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Subfossil Scots Pine (*Pinus sylvestris* L.) Wood from Northern Finland—Physical, Mechanical, and Chemical Properties and Suitability for Specialty Products

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Abstract: The physical, mechanical, and chemical properties of both stem wood and knot wood were investigated from two subfossil Scots pine (*Pinus sylvestris* L.) trunks retrieved from a lake in Finnish Lapland, dated to 404–486 CE and to 1318–1444 CE. Both the stem wood and the knot wood of the younger trunk had higher moisture content, lower density, and lower strength properties in comparison to the older trunk. The ash content of the stem wood of the younger trunk was lower, but the ash content of the knot wood was higher than that of the older trunk. Due to the degradation that occurred over time, all the values of physical and mechanical properties were lower compared to typical values of recently grown Scots pine wood. The chemical composition of both stem wood samples was close to the composition of the recently grown wood, and the only exception was the small decrease of the cellulose and hemicellulose in the subfossil samples. The bulk extractives were well-preserved, but terpenes and fatty acids underwent transformation, resulting in more stable compounds. The SWOT analysis (strengths, weaknesses, opportunities, and threats) showed pros and cons for the productization of subfossil wood, with the branding value of an ancient material being the potential enabler in developing commercial niche uses.

Keywords: natural modification; *Pinus sylvestris*; subfossil; wood composition; wood extractives; wood hardness; wood strength; SWOT analysis

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1. Introduction

Decay of dead wood may be a slow, centuries- to millennia-long process in certain environments [1]. In the northern regions, the decay rate of wood is characteristically slow due to the cold climate. In subarctic conditions, dead and decaying trees may remain subaerially preserved as standing (snags) or fallen tree trunks (coarse woody debris) for more than 1000 years on dry forest soils or mountainous terrain given that contact with moist and biogenic decay agents is limited [2,3]. However, a variety of taphonomic processes influence the rate of wood decay once the tree trunks are deposited in sedimentary environments [4]. In general, the preservation potential of deposited wood is increased by anoxic conditions [5]. In fact, reduced rates of both biological and mechanical degradation benefit the preservation of whole or nearly complete plants [6,7], such as tree trunks. Such conditions are typical to sedimentary archives of small lakes and peatlands in northern and central Europe and the British Isles, where considerable research efforts have been

underway over the past several decades to retrieve scientific sample collections from the discovered waterlogged tree trunks [8–15]. In the geoscientific literature, this material is commonly called subfossil wood as an indication of its sub-recent origin and, correspondingly, of the Holocene age (the geological epoch of the past 11.7 thousand years [16]. Alternatively, similar specimens of tree trunks may be called mega-fossils by virtue of their large size [10,17]. Many of these subfossil collections consist of Scots pine (*Pinus sylvestris* L.) stem wood used for tree-ring analyses of past climate variability, i.e., for purposes of palaeoclimate and palaeoecological research. Similar investigations carried out in northern (subarctic) Finland have resulted in a subfossil collection of more than 3000 Scots pine tree-ring samples [18–20]. Collected from sedimentary deposits of small subarctic lakes, this material could indeed be seen to have benefitted from several foregoing factors, leading to increased preservation potential of sizeable arboreal plant parts. The studies conducted so far in this region have been effective in mapping the lake sites with subfossil pine trunks and using the collected tree-ring materials for estimating the changes in climate and pine forests in the region over the past 7.6 thousand years [18–22]. It has been shown that the supply of pine wood to these lakes does not represent a monotonic process but fluctuates through millennia, mainly with varying success of tree recruitment. This means that several past millennia deeper in time, when the conditions were more beneficial for recruitment, may actually be more well-represented in the subfossil record than the more recent times [22,23]. Any of these studies have not, hitherto, delved into the physical, mechanical, and chemical properties of these subfossil materials, in comparison to recently felled and processed Scots pine wood. Generally, such properties are also less commonly studied elsewhere.

