and knots whereas only traces occur in sapwood (Holmbom 2011). Compounds belonging to phenolics represent a wide variety of chemical structures, featuring a benzene ring as a core structure to which one or more hydroxyl group(s) is/are attached, either free or substituted with various specific chemical functions (e.g. alkyl groups in ethers and esters, or mono/disaccharides in phenol glycosides) (Royer et al. 2012). These compounds can be grouped into several families, such as coumarins, lignans, stilbenes, flavonoids, phenolic acids, tannins (grouped into condensed and hydrolysable tannins), xanthenes, quinones etc. They range from monomers to polymers and include various types of complexes. Such a wide variety of structures explains the impressive range of physico-chemical and biological activities recorded, and which come from their significant chemical reactivity. The antioxidant activity of phenolics is mainly due to their redox properties, which allow them to act as reducing agents, hydrogen donors and singlet oxygen quenchers (Kähkönen et al. 1999). Additionally, they provide metal chelation potential. Another key factor with regards to their biopotential is their ability to interact with cellular proteins; in fact, polyphenols can function as activators or inhibitors of numerous cellular enzymes (Royer et al. 2012).

Polyphenols have the ability to scavenge free radicals (strong antioxidant activity), block enzymatic processes and stop fungal growth (Royer et al. 2012). They also contribute to antiseptic and antibacterial properties and have a positive incidence on product preservation, be it cosmetics, foods or pharmaceuticals. Their free-radical scavenging properties coupled with the antioxidant and anti-inflammatory properties are linked to the prevention of certain diseases that implicate oxidative stress and cellular ageing, cardiovascular and degenerative conditions: osteoporosis, cancer, arthritis and type II diabetes.

The amount of extractable phenolic compounds in the heartwood of Norway spruce knots can be close to 30% (w/w), but on average it is around 15% (w/w) (Willför et al. 2003a, b). The amounts of phenolic compounds in knot heartwood are usually 50–100 times that found in the stemwood. The amounts of extractable phenolic compounds in the heartwood of Scots pine knots can be as high as 10% (w/w) (Willför et al. 2003a, c). In a study where the antioxidant activities of phenolic extracts from edible and nonedible Finnish plant materials were examined by their inhibition of methyl linoleate oxidation, Scots pine bark was ranked among the most potent plant sources for natural phenolic antioxidants (Kähkönen et al. 1999).

Several phenolic compounds such as phenolic acid glycosides, stilbene glycosides, lignans and flavonoids have been previously isolated from the inner bark of Scots pine trees, and the bark of Norway spruce trees (Krogell et al 2012). Scots pine bark has been found rich in procyanidins as well (Karonen et al. 2004b).

6.1.1. Stilbenes

Coniferous trees contain relatively large amounts of stilbene compounds (Mannila & Talvitie 1992). In Norway spruce trees they are concentrated in the bark of the tree. The total amount of isorhapon-tigenin, piceatannol, resvatrol and their glucosides is 1–6% of the dry weight. Stilbenoids in Norway spruce bark are mainly in glucosidic form (Latva-Mäenpää 2017). Stilbenoids of Scots pine trees are mainly localized in the heartwood region of the tree (Latva-Mäenpää 2017).

Stilbenes, or stilbenoids, have been shown to be potential anti-inflammatory, anti-cancer, anti-oxidant, anti-ageing and chemoprotective agents (Mulat et al. 2014). In Table 7 some interesting stilbenes which are found in common Nordic softwoods are presented with the information about their properties for activities/functionalities.

Table 7. Interesting bioactive stilbenes in common Nordic softwood species (*Picea abies*, *Pinus sylvestris*)

Compound	Properties	Tree species and part	References
Piceatannol	antimicrobial, anticancer, cardioprotective, allelopathic, antioxidant, artemicide, fungicide, pesticide,	<i>P. abies</i> : bark <i>P. sylvestris</i>	Reinhold et al. 1980, Mannila & Talvitie 1992, Wolter et al. 2002, Latva-Mäenpää et al. 2014, 2017 Lim & Koffas 2010, Duke 2017 Siwale 2015
Resvatrol	antimicrobial, anti-cancer, antiviral, cardiovascular and neuroprotective, extends the life-span of cells i.e., anti-aging	<i>P. abies</i> : bark <i>P. sylvestris</i>	Välilmaa et al. 2007, Holmbom 2011, Mannila & Talvitie 1992
Pinosylvin	fungicide, antimicrobial, antioxidant, anticancer, anti-inflammatory, antifeedant, pesticide	<i>P. sylvestris</i> : heartwood, knots	Willför et al. 2003b Välilmaa et al. 2007, Fang et al. 2013 Latva-Mäenpää 2017 Duke 2017 Siwale 2015
Pinosylvin monomethyl ether	antimicrobial, anticancer, anti-inflammatory, antifungal	<i>P. sylvestris</i> : heartwood, knots	Willför et al. 2003b, Välilmaa et al. 2007 Latva-Mäenpää 2017 Siwale 2015
Pinosylvin dimethyl ether	antifungal	<i>P. sylvestris</i> : heartwood, knots	Willför et al. 2003b, Latva-Mäenpää 2017
Dihydripi-nosylvin	antibacterial, fungicide, pesticide	<i>P. sylvestris</i>	Duke 2017
Astringin	antibacterial, anticancer, antifungal, pesticide	<i>P. abies</i> : needles, bark	Latva-Mäenpää et al. 2014, 2017 Slimestad & Hostettmann 1996, Duke 2017

Isorhapontin	antibacterial, anti-leukemia, cardio protection, antifungal	<i>P. abies</i> : needles, bark	Mannila & Talvitie 1992, Latva-Mäenpää et al. 2014,2017 Slimestad & Hostettmann 1996
Isorhapontigenin	antibacterial, antifungal	<i>P. abies</i> : bark	Mannila & Talvitie 1992, Latva-Mäenpää et al. 2014, 2017
Piceid	antibacterial, antilipoperoxidant, antioxidant, fungicide, hepatoprotective, pesticide	<i>P. abies</i> : needles, bark	Latva-Mäenpää et al. 2014, Slimestad & Hostettmann 1996 Duke 2017

6.1.2. Flavonoids

A considerable amount of research has been directed toward the activity of flavonoids as antioxidants and radical scavengers, as well as their anti-mutagenic and anti-carcinogenic properties (Rauha 2001). Flavonoids have been suggested to play a preventive role in the development of cancer and heart diseases (Kähkönen et al. 1999). Flavonoids are divided into several subgroups, and it is important to keep in mind that the biological and chemical properties of flavonoids belonging to different subgroups can be quite different (Eklund 2004). Flavonoids are mainly present in plants as glycosides, whereas aglycones occur less frequently. Flavonoids can be found in the foliage of hardwoods and softwoods, and in the bark, at least in the rootbark of Norway spruce trees (Rauha 2001, Pan and Lundgren 1995). In Table 8 some interesting flavonoids and their properties for various activities/functionalities are presented.

Table 8. Interesting bioactive flavonoids in common Nordic wood species (*Picea abies*, *Pinus sylvestris*, *Betula pendula* and *Betula pubescens*)

Compound	Properties	Tree species and part	References
apigenin	Reduced risk of coronary heart disease, vasoprotective activity antiADD, anti aflatoxin, antiaggregant, antiaging, antiallergic, antiangiogenic, antiarrhythmic, antibacterial, anticancer antidermatitic, antiestrogenic, antiherpetic, antihistaminic, anti-HIV, anti-inflammatory, antimelanomic, antimutagenic, antioxidant, antiperistaltic, antiproliferant, antispasmodic, antistress, antithyroid, antiviral, anxiolytic, apoptotic, , choleric, CNS-depressant, cytotoxic, differentiator, diuretic, DNA-Protective, estrogenic, hypotensive, inotropic, musculotropic, mutagenic, myorelaxant, pesticide, progestational, radioprotective, sedative, sunscreen, uterotrophic	<i>B. pubescens</i> and <i>B. pendula</i> : leaves	Rauha 2001, Valkama et al. 2003, Keinänen & Julkunen-Tiitto 1998, Lim & Koffas 2010, Duke 2017

acacetin	protective potential against prostate cancer allergenic, antiaflatoxin, antiallergic, antihistaminic, antimalarial, antimutagenic, hepatoprotective, mutagenic, plasmodicide, protisticide	<i>B. pubescens</i> and <i>B. pendula</i> : leaves	Rauha 2001, Valkama et al. 2003, Keinänen & Julkunen-Tiitto 1998, Singh et al. 2005, Duke 2017
glycosides of kaempferol	anticancer, antioxidant, anti-inflammatory, antiaflatoxin, antiaggregant, antiallergic, antibacterial, antifertility, antigingivitic, antiherpetic, antihistaminic, anti-implantation, antilymphocytic, antimutagenic, antiperiodontic, antiplaque, antiradicular, antiseptic, anti-serotonin, antispasmodic, antistaphylococcal, antiulcer, antiviral, apoptotic, carcinogenic, choleric, cytotoxic, diuretic, estrogenic, fungicide, hepatoprotective, HIV-RT-Inhibitor, hypotensive, inotropic, mutagenic, natriuretic, neuroprotective, pesticide, protisticide, teratologic, uterotrophic, vasodilator	<i>B. pubescens</i> and <i>B. pendula</i> : leaves <i>P. abies</i> : needles <i>P. sylvestris</i> : needles	Rauha 2001, Lim & Koffas 2010, Svahn 2015, Räisänen et al. 2008, Duke 2017
quercetin and glycosides of quercetin	Reduced risk of coronary heart disease. Neuroprotective effects. Potent for treating or preventing cancer due to its antimutagenic, anti-proliferative, antioxidative activities and its role in cellular receptor interactions and modification of signal transduction. Anti-inflammatory.	<i>B. pubescens</i> : leaves* ¹ <i>P. abies</i> : needles <i>P. sylvestris</i> : needles	Rauha 2001, Oleszek et al. 2002, Ossipov et al. 1995, 1996, Keinänen & Julkunen-Tiitto 1998, Strack et al. 1989, Lim & Koffas 2010, Svahn 2015
glycosides of myricetin	Reduced risk of coronary heart disease, anti-oxidant, pro-oxidant, anticarcinogenic, mutagenic, antiviral, antidiabetic, lowers cholesterol level, prevents formation of blood-clots	<i>B. pubescens</i> : leaves <i>P. abies</i>	Rauha 2001, Ossipov et al. 1995, 1996, Keinänen & Julkunen-Tiitto 1998, Svahn 2015
isorhamnetin and glycosides of isorhamnetin	antibacterial, antihistaminic, anti-inflammatory, antioxidant, antispasmodic, cancer-preventive, hepatoprotective, pesticide, vasodilator	<i>P. abies</i> : needles, rootbark <i>P. sylvestris</i> : needles* ¹	Rauha 2001, Strack et al. 1989, Pan & Lundgren 1995, Kähkönen et al. 1999, Duke 2017
naringenin and glycosides of naringenin	anti-oxidant, anti-inflammatory, lowers cholesterol level anti-acetylcholinesterase, antiaflatoxin, antiaggregant, antialzheimeran, anti-amnesic, antibacterial, anticancer, antiescherichic, antiestrogenic, antifibrotic, anti-hepatotoxic, antiherpetic, anti-HIV, anti-inflammatory, antimutagenic, antiperistaltic, antiperoxidative, antiradicular, antisindhis, antispasmodic, antistaphylococcal, anti-tumor, , antiulcer, antiviral, aphidifuge, candidicide, choleric, embryotoxic, estrogenic, fungicide, fungistat, hepatoprotective, neuroprotective, pesticide, serotonin-inhibitor, teratogenic, uterotrophic	<i>B. pubescens</i> : leaves <i>P. abies</i> * ¹	Rauha 2001, Ossipov et al. 1995, 1996, Svahn 2015, Duke 2017

pinocembrin	anesthetic, antibacterial, antileukemic, antiseptic, artemicide, candidicide, cytotoxic, fungicide, pesticide	<i>P. sylvestris</i> : knotwood, heartwood	Rauha 2001, Willför et al. 2003b, Duke 2017
(+)-catechin	antiaggregant, anticoagulant, anticomplementary, anti-HIV, anti-inflammatory, antimutagenic, antioxidant, antiperoxidant, antiprostaglandin, antiradicular, antiulcer, cancer-preventive, cardiotoxic, dermatitogenic, hemostat, hepatoprotective, immunostimulant, neuroprotective, phagocytotic, vasoconstrictor	<i>B. pubescens</i> , <i>B. pendula</i> : leaves, bark, stemwood <i>P. abies</i> : needles, rootbark <i>P. sylvestris</i> : bark, needles**)	Rauha 2001, Ossipov et al. 1995, 1996, Keinänen & Julkunen-Tiitto 1998, Strack et al. 1989, Pan & Lundgren 1995, Karonen et al. 2004a, Kähkönen et al. 1999, Roitto et al. 2016, Duke 2017

