Extractives of Stemwood and Sawmill Residues of Scots Pine (*Pinus sylvestris* L.) for Biorefining in Four Climatic Regions in Finland—Phenolic and Resin Acid Compounds

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**Abstract:** This study aimed to identify and quantify phenolic and resin acid extractive compounds in Scots pine stemwood and sawmill residues in four climatic regions of Finland to evaluate their most optimal sources for bio-based chemical biorefining and bioenergy products. The sample consisted of 140 trees from 28 stands, and sawdust lots from 11 log stands. NMR for the overall extractive analysis and HPLC for the quantitative estimation of phenolic and resin acid compounds were employed. Correlation analysis, multivariate factor analysis, principle component analysis and multiple linear regression modelling were applied for statistical analysis. HPLC identified 12 extractive compounds and NMR five more resin acids. Pinosylvin (PS), pinoresinol monomethyl ether (PSMME), and partly neolignans/lignans occurred in the largest concentrations. Wood type caused the most variation, heartwood having larger concentrations than sapwood (sawdust between them). Regional differences in the concentrations were smaller, but factor analysis distinguished the northern and the southern regions into their own groups. The results indicated higher concentrations of PS, PSMME, and vanillic acid in southern regions and those of, e.g., PSMME glycoside, lignan 2, and neolignan 1 in northern regions. The rather low concentrations of extractives in stemwood and sawdust imply value-added products, efficient sorting and/or large raw material volumes.

**Keywords:** *Pinus* sp.; biorefining; raw material; wood chemistry; chemical analysis; statistical analysis; wood extractives; regional effects; climatic effects

1. Introduction

Forest biomass is an important feedstock to fulfil the demand of novel biomaterials, biofuels, and biorefinery products, along with the more traditional wood products, pulp and paper, and forest energy [1–3]. The recent industrial policies in Finland and Europe aim towards sustainable circular bioeconomy, including novel technologies and value-added products to forest biomass valorisation that may provide techno-chemical benefits or bioactive functionalities [4–6]. Therefore, the interest in biomass chemistry has been rising among the research and development societies of academia, research institutes, and industries.
Wood-based raw materials are composed of three main structural, high-molecular-weight biopolymers (cellulose, hemicelluloses, lignin), other polymeric components (pectins, starch, proteins), and numerous low-molecular-weight non-structural components [3,7]. The latter group consists of organic extractives and some water soluble organic and inorganic compounds [8–12]. Wood extractives can be classified into phenolic, aliphatic and other compounds (see Table 1). Their composition varies between tree species, tree individuals and tree parts (stem, root, branches), and wood type (sapwood or heartwood) as well as growth conditions and genetic background [3,8–13]. Few differences in the chemical composition of the three major cell wall components (cellulose, hemicelluloses, lignin) have been stated between tree species; on the other hand, there is a large diversity in extractive composition throughout the species [8–11].

Table 1. Classification of organic extractives in wood [3].

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

While Scots pine (Pinus sylvestris L.) is the most abundant tree species in Finland, particularly in northern and central regions, the interest in its chemical potential for novel materials and products is evident. Of the main species in Finland, extractive content of Scots pine is generally the highest, and there is a long history of the industrial utilization of its extractives for many products, such as pine tar, tall oil, and turpentine [1,2,14]. According to different reviews, the total extractive percentage in Scots pine biomass is typically as follows: stemwood, 3 to 5%; stump, 19%; roots, 13%; bark, 25%; branches, 17%; and needles, 40% [14–16]. Across the world, there are softwood species with both much higher and lower extractive contents than Scots pine [8,14,17,18].

Wood biopolymers and extractives have different roles to play in the secondary xylem formation, structural stability, energy reserve and resistance towards biological attacks and thermal degradation [8,12,14]. Many extractive compounds are intermediates in tree metabolism. Different extractive types perform a wide range of physical and mechanical properties, as well as odour and colour [7,8]. Extractives provide advantages to standing trees by defending them from various biological and physical attacks and stresses through their partly protective and toxic nature [8,14,19–22]. While in pulping processes extractives bring several disadvantages, such as increasing specific energy consumption and lowering pulp yield, the presence of extractives in its heartwood significantly improves the durability of Scots pine wood against fungal degradation, weathering, and moisture absorption [8,14,23].

In the past, targeting for the extractive parts of wood raw materials was questioned for economic reasons, mostly due to their low and irregular concentrations, uncertain sourcing, and lack of technology and proofs-of-concept [24]. Later, it was understood that true value can be gained in the biorefining of wood biomass with more focus on extractives [2,25]. Accordingly, several applications were suggested during the 2000s: biocides, insect repellents, pharmaceuticals, nutraceuticals, antioxidants, antimicrobials, cosmetic ingredients, detergents, anti-humectants, preservation agents of foods and chemicals, wood surface protectants, impregnation agents, adhesives and binders, miscellaneous industrial chemicals, and advanced fuels (liquid, gaseous) [2,26].

It has remained a question both among practitioners and researchers how to efficiently find the sources of the interesting wood extractives. The climatic region/geographical location has been demonstrated as one important factor for the variation in wood chemical
components, along with the soil properties, tree stand conditions, and characteristics of individual trees that affect several growth factors of trees and the properties of their wood [12,14,27–29]. Forest regeneration and management have a strong influence on the growth and wood properties as well [3,8,14]. According to the available literature, the total extractive contents of softwood species tend to increase toward the north in Northern Europe [27–29] and Canada [17]. However, the actual effects of temperature, light, and precipitation during the growth period on the extractives are not clear.

The data on other plant species also indicate benefits for northern locations, as regards the biosynthesis of some secondary metabolites (extractives); long days and low night temperatures were observed to add to the plant flavonoid production in Northern Finland and Norway [30]. Soluble phenolic and terpenoid content in juniper (Juniperus communis) needles increased with latitude in Finland [31]. Quercetin derivatives in white birch (Betula pubescens) leaves increased with growing latitude in Finland; on the other hand, apigenin and naringenin derivatives decreased and total flavonoid levels remained constant [32].

Biotic and abiotic stress factors may also affect the contents of phenolic compounds, often being induced in response to wounding, pathogen infection, frostbiting or chilling, ozone exposure, or nutrient deficiency [33]. Stilbenes that are biosynthesized during transition from sapwood to heartwood [34] have a role in defense mechanisms against harmful fungi in Scots pine [35,36]. Within the plant environment, different microorganisms coexist that can establish various interactions with the host plant; they are often the basis for the synthesis of specific phenolic extractives in response to these interactions [37].

In the procurement of raw materials, interesting extractive compounds may be obtained from certain parts of the tree biomass, or from by-products or residues of forest industries [17,38]. In principle, sourcing of the desired compounds can be performed most accurately in the forest; there, the most interesting stands, trees, or locations can be identified and truly fresh wood can be attained. This is possible if there is enough information available about the occurrence and concentration of extractives that can be found in different components of the tree biomass. However, low volumes and yields of extractives from stands can be a drawback. Instead, wood raw material is readily available in large volumes at sawmills and other wood product industries where mechanical fractionation and sorting of the materials to increase the yield of extractives is technically most feasible. In wood processing, the raw material is most often a mixture from different sources; this hampers the identification of side streams rich in the desired extractives.

The objective of this study was to map the general occurrence of extractive compounds and systematically examine the composition, concentration, and variation of the phenolic and resin acid extractives in Scots pine wood and sawmill residues (sawdust, chips) from four climatic regions of Finland. The differences between final felling and thinning stands, forest site types, and heartwood and sapwood were considered as well. The purpose was to identify and quantify the before-mentioned extractives in the raw materials to evaluate the most optimal sources for bio-based chemical biorefining and bioenergy products.

2. Materials and Methods

The experimental design consisted of four geographical regions in Finland that cover the full range of variation in latitude, effective thermal sum, and annual precipitation in the country (Table 2). The areas were named Lapland North (LN), Lapland South (LS), Middle Finland (MF) and South Finland (SF). Each area had eight forest plots (with the exception of Middle Finland, with four plots). One half of the plots in each region was in the mature development stage (final felling stands), and another half in the productive stage (thinning stands), as classified in the regional forest management instructions in Finland [39]. Tree stocks in all plots were of natural origin. Forest site types (fertility levels) of the study stands were typical for Scots pine in each region, covering poor sites (Calluna type, CT), less-fertile sites (Vaccinium type, VT), medium-fertile sites (Myrtillus type, MT) and fertile sites (Oxalis-Myrtillus type, OMT) [40].
In each plot, five study trees were selected and cut for the study between February and March 2014. The aim was to catch each sample during its dormancy period to provide a uniform physiological stage for all sample trees. For the trees representing the final felling stage, the age criterion was ca. 90 years or older in Lapland and ca. 70 years or older in Middle and South Finland, respectively. For the trees in the thinning stage, the age was aimed at ca. 30 to 80 years in Lapland and ca. 20 to 60 years in Middle and South Finland, respectively. In each stand, the sample trees were selected to cover the full diameter range of saw log-sized trees that provided conventional and/or small-diameter logs (diameter at breast height, \(d_{1.3} \geq 14\) cm).

After felling the sample trees, butt logs of 1.5 m in length were cross-cut from each sample tree. Disc samples of three centimetres in thickness were cut from the top part of each log, and stored in a freezer in \(-20\) °C. Key physical characteristics of the stemwood materials were measured from the disc samples—growth rate and latewood proportion, heartwood proportion, moisture content, and basic density. Basic statistics on the tree and wood properties of the sample trees are shown by region and development stage in Table 3.