In addition to naturally deposited wood, previous physical, mechanical, and chemical analyses of ancient timber also involve archaeological materials that may have been preserved in similar waterlogged conditions [24–26]. Combined, many of the studies focus on the effects of the long period of underground preservation (i.e., in an uncontrolled environment) that have resulted in the properties of predominantly pine, spruce, oak, ash, and elm wood retrieved from natural deposits or archaeological sites. These analyses have characterised a range of changes in wood chemical composition [27], reductions in subfossil wood density [28], deterioration of the cell wall ultrastructure [29], delignification and narrowing of the secondary walls of fibres, vessels, and parenchyma cells [30], degradation and decomposition of holocellulose and lignin [31,32], increases in the proportions of ash, calcium, and lignin at the expense of polysaccharides, with concomitant changes in the shrinkage and mechanical deterioration of subfossil wood [33,34], changes in the bending strength values [35], decreases in the hardness and modulus of elasticity and changes in cell wall composition, cellulose crystallinity, and porosity [36], differing forms of microbial decay [37,38], and arrays of potentially adsorbed elements in the subfossil wood [39]. Previous analyses concentrating on this species have shown that the samples (900 to 2200 years old in their post-mortem age) may retain almost their normal macroscopic appearance and properties, in spite of the changes in the micromorphology and breakdown of certain elements at the ultrastructural level [40]. The speed and extent of deterioration is not related only to post-mortem age and intrinsic wood properties, such as density, extractives content, and heartwood proportion, as well as the depositional environment. Moreover, a large amount of original lignin seems to remain in the Scots pine samples, but their ash content appears to increase due to the accumulation of inorganic matters in comparison to recent wood [41]. No significant differences were found for the physical and mechanical properties of old Scots pine wood (representing 17th century buildings) compared to recent Scots pine samples. However, indications of reductions in resin content and hydrolysis of xylan but not of cellulose were evident [42]. More recently, extractives soluble in acetone were found to account for approximately four percent of the subfossil sample (300 to 700 years old) weights, with the occurrence of extractives in different portions of Scots pine wood being further determined by dendrochronological comparisons of tree-ring records before and after the extraction [23]. Moreover, Tintner et al. [43] used FTIR (Fourier transform

infrared) spectroscopy to demonstrate a molecular decay in pine wood (including Scots pine) samples as a function of their post-mortem age, expressing the extent of complex molecular changes proceeding statistically predictably during the ageing processes over the past 14,000 years.

The well-preserved Scots pine subfossil trees in the lakes of northern Finland and elsewhere on earth at high latitudes are a unique but completely unused wood raw material with great potential. This material is several hundred to several thousand years old, and the year of formation of the annual ring of each tree trunk can be dated accurately. Long periods of time under extreme conditions have also altered the physical and chemical properties of wood, allowing for exceptional properties in the final products. These features make it possible to create compelling brand stories: the best brands are always built on great stories. However, there is no documented information on the technical and chemical properties and treatment possibilities of subfossil wood.

A specific motivation of this study is the potential of using the subfossil Scots pine materials for different added-value applications, such as wood arts or crafts. Detailed knowledge of the properties of this specific material is essential to appropriately utilise it for different types of value-added applications. With these regards, a wide range of properties need to be tested to gain deeper knowledge on the property range and subsequent usability of the subfossil pine wood. For this purpose, variations in colour and in physical and mechanical properties [44] of tree-ring-dated subfossil samples of this species were determined together with the chemical analyses, providing the composition analysis of lignin, hemicellulose, cellulose, and total extractives, in addition to ICP-MS (Inductively Coupled Plasma Mass Spectrometry) analyses. The objective of this study was to determine a spectrum of effects that the prolonged exposure to water, mineral, and organic matter may have caused to this type of wood and, accordingly, to outline its potential applications as well as limitations for commercial use.