*) Only as glycosides, **) Also as glycoside

6.1.3. Tannins

Tannins are polyphenolic compounds based either on flavan-3-ol monomers (condensed tannins, also called proanthocyanidins), or on gallic or hexahydroxydiphenic acid esters linked to a sugar moiety (hydrolysable tannins) (Kempainen 2014). Tannins are the main components of softwood (*P. abies* and *P. sylvestris*) extracts (see table 6). The tannins in wood bark are mainly condensed tannins (Tamminen et al. 2017).

Tannins also have bioactive properties, including antioxidative and radical-scavenging power, thus, they are also of great interest in nutrition and health (Holmbom 2011). The use of tannins is presently expanding into nutritional and pharmaceutical areas. Tannins are known to display antimicrobial activity and they can also complex with the proteins in bacterial cell membranes. Tannins are used in pharmaceuticals which aim at curing bacterial intestinal infections. Additionally, tannins have been indicated to have antitumor and anticancer properties as well as antiviral effects. There has been interest in the antimutagenic and antitumorigenic properties of tannic acid especially (Rauha 2001). In Table 9 interesting tannins and their properties for activities/functionalities are presented.

Table 9. Interesting bioactive tannins in common Nordic softwood species (*Picea abies*, *Pinus sylvestris*)

Compound	Properties	Tree species and part	References
epigallocatechin-3-gallate	antiangiogenic, antitumor	<i>P. sylvestris</i>	Duke 2017
tannic acid	allergenic, antianacarditic, antibacterial, anticariogenic, anticolitic, antidecubitic, antidermatotic, antidiarrheic, antidote, antidysenteric, antiencephalitic, antienteritic, antifeedant, antigargantitic, antigingivitic, antihemorrhoidal, antiherpetic, anti-HIV, antimutagenic, antinitrosaminic, antiobesity, antiophidic, antioxidant, antipharyngitic, antipolio, antirhinitic, antiseptic, antistomatitic, antitonsillitic, antiulcer, antiviral, astringent, cytotoxic, detoxicant, emetic, flavor, hemostat, hepatotoxic, immunostimulant, pesticide	<i>P. abies</i> : needles	Duke 2017, Adamczyk et al. 2011

gallic acid	analgesic, antiadenovirus, antiallergenic, antianaphylactic, antiangiogenic, antiasthmatic, antibacterial, antibronchitic, anticancer, c, antiescherichic, antifibrinolytic, antifu, antihepatotoxic, antiherpetic, antiHIV, anti-inflammatory, antileishmanic, antiMRSA, antimutagenic, antinitrosaminic, antioxidant, antiperiodontic, antiperoxidant, antipolio, antiproteolytic, antiradicular, antiseptic, antistaphylococcic, antitumor, , antiviral, apoptotic, astringent, bacteristat, bronchodilator, candidicide, carcinogenic, choleric, cytotoxic, gram(+)icide, gram(-)icide, hemostat, hepatoprotective, immunomodulatory, immunostimulant, immunosuppressant, insulin-sparing, myorelaxant, nephrotoxic, pesticide, styptic	<i>P. sylvestris</i>	Duke 2017
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6.1.4. Lignans

Lignans have attracted much interest due to their broad range of biological activity (Eklund et al. 2004). The knots, i.e., the branch bases of softwood tree species are the richest sources of lignans. Lignan 7-hydroxymatairesinol (HMR), has been stated to have a positive influence on the development of breast, prostate and colon cancer which rely specifically on estrogens in order to progress (Holmbom 2011). Lignans also help to maintain good cardiovascular health and to moderate other estrogen dependent health problems (menopause, osteoporosis). Lignans and oligolignans are strong antioxidants and radical scavengers, however according to tests performed by Välimaa et al. (2007), these mechanisms are not directly associated with antimicrobial effects. In Table 10 interesting bioactive lignans and their properties for activities/functionalities are presented.

Table 10. Interesting bioactive lignans in common Nordic softwood species (*Picea abies*, *Pinus sylvestris*)

Compound	Properties	Tree species and part	References
matairesinol	antileukemic, fungicide, insecticide-synergist	<i>P. abies</i> : Knotwood, heartwood <i>P. sylvestris</i> : Knotwood, bark	Willför et al. 2003a, b, Duke 2017, Karonen et al. 2004a, Fengel & Wegener 1989
hydroxymatairesinol	chemopreventive effects, antioxidant,	<i>P. abies</i> : Knotwood <i>P. sylvestris</i> : Knotwood	Willför et al. 2003a, b, Eklund et al. 2004
matairesinol dimethyl ether		<i>P. abies</i> : Knotwood	Willför et al. 2003a

pinoresinol	antioxidant	P. abies: Knotwood, heartwood P. sylvestris: bark	Willför et al. 2003a, Duke 2017, Karonen et al. 2004a, Fengel & Wegener 1989
dimethyl pinoresinol		P. abies: Knotwood	Willför et al. 2003a
nortrache- logenin	antileumic, antifungal mechanism against pathogenic fungi	P. sylvestris: Knotwood P. abies: Knotwood	Torrance et al 1979, Willför et al. 2003a, b, Ekman et al 2002, Lee et al 2016
secoisolar- iciresinol	antioxidant, cancer-preventive	P. abies: Knotwood , heartwood, P. sylvestris: Knotwood	Willför et al. 2003a, b, Duke 2017, Fengel & Wegener 1989
α- Conidendrin		P. abies: Knotwood, heartwood	Willför et al. 2003a, Fengel & Wegener 1989
liovil		P. abies: Knotwood, heartwood P. sylvestris: Knotwood	Willför et al. 2003a, Fengel & Wegener 1989
lariciresinol	antibacterial	P. abies: Knotwood, heartwood	Willför et al. 2003a, Bajpai et al. 2017, Fengel & Wegener 1989
isolaricires- inol	anti-inflammatory	P. abies: Knotwood, heartwood P. sylvestris	Willför et al. 2003a, Cho et al.2001, Fengel & Wegener 1989
lignan A		P. abies: Knotwood	Willför et al. 2003a
hinokiresinol	insecticide-synergist, pesticide	P. abies: Knotwood	Willför et al. 2003a, Duke 2017

6.2. Terpenes and terpenoids

The vast majority of terpenes exhibit some type of bioactivity thus possessing therapeutic applications. Numerous studies have attributed the following properties to terpenes: antimicrobial, fungicidal, antiviral, anti-inflammatory, cytotoxic, anticancer, etc. Often implicated in a tree's resistance to disease and microbial attack, their concentration increases following intrusions by predators or parasitic organisms (Royer et al. 2012). High concentrations of terpenoids exhibit toxic effects and play a protective role against pathogens and herbivorous animals. Monoterpenes and sesquiterpenes form the main constituents of essential oils and oleoresins volatile fractions. In Table 11 some examples of interesting terpenoids and their properties for activities/functionalities are presented.

Table 11. Interesting bioactive terpenoids in common Nordic species (*Picea abies*, *Pinus sylvestris*, *Betula pendula* and *Betula pubescens*)

Compound	Properties	Tree species and part	References
dehydroabietic acid	anti-inflammatory, allergenic, antifeedant, pesticide, protisticide, schistosomicide	<i>P. sylvestris</i> : stemwood, bark, knot-wood <i>P. abies</i> : stemwood, bark	Goto et al. 2010 Holmbom & Ekman 1978, Arshadi et al. 2013, Willför et al. 2003b, Valentín et al. 2010, Duke 2017, Anttonen et al. 2002, Salem et al. 2016
sitosterol	decreases the absorption of cholesterol in the digestive system and decreases the amount of cholesterol produced by the liver, analgesic, anthelmintic, antimutagenic, antitumor (breast, cervix, lung), and hypoglycaemic Androgenic, angiogenic, anorexic, antiadenomic, antiandrogenic, antibacterial, anticancer (breast, cervix, lung), antiedemic, antiestrogenic, antifeedant, antifertility, antigonadotrophic, antihyperlipoproteinaemic, anti-inflammatory, antileukemic, antilymphomic, antiophidic, antioxidant, antiprogestational, antiprostaglandin, antiprostadenomic, antiprostatic, antipyretic, antiviral, apoptotic, artemicide, cancer-preventive, candidicide, estrogenic, febrifuge, gonadotrophic, hepatoprotective, hypocholesterolemic, hypoglycemic, hypolipidemic, pesticide, spermicide, ubiquestrol, ulcerogenic	<i>P. sylvestris</i> : stemwood, bark <i>P. abies</i> : stemwood, bark <i>B. pendula</i> : stemwood, bark <i>B. pubescens</i>	Villasenõr et al. 2002, Mbambo et al. 2012, Norin & Winell 1972, Holmbom & Ekman 1978, Piispanen & Saranpää 2004, Valentín et al. 2010, Duke 2017, Ferreira et al 2017
betulinol	anti-bacterial, anti-mycotic, anti-itching, anti-inflammatory, antiviral, hepatoprotective effects against ethanol induced cytotoxicity, anticarcinomic, antifeedant, antiflu, antiHIV, anti-inflammatory, antitumor, antiviral, aphidifuge, cytotoxic, hypolipemic	<i>B. pendula</i> : bark <i>B. pubescens</i> : bark	Holmbom 2011, Kratsutsky 2006, Roitto et al. 2016 Duke 2017
betulinic acid	anticancer, anti-HIV, antimalarial, anti-inflammatory, antibacterial, anti-oxidant, anti-viral, hepatoprotective effects against ethanol induced cytotoxicity, anthelmintic, anticarcinomic, antiedemic, antileukemic, antimalarial, antimelanomic, antinociceptive, antiplasmodial, antitumor, apoptotic	<i>B. pendula</i> : bark <i>B. pubescens</i> : bark	Royer et al. 2012, Holmbom 2011, Kratsutsky 2006, Duke 2017 Ferreira et al. 2017