Four sample blocks (6 cm\(^3\)) were cut from each wood disc, two of them from sapwood close to the surface and two from the heartwood. Two replicate pieces were taken from opposite sides of the disc. From the discs of early-thinning trees, only sapwood samples were taken, because of the narrow heartwood area in the core. The wood samples were air-dried at standard room temperature (20 °C) with a relative humidity of approximately 40%. Dried wood was milled into fine powder using an IKA A11 and an IKA A10 Basic Analytical Grinder equipped with a water cooling system.

Sawmill residues were sampled from similar regions as the sample trees in collaboration with three sawmills (see Table 2). Sawdust samples of ca. 10 L and sawmill chip samples of ca. 50 L were taken from the flow of wood residues after primary sawing of fresh logs from 11 final felling stands, their origin being individually identified and location, forest site type, and tree age recorded before cutting. Each sample was packed in an airtight plastic bag and stored in a freezer at \(-20\) °C. Sawdust samples were used in this study, and sawmill chip samples used in further studies. Drying and milling of sawdust were performed with a similar protocol to the wood disc samples. Descriptive data on the sources of sawmill residue samples are listed in Table 4.
| Variable                        | Stand Type and Region | N  | Mean   | Minimum | Maximum | Std. Deviation |
|--------------------------------|-----------------------|----|--------|---------|---------|----------------|
| Age (y)                        | Final felling LN      | 20 | 100.0  | 77      | 141     | 23.1           |
|                                | Final felling LS      | 20 | 100.7  | 71      | 155     | 31.9           |
|                                | Final felling MF      | 10 | 80.9   | 54      | 123     | 21.5           |
|                                | Final felling SF      | 20 | 83.6   | 51      | 116     | 16.7           |
|                                | Thinning LN           | 20 | 64.2   | 28      | 93      | 23.7           |
|                                | Thinning LS           | 20 | 52.6   | 36      | 71      | 12.3           |
|                                | Thinning MF           | 10 | 29.4   | 26      | 32      | 1.8            |
|                                | Thinning SF           | 20 | 36.8   | 20      | 76      | 18.2           |
| Height (m)                     | Final felling LN      | 20 | 16.7   | 11.9    | 20.5    | 2.5            |
|                                | Final felling LS      | 20 | 17.6   | 14.5    | 21.6    | 2.2            |
|                                | Final felling MF      | 10 | 22.1   | 18.7    | 25.2    | 2.0            |
|                                | Final felling SF      | 20 | 22.1   | 16.8    | 29.2    | 4.2            |
|                                | Thinning LN           | 20 | 10.6   | 8.4     | 12.8    | 1.2            |
|                                | Thinning LS           | 20 | 11.1   | 8.8     | 12.6    | 1.0            |
|                                | Thinning MF           | 10 | 11.6   | 9.3     | 13.4    | 1.5            |
|                                | Thinning SF           | 20 | 13.2   | 9.7     | 20.2    | 3.0            |
| Diameter at breast height, d_{1.3} (mm) | Final felling LN      | 20 | 228.9  | 212     | 254     | 11.9           |
|                                | Final felling LS      | 20 | 227.1  | 210     | 258     | 14.4           |
|                                | Final felling MF      | 10 | 265.9  | 204     | 336     | 41.8           |
|                                | Final felling SF      | 20 | 242.5  | 181     | 356     | 47.0           |
|                                | Thinning LN           | 10 | 130.8  | 94      | 139     | 11.4           |
|                                | Thinning LS           | 20 | 113.9  | 91      | 140     | 12.9           |
|                                | Thinning MF           | 10 | 129.4  | 96      | 168     | 24.7           |
| Basic density (g cm\(^{-3}\)) | Final felling LN      | 20 | 400.3  | 345.8   | 460.3   | 30.8           |
|                                | Final felling LS      | 20 | 410.0  | 365.3   | 482.3   | 31.9           |
|                                | Final felling MF      | 10 | 441.2  | 401.0   | 489.8   | 36.2           |
|                                | Final felling SF      | 20 | 449.7  | 398.5   | 514.8   | 31.9           |
|                                | Thinning LN           | 10 | 411.1  | 342.4   | 548.9   | 53.8           |
|                                | Thinning LS           | 20 | 386.6  | 337.5   | 443.5   | 26.5           |
|                                | Thinning MF           | 10 | 373.6  | 354.0   | 436.1   | 24.3           |
|                                | Thinning SF           | 20 | 383.2  | 303.8   | 494.3   | 52.0           |
| Moisture content (%)           | Final felling LN      | 20 | 80.2   | 64.8    | 103.5   | 12.9           |
|                                | Final felling LS      | 20 | 78.9   | 58.6    | 107.2   | 11.4           |
|                                | Final felling MF      | 10 | 76.5   | 44.3    | 104.0   | 16.8           |
|                                | Final felling SF      | 20 | 65.0   | 49.1    | 89.4    | 9.4            |
|                                | Thinning LN           | 20 | 118.0  | 78.2    | 164.9   | 22.9           |
|                                | Thinning LS           | 20 | 129.6  | 98.1    | 165.4   | 18.0           |
|                                | Thinning MF           | 10 | 139.5  | 106.6   | 156.4   | 17.4           |
|                                | Thinning SF           | 20 | 116.2  | 73.1    | 174.8   | 29.3           |
| Heartwood proportion (%)       | Final felling LN      | 20 | 30.8   | 9.2     | 44.9    | 10.0           |
|                                | Final felling LS      | 20 | 30.7   | 14.2    | 53.3    | 10.8           |
|                                | Final felling MF      | 10 | 26.7   | 10.2    | 26.7    | 17.4           |
|                                | Final felling SF      | 20 | 34.0   | 20.2    | 58.1    | 10.0           |
|                                | Thinning LN           | 20 | 11.7   | 4.2     | 27.1    | 6.5            |
|                                | Thinning LS           | 20 | 10.3   | 2.8     | 20.1    | 5.1            |
|                                | Thinning MF           | 10 | 10.3   | 5.4     | 19.0    | 4.6            |
|                                | Thinning SF           | 20 | 17.7   | 5.1     | 40.6    | 9.0            |
| Ring width (mm)                | Final felling LN      | 20 | 1.37   | 0.99    | 1.70    | 0.17           |
|                                | Final felling LS      | 20 | 1.34   | 0.70    | 1.74    | 0.36           |
|                                | Final felling MF      | 10 | 1.90   | 1.27    | 2.60    | 0.53           |
|                                | Final felling SF      | 20 | 1.51   | 0.90    | 2.33    | 0.48           |
|                                | Thinning LN           | 20 | 1.61   | 0.65    | 3.31    | 0.90           |
|                                | Thinning LS           | 20 | 1.67   | 0.94    | 2.40    | 0.56           |
|                                | Thinning MF           | 10 | 2.70   | 1.86    | 4.04    | 0.66           |
|                                | Thinning SF           | 20 | 2.70   | 1.07    | 4.26    | 1.06           |
| Latewood proportion (%)        | Final felling LN      | 20 | 30.1   | 21.8    | 37.6    | 4.6            |
|                                | Final felling LS      | 20 | 32.9   | 23.0    | 39.4    | 3.9            |
|                                | Final felling MF      | 10 | 32.8   | 26.5    | 37.4    | 3.6            |
|                                | Final felling SF      | 20 | 34.0   | 27.3    | 41.5    | 4.2            |
|                                | Thinning LN           | 20 | 29.6   | 23.7    | 38.2    | 3.8            |
|                                | Thinning LS           | 20 | 31.3   | 26.4    | 40.7    | 3.2            |
|                                | Thinning MF           | 10 | 37.4   | 32.4    | 42.0    | 3.2            |
|                                | Thinning SF           | 20 | 32.6   | 26.0    | 41.4    | 4.5            |
Table 4. Geographic origin and stand properties of logs for the sawmill residue samples by study region (LN = Lapland North, LS = Lapland South, MF = Middle Finland, SF = South Finland).

| Sawmill Region | Location | Forest Site Type | Tree Age, Years |
|----------------|----------|------------------|-----------------|
| Jutos Timber AB, | Norrbotten, Puljukka | VT | 124 |
| Pajala (Sweden) | Norrbotten, Lumipalo | VT | 109 |
| | Norrbotten, Kursunkangas | CT | 130 |
| Veljekset Vaara Oy | Simo, Yli-Kärppä | VT | 90 |
| Tervola (Finland) | Rovaniemi, Marivaara | VT | 126 |
| | Sodankylä, Päivivaara | VT | 196 |
| | Pello, Martinjärvi | MT | 104 |
| Lopen Rakennuspuu Oy | Pälkäne, Rautajärvi | MT | 150 |
| Loppi (Finland) | Pälkäne, Rautajärvi | MT | 120 |
| | Urjala, Nenosenkylä | OMT | 110 |
| | Mäntsälä | VT | 120 |

Laboratory experiments included two different analyses. For the first, NMR analysis was performed to show the general profile and relative concentrations of extractive compounds. The analysis covered all sample trees from final felling stands as well as sawmill residue samples of the four regions. Sample trees from thinning stands with no or little heartwood were excluded. In total, the NMR sample set comprised 140 samples from sample trees (duplicates included) and 11 samples from sawmill residues.