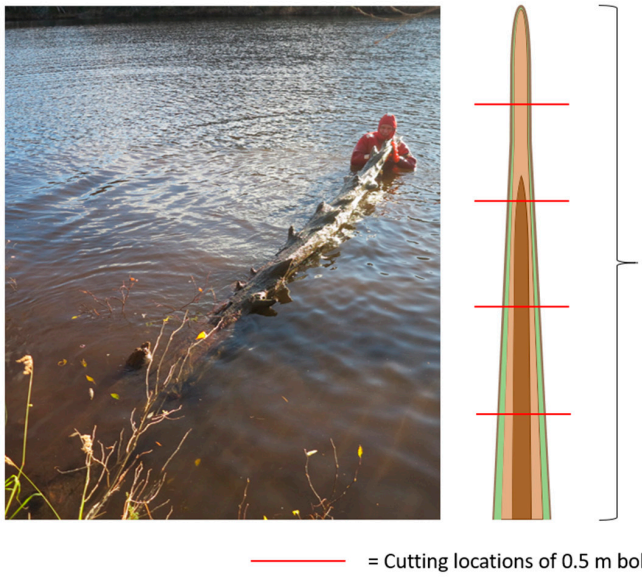
2. Materials and Methods

2.1. Subfossil Material

Fieldwork was targeted to the Lohikoste site (69.84° N, 26.35° E) situated in northwest Finnish Lapland, around 370 km north of the Arctic Circle. Two Scots pine trunks were retrieved from the lake (Figure 1). Sample disks I and II were cut from trunks 1 and 2, respectively, and transported to the tree-ring laboratory. Cross-sectional surface areas of the discs were sanded and scanned for analyses of digital images. The resulting ring-width series were cross-dated visually and statistically [45]. As a result, disc I was tree-ring-dated to 404–483 CE, whereas disc II was dated to 1318–1444 CE. The remaining parts of the trunks were used for testing the physical, chemical, and mechanical properties of stem wood and knot wood of this subfossil material.

2.2. Physical and Mechanical Analyses

The retrieved trunks were cut into five 0.5 m-long bolts and sawn into 30 mm-thick planks (Figures 1 and 2). After air-drying and conditioning at 20 °C and 65% relative humidity, specimens of stem wood were prepared from the planks for the following physical and mechanical property measurements: moisture content (MC), basic density (ϱ_y), modulus of elasticity (E_b) and modulus of rupture (σ_b) in static 3-point bending, Brinell hardness (HB), colour, and ash content (AC). The basic density and the ash content were measured by the gravimetric method from intact parts of bending test specimens after the bending tests. Since the trunks, and subsequently the planks, contained large knots, knot wood specimens were also prepared from randomly selected planks of both trunks for analyses of MC, ϱ_y, HB, and AC.



Analysis	Number of specimens
Moisture content	Stem wood: 10 Knot wood: 10
Basic density	Stem wood: 31 Knot wood: 8
Modulus of elasticity	Stem wood: 56
Modulus of rupture	Stem wood: 28
Brinell hardness	Stem wood: 50 Knot wood: 20
Ash content	Stem wood: 15 Knot wood: 15
Chemical properties	Stem wood: 20 Knot wood: 20

Figure 1. Photo of retrieving the subfossil trunk from the lake and schematic presentation of sampling the specimens for different types of analysis with the total number of specimens.

The physical and mechanical properties and the colour values were measured according to respective ISO standards (Table 1). The mechanical properties were tested using the Zwick Z050 (ZwickRoell GmbH, Germany) material testing device.

The reflectance spectra of the wood surface were measured using a portable spectrophotometer (Konica Minolta, Japan) over three 8 mm-diameter regions located at each end and in the middle of the bending test specimens. Spectral data between the 360 and 740 nm visible wavelength range were converted to CIEL*a*b* colour space using a 2° standard observer and D65 light source. The colour values a* and b* represent red and yellow tones, respectively. The coordinate L* represents lightness, ranging from 0 (black) to 100 (white). Lastly, the colour differences (ΔE^*_{ab}) between the subfossil wood and recently grown wood [46] were calculated.

Table 1. Standards applied for the analysis of different physical and mechanical wood properties.

Wood Property	Standard
Moisture content (MC)	ISO 13061-1:2014
Basic density (ϱ_y)	ISO 13061-2:2014
Ash content (AC)	TAPPI T 211:2007
Modulus of elasticity (E_w)	ISO 13061-3:2014
Modulus of rupture (σ_b)	ISO 13061-4:2014
Colour	ISO 11664-2: 2007. Colorimetry. Part 2: CIE standard illuminants. ISO 11664-4: 2008: Colorimetry. Part 4: CIE 1976 L*a*b* colour space. ISO 11664-6: 2013. Colorimetry. Part 6: CIEDE2000 Colour-difference formula.
Brinell hardness (HB)	EN 1534:2010



Figure 2. A set of unedged subfossil Scots pine boards prepared for the manufacturing of a physico-mechanical test specimen.

2.3. Chemical Analyses

2.3.1. Specimen Preparation

Specimens for chemical analysis were cut and freeze-dried from the stem wood and knot wood of a plank of each bolt. The masses of specimens were measured before and after drying to determine the moisture content (MC) of the wood.

The subfossil wood specimens were cut into small pieces and ground with a mill (Arthur H. Thomas Co. Scientific Apparatus, Philadelphia, PA USA) equipped with a 1 mm sieve. The ground wood samples were freeze-dried and stored at −19 °C in the dark.

2.3.2. Structural Compounds

The cellulose content in the wood samples was analysed by acid hydrolysis combined with GC [47]. The cellulose content in the sample was calculated based on the amount of glucose obtained by acid hydrolysis minus glucose obtained from hemicelluloses, i.e., glucose in galactoglucomannan determined by acid methanolysis with GC.