lupeol	anti-inflammatory, antiangiogenic, anti-EBV, antiedemic, antifu, antihyperglycemic, antilithic, antimalarial, antioxalate, antioxidant, antiperoxidant, antiprostaglandin, antirheumatic, antitumor, antiurethrotic, antiviral, cytotoxic, hypotensive, pesticide	<i>B. pendula</i> : bark <i>B. pubescens</i> : bark	Royer et al. 2012, Duke 2017, Ferreira et al. 2017
betulin 3-caffeate	anti-proliferative, UV-protective, anti-melanoma	<i>B. pendula</i> : bark	Krasutsky 2006
oleanolic acid	anti-inflammatory, antibacterial, anti-cancer, anti-viral Abortifacient, antiallergic, antiarrhythmic, antiatherosclerotic, anticarcinomic, anticariogenic, anticomplement, antiedemic, antifertility, antigingivitic, antihepatotoxic, antiHIV, antihyperlipidemic, antiischemic, antileukemic, antileukotriene, antimalarial, antinephritic, antioxidant, antiperiodontic, antiperoxidant, antiPGE2, antiplaque, antiplasmodial, antisarcomic, antiseptic Antitumor (breast, colon, kidney, lung, pancreas), antiulcer, beta-blocker, cancer-preventive, cardioprotective, cardiotonic, diuretic, hepatoprotective, hypolipemic, hypotensive, immunomodulatory, leucocytogenic, phagocytotic, piscicide, sedative, uterotonic, vasopressor	<i>B. pendula</i> : bark <i>B. pubescens</i> : bark	Krasutsky 2006, Duke 2017, Ferreira et al 2017
α-Pinene	allelochemic, allergenic, antiacne, antibacterial, antifeedant, antifu, anti-inflammatory, antipneumonic, antiseptic, antispasmodic, antistaphylococcic, antiviral, cancer-preventive, coleoptophile, expectorant, flavor, herbicide, insecticide, insectifuge, insectiphile, irritant, perfumery, pesticide, sedative, spasmogenic, tranquilizer, transdermal	<i>P. sylvestris</i> : stemwood, root, needles, resin, exudate, sap <i>P. abies</i>	Duke 2017, Räsänen et al. 2008, Williams 2011, Sadof & Grant 1997, Thorin & Nommik 1974
D-Limonene	antiacetylcholinesterase, anticancer & antitumor (breast, gastric), antimelanomic, apoptotic, cancer-preventive, chemopreventive, flavor, hypocholesterolemic, insecticide, insectifuge, litholytic, nephrotoxic, pesticide	<i>P. sylvestris</i> : stemwood	Duke 2017, Sadof & Grant 1997, Thorin & Nommik 1974
β-carotene	allergenic, antiacne, antiaging, antiarthritic, antiasthmatic, anticancer, anticarcinomic, anticervicaldysplastic, anticoronary, antihyperkeratotic, antiichthyotic, antileukoplakic, antilipoperoxidant, antilupus, antimaculitic, antimastitic, antimutagenic, antioxidant, antiozenic, antipapil-	<i>P. sylvestris</i> : needles	Duke 2017, Matysiak 2001

	lomic, antiphotophobic, antipityriasic, anti-PMS, antiporphyric, antiproliferant, antipsoriatic, antiradicular, antirheumatic, antistress, antitumor (breast, CNS, colon, lung, prostate, stomach), antiulcer, antixerophthalmic, cancer-preventive, chemopreventive, colorant, gastroprotective, immunostimulant, interferon-synergist, mucogenic, phagocytotic, prooxidant, thymoprotective, ubiquot		
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Already in the 1950s it was documented that plant sterols can lower serum cholesterol (Holmbom 2011). Today, there are broad selections of plant sterol products available on the consumer markets, for example, cream cheese, pasta, yoghurts, sour-milk and meat products. The total production of sitosterol, for use primarily in functional foods, is now about 10,000 tons per year and is growing by about 10% per year.

A range of bioactivities have been assigned to pentacyclic triterpenes with lupane structures (including betulin): i.e. bactericidal, antiviral, anti-inflammatory, cytotoxic and antitumoral (Royer et al. 2012). Within the lupane series, betulinic acid stands out with its proven antiviral activity towards type I human immunodeficiency virus (HIV), apart from its selective cytotoxicity towards human melanoma.

Much fundamental research into the bioactivity of betulin and its derivatives is ongoing (Krasutsky 2006). Research has shown, for example, that betulin and dihydrobetulin derivatives are usually more active than pure betulin as anti-cancer compounds, or anti-HIV compounds (Krasutsky 2006). It has been shown as well that simple modifications to the parent structure of lupane triterpenoids produce agents that are effective against influenza-A and herpes simplex type-1 viruses. Betulin and birch bark extract are also patented as adaptogenic remedies, interferon inducers, antihypoxic products, hepatitis-C preventatives and treatments, anti-influenza and tuberculosis prophylactics, and as additives in cosmetics, pet foods, lipase inhibitors, and foods containing triterpenes (Krasutsky 2006). The presence of betulin 3-caffeates makes birch bark extracts good sun-blocker ingredients for cosmetics because of its good UV-absorption.

6.3. Fats, waxes and their components

Fatty acids of type Δ^5 , i.e., pinolenic, taxoleic, and sciadonic acids, have lipid modulating and other effects in animals, thus, they have raised interest among researchers (Holmbom 2011). Pinolenic acid has also been shown to promote a feeling of satiety and to suppress appetite.

Over the past two decades numerous health benefits have been attributed to conjugated linoleic acid (CLA) in experimental animal models including actions to reduce carcinogenesis, atherosclerosis, insulin resistance and body fat mass (Rastmanesh 2011). The cis-9, trans-11 CLA seems to have an anticarcinogenic effect, whereas the trans-10, cis-12 CLA seems to modulate body composition mainly through the reduction of body weight and fat percentage, besides promoting beneficial alterations in lipid metabolism. Furthermore, results of both in vivo and in vitro studies have shown that CLA has anticarcinogenic effects in a range of human breast cells and tumors.

6.4. Suberin and its components

Suberin is a complex aromatic–aliphatic cross-linked biopolyester (Pinto 2009), mainly found in wood bark. Suberin is of interest mainly because it constitutes an abundant source of rare ω -hydroxyfatty acids, α , ω -dicarboxylic acids and homologous mid-chain dihydroxy or epoxy derivatives that, apart from in birch, cork oak bark, are not abundant in nature. Only these species produce suberin-rich biomass residues in amounts that can justify their exploitation as renewable sources of chemicals. According to Holmbom (2011), the outer bark of silver birch trees may contain up to 45% suberin, therefore, birch bark residues could serve as an industrially valuable feedstock for extracting suberin derived compounds.

The most interesting applications for suberin components involve their use in the synthesis of new biopolymers, as well as novel coating materials (Alakurtti 2006, 2013, Dzubak 2006, Gandini 2006). The exceptional chemistry of suberinic hydroxyl/epoxy fatty acids provide interesting routes for further upgrading into versatile building blocks for a variety of materials. Other possible attractive applications presented for suberin monomers according to the literature include applications in the cosmetics industry, for example. Suberinic ω -hydroxyfatty acids could be used in skin-care, anti-aging, hair-care, individual chemicals for drug design, dietary supplements, anti-cholesterol, and anti-obesity products (Krasutsky 2011). Whereas suberinic ω -acids salts could be used in special washing materials, shampoos, and hair care.

7. Applications utilizing extractives from wood-based biomass

Since ancient times, man utilized trees as a source of useful chemicals (Holmbom 2011). Birch bark tar was prepared in Europe already about 40,000 years ago by the Neandertals. Oleoresin has been used for thousands of years as such, or as tar, to preserve different wooden and other organic materials. Tall oil and turpentine came on the market about one hundred years ago. In 1899 the production of crude tall oil (CTO) started in Sweden, and in 1913 the first CTO distillation plant started in Finland (Baumassy 2014).

Global markets are featuring an increasingly high demand for nature-derived ingredients replacing synthetic chemicals. In Figure 8 some examples are shown of how extractives-based chemicals could substitute fossil feedstock based and edible vegetable oil based chemicals. Although this figure is for tall oil based chemicals, fatty acids, resin acids and sterols from other sources may similarly be utilized. Crude tall oil is bio-based raw material with a constrained annual global volume of around 2 million tons and an EU wide availability of approximately 650,000 tons (Rajendran et al. 2016).

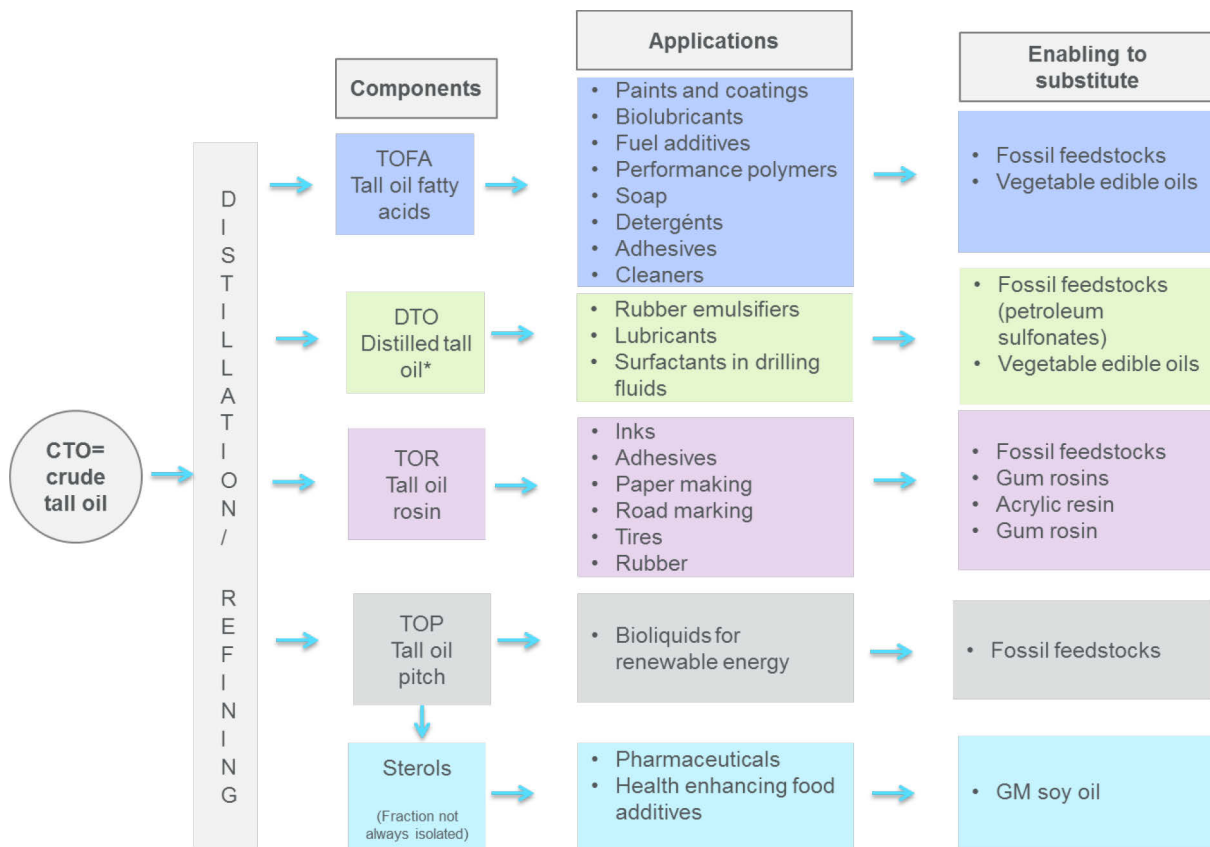


Figure 8. The cascading use of crude tall oil (CTO), starting from refining and processing of CTO to making the highest value bio-based chemicals before utilizing the final residue for biofuels and energy use will not only address the issue of resource efficiency but also contribute to the European Union’s ambitious circular economy goals (modified from refs. Arizona chemicals 2009, Polastro & Tuovinen 2010 and HARRPA 2015).