NMR spectra were measured using a 600 MHz Bruker NMR spectrometer, equipped with a cryoprobe (Bruker Prodigy TCI 600 S3 H&F-C/N-D-05 Z) and an automatic cooled SampleJet sample changer. Prior to the NMR measurements, 20 µL of sample liquid was transferred to a 5 mm NMR tube followed by the addition of CD$_3$OD (480 µL) and 3-(trimethylsilyl)-propionic-d$_4$ acid (25 µL, 20 mM) in CD$_3$OD as an internal standard of known concentration. The compounds were identified from routine two-dimensional proton-proton and proton-carbon correlated spectra. $^1$H NMR spectra were collected using “zg” automation program using the following parameters: 30° pulse angle, total relaxation delay 7 s, and four scans at 300 K.

For the second, extraction of phenolic compounds was done on the full set of samples using the ball mill extraction method, according to the procedure of Nybakken et al. [41]. Milled wood (30 mg) in a 2 mL vial was homogenized for 25 s in 100% ice-cold methanol (800 µL) with a Precellys 24 homogenizer. Homogenization was followed by 15 min incubation in an ice bath at 4 °C. The samples were re-homogenized for 30 s, centrifuged (Eppendorf® centrifuge 5415 R, Eppendorf, Hamburg, Germany) for 3 min at 13,000 rpm, and the supernatant separated into a 6 mL glass tube. The residue was re-homogenized three times, each with 600 µL methanol and 5 min of ice bath incubation. The combined supernatants were evaporated to dryness in a vacuum centrifuge (Eppendorf® 270 concentrator, Eppendorf, Hamburg, Germany). The dried extracts were stored at −18 °C in a freezer.

High Performance Liquid Chromatography (HPLC, 1100 series; Agilent USA) was used to analyse the phenolic compounds. Extracts were dissolved in 0.25 mL 100% methanol and diluted by adding 0.25 mL milli-Q water to bring the total volume to 0.5 mL. The injection volume was 30 µL. Phenolic extractives were separated using a Zorbax SBC18 (4.6 mm × 60 mm) HPLC column (AgilentTechnologies, Waldbronn, Germany) [41]. The phenolic compounds were identified by comparing their retention times and UV spectrum with those of references. The phenolic compounds were quantified at 220 nm against standards. Pinosylvin, pinosylvin monomethyl ether, pinosylvin glycoside, pinosylvin monomethyl ether glycoside, and piceatannol were quantified with the reference coefficient and responses factor of piceatannol [41]. Lignans and neolignans were quantified against salicin and vanillic acid against vanillic acid, and eriodictyol against eriodictyol, respectively.
Statistical analysis of the data was performed using the IBM SPSS Statistics program, Version 25 (2017). Significance levels of $\alpha = 0.01$ (**) and $\alpha = 0.05$ (*) were used in all statistical tests. Multivariate factor analysis and principal component analysis were used to identify the common dimensions of the pattern and structure of the occurrence of phenolic compounds in stemwood samples. Linear relationships between the studied variables were analysed with Pearson’s correlation coefficients. Based on significant and strong correlations, the relationships between the variables were modelled using multiple linear regression models. Extractives in sawdust samples were analysed using descriptive statistics only, because few variables could be obtained on the origin and properties of saw logs. Finally, results on the concentration of phenolic and resin acid compounds of Scots pine heartwood that were obtained with the NMR and HPLC methods were benchmarked using comparison with a correlation analysis to ensure consistency.

3. Results

3.1. Profile of Extractive Compounds

In general, $^1$H NMR spectroscopy is an easy and excellent method to evaluate simultaneously different types of organic compounds, functional groups present in compounds, and roughly the amount of these compounds in the measured samples, if concentrations of compounds are at least on mM level. Exact quantification of individual compounds is possible if at least one $^1$H NMR signal from each studied molecule can integrate without overlapping other signals. Moreover, NMR is an excellent tool to compare alterations between different wood samples, like compounds present in heartwood and sapwood.

In this study, $^1$H NMR spectra were measured from 140 stemwood samples and 11 sawmill residue samples. In Figure 1, selected $^1$H NMR spectra of the extracted samples from the opposite latitude regions of Finland, Lapland North (LN) and South Finland (SF) are presented, with a comparison of compounds present in heartwood, sapwood, and sawdust. The graph also includes approximate chemical shift values (ppm scale) for each functional group. The major differences were observed between heartwood (e.g., violet spectrum) and sapwood (e.g., green spectrum). Aromatic and phenolic compounds (red rectangle) were almost absent in sapwood, whilst in heartwood the height of these signals was comparable to other major signals observed at the hydrocarbon region. Based on the reference compounds and two dimensional $^1$H-$^1$H and $^1$H-$^{13}$C correlated NMR measurements, these compounds were identified as dehydroabietic acid (DAA), pinosylvin, and its derivative monomethyl ether (signal in light blue rectangle belongs to Ar-OCH$_3$ group). In sapwood, DAA was the only aromatic compound visible in the spectrum, though it was also present in heartwood. Another clearly visible dissimilarity between heartwood and sapwood was observed in the amounts of other resin acids (abietic, pimaric, and isopimaric acids). These compounds were identified based on double-bond signals at ca. 5.5 ppm; more easily, the presence of these compounds was identified based on sharp singlets in the region of 1.25 ppm to 0.75 ppm, characteristic for isolated methyl signals. In the sapwood, these methyl singlets were hardly visible, but in heartwood, these signals could be rather intensive.

The only major difference was found in the amounts of extractable compounds between Lapland North and South Finland samples, being ca. three-fold in the South Finland region. In sawdust, the composition of these compounds was roughly an average of weights of heartwood and sapwood. The other compounds that were easily identified and quantified from the spectra were resin acids, abietic, pimaric, and isopimaric acids, as shown in Section 3.2.1. Note that these resin acids had signals both on alkene and hydrocarbon regions.

NMR profiles of the extractive compounds from the four regions are shown and discussed in more details in Appendix A. In each region, stemwood from one sample tree from an old forest stand (final felling) and a middle-aged forest stand (thinning), and sawdust from the typical origin of saw logs were included in the presentation to exhibit the range of variation in the occurrence and concentration of the compounds.
Figure 1. Typical $^1$H NMR spectra of wood extractives and other chemical compounds in wood samples and sawmill residues (sawdust). The examples represent the range of variation in the growth attributes (region, tree age, forest site type) and the differences between heartwood and sapwood that were observed to mainly affect the concentration of extractive compounds.

3.2. Phenolic and Resin Acid Compounds

3.2.1. Stemwood

Of the extractive compounds, only pinosylvin (PS), pinosylvin monomethyl ether (PSMME), and vanillic acid were detected in the wood from thinning and in the sapwood from final felling (Table 5). Additionally, the concentrations of these compounds, except for vanillic acid, were much lower in the wood from thinning and sapwood from final felling than in the heartwood from final felling, and lower in the sapwood from wood from thinning compared to the sapwood from final felling.

In the heartwood the concentrations of PSMME and pinosylvin were more than 2.5 mg/g while the concentrations of the other compounds remained below 1 mg/g, neolignans, lignans and eriodictyol (flavanone) showing up as the most abundant of them. The difference in the concentration of PSMME and pinosylvin between the stand types was significant, the minimum and maximum values being clearly higher in the heartwood from final felling than in the sapwood from final felling or in the wood from thinning.

The concentrations of pinosylvin and PSMME were higher in the sapwood from final felling than in the sapwood from thinning (Table 5). Vanillic acid was the dominant compound in the sapwood first thinning samples, its concentration being even higher than those of pinosylvin and PSMME.

Principal component analysis was used to examine the dimensionality of the concentration of all 12 extractive compounds detected by HPLC in the Scots pine heartwood. The Varimax orthogonal rotation method explained 75.7 percent of the variance of the twelve variables (Table 6). The rotation matrix showed that the compounds were charged to the four main components. The first major component (PC 1) of six compounds alone explained 37.5 percent and the remaining three major components (PC 2–PC 4) explained 38.2 percent of the variance of the concentration. The PC 1 consisted of three lignan compounds (Lignan 2, Neolignan 1, Neolignan 2) and three stilbene compounds (PSMME Glycoside, PSMME, PS Glycoside). All phenolic compounds included in PC 1 were strongly correlated with each other (Table 7). The other three PCs contained compounds from three or more phenolic groups and were thus more heterogeneous than PC 1.
Table 5. Concentrations of phenolic and resin acid compounds in sapwood and heartwood of Scots pine from final felling and thinning stands in all regions (mg/g dry weight).

| Compound         | Stand Type and Wood Type | N  | Mean     | Minimum | Maximum | Std. Deviation |
|------------------|--------------------------|----|----------|---------|---------|----------------|
| Pinosylvin       | Final felling sapwood    | 66 | 0.021    | 0.004   | 0.086   | 0.014          |
|                  | Final felling–heartwood  | 69 | 2.554    | 0.634   | 6.650   | 1.260          |
|                  | Thinning–sapwood         | 69 | 0.005    | 0.001   | 0.026   | 0.005          |
|                  | Total                     | 204| 0.872    | 0.001   | 6.650   | 1.409          |
| PSMME            | Final felling–sapwood    | 66 | 0.026    | 0.006   | 0.120   | 0.023          |
|                  | Final felling–heartwood  | 69 | 4.881    | 1.691   | 11.396  | 2.170          |
|                  | Thinning–sapwood         | 69 | 0.003    | 0.000   | 0.014   | 0.003          |
|                  | Total                     | 204| 1.660    | 0.000   | 11.396  | 2.628          |
| Vanillic acid    | Final felling–sapwood    | 66 | 0.006    | 0.003   | 0.013   | 0.002          |
|                  | Final felling–heartwood  | 69 | 0.007    | 0.003   | 0.013   | 0.003          |
|                  | Thinning–sapwood         | 69 | 0.008    | 0.003   | 0.032   | 0.004          |
|                  | Total                     | 204| 0.007    | 0.003   | 0.032   | 0.003          |
| PS Glycoside     | Final felling–heartwood  | 69 | 0.061    | 0.015   | 0.181   | 0.035          |
| PSMME-Glycoside  | Final felling–heartwood  | 69 | 0.091    | 0.013   | 0.375   | 0.065          |
| Piceatannol      | Final felling–heartwood  | 69 | 0.007    | 0.001   | 0.028   | 0.006          |
| Eriodictyol      | Final felling–heartwood  | 69 | 0.123    | 0.042   | 0.526   | 0.069          |
| Lignan 1         | Final felling–heartwood  | 69 | 0.096    | 0.041   | 0.173   | 0.027          |
| Lignan 2         | Final felling–heartwood  | 69 | 0.077    | 0.018   | 0.344   | 0.050          |
| Lignan 3         | Final felling–heartwood  | 69 | 0.073    | 0.028   | 0.165   | 0.029          |
| Neolignan 1      | Final felling–heartwood  | 69 | 0.303    | 0.058   | 1.398   | 0.206          |
| Neolignan 2      | Final felling–heartwood  | 69 | 0.166    | 0.008   | 0.920   | 0.177          |

Table 6. Factor loadings of the principal component analysis for grouping phenolic and resin acid compounds in heartwood of Scots pine from final felling in all regions. Results of the correlation matrix are shown as subscript capital letters.

| Total Variance Explained | PC I | PC II | PC III | PC IV |
|--------------------------|------|-------|--------|-------|
| Initial Eigenvalue       | 4.51 | 2.10  | 1.41   | 1.07  |
| % of variance            | 37.55| 17.47 | 11.73  | 8.91  |
| Rotation SSL             | 3.54 | 2.31  | 1.87   | 1.36  |
| % of variance SSL        | 29.48| 19.28 | 15.60  | 11.30 |

Rotated component matrix

|                | Lignan 2 | Neolignan 1 | PSMME Glycoside | Neolignan 2 | PSMME | Vanillic acid | Pinosylvin | Lignan 1 | Piceatannol | PS Glycoside | Eriodictyol | Neolignan 3 |
|----------------|----------|-------------|-----------------|-------------|-------|--------------|------------|----------|-------------|--------------|-------------|-------------|
| Lignan 2       | 0.902    | -           | -               | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| Neolignan 1    | 0.875    | -           | -               | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| PSMME Glycoside| 0.749    | 0.316       | 0.357           | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| Neolignan 2    | 0.729    | -           | -               | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| PSMME          | 0.682    | 0.572       | -               | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| Vanillic acid  | -        | -0.821      | -               | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| Pinosylvin     | -        | 0.696       | -               | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| Lignan 1       | -        | -0.686      | -               | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| Piceatannol    | -        | -           | 0.868           | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| PS Glycoside   | 0.409    | -           | 0.822           | -           | -     | -            | -          | -        | -           | -            | -           | -           |
| Eriodictyol    | -        | -           | -               | 0.873       | -     | -            | -          | -        | -           | -            | -           | -           |
| Neolignan 3    | -        | -0.340      | 0.466           | 0.589       | -     | -            | -          | -        | -           | -            | -           | -           |

Initial Eigenvalues (>1) and rotation sums of squared loadings SSL (after rotation) are listed, additionally the % of variance explained by the PCs are given. Only variable loadings >0.3 are listed to highlight the patterns revealed.
Table 7. Pearson’s correlation coefficients between the phenolic and resin acid compounds detected by HPLC in Scots pine heartwood.

|                | Pinosylvin | PSMME | Vanillic_Acid | Psglycoside | PSMMEgly | Piceatannol | Eriodictyol | Lignan 1 | Lignan 2 | Lignan 3 | Neolignan 1 |
|----------------|------------|-------|---------------|-------------|----------|-------------|-------------|----------|----------|----------|-------------|
| PSMME glycoside | 0.689 **   |       |               |             |          |              |             |          |          |          |             |
| Vanillic acid   | −0.456 **  | −0.504** |               |             |          |              |             |          |          |          |             |
| Psglycoside     | 0.342 **   | 0.527** | −0.338 **     |             |          |              |             |          |          |          |             |
| PSMME gly        | 0.323 **   | 0.707** | −0.391 **     | 0.719 **    |          |              |             |          |          |          |             |
| Piceatannol     | 0.254      | 0.130 | −0.171        | 0.622 **    | 0.148    |              |             |          |          |          |             |
| Eriodictyol     | 0.267      | 0.389** | −0.059        | 0.154       | 0.249*   | −0.063       |             |          |          |          |             |
| Lignan 1        | −0.288*    | −0.184| 0.392**       | −0.131      | −0.140   | −0.078       | −0.071      |          |          |          |             |
| Lignan 2        | 0.170      | 0.518** | 0.028         | 0.328**     | 0.550    | −0.082       | 0.152       | 0.221    |          |          |             |
| Lignan 3        | 0.032      | 0.232 | 0.212         | 0.486**     | 0.377**  | 0.108        | 0.263*      | 0.125    | 0.263*   |          |             |
| Neolignan 1     | 0.218      | 0.541** | −0.053        | 0.333**     | 0.536**  | −0.072       | 0.076       | 0.150    | 0.678**  | 0.289**   |             |
| Neolignan 2     | 0.161      | 0.607** | −0.209        | 0.412**     | 0.725**  | −0.021       | 0.165       | 0.068    | 0.482**  | 0.309**   | 0.422**    |

$\alpha = 0.01$ (**) and $\alpha = 0.05$ (*).

Figure 2 visualizes the multiple correlations between specific extractive compounds by factor loadings of PC 1 and PC 2. The compounds that composed PC 1 were highly correlated with each other. In addition, they were grouped together with PC 2 by PSMME, PSMME Glycoside and PS Glycoside. Vanillic acid located in the negative side in relation to factor loading PC 1 showed a significant negative correlation with stilbenes (Table 7).

Detailed information on the concentration of each extractive compound by region is provided in Appendix B. No general statistically significant effect of the location to explain the variation in the concentrations in the north–south axis was observed by simple general linear models. For most compounds, however, the highest mean and maximum concentrations were observed in the regions of Lapland, which indicated eventual effects of latitude. On the other hand, different groups of compounds differed from each other in such a way that the highest concentrations of pinosylvins were generally observed in southern Finland and the highest concentrations of lignans and neolignans in Lapland. In order to statistically validate this finding further, the effects of the geographical location were investigated by calculating the regional averages of the factor loadings given by the factor analysis (Figure 3). Indeed, in this analysis the locations in Lapland were distinguished into their own group and the locations in Middle and Southern Finland into their own. The result indicated that the concentrations of compounds charged with PC 1 are higher in Lapland (e.g., lignan 2, neolignan 1, PSMME glycoside) and those charged with PC 2 are higher in South Finland (e.g., vanillic acid, pinosylvin, PSMME).
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Figure 3. Factor loadings generated by factor analysis for different geographical locations.

In the sapwood, the age of the wood at the sampling height, d1.3, tree length, and heartwood proportion showed significant positive correlations (p < 0.01) with the concentration of pinosylvin and PSMME, but negative correlations with the concentration of vanillic acid (Table 8). In addition, a negative correlation was found between the latewood proportion and the concentration of vanillic acid.

Table 8. Relationships between the concentrations of phenolic and resin acid compounds and physical properties of wood in Scots pine sapwood by stand type.

| Compound | Stand Type | Disc Age 1 | d1.3 | Tree Length | Ring Width | Density | Heartwood Proportion | Latewood Proportion |
|----------|------------|------------|------|-------------|------------|---------|---------------------|---------------------|
| Pinosylvin | Final felling N = 66 | 0.344 ** | −0.016 | −0.120 | −0.264 * | −0.188 | 0.332 ** | −0.113 |
|          | Thinning N = 69 | −0.355 ** | 0.170 | −0.119 | 0.426 ** | −0.462 ** | −0.223 | −0.187 |
|          | Total N = 135 | 0.599 ** | 0.576 ** | 0.434 ** | 0.210 * | 0.056 | 0.559 ** | −0.076 |
| PSMME    | Final felling N = 66 | 0.284 * | 0.023 | −0.064 | −0.192 | −0.111 | 0.342 ** | 0.080 |
|          | Thinning N = 69 | −0.188 | 0.047 | −0.163 | 0.215 | −0.288 * | −0.203 | −0.280 * |
|          | Total N = 135 | 0.566 ** | 0.524 ** | 0.412 ** | −0.248 ** | 0.127 | 0.553 ** | 0.037 |
| Vanillic acid | Final felling N = 66 | 0.072 | −0.186 | −0.545 ** | −0.171 | −0.387 ** | 0.124 | −0.310 * |
|          | Thinning N = 69 | 0.059 | −0.145 | −0.155 | −0.163 | 0.201 | −0.118 | −0.199 |
|          | Total N = 135 | −0.175 * | −0.303 ** | −0.392 ** | −0.050 | −0.083 | −0.195 * | −0.230 ** |

1 Disc age = age of wood at the sampling height in a tree. α = 0.01 (**) and α = 0.05 (*).

In the heartwood of final felling trees, pinosylvin correlated positively with d1.3, tree length, and latewood proportion and PSMME with the age of wood at the sampling height (Table 9). The age showed a positive correlation with PS Glycoside, PSMME glycoside and neolignan 2. The heartwood proportion showed a negative correlation with SMME glycoside and neolignan 2.