Currently, there are only two larger distillation plants for sulphate turpentine in Europe, one of them in Finland (Arizona Chemicals, Oulu) (Holmbom 2011). Turpentine is used as a raw material for chemicals, perfumes, vitamins and polymers (Niemelä 2015). Turpentines are produced by steam-

distillation of tapped or solvent-extracted oleoresin gum, or by recovery from kraft pulping (Holmbom 2011). In the Nordic countries no gum resin is collected (Niemelä 2015).

Extractives may not only substitute fossil based feedstocks in specialty chemicals but instead they may partially replace fossil based fuels. Sunpine Inc. in Sweden employed its first tall oil based diesel plant in 2010, with a yearly production capacity of 100,000 m³ of tall oil diesel (Aro & Fatehi 2017). UPM started the production of crude tall oil based renewable diesel in the UPM Lappeenranta Biorefinery in January 2015. The production capacity of the biorefinery is 120 million liters of renewable diesel annually (UPM 2016). However, according to a recent study (Rajendran et al. 2016), the economic added value generated by the entire pine chemicals industry (CTO refiners and the extended downstream operators along the value chain) is at least four times more than the added value generated from the production of renewable diesel.

Sources of the other bioactive extractives, especially phenolics, and their applications were shown in Chapter 6, Figure 7.

In 1998 it was discovered at Åbo Akademi that spruce knots constitute an extraordinarily rich source of lignans (Holmbom 2011). This was the start for extensive research into tree knots, and finally to clearance for a new dietary ingredient from the US FDA in 2004. In 2006, the HMRLignanTM product (dietary supplement) came onto the market in the form of capsules (Holmbom 2011). The knots can be separated from chips before pulping by a proven technology named “ChipSep”.

Condensed tannins were already extracted from oak wood in Europe in ancient times and used for tanning hides into leather (Holmbom 2011). Today, the main source of condensed tannins is the bark of black wattle (*Acacia mearnsii*) and quebracho wood (*Schinopsis balansae*). Condensed tannins are still used in leather production, but are also used as a component in adhesives. However, the use of tannins is expanding into nutritional and pharmaceutical areas. Extraction of pine and spruce bark has been shown to give economical yields of condensed tannins (Lacoste 2015). Currently, there is an available commercial pine bark extract named FenoprolicTM which contains oligomeric proanthocyanidins (Eevia Health). It is marketed to support joint, heart and circulatory system health.

Spruce bark stilbenes contain compounds such as resvatrol which have a multitude of beneficial health properties (see chapter 6) (Holmbom 2011). However, further research is required to develop applications for these compounds.

Resin scraped from the bark of old Norway spruce trees has been used as a resin salve in northern Sweden and Finland for centuries. This invention was rediscovered in Finland and developed into a salve with the trade name “Abilar” in 2008 (Holmbom 2011, Bioeconomy 2015). When a tree is damaged it produces a sticky resin to plug the wound and protect the tree from infection (Repolar). Over a period of 3 or more years this resin seals the tree wound. At this time, the resin can be harvested by hand.

There are many cosmetic products containing pure betulin or birch bark extracts on the market (Holmbom 2011). Innomost Oy isolates betulin from Finnish birch bark and sells it to be used as active ingredient in cosmetics. The company also markets dry birch bark and suberin for the cosmetics industry (Innomost).

8. Conclusions

The Finnish governmental bio-economy strategy aims to create new innovations and products based on natural resources in a sustainable way. The production volumes of the current main products such as pulp and wood products are often high and their unit price is relatively low. In the production chain remarkable quantities of side products are produced, such as bark and wood residues, which are utilized mainly in energy production today, where the added value has been decreasing due to globally low energy prices. Biomass and especially the side products mentioned above contain extractives which could be utilized in developing added value products for the pharmaceutical, food and cosmetics industries, for example.

Small group of experts were interviewed in this study to identify potential sources and uses of extractives from wood-based biomass. The experts emphasized some extractive groups (stilbenes, tannins, lignans and terpenes), but also some interesting single chemical compounds (pinosylvin, pinosylvin monomethyl ether, hydroxymatairesinol, betulin, α -/ β -pinene, resin- and fatty acids). The same extractive groups and individual compounds were also found in the literature review of this study.

Trees can be a large and valuable source of extractives, and large amounts of extractives could be utilized from raw materials which are not currently seen as valuable components and are considered mainly waste materials which usable for second purposes, such as bark or knotwood. The forest industries produce a great deal of bark waste which contains 2–6 times more extractives than stemwood. Knots are undesirable in papermaking and manufacturing advanced wood products. It could be economically advantageous to remove the knot fractions before pulping or further processing sawn timber and utilize their lignans. Knots contain 4–5 times more lignans than stemwood.

Wood-based lignans can be used in functional foods and for pharmaceutical purposes. The most abundant lignan hydroxymatairesinol is already used as a health beneficial dietary supplement, and the development of hydroxymatairesinol as a natural antioxidant is ongoing. However, hydroxymatairesinol is also a valuable optically pure compound, which could be utilized in high value applications in the field of organic chemistry.

Sitosterol is used primarily in functional foods, for example in some margarines that are designed for use as part of a cholesterol-lowering diet. The overall production of sitosterol, is now about 10,000 tons per year and is growing at a rate of about 10% per year (Nilsson et al. 2011).

Tannins have been indicated to have anti-tumor and anticancer properties and antiviral effects. Additionally, the use of tannins is presently expanding into nutritional and pharmaceutical areas. The global tannin demand was 1,076 million tons in 2015 and it is expected to grow at a rate of 5.8% from 2016 to 2025. The tannin market is expected to grow globally and is expected to reach 3.39 billion USD by 2025 (Grand View Research).

Fatty and resin acids are generally regarded as problematic compounds in paper and board making (Farrell et al. 1997, Sun & Tomkinson 2001). However, fats are valuable resources for producing fuels such as biodiesel, while resins are suitable for producing glues and inks (Demirbas 2011).

Talloil –based diesel production is already running and talloil is also an important compound in the paint industry.

Knowledge of both the amount and type of extractive compounds in the available wood raw material is vital when assessing options for its use. Furthermore, the factors affecting the aforementioned should be known. All tree species in Finland contain at least moderate amounts of extractives, but the contents of extractives are specific to each species. The volumes of extractive compounds are relatively small compared to the main products of pulp-mills and sawmills. Additionally, their markets

are very different from those of the main products. Therefore, new industrial partnerships and value networks need to be developed further to bring actors from the food and feed industries, among others, to the sites of wood processing industries.

The results of the literature survey in this study showed that the extractives contents decrease notably during the storage of wood biomass, even during the first four weeks. The composition of this fraction also changes during storage and valuable bioactive compounds may be lost. Thus, the freshness of the feedstock and fast recovery logistics are major factors to consider when designing and implementing processes intended to recover extractives.

This report showed that even within species there is a lot of variation in the quantity of extractives found. Site-to-site variability to quantify how much the extractive content varies within a species has been investigated in a few studies only. This makes it difficult to quantify the amounts of extractives that could be recovered, and virtually impossible to visually identify trees or stands of trees that could potentially have higher yields of extractives. New research has been started in this area in recent years.

Accelerated wood supply is a key issue for practitioners aiming to reduce capital costs and dry matter losses during the supply chain of wood-based biomass. It is also essential to utilize the extractives of wood biomass. In the future, studies on the feasibility, availability, supply and demand, costs and methods are needed.

The results of this review can be used in assessing the availability of various extractives at a general level, as well as for planning their procurement in connection with industrial round-wood. However, further research is needed on the effects of different forest and supply chain factors on the extractive concentrations found in wood-based biomass – in addition to their characteristics and functionalities for different industrial and consumer uses. In the future, availability maps for different chemical compounds could be generated by linking forest inventory data with the chemical analysis data to support the optimal location of production lines for new biorefinery products.

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References

- Adamczyk, B., Adamczyk, S., Smolander, A. and Kitunen, V. 2011. Tannic acid and Norway spruce condensed tannins can precipitate various organic nitrogen compounds. *Soil Biology & Biochemistry* 43: 628–637.
- Alakurtti, S., Mäkelä, T., Koskimies, S and Yli-Kauhaluoma, J. 2006. Pharmacological properties of the ubiquitous natural product betulin. *European journal of pharmaceutical sciences* 29:1–13.
- Alakurtti, S. 2014. Synthesis of botulin derivatives against intracellular pathogens. Academic Dissertation. Division of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Helsinki, Finland, p. 99.
- Alam, A., Kilpeläinen, A., & Kellomäki, S. 2010: Potential energy wood production with implications to timber recovery and carbon stocks under varying thinning and climate scenarios in Finland. – *Bioenergy Research* 3: 362–372.
- Alen, R. 2000: Structure and chemical composition of wood. In: Stenius P (ed.) *Forest Products Chemistry*: 11–57. Gummerus Printing. Jyväskylä, Finland.
- Alen, R. 2011: Structure and chemical composition of biomass feedstocks. – In: Alen, R (ed.) *Biorefining of forest resources*: 17–54. Paperi ja Puu Oy. Finland.
- Anttonen, S., Piispanen, R., Ovaska, J., Mutikainen, P., Saranpää, P. & Vapaavuori, E. 2002. Effects of defoliation on growth, biomass allocation, and wood properties of *Betula pendula* clones grown at different nutrient levels. *Canadian Journal of Forest Research* 32: 498–508
- Arizona chemicals. 2009. The carbon footprint of Arizona Chemical's US operations and CTO/CST derivatives. Summary report. Available: http://www.adlittle.be/in-the-press_be.html?&download=201&file=CTO-fractionation-orig.pdf&anchor=set201. Accessed: 17.10.2017.
- Arshadi, M., Backlund, I., Geladi, P. & Bergsten, U. 2013. Comparison of fatty and resin acid composition in boreal Lodgepole pine and Scots pine for biorefinery applications. *Industrial Crops and Products*, 49, 535-541.
- Aro, T. & Fatehi, P. 2017. Tall oil production from black liquor: Challenges and opportunities. *Separation and Purification Technology* 175: 469–480.
- Assarsson, A., Croon, I and Donetzhuber, A. 1963. Studies on wood resin especially change in chemical composition during seasoning of wood. *Svensk Papperstidning* 22: 940–948.
- Assarsson, A. & Åkerlund, G. 1967. Studies on wood resin, especially the change in chemical composition during seasoning of the wood, part 5. changes in composition of nonvolatile extractives during water seasoning of unbarked spruce, pine, birch, and aspen logs. *Svensk Papperstidning*. 6 :205–212.
- Bajpai, VK, Shukla, S., Paek, WK., Lim, J., Kumar, P. and Na, M. 2017. Efficacy of (+)-Lariciresinol to Control Bacterial Growth of *Staphylococcus aureus* and *Escherichia coli* O157:H7. *Front Microbiol.* 3:8:804
- Barnett, J. & Jeronimidis, G. 2003 *Wood Quality and its Biological Basis*. 226p.
- Baumassy, M. 2014. The Talloil Industry: 100 years of Innovation. 2014 PCA International Conference September 21–23, Seattle, USA.
- Belt, T. 2013. Wood preservative potential of Scots pine bark and knot extractives. Master Thesis, Aalto University, School of Chemical Technology . 56 p.
- Bertaud, F. and Holmbom, B. 2004. Chemical composition of earlywood and latewood in Norway spruce heartwood, sapwood and transition zone wood. *Wood Sci. Technol* 38:245–256.
- Bergstrom, B., Gustafsson, G., Gref, R. & Ericsson, A. 1999. Seasonal changes of pinosylvin distribution in the sapwood/heartwood boundary of *Pinus sylvestris*. *Trees-Structure and Function*, 14, 65-71.
- Bioeconomy. Available: <http://www.bioeconomy.fi/kuusesta-saadaan-suojavia-ja-hoitavia-ainesosia-myos-ihmisten-hyvinvointiin/> . Accessed 17.10.2017.
- Boutelje, J.B. 1966. On the anatomical structure moisture content, density, shrinkage, and resin content of the wood in and Swedish spruce (*Picea abies* Karst.). *Sven. Papperstidn.* 69:1–10.
- Campbell, A., Kim, W-J. and Koch, P. 1990. Chemical variation in lodgepole pine with sapwood/heartwood, stem height, and variety. *Wood and Fiber Science*, 22: 22–30.
- Cho, J.Y, Kim, A. R and Park, M. H. 2001. Lignans from the Rhizomes of *Coptis japonica* Differentially Act as Anti-Inflammatory Principles. *Planta Med* 2001; 67(4): 312–316
- Co, M., Fagerlund, A., Engman, L., Sunnerheim, K., Sjöberg, P. and Turner, C. 2012. Extraction of antioxidants from spruce (*Picea abies*) bark using eco-friendly solvents. *PhytochemAnal.*23:1–11.