Multiple linear regression was used to analyse the effects of physical properties of trees and wood on the concentration of extractive compounds in the Scots pine heartwood and sapwood. The physical variables which gave the highest correlations with the compounds
in correlation analysis were selected as independent variables of the analysis. The age of wood at the sampling height explained most of the variation in the concentration of the compounds in the heartwood (Table 10). Increase in the age had a positive effect on the concentration of stilbenes (pinoresinol, PSME, PS Glycoside, PSMME Glycoside), neolignan 2 and abietic acid, and a negative effect on the concentration of vanillic acid and lignan 1. Tree ring width increased the concentration of acids detected by NMR. In addition, the increase in the heartwood proportion and effective thermal sum (d.d) were found to increase the concentration of lignan 1 and neolignan 2, respectively.

Table 9. Relationships between the concentrations of phenolic and resin acid compounds and physical properties of wood in Scots pine heartwood in final felling stands, N = 70.

| Compound          | Disc Age | dL3     | Tree Length | Ring Width | Density | Heartwood Proportion | Latewood Proportion |
|-------------------|-----------|---------|-------------|------------|---------|----------------------|---------------------|
| Pinosylvin        | 0.214     | 0.380 **| 0.431 **    | 0.074      | 0.308 * | 0.198                | 0.415 **            |
| PSME              | 0.504 **  | 0.169   | 0.143       | −0.294 *   | 0.224   | 0.158                | 0.227               |
| Vanillic acid     | −0.187    | −0.394 **| −0.426 **   | −0.083     | −0.430 **| 0.109                | −0.404 **           |
| PS Glycoside      | 0.339 **  | 0.096   | 0.176       | −0.158     | 0.237   | −0.036               | 0.205               |
| PSMME Glycoside   | 0.574 **  | 0.014   | 0.073       | −0.421 **  | 0.189   | 0.080                | 0.017 **            |
| Piceatannol       | 0.063     | 0.193   | 0.275 *     | 0.047      | 0.196   | 0.008                | 0.128               |
| Eriodictyol       | 0.128     | 0.024   | 0.035 *     | −0.046     | 0.186   | 0.086                | 0.258 *             |
| Lignan 1          | −0.077    | −0.227  | −0.222      | −0.145     | −0.136  | 0.315 **             | −0.138              |
| Lignan 2          | 0.204     | −0.068  | −0.197      | −0.238 *   | −0.064  | 0.075                | −0.207              |
| Lignan 3          | 0.229     | −0.090  | −0.169      | −0.181     | −0.040  | 0.028                | 0.001               |
| Neolignan 1       | 0.123     | −0.052  | −0.155      | −0.121     | −0.033  | −0.045               | −0.154              |
| Neolignan 2       | 0.702 **  | −0.060  | −0.005      | −0.575 **  | 0.157   | 0.276 *              | 0.048               |

1 Disc age = age of wood at the sampling height in a tree. α = 0.01 (**) and α = 0.05 (*).

Table 10. Standardized coefficients (β) for independent variables and model fit statistics obtained from multiple regression analysis of phenolic and resin acid compound concentrations in Scots pine heartwood and sapwood.

| Dependent Variables | Effective Thermal Sum | Density | Heartwood Proportion | Tree Length | Ring Width | Disc Age 1 | R² | F-Value |
|--------------------|-----------------------|---------|----------------------|-------------|------------|-------------|----|---------|
| HPLC–heartwood     |                       |         |                      |             |            |             |    |         |
| Pinosylvin         | −0.119                | 0.266   | 0.124                | 0.179       | 0.542 *    | 0.516 *     | 0.304 | 4.521 **|
| PSME               | 0.044                 | 0.149   | −0.044               | −0.092      | 0.334      | 0.769 **    | 0.305 | 4.535 **|
| Vanillic acid      | −0.036                | −0.296 *| 0.239 *              | −0.116      | −0.525 *   | −0.639 **   | 0.379 | 6.305 **|
| PS Glycoside       | 0.063                 | 0.114   | −0.220               | 0.002       | 0.281      | 0.636 **    | 0.214 | 2.806 **|
| PSMME Glycoside    | 0.263                 | −0.044  | 0.214                | −0.115      | 0.084      | 0.772 **    | 0.395 | 6.741 **|
| Piceatannol        | −0.062                | 0.088   | −0.057               | 0.253       | 0.088      | 0.116       | 0.087 | 0.988   |
| Eriodictyol        | −0.149                | 0.379 * | 0.131                | −0.195      | 0.352      | 0.277       | 0.093 | 1.058   |
| Lignan 1           | 0.056                 | −0.010  | 0.466 **             | −0.192      | −0.460 *   | −0.611 **   | 0.299 | 4.411 **|
| Lignan 2           | −0.188                | 0.084   | 0.053                | −0.125      | −0.029     | 0.132       | 0.102 | 1.174   |
| Lignan 3           | 0.023                 | 0.052   | −0.028               | −0.291      | 0.223      | 0.428       | 0.101 | 1.156   |
| Neolignan 1        | −0.131                | 0.099   | −0.059               | −0.151      | 0.118      | 0.218       | 0.058 | 0.639   |
| Neolignan 2        | 0.408 **              | −0.080  | −0.028               | −0.293 *    | 0.006      | 0.796 **    | 0.567 | 13.555 **|

| HPLC–sapwood       |                       |         |                      |             |            |             |    |         |
| Pinosylvin         | 0.099                 | −0.243  | 0.197                | −0.137      | 0.081      | 0.406       | 0.153 | 2.954 **|
| PSME               | 0.068                 | −0.092  | 0.274                | −0.177      | 0.169      | 0.346       | 0.091 | 2.084   |
| Vanillic acid      | −0.408 **             | 0.096   | 0.238 **             | −0.428 **   | 0.246      | 0.121       | 0.376 | 7.525 **|

| NMR–heartwood      |                       |         |                      |             |            |             |    |         |
| Dehydroabietic acid| −0.157                | 0.131   | 0.034                | −0.193      | 0.687 **   | 0.365       | 0.142 | 1.739   |
| Abietic acid       | −0.108                | 0.282   | 0.050                | −0.174      | 0.658 **   | 0.645 **    | 0.165 | 2.075   |
| Isopimaric acid    | −0.248                | 0.219   | 0.038                | −0.038      | 0.379      | 0.322       | 0.070 | 0.790   |
| Pinamaric acid     | −0.226                | 0.314   | −0.006               | −0.268      | 0.736 **   | 0.557 *     | 0.158 | 1.964   |
| Levopimaric acid   | −0.226                | 0.350   | −0.127               | −0.253      | 0.771 **   | 0.306       | 0.206 | 2.793 * |
| Pinosylvin         | −0.108                | 0.253   | 0.078                | 0.173       | 0.508 *    | 0.485 *     | 0.265 | 3.783 **|
| PSME               | 0.032                 | 0.140   | −0.082               | −0.084      | 0.317      | 0.752 **    | 0.287 | 4.223 **|

1 Disc age = age of wood at the sampling height in a tree. α = 0.01 (**) and α = 0.05 (*).

In the sapwood, physical properties only explained the variation in the concentration of vanillic acid, which was most affected by the length of the tree, the effective thermal sum, and the heartwood proportion.
3.2.2. Sawmill Residues

In sawmill residues (sawdust), there were some small between-region differences in the concentration of extractive compounds, but no general north–south trend was observed (Table 11). The highest concentrations of pinosylvin and its derivatives were generally found in sawmill residues from South Finland, but lignan concentrations were higher in Lapland than in Middle or South Finland. The mean age of the timber stock in the stands that were the origin for sawmill residues was almost the same in the three regions, 121 to 129 years, but the between-stand variation was very large in Lapland South, 106 years, compared to Lapland North, 21 years, and Middle and South Finland, 40 years (see Table 4). However, the variation in the concentrations of almost all individual compounds was larger in Middle and Southern Finland than in Lapland, indicating that tree age was not the first factor for their concentrations in sawmill residues. Since the residues consisted of both heartwood and sapwood, the mean values were lower than in the heartwood but higher than in the sapwood of the wood collected from standing trees (Table 5).

### Table 11. Concentrations of phenolic and resin acid compounds in the sawmill residues (sawdust) of Scots pine by region (mg/g dry weight).

| Compound         | Region                  | N  | Mean  | Minimum | Maximum | Std. Deviation |
|------------------|-------------------------|----|-------|---------|---------|----------------|
| Pinosylvin       | Lapland North           | 3  | 0.629 | 0.569   | 0.681   | 0.057          |
|                  | Lapland South           | 4  | 0.435 | 0.393   | 0.511   | 0.053          |
|                  | Middle & South Finland  | 4  | 0.767 | 0.594   | 1.082   | 0.188          |
|                  | Total                   | 11 | 0.609 | 0.393   | 1.082   | 0.194          |
| PSMME            | Lapland North           | 3  | 1.167 | 1.267   | 2.027   | 0.381          |
|                  | Lapland South           | 4  | 0.986 | 0.916   | 1.030   | 0.049          |
|                  | Middle & South Finland  | 4  | 1.462 | 1.025   | 2.216   | 0.578          |
|                  | Total                   | 11 | 1.335 | 0.916   | 2.216   | 0.458          |
| Vanillic acid    | Lapland North           | 3  | 0.010 | 0.007   | 0.015   | 0.004          |
|                  | Lapland South           | 4  | 0.011 | 0.008   | 0.016   | 0.004          |
|                  | Middle & South Finland  | 4  | 0.010 | 0.005   | 0.014   | 0.004          |
|                  | Total                   | 11 | 0.010 | 0.005   | 0.016   | 0.003          |
| PS Glycoside     | Lapland North           | 3  | 0.021 | 0.014   | 0.027   | 0.007          |
|                  | Lapland South           | 4  | 0.015 | 0.012   | 0.017   | 0.002          |
|                  | Middle & South Finland  | 4  | 0.021 | 0.016   | 0.032   | 0.006          |
|                  | Total                   | 11 | 0.019 | 0.012   | 0.032   | 0.006          |
| PSMME-Glycoside  | Lapland North           | 3  | 0.048 | 0.027   | 0.065   | 0.020          |
|                  | Lapland South           | 4  | 0.026 | 0.022   | 0.031   | 0.003          |
|                  | Middle & South Finland  | 4  | 0.026 | 0.013   | 0.047   | 0.017          |
|                  | Total                   | 11 | 0.032 | 0.013   | 0.065   | 0.016          |
| Eriodictyol      | Lapland North           | 3  | 0.032 | 0.030   | 0.035   | 0.002          |
|                  | Lapland South           | 4  | 0.034 | 0.024   | 0.050   | 0.011          |
|                  | Middle & South Finland  | 4  | 0.046 | 0.026   | 0.084   | 0.027          |
|                  | Total                   | 11 | 0.038 | 0.024   | 0.084   | 0.017          |
| Lignan 1         | Lapland North           | 3  | 0.013 | 0.011   | 0.015   | 0.002          |
|                  | Lapland South           | 4  | 0.024 | 0.017   | 0.029   | 0.005          |
|                  | Middle & South Finland  | 4  | 0.015 | 0.008   | 0.022   | 0.004          |
|                  | Total                   | 11 | 0.018 | 0.008   | 0.029   | 0.007          |
| Lignan 2         | Lapland North           | 3  | 0.013 | 0.010   | 0.016   | 0.003          |
|                  | Lapland South           | 4  | 0.007 | 0.005   | 0.009   | 0.002          |
|                  | Middle & South Finland  | 4  | 0.007 | 0.005   | 0.009   | 0.002          |
|                  | Total                   | 11 | 0.009 | 0.005   | 0.016   | 0.003          |
3.2.3. Comparison of HPLC and NMR Results

The correlations of the concentrations of phenolic and resin acid compounds in Scots pine heartwood analysed either using NMR or HPLC methods are shown in Table 12. Of the total of 17 compounds, both analytical methods were used for pinosylvin and pinosylvin monomethylether (PSMME) only. Concentrations of these two compounds obtained by different methods had a high and significant correlation with each other. In addition, pinosylvin and PSMME analysed by NMR had a significant correlation with other stilbene compounds (PS Glycoside, PSMME Glycoside) analysed by HPLC. Most of the acids analysed by NMR had a significant correlation with pinosylvin and PSMME analysed by HPLC. However, acids did not correlate with lignans.

| Compound  | Region          | N  | Mean  | Minimum | Maximum | Std. Deviation |
|-----------|-----------------|----|-------|---------|---------|----------------|
| Lignan 3  | Lapland North   | 3  | 0.017 | 0.013   | 0.023   | 0.006          |
|           | Lapland South   | 4  | 0.016 | 0.011   | 0.020   | 0.005          |
|           | Middle & South Finland | 4  | 0.013 | 0.010   | 0.016   | 0.003          |
|           | Total           | 11 | 0.015 | 0.010   | 0.023   | 0.004          |
| Neolignan 1 | Lapland North   | 3  | 0.020 | 0.018   | 0.022   | 0.002          |
|           | Lapland South   | 4  | 0.016 | 0.014   | 0.018   | 0.002          |
|           | Middle & South Finland | 4  | 0.013 | 0.008   | 0.022   | 0.008          |
|           | Total           | 11 | 0.016 | 0.008   | 0.022   | 0.005          |
| Neolignan 2 | Lapland North   | 3  | 0.014 | 0.012   | 0.015   | 0.002          |
|           | Lapland South   | 4  | 0.011 | 0.008   | 0.014   | 0.003          |
|           | Middle & South Finland | 4  | 0.020 | 0.011   | 0.037   | 0.011          |
|           | Total           | 11 | 0.015 | 0.008   | 0.037   | 0.008          |

4. Discussion

The present study evaluated the variations in phenolic and resin acid extractives within Scots pine tree stems and showed some notable differences between the four climatic regions in Finland. According to the available literature, the amount and composition of the extractives can vary significantly between trees of the same species due to genetic factors, growth location, climatic conditions and the rate of tree growth [8,9,12,42–51]. Furthermore, extractive occurrence and specified extractive contents vary between tree age classes/felling types, heartwood/sapwood, forest site types, and between sawmill residues and standing trees.

A total of twelve extractive compounds, stilbenes and their derivatives, lignans and neolignans, hydroxybenzoic acid (vanillic acid), and flavanone (eriodictyol) were quantified in the heartwood of final felling trees in this study. Only three compounds (pinosylvin, pinosylvin monomethylether (PSMME), vanillic acid) were quantified by HPLC in the
Sapwood of final felling trees and in the wood of thinning trees. In addition, five resin acids were detected in all materials by NMR. In the heartwood, pinosylvin (PS) and pinosylvin monomethyl ether (PSMME) occurred in the largest concentrations, the next abundant groups being neolignans, lignans, and eriodictyol (flavanone). Consistently, it has been observed in many previous studies that total resin acid concentrations in Scots pine heartwood are much higher than in the sapwood, up to five-fold, but the composition of resin acids is rather similar [42,49]. In the study conducted by Nisula [42], which considered all pine species, resin acids were the dominant extractives in the heartwood and the average stemwood. Significant amounts of stilbenes and flavonoids were present in the heartwood as well, and similar also in the knotwood. Esterified fatty acids were dominant in the sapwood. There were hardly any lignans in the stemwood.

The regional differences in the concentrations of individual extractives and groups of extractives were generally small between the four regions. For most compounds, however, the highest mean and maximum concentrations were observed in the northern regions. The highest concentrations of lignans and neolignans were observed in Lapland, with concentrations of pinosylvins highest in South Finland. It is also notable that no significant latitudinal effect connected to the effective thermal sum was observed with the main compounds pinosylvin or PSMME.

Although no general statistically significant trend regarding the north–south axis was shown by simple general linear models, multiple factor analysis distinguished the regions to two groups, North Finland vs. South and Middle Finland. The analysis showed that geographical location affects the content of phenolic compounds in wood, but responses between compounds are quite variable at different development stages and in wood sections belonging to either heartwood or sapwood. This means that the compounds studied do not have a uniform trend in relation to geographical location. The results, however, indicated higher concentrations of pinosylvin, PSMME, and vanillic acid in southern regions and those of, e.g., PSMME glycoside, lignan 2, and neolignan 1 in northern regions. In the literature, observations of geographical variation in the content of individual phenolic compounds are minor and they apply to deciduous tree species or flowering plants but show responses to the local light and temperature conditions [30–32,52,53].

Sawmill residues were present in the study as sawdust, which to some extent resembled sawmill chips in chemical composition; however, the volume and dry mass of sawmill chips usually contain less heartwood because they are made from more wood from outer parts of saw logs [3,14]. In sawdust, the composition of extractive compounds was roughly an average of weights of heartwood and sapwood. Pinosylvin and PSMME were as dominant as in heartwood, but the concentrations of neolignans and lignans were very small. Pinosylvin and PSMME occurred generally more in South Finland compared to North Finland. In contrast, lignans had larger concentrations in North Finland compared to Middle or South Finland. The variation for all extractives was also clearly larger in Middle and Southern Finland than in Lapland.

We used several tree growth and wood physical parameters to identify relationships among the contents of phenolic and resin acid compounds. It is known that the contents of pinosylvin, PSMME and resin acids in Scots pine wood are strongly genetically controlled, but their content is affected by differences in the environment, and/or tree and wood age or tree size [13]. The concentration of pinosylvin in the heartwood of Scots pine is usually about one to three percent of the dry mass [35].

In this study, the age of wood at the sampling height explained most of the variation in the proportion of heartwood extractives, of which stilbenes, neolignan 2, and abietic acid increased with the increasing age of wood. The highest pinosylvin content observed in the heartwood of individual trees was ten-fold compared to the lowest observations. The high between-tree variations make it difficult to establish the relationship between extractives, tree growth, and physical properties. Bergstöm et al. [34] found no correlation between pinosylvin content in Scots pine wood and tree age, height, crown width, stem diameter, or climatic conditions. A clear relationship between high pinosylvin and PSMME contents in
the Scots pine heartwood and resistance to wood decay has been shown, however [35,36]. In the study by Hovelstad et al. [28], an 87-year-old Scots pine tree had a higher content of stilbenes and resin acids compared to a 34-year-old tree.

Principal component analysis revealed the highest multiple correlations for pinosylvin and neolignans in the heartwood of final felling trees, which indicates that the presence of these compounds in wood is dependent on the same background factors (see, e.g., [29]). Multiple correlations between lignans and neolignans were low; therefore, they were found on two different principal components, indicating their different synthetization. Vanillic acid, which correlated negatively with the age of wood at the sampling height, also showed high negative correlations with pinosylvin and its derivatives, which might indicate that it is synthesized and stored primarily in the sapwood.