- Conde, E., Fang, W., Hemming, J., Willför, S., Moure, A., Dominguez, H and Parajo JC: 2013. Water soluble components of *Pinus pinaster* wood. *BioResources* 8:2047–2063.
- Demirbas, A. 2011. Methylation of wood fatty and resin acids for production of biodiesel. *Fuel* 90:2273–2279.
- Duke 2017. U.S. Department of Agriculture, Agricultural Research Service. 1992–2016. Dr. Duke's Phytochemical and Ethnobotanical Databases. Home Page, <http://phytochem.nal.usda.gov/> <http://dx.doi.org/10.15482/USDA.ADC/1239279> Accessed 15.9.2017
- Dzubak, P., Hajduch, M., Vydra, D., Hustova, A., Kvasnica, M., Biedermann D., Markova, L., Urban, M. and Sarek, J. 2006. Pharmacological activities of natural triterpenoids and their therapeutic implications. *Nat Prod Rep.* 23:394–411.
- Eevia Health. Available: <https://www.eeviahealth.com/ingredients/fenoprolic/> Accessed 17.10.2017.
- Ekeberg, D., Flaete, P-O., Eikemnes, M., Fongen, M and Naess Anderssen, C.F. 2006. Qualitative and quantitative determination of extractives in heartwood of Scots pine (*Pinus sylvestris* L.) by gas chromatography. *Journal of Chromatography A*, 1109:267–272.
- Eklund PC, Willför SM, Smeds AI, Sundell FJ, Sjöholm RE, Holmbom BR. A new lariciresinol-type butyrolactone lignan derived from hydroxymatairesinol and its identification in spruce wood. *J Nat Prod.* 2004;67(6):927–931.
- Ekman, R. 1979. Analysis of the nonvolatile extractives in Norway spruce sapwood and heartwood. *Acta Acad. Abo. Ser. B* 39:1–20.
- Ekman, R. 1983. The suberin monomers and triterpenoids from the outer bark of *Betula verrucosa* Ehrh. *Holzforschung* 37:205–211.
- Ekman, R. 2000. Resin during storage and in biological treatment, In E-L. Back, (Ed); *Pitch Control, Wood resin and Deresination*, Tappi Press: Atlanta, USA, pp. 37–76.
- Ekman, R., Willför, S., Sjöholm, R., Reunanen, M., Mäki, J., Lehtila R., Eckerman, C. 2002. Identification of the lignan nortrachelogenin in knot and branch heartwood of Scots pine (*Pinus sylvestris* L.). *Holzforschung* 56:253–256.
- Erdtman, H. & Rennerfelt, E. 1944. Der Gehalt des Kiefern Kernholzes an Pinosylvin-phenolen. *Sven. Papperstidn.* 47:45–56.
- Fang W, Hemming J, Reunanen M, et al. Evaluation of selective extraction methods for recovery of polyphenols from pine. *Holzforschung.* 2013;67(8):843–851.
- Farrell R.L., Hata, K. and Wall, M.B. 1997. Solving pitch problems in pulp and paper processes by the use of enzymes or fungi. *Adv. Biochem. Eng. Biot.* 57:197–212.
- Fengel, D. and Wegener, G. 1984. Constituents of bark. In: *Wood, Chemistry, ultrastructure, Reactions.* Walter de Gruyter, Berlin. pp.240–267.
- Fengel, D., Wegener, G. 1989. *Wood. Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, Germany, 613p.
- Ferreira, J., Quilho, T. and Pereira, H. 2017. Characterization of *Betula pendula* outer bark regarding cork and phloem components at chemical and structural levels in view of biorefinery integration. *Journal of chemistry and technology* 37:10–25.
- Fischer, C. and Höll, W. 1992. Food reserves of Scots pine (*Pinus sylvestris* L.). II. Seasonal changes and radial distribution of carbohydrate and fat reserves in pine wood. *Trees* 6:147–155
- Fries, A., Ericsson, T. and Gref, R. 2000. High heritability of wood extractives in *Pinus sylvestris* progeny tests. *Can. J. For. Res* 30:1701–1713.
- Fuller, WS. Chip pile storage—a review of practices to avoid deterioration and economic losses. 1985. *Tappi J.* 68(8):48–52.
- Gandini, A., Neto, C. and Silvestre, A. 2006. Suberin: A promising renewable resource for novel macromolecular materials. *Prog. Polym. Sci.* 31:878–892.
- Goto T, Takahashi N, Hirai S, Kawada T. 2010. Various terpenoids derived from herbal and dietary plants function as PPAR modulators and regulate carbohydrate and lipid metabolism. *PPAR Res.* (10):1–9.
- Grand View Research. *Tannin Market Analysis By Sources (Plants, Brown Algae), By Product (Hydrolysable, Non-hydrolysable, Phlorotannins), By Application (Leather Tanning, Wine Production, Wood Adhesives), & Segment Forecasts, 2014 – 2025.* Available: <http://www.grandviewresearch.com/industry-analysis/tannin-market>. Accessed 30.10.2017.
- Hakkila, P. 1968. Geographical variation of some properties of pine and spruce pulpwood in Finland. *Commun Inst For Fenn* 66:1–59.
- Hakkila, P. 1975. Kanto- ja juuripuun kuortiprosentti, puuaineen tiheys ja asetoniutteitten määrä. *Folia For.* 224. Pp. 1–14.
- Hakkila, P. 1989. Technical properties of residual tree components. In: *Utilization of residual forest biomass.* Springer; p.100–203.

- Hakkila, P. & Verkasalo, E. 2009. Structure and properties of wood and woody biomass. In: Kellomäki, S. (ed.). *Forest Resources and Sustainable Management. Papermaking Science and Technology, Volume 2. 2nd Updated Edition.* Suomen paperi-insinöörien yhdistys ry., Helsinki. p. 133–215.
- Hammerbacher, A., Ralph, S., Bohlmann, J., Fenning, T., Gersenzon, J. and Schmidt, A. 2011. Biosynthesis of the major tetrahydroxystilbenes in spruce, astrigin and isorhapontin, proceeds via resveratrol and is enhanced by fungal infection. *Plant Physiology* 157:876–890.
- Harju, A., Kainulainen, P., Venäläinen, M., Tiitta, M. and Viitanen, H. 2002. Differences in resin acid concentration between brown-rot resistant and susceptible scots pine heartwood. *Holzforschung* 56:479–486.
- Harkin J.M. and Rowe J.W., 1971, *Forest Products Laboratory, 2 Forest Service; Bark and its possible uses.*
- HARRPA 2015 Hydrocarbon Resins, Rosin Resins and Pine Chemicals Producers Association (HARRPA). Crude tall oil- Valuable biomass based raw material for the chemical industry. Available: <http://www.circulary.eu/project/harrpa-biorefineries/> Accessed 17.10.2017.
- Hedmark, Å. & Scholz, M. 2008. Review of environmental effects and treatment of runoff from storage and handling of wood. *Bioresource Technology* 99, p. 5997–6009.
- Heijari, J., Nerg, A.-M., Kaakinen, S., Vapaavuori, E., Raitio, H., Levula, T., Viitanen, H., Holopainen, J.K., Kainulainen, P. 2005. Resistance of Scots pine wood to brown-rot fungi after long-term forest fertilization. *Trees* 19:728–734.
- Hillis, W.E. 1962. *Wood extractives and their significance to the pulp and paper industry.* Academic press. 485 p.
- Hillis, W.E. 1971: Distribution, properties and formation of some wood extractives. – *Wood Science and Technology* 5: 272–298.
- Hoch, G., Richter, A. and Körner, C. 2003. Non-structural carbon compounds in temperate forest trees. *Plant, cell and environment* 26: 1067–1081.
- Holmbom B, Ekman R. 1978. Tall oil precursors of scots pine and common spruce and their change during sulphate pulping. *Acta Acad Aboensis B.* 38(3):1–11.
- Holmbom, B. 1999. Extractives. In: Sjöström, E., Alen, R(eds), *Analytical methods in wood chemistry pulping and papermaking.* Springer-Verlag, Germany p. 125–148.
- Holmbom, B., Eckerman, C., Eklund, P., Hemming, J., Reunanen, M., Sjöholm, R., Sundberg, A. and Willför, S. 2003. Knots in trees—a new rich source of lignans. *Phytochem.* 2: 331–340.
- Holmbom B, Hemming J, Eckerman C, et al. 2007. Fractionation and chemistry of bark components in wood material and science engineering final report – Finnish-Swedish research programme 2003–2007.
- Holmbom 2010. Utilization of extractives. Course “The Forest-based Biorefinery – Chemical and Engineering Challenges and Opportunities” http://www.aboakademi.fi/institut/pcc/presentations_pdf/Holmbom_Extractives.pdf Accessed 20.9.2017
- Holmbom B. 2011. Extraction and utilization of non-structural wood and bark components. In: Alén R, ed. *Biorefining of forest resources.* Helsinki, Finland: Paperi ja Puu Oy, p. 178–224.
- Holopainen JK, Rikala R, Kainulainen P, Oksanen J 1995. Resource partitioning to growth, storage and defence in nitrogen-fertilized Scots pine susceptibility of the seedlings to the tarnished plant bug *Lygus rugulipennis*. *New Phytol* 131:521–532.
- Hovelstad, H., Leirset, I., Oyaas, K., Fiksdahl, A. 2006. Screening analyses of pinosylvins, resin acids and lignans in Norwegian conifers and hardwood. *Molecules* 11:103–114.
- Höll, W. 1981. Eine dünnsichtchromatographische Darstellung des Jahresgangs löslicher Zucker im Stammholz von drei Angiospermen und einer Gymnosperme. *Holzforschung* 35:173–175
- Höll, W. and S. Priebe. 1985. Storage lipids in the trunk- and rootwood of *Tilia cordata* Mill. from the dormant to the growing period. *Holzforschung* 39:7–10.
- Höll, W. 1985. Seasonal fluctuation of reserve materials in the trunkwood of spruce (*Picea abies* (L) Karst). *J. Plant Physiol.* 117: 355–362.
- Ingram, L.L Templeton, M.C., McGraw, G.W and Hemingway, R. W. 2000. Knot, Heartwood, and Sapwood Extractives Related to VOCs from Drying Southern Pine Lumber, *Journal of Wood Chemistry and Technology*, 20:4, 415–439,
- Innomost. Available: (<http://www.innomost.com/products/betulin/>. Accessed 17.10.2017.
- Jewell, I.J., Cavell, K.J., Blackman, A.J. 1991. “Chemistry of *Eucalyptus regnans* Extractives and Effects on Peroxide Bleaching”. *Appita 6th Int. Symp. Wood & Pulping Chem. Proc.* Vol.1: 45
- Jirjis, R. and Theander, O. 1990. The effect of seasonal storage on the chemical composition of forest residue chips. *Scand. J. G. For. Res.* 5:437–448.
- Jyske, T., Laakso, T., Latva-Mäenpää, H., Tapanila, T. and Saranpää, P. 2014 Yield of stilbene glucosides from the bark of young and old Norway spruce stems. *Biomass and Bioenergy* 71: 216–227.