In $^1$H NMR spectroscopy, the identification and comparison of compounds with different types of functional groups from hydrocarbons to aldehydes in the samples was straightforward when the studied spectra were plotted above each other in the same scale-based internal standard. Based on that, heartwood and sapwood extracts were easy to distinguish from each other regarding phenols, pinosylvin and its methyl-ether, since these compounds were present only in heartwood samples. In sapwood, the only aromatic compound was dehydroabietic acid (DAA). There were also clear differences between heartwood and sapwood in other resin acids; they were hardly visible in sapwood, but rather intensive in heartwood. In the case of sawmill residues, $^1$H NMR spectra were located between heartwood and sapwood; however, the spectra of sawmill residues slightly resembled those of heartwood samples.

Our study design provided a systematic approach and full cover to map the occurrence, composition, and relative amounts of extractive compounds in Scots pine trees and sawmill residues in the geographic area between the 60th to 70th degrees of northern latitude, with an altitude of 60 to 320 m, 500 to 650 mm of annual precipitation and, as a result, 550 to 1600 d.d. of effective thermal sum in a boreal climate. Our sampling design was based on pre-determined stratification according to four climatic regions, prevalent stand and soil types, typical stand age classes as well as wood types according to their maturity. The study stands were selected from the long-term research plot network of the Finnish Forest Research Institute which have been managed and monitored for decades. Therefore, the origin and history of the study material was fully known.

Stand and tree age in the study material of standing tree stock was realistic in each region for commercial timber harvesting [39], whereas sawmill residues came from logs from rather old forest stands and slow diameter growth in Southern and Middle Finland. All study stands were naturally born, so the most fast-growing Scots pine tree material with wide growth rings and low wood density that typically occur in planted forests was not present in the data—see also [14,27].

We used well-established analysis methods on extractives with well-controlled storage and preparation of sample materials and credible references of extractives in qualified research laboratories, the findings being based on NMR analysis of all the extractives and HPLC analysis on the phenolics and selected resin acids. The well-balanced and ample data made it possible to apply statistical analysis methods that are rarely used in the research of wood chemistry—multivariate factor-analysis and principal component analysis, multiple linear regression modelling—in addition to descriptive statistics and Pearson’s correlation analysis. It is our understanding that the basis of this study for reliable, valid, and generalizable results on wood extractives, starting from the regions and forests and ending at wood processing, was unique in Northern Europe, and also globally.

In this study, we did not aim to quantify the total extractive contents. However, total quantification is an important issue for the overall approach of wood chemistry from the viewpoint of establishing both useful and harmful components in the raw materials. It is well-known that the results on the quantities of chemical compounds depend on the extraction method [54–56]. In most studies, the individual research teams from different decades have used wood raw materials from different types of forests and different analysis
methods to estimate phenolic and resin acids. This limits the opportunity to compare the results and generalize them to different operating environments.

During the late 1960s, total percentages of wood extractives of 5.0 to 5.7 and 3.0 to 3.2 were reported for Scots pine heartwood and sapwood in Finland, depending on the geographic region, using acetone extraction in the analysis [27]. During the late 2010s, the respective percentages of 2.3 to 8.9 and 0.76 to 3.7 were observed when sequential extraction using an accelerated solvent extractor (ASE) was applied without regional justification, but with a more detailed stratification of the groups of samples than in the study from the 1960s [42]. It was notable in the latter study that the internal knots of the stems contained 0.82 to 30% of the extractives, three-fold compared to the heartwood. Textbooks often present an average total extractive percentage of three to five percent for Scots pine stemwood in Northern Europe [3,7,14], but as high a variation as 1.0 to 6.8 has been shown in different studies [49]. In a European context, the average value of Scots pine is between the values of typical low-extractive species of Norway spruce (1.7) and high-extractive species of Douglas fir (5.3).

Currently known potential applications of individual phenolic compounds of Scots pine wood may be in high value-added bioactive substances replacing synthetic compounds in the food and pharmaceutical industries due to their antioxidant, antimicrobial, anti-inflammatory, and antitumor effects [12,57,58]. Typical applications for resin acids, which make up of 40 to 50% of heartwood extractives and 3 to 4% of sapwood extractives in pine species on average [42], include perfumed compounds for cosmetics, additives for food and beverages, antimicrobial food protection, and biomedical applications [42,59,60]. Stilbenes, lignans, and flavonoids are the other main extractive compounds in Scots pine with known bioactive effects, albeit occurring almost only in the heartwood. Extractives to be applied as effective agents in wood treatment and processing were introduced as well, but they have so far been used only on a limited scale (surface treatment, impregnation, gluing) [2,16]. In a recent study, Scots pine was classified as a moderate species for sourcing resin acids (heartwood), fatty acids (sapwood), stilbenes (especially knotwood, also stemwood), or sterols (stemwood) [42].

In the production of large-volume industrial chemicals and advanced biofuels from the biomass, the wood extractives are usually managed as a whole entity without aiming to individual compounds in the process [2,26]. The main commercial products of pine extractives are tall oil rosins which are the solid form of resin and distilled from the waste liquor recovered from kraft pulping, the total yield typically being 30 to 50 kg/t pulp, but exceeding 50 kg/t pulp in northern Finland [2,42]. The yield is strongly dependent on the heartwood percentage in the raw material, leading to the benefits of Scots pine with slow growth (also compared with faster growing pine species), high tree age and origin from final felling, and drawbacks with low tree age and origin from early thinning or sawmill residues [42]. Tall oil rosin contains 85 to 96% of resin acids, the rest being fatty acids and neutral compounds [61], but only about 20% of tall oil present in pine trees can be recovered in the kraft process [62]. In addition to liquid biofuels, the most important application areas of tall oil resin acids are printing inks, adhesives and sealants, paper size, and emulsifiers and coatings [2,63]. Market trends show decreasing demand in printing and writing paper applications, and increasing demand in adhesives, sealants, and emulsifiers [42,63]. It should be mentioned that industrial pilot scale segregation of individual extractives such as in pyrolysis processes have been attempted during the 2000s, along with bioenergy products as the main target e.g., [2,6,60].

The recovery of phenolic compounds and resin acids from wood materials on an industrial scale is mainly limited by the low economic feasibility and negative ecological impacts of the extraction methods [56,64]. Other limitations include differences in the concentrations and types of individual compounds as well as the strength of the bioactive effects due to the natural variability. In addition, the polarity of the solvent and the extraction method chosen influence the content of the natural antioxidant extracted and the antioxidant activity of the extracts. Studies for alternative extraction techniques and
solvents for obtaining environmentally healthy, sustainable, and viable processes have been done to replace conventional methods [1,2,56,57]. These include ultrasound and microwave-assisted extractions, supercritical fluid extraction, pressurized liquid extraction and ohmic heating extraction.

5. Conclusions

Scots pine, as one of the two main softwood species in Northern Europe, is an important source of raw material for a diversity of products in value-added biorefining and advanced bioenergy generation. The results of this study contribute to evaluating the most optimal sources of extractives of interest, finding the realistic raw material basis for product and technology development, and developing the platform for industrial investments. In addition, the results reveal the relative significance of different tree, stand and regional-level factors affecting the availability of the extractives analysed.

Pinosylvin (PS) and pinosylvin monomethyl ether (PSMME), present in the largest concentrations in heartwood, exhibited at least a moderate potential for utilization, the next abundant groups being neolignans, lignans, and eriodictyol (flavanone). Sapwood did not show very promising concentrations of any of the extractives analysed. Sawdust as a mixture of heartwood and sapwood seemed, however, to more closely resemble heartwood. Sawmill chips could be considered to be closer to sapwood. PSMME and pinosylvin were more abundant and their variation was higher in the heartwood from final felling than in the sapwood from final felling or thinning wood.

Regional differences in the concentration were smaller than what we expected, but still notable for some extractives. The results indicated higher concentrations of pinosylvin, PSMME, and vanillic acid in southern regions and those of, for example, PSMME glycoside, lignan 2, and neolignan 1 in northern regions. This did not show up directly due to the climate (effective thermal sum), but the regional differences in tree age and heartwood proportion had a significant effect in the background.

The focus on strategic planning and practical operations should involve collecting volumes and/or identifying individual interesting fractions of extractives for biorefining. The wood raw material rich in heartwood should be targeted to maximize the recovery of extractives from Scots pine. Raw material sourcing in connection to roundwood harvesting may be operationalized in final felling forests if the wood is sorted according to heartwood proportion; then, stems with inferior quality for saw logs and large pulpwood could be preferred. Wood raw material readily available at saw mills could be used as well, if the lower concentrations of extractives in wood residues can be accepted, and if material sorting can be applied to increase the yield of the extractives. It is utterly important to keep the freshness of the raw material to maximize the quantity and maintain the quality of the extractives, because they tend to reduce during the storage.

The systematic sampling design and well-established research protocol of our study could be applied in other macro-regions as well to get a picture of the chemistry of wood raw materials. The vertical variation of extractives in trees as well their concentrations in other biomass components should be studied for better sourcing of extractives. Considering genetics as a source of variation could provide more power to manage chemical properties in forest management, tree breeding, and nursery production. Moreover, chemical constituents of wood could be connected to forest inventory and planning data through modelling to quantify their amounts and assess their availability at different geographic levels.

Further research and development should also focus on how to implement the application potential and pursue business development and to assess how close we are to industrial outbreaks of novel value-added uses of extractives. Previous studies and practical experiences stress the need for well-adjusted materials and technology, product and market pilots and credible proofs-of-concept. Technology readiness level (TRL) varies much between the different raw material and product incentives. Accordingly, upscaling laboratory knowledge toward commercial utilization calls for detailed analysis of opportunities.
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Appendix A
Figure A1. Cont.
Figure A1. NMR spectra of wood extractives and other chemical compounds in wood samples and sawmill residues (sawdust) in the four regions. The examples represent the range of variation in tree age and the differences between heartwood and sapwood in each region. Explanation of abbreviations: HW = heartwood; SW = sapwood; SMC = sawmill residues; LN = Lapland North; LS = Lapland South; MF = Middle Finland; SF = South Finland; FF = final felling stands; Th = thinning stands; CT = Calluna type, poor sites; VT = Vaccinium type, less fertile sites; MT = Myrtillus type, medium fertile sites; OMT Oxalis-Myrtillus type, fertile sites.

Appendix B

Table A1. HPLC concentrations of phenolic and resin acid compounds in sapwood and heartwood of Scots pine from final felling and thinning stands in the four regions (mg/g dry weight).

| Compound | Stand Type and Wood Type | Region          | N   | Mean  | Minimum | Maximum | Std. Deviation |
|----------|--------------------------|-----------------|-----|-------|---------|---------|---------------|
| Pinosylvin | Final felling– sapwood    | Lapland North   | 20  | 0.021 | 0.007   | 0.039   | 0.010         |
|          |                          | Lapland South   | 19  | 0.025 | 0.008   | 0.057   | 0.013         |
|          |                          | Middle Finland  | 9   | 0.016 | 0.004   | 0.033   | 0.009         |
|          |                          | South Finland   | 18  | 0.019 | 0.006   | 0.086   | 0.018         |
|          | Final felling– heartwood  | Lapland North   | 20  | 2.347 | 1.104   | 4.615   | 1.066         |
|          |                          | Lapland South   | 20  | 2.762 | 0.634   | 5.034   | 1.310         |
|          |                          | Middle Finland  | 10  | 2.843 | 1.691   | 4.846   | 0.977         |
|          |                          | South Finland   | 19  | 2.928 | 0.711   | 6.650   | 1.475         |
|          | Thinning– sapwood        | Lapland North   | 20  | 0.004 | 0.000   | 0.013   | 0.004         |
|          |                          | Lapland South   | 20  | 0.005 | 0.001   | 0.009   | 0.002         |
|          |                          | Middle Finland  | 9   | 0.002 | 0.001   | 0.004   | 0.001         |
|          |                          | South Finland   | 20  | 0.007 | 0.001   | 0.026   | 0.007         |
| PSMME    | Final felling– sapwood    | Lapland North   | 20  | 0.026 | 0.006   | 0.071   | 0.020         |
|          |                          | Lapland South   | 19  | 0.031 | 0.006   | 0.106   | 0.028         |
|          |                          | Middle Finland  | 9   | 0.017 | 0.009   | 0.035   | 0.008         |
|          |                          | South Finland   | 18  | 0.025 | 0.006   | 0.120   | 0.026         |
|          | Final felling– heartwood  | Lapland North   | 20  | 4.503 | 1.691   | 11.396  | 2.697         |
|          |                          | Lapland South   | 20  | 5.114 | 1.971   | 10.498  | 2.477         |
|          |                          | Middle Finland  | 10  | 4.792 | 1.834   | 9.112   | 2.079         |
|          |                          | South Finland   | 19  | 5.079 | 2.640   | 7.326   | 1.103         |
|          | Thinning– sapwood        | Lapland North   | 20  | 0.003 | 0.000   | 0.014   | 0.004         |
|          |                          | Lapland South   | 20  | 0.003 | 0.001   | 0.009   | 0.002         |
|          |                          | Middle Finland  | 9   | 0.001 | 0.000   | 0.002   | 0.001         |
|          |                          | South Finland   | 20  | 0.003 | 0.000   | 0.011   | 0.003         |
Table A1. Cont.

| Compound         | Stand Type and Wood Type | Region          | N  | Mean   | Minimum | Maximum | Std. Deviation |
|------------------|--------------------------|----------------|----|--------|---------|---------|---------------|
| Vanillic acid    | Final felling–sapwood    | Lapland North  | 20 | 0.008  | 0.005   | 0.013   | 0.002         |
|                  |                          | Lapland South  | 19 | 0.007  | 0.004   | 0.009   | 0.001         |
|                  |                          | Middle Finland | 9  | 0.006  | 0.004   | 0.010   | 0.002         |
|                  |                          | South Finland  | 18 | 0.005  | 0.003   | 0.007   | 0.001         |
|                  | Final felling–heartwood  | Lapland North  | 20 | 0.008  | 0.003   | 0.013   | 0.003         |
|                  |                          | Lapland South  | 20 | 0.007  | 0.003   | 0.012   | 0.003         |
|                  |                          | Middle Finland | 10 | 0.006  | 0.004   | 0.010   | 0.002         |
|                  |                          | South Finland  | 19 | 0.006  | 0.003   | 0.012   | 0.002         |
|                  | Thinning–sapwood         | Lapland North  | 20 | 0.010  | 0.005   | 0.032   | 0.006         |
|                  |                          | Lapland South  | 20 | 0.008  | 0.005   | 0.012   | 0.002         |
|                  |                          | Middle Finland | 9  | 0.007  | 0.005   | 0.009   | 0.001         |
|                  |                          | South Finland  | 20 | 0.007  | 0.003   | 0.015   | 0.003         |
|                  | PS-                      | Final felling–heartwood | Lapland North | 20 | 0.054  | 0.019   | 0.098   | 0.024         |
|                  |                          | Lapland South  | 20 | 0.061  | 0.015   | 0.179   | 0.045         |
|                  |                          | Middle Finland | 10 | 0.081  | 0.028   | 0.181   | 0.047         |
|                  |                          | South Finland  | 19 | 0.058  | 0.023   | 0.124   | 0.024         |
|                  | PSMME-                   | Final felling–heartwood | Lapland North | 20 | 0.072  | 0.013   | 0.269   | 0.058         |
|                  |                          | Lapland South  | 20 | 0.105  | 0.034   | 0.375   | 0.085         |
|                  |                          | Middle Finland | 10 | 0.088  | 0.015   | 0.202   | 0.062         |
|                  |                          | South Finland  | 19 | 0.096  | 0.040   | 0.190   | 0.045         |
| Piceatannol      | Final felling–heartwood  | Lapland North  | 20 | 0.007  | 0.001   | 0.022   | 0.006         |
|                  |                          | Lapland South  | 20 | 0.005  | 0.001   | 0.014   | 0.004         |
|                  |                          | Middle Finland | 10 | 0.010  | 0.003   | 0.024   | 0.007         |
|                  |                          | South Finland  | 19 | 0.007  | 0.003   | 0.028   | 0.006         |
| Eriodictyol      | Final felling–heartwood  | Lapland North  | 20 | 0.134  | 0.044   | 0.526   | 0.104         |
|                  |                          | Lapland South  | 20 | 0.111  | 0.042   | 0.190   | 0.041         |
|                  |                          | Middle Finland | 10 | 0.109  | 0.074   | 0.175   | 0.033         |
|                  |                          | South Finland  | 19 | 0.130  | 0.057   | 0.340   | 0.063         |
| Lignan 1         | Final felling–heartwood  | Lapland North  | 20 | 0.096  | 0.055   | 0.162   | 0.028         |
|                  |                          | Lapland South  | 20 | 0.102  | 0.055   | 0.173   | 0.029         |
|                  |                          | Middle Finland | 10 | 0.084  | 0.041   | 0.138   | 0.028         |
|                  |                          | South Finland  | 19 | 0.096  | 0.054   | 0.126   | 0.022         |
| Lignan 2         | Final felling–heartwood  | Lapland North  | 20 | 0.088  | 0.023   | 0.344   | 0.070         |
|                  |                          | Lapland South  | 20 | 0.087  | 0.031   | 0.164   | 0.041         |
|                  |                          | Middle Finland | 10 | 0.061  | 0.018   | 0.111   | 0.024         |
|                  |                          | South Finland  | 19 | 0.065  | 0.021   | 0.203   | 0.041         |
| Lignan 3         | Final felling–heartwood  | Lapland North  | 20 | 0.077  | 0.030   | 0.165   | 0.037         |
|                  |                          | Lapland South  | 20 | 0.074  | 0.028   | 0.130   | 0.029         |
|                  |                          | Middle Finland | 10 | 0.075  | 0.043   | 0.136   | 0.025         |
|                  |                          | South Finland  | 19 | 0.065  | 0.034   | 0.125   | 0.020         |
| Neolignan 1      | Final felling–heartwood  | Lapland North  | 20 | 0.335  | 0.058   | 1.398   | 0.301         |
|                  |                          | Lapland South  | 20 | 0.325  | 0.097   | 0.711   | 0.145         |
|                  |                          | Middle Finland | 10 | 0.285  | 0.077   | 0.650   | 0.180         |
|                  |                          | South Finland  | 19 | 0.256  | 0.092   | 0.743   | 0.147         |
| Neolignan 2      | Final felling–heartwood  | Lapland North  | 20 | 0.112  | 0.017   | 0.307   | 0.084         |
|                  |                          | Lapland South  | 20 | 0.222  | 0.020   | 0.800   | 0.218         |
|                  |                          | Middle Finland | 10 | 0.097  | 0.021   | 0.185   | 0.057         |
|                  |                          | South Finland  | 19 | 0.199  | 0.008   | 0.920   | 0.221         |

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