- Kaakinen, S., Saranpää, P. and Vapaavuori, E. 2007. Effects of growth differences due to geographic location and N-fertilization on wood chemistry of Norway spruce. *Trees* 21:131–139.
- Kaakinen, S., Piispanen, R., Lehto, S., Metsometsä, J., Nilsson, U., Saranpää, P., Linder, S. & Vapaavuori, E. 2009. Growth, wood chemistry, and fiber length of Norway spruce in a long-term nutrient optimization experiment. *Canadian Journal of Forest Research* 39: 410–419.
- Kainulainen P, Holopainen JK, Palomäkii V, Holopainen, T. 1996. Effects of nitrogen fertilization on secondary chemistry and ectomycorrhizal state of Scots pine seedlings and on growth of grey pine aphid. *J Chem Ecol* 22:617–636.
- Karonen M, Hämäläinen M, Nieminen R, et al. 2004a. Phenolic extractives from the bark of *Pinus sylvestris* L. and their effects on inflammatory mediators nitric oxide and prostaglandin E2. *J Agric Food Chem*. 52:7532–7540.
- Karonen, M., Loponen, J., Ossipov, V., Pihlaja, K. 2004b. Analysis of procyanidins in pine bark with reversed-phase and normal-phase high-performance liquid chromatography-electrospray ionization mass spectrometry. *Anal. Chim. Acta* 522: 105–112.
- Karppanen, O., Venäläinen, M., Harju, A., Willför, S., Pietarinen, S., Laakso, T. and Kainulainen, P. 2007. Knotwood as a window to the indirect measurement of the decay resistance of Scots pine heartwood. *Holzforchung* 61: 600–604.
- Karppanen, O., Venäläinen, M., Harju, A. and Laakso, T. 2008. The effect of brown-rot decay on water adsorption and chemical composition of Scots pine heartwood. *Ann. For. Sci.* 65.
- Kasmani, J., Nemati, M., Samariha, A., Chitsazi, H., Mohammadi, N. and Nostrati, H. 2011. Studying the effect of the age in *Eucalyptus camaldulensis* species on wood chemical compounds used in pulping process. *American-Eurasian J. Agric. & Environ. Sci.* 11: 854–856.
- Kebbi-Benkeder, Z., Colin, F., Dumarcay, S. & Gerardin, P. 2015. Quantification and characterization of knotwood extractives of 12 European softwood and hardwood species. *Annals of Forest Science* 72: 277-284
- Keinänen M, Julkunen-Tiitto R. 1998. High-performance liquid chromatographic determination of flavonoids in *Betula pendula* and *Betula pubescens* leaves. *Journal of Chromatography A* :793:370–377.
- Kemppainen K, Siika-Aho M, Pattathil S, Giovando S, Kruus K. 2014. Spruce bark as an industrial source of condensed tannins and non-cellulosic sugars. *Industrial Crops and Products*. 52:158–168.
- Kimland B, Norin T. 1972. Wood extractives of common spruce, *Picea abies* (L.) Karst. *Svensk papperstidning* 75(10):403–409.
- Kilpeläinen, A., Peltola, h., Ryyppö, A., Sauvala, K., Laitinen, K. and Kellomäki, S. 2003. Wood properties of Scots pines (*Pinus sylvestris*) grown at elevated temperature and carbon dioxide concentration. *Tree Physiology* 23:889–897.
- Kinnari, H. Kuusen (*Picea abies*) uuteaineet ja niiden pitoisuusvaihtelut vuosikasvun ja varastoinnin aikana. Kuorimon jätevesien myrkylliset yhdisteet ja kenttäkastelun vaikutus vesistöön, Pro Gradu ja erikoistyö, Jyväskylän yliopisto, 2002. [in Finnish]
- Kostiainen, K., Kaakinen, S., Saranpää, P., Sigurdsson, B.D., Linder, S. and Vapaavuori, E. 2004. Effect of elevated [CO₂] on stem wood properties of mature Norway spruce grown at different soil nutrient availability. *Global Change Biol* 10: 1526–1538
- Krasutsky, P.A. 2006. Birch bark research and development. *Nat Prod Rep.* 23:919–42.
- Krasutsky, P.A. 2011. Laboratory of Chemical Extractive. Available: http://www.nati.net/media/7446/pavel_a_krasutsky__oct2011.pdf Accessed 15.09.2017.
- Krogell, J., Holmbom, B., Pranovich, A., Hemming, J. and Willför, S. 2012. Extraction and chemical characterization of Norway spruce inner and outer bark. *Nordic Pulp and Paper Research Journal*. Vol 27, no 1/ 2012.
- Kähkönen, M., Hopia, A., Vuorela, H., Rauha, J-P., Pihlaja, K., Kujala, T. and Heinonen, M. 1999. Antioxidant activity of plant extracts containing phenolic compounds. *J. Agric. Food Chem.* 47:3954–3962.
- Lacoste C, Čop M, Kemppainen K, et al. 2015. Biobased foams from condensed tannin extracts from Norway spruce (*Picea abies*) bark. *Industrial Crops and Products*. 73:144–153.
- Latva-Mäenpää, H., Laakso, T., Sarjala, T., Wähälä, K. and Saranpää, P. 2013. Variation of stilbene glucosides in bark extracts obtained from roots and stumps of Norway spruce (*Picea abies* [L.] Karst.) *Trees* 27:131–139.
- Latva-Mäenpää H, Laakso T, Sarjala T, Wähälä K, Saranpää P. 2014. Root neck of Norway spruce as a source of bioactive lignans and stilbenes. *Holzforchung*;68(1):1–7.
- Latva-Mäenpää, H. 2017. Bioactive and protective polyphenolics from roots and stumps of conifer trees (Norway spruce and Scots pine). Academic Dissertation. Chemistry Faculty of Science University of Helsinki Finland, p.74.

- Lappi, H., Läspä, O. and Nurmi, J. 2014a. Decrease in extractives of chain-flail residue. Forest Refine info sheet.3 p.[Available 28.8.2017: http://biofuelregion.se/wp-content/uploads/2017/01/3_13_IS_2014-08-12_Decrease_in_Extractives_of_CFResid_Lappi_Nurmi.pdf]
- Lappi, H., Läspä, O. and Nurmi, J. 2014b. Decrease in extractives of stumps. Forest Refine info sheet.3 p. [Available 28.8.2017: http://biofuelregion.se/wp-content/uploads/2017/01/3_12_IS_2014-08-12_Decrease_in_Extractives_of_Stumps_Lappi_Nurmi.pdf]
- Lappi, H., Nurmi, J., and Läspä, O. 2014c. Decrease in extractives of tree bark during storage. Forest Refine info sheet. 4 p. [Available 28.8.2017: http://biofuelregion.se/wp-content/uploads/2017/01/3_11_IS_2014-08-11_Decrease_in_Extractives_Lappi_Nurmi_Laspa.pdf]
- Lee, H., Wo, E-R and Lee, D.G. 2016 (–)-Nortrachelogenin from *Partrinia scabiosaefolia* elicits an apoptotic response in *Candida albicans*. *FEMS Yeast Research*, 2016, Vol. 16, No. 3
- Leinonen, A., Harju, A., Venäläinen, M., Saranpää, P. and Laakso, T. 2008. FT-NIR spectroscopy in predicting the decay resistance related characteristics of solid Scots pine (*Pinus sylvestris* L.) heartwood. *Holzforschung* 62: 284–288.
- Lim C., Koffas M. 2010. Bioavailability and recent advances in the bioactivity of flavonoid and stilbene compounds. *Current Organic Chemistry* 14:1727–1751.
- Lindberg, M., Lundgren, L., Gref, R., Johansson, M. 1992. Stilbenes and resin acids in relation to the penetration of *Heterobasidion annosum* through the bark of *Picea abies*. *Eur J For Pathol* 22:95–106.
- Lukkari, J., Hyppölä, A., Kärkkäinen, M., Lipponen, P., Mäkelä, M., Paananen, S., Rumpunen, H. and Thesslund, O. 2004. Puun laadun säilyttäminen.” Storing the quality of the wood”. Metsäteho Oy, Helsinki 2004. 24 p. (in Finnish).
- Lätti A.K., Riihinen K.R., Kainulainen P.S.: Analysis of anthocyanin variation in wild populations of bilberry (*Vaccinium myrtillus* L.) in Finland. *J Agric Food Chem*. 2008, 56: 190–196.
- Mbambo, B., Odhav, B. and Mohanlall, V. 2012. Antifungal activity of stigmasterol, sitosterol and ergosterol from bulbine *natalensis* baker (asphodelaceae). *Journal of Medicinal Plants Research*. 6:5135–5141.
- Mantau, U. and Saal, U.2010. Material uses. In: EU wood-Final Report, Hamburg, Germany. pp.35–42.
- Mannila, E. and Talvitie, A. 1992. Stilbenes from *Picea Abies* bark. *Phytochemistry* 31:3288–3289.
- Martinez-Inigo, M., Immerzeel, P., Gutierrez, A., del Rio, J.C. and Sierra-Alvarez, R. 1999. Biodegradability of Extractives in Sapwood and Heartwood from Scots Pine by Sapstain and White Rot Fungi. *Holzforschung* 53:247–252.
- Matthews, S., Mila, I., Scalbert, A., Donnelly, D. 1997. Extractable and non-extractable proanthocyanidins in barks. *Phytochemistry* 45: 405–410. Martínez-Iñigo, M., Immerzeel, P., Gutierrez, A., Río, J. and Sierra-Alvarez, R. 1999. Biodegradability of Extractives in Sapwood and Heartwood from Scots Pine by Sapstain and White Rot Fungi. *Holzforschung* 53:247–252
- Matysiak, R. 2001. Content of carotenoids in needles of *Pinus sylvestris* L. growing in a polluted area. *Dendrobiology* 46:39–42.
- Metsämuuronen S, Siren H (2014) Antibacterial Compounds in Predominant Trees in Finland: Review. *J Bioprocess Biotech* 4.
- Mulat, D. G., Latva-Mäenpää, H., Koskela, H., Saranpää, P. & Wähälä, K. 2014. Rapid Chemical Characterisation of Stilbenes in the Root Bark of Norway Spruce by Off-line HPLC/DAD-NMR. *Phytochemical Analysis*, 25: 529-536.
- Muzika R-M.1993. Terpenes and phenolics in response to nitrogen fertilization: a test of the carbon/nutrient balance hypothesis. *Chemoecology* 4:3–7.
- Nascimento, M.S., Santana, A.L., Maranhao, C.A., Oliveira, L.S., & Bieber, L. 2013: Phenolic extractives and natural resistance of wood. – In *Biodegradation – Life of Science*, Edited by Chamy, R. and Rosenkranz, F. In Tech, 378 p,
- Nerg, A., Kainulainen, P., Vuorinen, M., Hanso, M., Holopainen, J.K., Kurkela, T. 1994. Seasonal and geographical variation of terpenes, resin acids and total phenolics in nursery grown seedling of Scots pine (*Pinus sylvestris* L.), *New Phytol.* 128, p. 703–713.
- Niemelä, K. 2015. By-products from pulping of wood and non-wood raw materials. FIBRA seminar, March 23rd, 2015. Available: http://www.fibrafp7.net/Portals/0/7_Niemela.pdf. Accessed 17.10.2017.
- Nilsson, K., Sangster, M., Gallis, C., Hartig, T., Vries, S., Seeland, K. and Schipperijn, J. (Eds). 2011. *Forests, trees and human health*. Springer, New York. pp. 426.

- Norin, T. and Winell, B. 1972. Extractives from the bark of common spruce, *Picea abies* L. Karst.. Acta Chemica Scandinavica 26: 2289–2296.
- Nurmi, J. 1993. Heating values of the above ground biomass of small-sized trees. Acta Forestalia Fennica 236.
- Nurmi, J. 1997. Heating values of mature trees. Acta Forestalia Fennica 256.
- Nurmi J. 1999. The storage of logging residue for fuel. BIOMASS BIOENERG 17: 41–47.
- Official Statistics of Finland 2017 a: Forest industries' wood consumption 2016. [web publication]. Helsinki: Natural Resources Institute Finland [Accessed 23.8.2017].
- Official Statistics of Finland 2017 b: Wood in energy generation 2016. [web publication]. Helsinki: Natural Resources Institute Finland [Accessed 24.3.2017].
- Oleszek, W., Stochmal, A., Karolewski, P., Simonet, A.M., Macias, F.A., Tava, A. 2002. Flavonoids from *Pinus sylvestris* needles and their variation in trees of different origin grown for nearly a century at the same area. Biochemical Systematics and Ecology 30, p. 1011–1022.
- Ossipov, V., Nurmi, K., Loponen, J., Prokopiev, N., Haukioja, E. and Pihlaja, K. 1995. HPLC isolation and identification of flavonoids from white birch *Betula pubescens* leaves. Biochem Syst Ecol. 23:213–222.
- Ossipov, V., Nurmi, K., Loponen, J., Haukioja, E., and Pihlaja, K. 1996. High-performance liquid chromatographic separation and identification of phenolic compounds from leaves of *Betula pubescens* and *Betula pendula*. Journal of Chromatography A. 721:59–68.
- Pan, H. and Lundgren, L. 1996. Phenolics from inner bark of *Pinus sylvestris*. Phytochemistry 42: 1185–1189.
- Partanen, J., Harju, A.M., Venäläinen, M and Kärkkäinen, K. 2011. Highly heritable heartwood properties of Scots pine: possibilities for selective seed harvest in seed orchards. Can. J. Forest. Res. 41:1993–2000.
- Pasztory, Z., Mohacsine, I., Gorbacheva, G. and Börcsök, Z. 2016. The utilization of tree bark. Bioresources 11:7859–7888.
- Pereira H., Graca J., Rodrigues J.C. 2003. Wood chemistry in relation to quality. In: Barnett JR, Jeronimidis G (eds) Wood quality and its biological basis. Blackwell & CRC Press, London & Boca Raton, FL. Biological Sciences Series, pp 53–86
- Pietarinen, S., Willför, S., Vikström, F. & Holmbom, B. 2006a. Aspen Knots, a Rich Source of Flavonoids. Journal of Wood Chemistry and Technology, 26: 245–258.
- Pietarinen, S., Willför, S., Ahotupa, M., Hemming, J. & Holmbom, B. 2006b. Knotwood and bark extracts: strong antioxidants from waste materials. J Wood Sci. 52:436–444.
- Piispanen, R. & Saranpää, P. 2001. Variation of non-structural carbohydrates in silver birch (*Betula pendula* Roth) wood. Trees – Structure and Function 15: 444–451.
- Piispanen, R. & Saranpää, P. 2002. Neutral lipids and phospholipids in Scots pine (*Pinus sylvestris*) sapwood and heartwood. Tree Physiology 22(9): 661–666.
- Piispanen, R. & Saranpää, P. 2004. Seasonal and within-stem variations of neutral lipids in silver birch (*Betula pendula*) wood. Tree Physiology 24(9): 991–999.
- Piispanen, R., Willför, S., Saranpää, P. & Holmbom, B. 2008. Variation of lignans in Norway spruce (*Picea abies* [L.] Karst.) knotwood: within-stem variation and the effect of fertilisation at two experimental sites in Finland. Trees – Structure and Function 22(3): 317–328.
- Pinto, P. C. R. O., Sousa, A. F., Silvestre, A. J. D., Neto, C. P., Gandini, A., Eckerman, C., Holmbom, B. 2009. *Quercus suber* and *Betula pendula* outer bark as renewable sources of oleochemicals: A comparative study. Industrial crops and products 29: 126–132.
- Pohjamo, S., Hemming, J., Willför, S., Reunanen, M. and Holmbom, B. 2003. Phenolic extractives in *Salix caprea* wood and knots. Phytochemistry 63: 165–169.
- Polastro, E., Tuovinen, J., Little, A.D. 2010. CTO fractionation, A role model of a sustainable chemical business? Chemistry Today 28(2), 39–41.
- Promberger A, Weber HK, Stockinger A, Sixta H. Investigation of storage conditions on beech wood logs and chips and its influence on the production of dissolving sulfite pulp. Lenzinger Berichte. 2004; 83:1.
- Rajendran, V. K., Breitkreuz, K., Kraft, A., Maga, D. and Brucart, M. 2016. Analysis of the European crude tall oil industry – environmental impact, socioeconomic value & downstream potential. Fraunhofer Institute for Environmental, Safety and Energy Technology. p. 77.
- Rastmanesh, R. 2011. An urgent need to include risk-benefit analysis in clinical trials investigating conjugated linoleic acid supplements in cancer patients. Contemp Clin Trials. 32(1):69–73.
- Rauha, J-P. 2001. The search for biological activity in Finnish plant extracts containing phenolic compounds. Academic Dissertation. University of Helsinki, Faculty of Science, Department of Pharmacy, p. 72

- Reinhold, L., Harborne, J. B., and Swain, T. (editors) 1980. *Progress in Phytochemistry*, vol 6. , Pergamon Press Ltd. p. 294.
- Richter, A. K., Frossard, E. and Brunner, I. 2007. Polyphenols in the woody roots of Norway spruce and European beech reduce TTC. *Tree Physiology*, 27: 155-160
- Repolar. Available:<https://www.repolar.com/wp-content/uploads/2016/07/Abilar-5-FAQ-ENGL.pdf>. Accessed 17.10.2017.
- Rhen, C. 2004. Chemical composition and gross calorific value of the above-ground biomass components of young *Picea abies*. *Scandinavian Journal of Forest Research* 19:72–81.
- Richter, A., Frossard, E. and Brunner, I. 2007. Polyphenols in the woody roots of Norway spruce and European beech reduce TTC. *Tree Physiology* 27, 155–160.
- Roitto, M., Siwale, W., Tanner, J., Ilvesniemi, H., Julkunen-Tiitto, R. and Verkasalo, E. 2016. Characterization of extractives in tree biomass and by-products of plywood and saw mills from Finnish birch in different climatic regions for value-added chemical products. 5th International scientific conference on hardwood processing 2015, International academy of wood science – annual meeting, Sept. 15–17, 2015, Quebec City, Canada: Proceedings: 174–181.
- Routa, J., Pyörälä, P., Alam, A., Kilpeläinen, A., Peltola, H., & Kellomäki, S. 2013: Integrated production of timber and energy biomass in forestry. – In: Kellomäki, S., Kilpeläinen, A., & Alam, A. (eds.) *Forest BioEnergy Production: Management, Carbon Sequestration and Adaptation*: 57–80. Springer. New York.
- Royer M, Houde R, Viano Y, Stevanovic T. 2012. Non-wood forest products based on extractives-A new opportunity for the Canadian forest industry part 1: Hardwood forest species. *Journal of Food Research*.1(3), p.
- Rupar, K. and Sanati, M 2005. The release of terpenes during storage of biomass. *Biomass and Bioenergy* 28, p. 29–34.
- Rydholm, S.1967. Relationship of pulp and paper properties. In: Rydholm S (ed) *Pulping processes*. Interscience Publishers, New York, pp 1152–1166
- Räisänen, T., Ryyppö, A. and Kellomäki, S. 2008.Effects of elevated CO₂ and temperature on monoterpene emission of Scots pine (*Pinus sylvestris* L.) *Atmos. Environ.*, 2008, 42, 18, 4160–4171
- Saal, U.2010. Industrial wood residues. In: EU wood-Final Report, Hamburg, Germany. pp.97–107.
- Sadof, C. S. and Grant G. 1997. Monoterpene composition of *Pinus sylvestris* varieties resistant and susceptible to *Dipteris zimmermani*. *Journal of Chemical Ecology* vol 23, no. 8.
- Sakai, K. 2001. Chemistry of bark. In: *Wood and Cellulosic Chemistry*. Hon, D.N.-S and Shiraishi, N. (Eds) Marcel Dekker, New York, pp.244–273.
- Salem, M., Elansary, H-O, Elkelish, A., Zeidler, A., Ali, H., El-Hefny, M and Yessoufou, K. 2016. In vitro Bioactivity and Antimicrobial Activity of *Picea abies* and *Larix decidua* wood and bark extracts. *Bioresources* 11:9421–9437.
- Saranpää, P. and H. Nyberg. 1987. Seasonal variation of neutral lipids in *Pinus sylvestris* L. sapwood and heartwood. *Trees* 1:139–144.
- Seyed Mohammadi, N., Nemat, M., Samariha, A., Tabei, A., Ravanbakhsh, F. and Kiaei, M. 2011. Studying the effect of the age of a tree on chemical composition and degree of polymerization cellulose. *Indian Journal of Science and Technology* 12: 1679–1680.
- Shain L. 1971. The response of sapwood of Norway spruce to infection by *fomes annosus*. *Phytopathology* 61(3):301–307.
- Singh, RP., Agrawal, P., Yim, D., Agarwal, C. and Agarwal, R. 2005. Acacetin inhibits cell growth and cell cycle progression, and induces apoptosis in human prostate cancer cells: structure–activity relationship with linarin and linarin acetate. *Carcinogenesis* 26 :745–854.
- Sipi, M. *Sahatavaratuotanto Opetushallitus Helsinki* 2006
- Siwale, W. 2015. Phenolic compounds in stem wood of Scots pine (*Pinus sylvestris* L.) grown in different north-south locations in Finland. University of Eastern Finland, Department of Biology / School of Forest Science. Master's thesis in wood material science. 45 p.
- Sjöström, E. 1993. *Wood Chemistry, fundamentals and applications*. Academic press, California. p.295
- Slimestad R, Hostettmann K. 1996. Characterisation of phenolic constituents from juvenile and mature needles of Norway spruce by means of high performance liquid chromatography–mass spectrometry. *Phytochem Anal.* 7:42–48.
- Solhaug, K. 1990. Stilbene glucosides in bark and needles from *Picea* species. *Scandinavian Forest Research* 5:59–67.
- Spicer, R. 2005. Senescence in secondary xylem: heartwood formation as an active developmental program. In: Holbrook NM, Zwieniecki MJ (eds) *Vascular transport in plants*. Elsevier Academic Press, Amsterdam, pp 457–475
- Steinshamn H. Bark in feed - for improved feed utilization and animal health. *Bioforsk Fokus*. 2014;9(10):1–53.

- Strack, D., Heilemann, J., Wray, V. and Dirks, H. 1989. Structures and accumulation patterns of soluble and insoluble phenolics from Norway spruce needles. *Phytochemistry* 28:2071–2078
- Sun, R. & Tomkinson, J. 2001. Extraction and characterization of lipophilic extractives from wheat straw. *Cellulose Chemistry and Technology* 35: 471–485.
- Sutela, S., Niemi, K., Edesi, J., Laakso, T., Saranpää, P., Vuosku, J., Mäkelä, R., Tiimonen, H., Chiang, V., Koskimäki, J., Suorsa, M., Julkunen-Tiitto, R., and Häggman, H. 2009. Phenolic compounds in ectomycorrhizal interaction of lignin modified silver birch. *BMC Plant Biology* 2009, 9:124
- Sutela, S., Hahl, H., Tiimonen, H., Aronen, T., Ylioja, T., Laakso, T., Saranpää, P., Chiang, V., Julkunen-Tiitto, R., and Häggman, H. 2014. Phenolic Compounds and Expression of 4CL Genes in Silver Birch Clones and Pt4CL1a Lines. *PLoS ONE* 9(12): e114434. doi:10.1371/journal.pone.0114434.
- Svahn, T. 2015. Uuteaineiden fysiologiset vaikutukset. Pro gradu. Jyväskylän yliopisto 2015. p. 1–65. Master's Thesis [in Finnish]
- Tamminen, T., Ruuskanen, M., Grönqvist, S. "The influence of softwood bark origin on tannin recovery by hot-water extraction." 19th International Symposium on Wood, Fiber and Pulping Chemistry, ISWFPC. Porto Seguro, Brazil. Aug. 28–Sept. 01, 2017.
- Taylor, A.M., Gartner, B.L., Morrell, J.J. 2002. Heartwood formation and natural durability—a review. *Wood Fiber Sci* 34:587–611
- Tiitta, M., Tomppo, L., Järnström, H., Löija, M., Laakso, T., Harju, A., Venäläinen, M., Iitti, H., Paajanen, L., Saranpää, P., Lappalainen, R. and Viitanen, H. 2009. Spectral and chemical analyses of mould development on Scots pine heartwood. *Eur. J. Wood Prod.* 67: 151–158.
- Turtola S, Manninen A-M, Holopainen JK, Levula T, Raitio H, Kainulainen P. 2002. Secondary metabolite concentrations and terpene emissions of Scots pine xylem after long-term forest fertilization. *J Environ Qual* 31:1694–1701
- Toscano Underwood C, Pearce R. 1991. Astringin and isorhapontin distribution in Sitka spruce trees. *Phytochemistry* 30:2183–2189
- Thorin, J. and Nommik, H. 1974. Monoterpene composition of cortical oleoresin from different clones of *Pinus sylvestris*. *Phytochemistry* 13, 1879–1881.
- Torrance, S.J, Hoffmann, J.J, Cole, J.R. 1979. Wikstromol, antitumor lignin from *Wikstroemia foetida* var *oahuensis* gray and *wikstroemia uva-ursi* gray (thymelaeaceae). *J Pharm Sci*, 68: 664–5.
- Uleberg E., Roteh, G. and Martinussen, I. 2009. Cloudberry breeding in Norway. *Latv. J. Agron.* 12. 122–125.
- Uleberg, E., Rohloff, J., Jaakola, L., Trost, K., Junntila, O., Häggman, H. and Martinussen, I. 2012. Effects of temperature and photoperiod on yield and chemical composition of northern and southern clones of bilberry (*Vaccinium myrtillus* L.). *J Agric Food Chem.* 60: 10406–10414.
- Umezawa, T. 2000. Chemistry of extractives. In: *Wood and Cellulosic Chemistry*. Hon, D.N.-S and Shiraishi, N. (Eds) Marcel Dekker, New York, pp.213–241.
- UPM 2017. <http://www.upmbiofuels.com/upm-biofuels/production/Pages/Default.aspx>. Accessed 17.10.2017
- Uprichard, J.M. and Lloyd, J.A. 1980. Influence of tree age on the chemical composition of radiate pine. *NZJ For Sci* 10: 551–557.
- Välimaa A, Honkalampi-Hämäläinen U, Pietarinen S, Willför S, Holmbom B, von Wright A. 2007. Antimicrobial and cytotoxic knotwood extracts and related pure compounds and their effects on food-associated microorganisms. *Int J Food Microbiol.* 115(2), p. 235–243.
- Valentín, L., Kluczek-Turpeinen, B., Willför, S., Hemming, J., Hatakka, A., Steffen, K. and Tuomela, M. 2010. Scots pine (*Pinus sylvestris*) bark composition and degradation by fungi: Potential substrate for bioremediation. *Bioresource Technology* 101:2203–2209
- Valkama E, Salminen JP, Koricheva J, Pihlaja K. 2003. Comparative analysis of leaf trichome structure and composition of epicuticular flavonoids in Finnish birch species. *Ann Bot.* 91:643–655.
- Viiri, H., Annala, E., Kitunen, V. and Niemelä, P. 2001. Induced responses in stilbenes and terpenes in fertilized Norway spruce after inoculation with blue-stain fungus, *Ceratocystis polonica*. *Trees* 15:112–122.
- Villaseñor, I. M., Angelada, J., Canlas, A. P. and Echegoyen, D. 2002. Bioactivity studies on β -sitosterol and its glucoside. *Phytother. Res.* 16: 417–421.
- Voipio, R. & Laakso, T. 1992. Pienikokoisten puiden maanpäällisen biomassan kemiallinen koostumus. Chemical composition of the above ground biomass of small-sized trees. *Folia Forestalia* 789. [in Finnish].

- Wajs, A., Pranovich, A., Reunanen, M., Willför, S. and Holmbom, B. 2006. Characterization of volatile organic compounds (VOCs) in stemwood using solid phase microextraction. *Phytochem. Anal* 17:91–101.
- Wajs, A., Pranovich, A., Reunanen, M., Willför, S. and Holmbom, B. 2007. Headspace- SPME analysis of the sapwood and heartwood of *Picea abies*, *pinus sylvestris* and *Larix Decidua*. *J. Essent. Oil Res.* 19:125–133.
- Weissman, G. 1984. Zusammensetzung der wässrigen Rindenextrakte von *Picea abies* [Karst.] im Verlauf einer Vegetationsperiode. *Holzforschung* 38:7–10 [in German].
- Willför, S., Hemming, J., Reunanen, M., Eckerman, C. and Holmbom, B. 2002. Wood knots – A novel rich source of bioactive phenolic compounds. In: 7th European Workshop on Lignocellulosics and Pulp, Åbo Akademi University, Åbo, Finland, pp 43–46
- Willför, S., Hemming, J., Reunanen, M., Eckerman, C. and Holmbom, B. 2003a. Lignans and lipophilic extractives in Norway spruce knots and stemwood. *Holzforschung* 57:27–36
- Willför, S., Hemming, J., Reunanen, M. and Holmbom, B. 2003b. Phenolic and lipophilic extractives in Scots pine knots and stemwood. *Holzforschung* 57(4):359–372
- Willför, S., Nisula, L., Hemming, J., Reunanen, M. and Holmbom, B. 2003c. Lignans in knots of some *Abies* species used as pulpwood. In: *Phytochemistry and Biology of Lignans*, April 6–9, Bornheim-Walberger, Germany, Phytochemical Society of Europe, p 101
- Willför SM, Ahotupa MO, Hemming JE, et al. Antioxidant activity of knotwood extractives and phenolic compounds of selected tree species. *J Agric Food Chem.* 2003d;51(26):7600–7606.
- Willför, S., Nisula, L., Hemming, J., Reunanen, M. and Holmbom, B. 2004. Bioactive phenolic substances in industrially important tree species. *Holzforschung* 58: 335–344.
- Willför, S., Sundberg, A., Rehn, P., Saranpää, P. and Holmbom, B. 2005. Distribution of lignans in knots and adjacent stemwood of *Picea abies*. *Holz als Roh- und Werkstoff* 63: 353–357
- Williams, C. 2011. *Medicinal Plants in Australia Volume 2: Gums, Resins, Tannin and Essential Oils*. Rosenberg Publishing Pty Ltd, Australia, p. 1–338.
- Wolter F., Clausnitzer A., Akoglu B., Stein J. Piceatannol, a natural analog of resveratrol, inhibits progression through the S phase of the cell cycle in colorectal cancer cell lines. *J Nutr.* 2002;132(2): 298–302.
- Xavier D, Emmanuel F, Philippe G, Eric M. 2012. Spruce bark hydrolysis to optimize phenolic content. *CELLULOSE CHEMISTRY AND TECHNOLOGY* 46(9–10) p. 541–550.
- Yanchuk, A.D., Spilda, I. and Micko, M.M. 1988. Genetic variation of extractives in the wood of trembling aspen. *Wood Sci. Technol.* 22:67–71.
- Zabel, R.A. & Morrell, J.J. 1992. *Wood Microbiology – Decay and its Preservation*, Academic Press, Inc., New York.
- Zahri, S., Belloncle, C., Charrier, F., Pardon, P., Quideau, S., Charrier, B. 2007. UV light impact on ellagitannins and wood surface colour of European oak (*Quercus petraea* and *Quercus robur*), *Applied Surface Science* 253, p. 4985–4989.
- Zhang, L. and Gellerstedt, G. "Reactive Structures in Wood and High-yield Pulps. IV.* Daylight-induced Oxidation of Stilbene Structures in." *Acta Chemica Scandinavica* 48 (1994): 490–497.
- Zobel, B.J. and van Buijtenen, J.P. 1989. *Wood Variation: Its Causes and Control*. Springer-Verlag, Berlin, Germany (1989) p. 363
- Åkerström A, Jaakola L, Bång U, Jaderlund A: Effects of latitude-related factors and geographical origin on anthocyanidin concentrations in fruits of *Vaccinium myrtillus* L. (bilberries). *J Agric Food Chem.* 2010, 58: 11939–11945.
- Ånäs, E., Ekman, R and Holmbom, B. 1983. Composition of nonpolar extractives in bark of Norway spruce and Scots pine. *Journal of wood chemistry and technology* 2:119–130.



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