To characterise the chemical composition of hemicelluloses and pectins in the wood samples, acid methanolysis and GC were carried out as described by Sundberg et al. [47].

Klason lignin, i.e., acid-insoluble lignin, was determined with the conventional method using 72% H_2SO_4 and 100 mg of the pre-extracted and dried wood sample [48]. An analytical balance (Mettler Toledo Excellence Plus XP Analytical balance XP205) equipped with an antistatic kit was used to weigh the samples accurately.

Acid-soluble lignin (AS lignin) was determined by the UV absorption method (Shimadzu 2600 UV-VIS spectrophotometer) in accordance with TAPPI UM250 at 205 nm.

2.3.3. Extractives

The extractives were isolated from the ground and freeze-dried wood with a Soxhlet apparatus using acetone:water (90:10 *v/v*) as a solvent for 6 h (ca. 40 percolations).

The volumes of the extracts obtained were adjusted to 50 mL and their aliquots were taken for the Total Dissolved Substances (TDS) determination. Then, 20 mL of each extract was evaporated with N_2 flow at 40 °C and the extracted solids were dried in the vacuum-desiccator at 40 °C until constant weight. An aliquot of each extract, which contained approximately 1 mg of TDS, was taken for the extractives' composition analyses.

Depending on the TDS, 0.25–1.0 mL of the extracts was transferred into a 10 mL test tube equipped with a hermetically sealing Teflon-coated screw cap; then, 2 mL of the internal standards in methyl-tert-butyl ether (MTBE) solution, containing exactly 0.02 mg/mL of each: heneicosanoic acid, cholesteryl heptadecanoate, 1,3-dipalmitoyl-2-oleyglycerol (Sigma Chemical Co., St. Louise MO, USA), and betulinol (isolated and purified in the

Laboratory of Wood and Paper Chemistry at Åbo Akademi University, Finland) was added, and the tube content was evaporated with a nitrogen flow in a water bath at 40 °C. To secure the moisture removal from the samples, 1 mL of acetone was added to the test tube and evaporated again with a nitrogen flow as above. After additional drying in a vacuum desiccator at 40 °C for 30 min, the extractives were silylated with 80 µL of BSFTA + 40 µL of TMCS + 40 µL of pyridine at room temperature overnight in the dark.

The extractives were analysed by the Gas Chromatography (GC) method using long and short capillary columns [47]. The long column was used to determine the component composition of fatty and resin acids as well as the other relatively low-molar-mass compounds. The short column was used for the group analysis of high-boiling steryl esters and triglycerides. To confirm the component identification with the long column, the GC-MS analysis of the extractives on a Hewlett-Packard HP 6890 GC instrument equipped with an HP 5973 Mass Selective Detector (MSD) was applied. The GC-MS analysis was performed with the HP-1 capillary column, at conditions similar to those used for the GC-FID instrument. The compounds were identified as silylated derivatives, by comparing the mass spectra of their chromatographic peaks with the spectra of pure compounds from the in-house Spectral Library and the commercial Wiley 10th/NIST 2012 spectral library.

2.4. SWOT Analysis

SWOT analysis was used to examine the strengths and weaknesses of the subfossil wood as a raw material for wood products, as well as opportunities and threats for the products in the market. The data for the SWOT analysis were collected in a brainstorming session of the research team and by interviewing colleagues from the Natural Resources Institute Finland (Luke).

2.5. Statistical Analyses and Comparison to the Recently Grown Scots Pines

The two-tailed *t*-test with significance at the 5% level was used to compare the means of the physical and mechanical properties of wood in the older and younger trunks. The method of either the equal or unequal variances was used when the number of samples in each group was the same or different, respectively. The typical values of wood properties reported in the literature for mature Scots pine trees in Finland were used as reference values of wood properties for recently grown wood.

3. Results

3.1. Moisture Content, Basic Density, and Ash Content

Hereinafter, the older subfossil trunk is defined as the tree grown in the years 404–483 CE, as determined by the tree-ring dating method (see Section 2.1), and the younger subfossil trunk is the tree grown in the years 1318–1444 CE.

The average moisture contents of green stem wood and knot wood from subfossil trunks were 221% and 97%, respectively (Table 2). For both stem wood and knot wood, the *MC*s were higher in the younger trunk than in the older trunk.

The basic density of stem wood of the younger trunk was 30.8 kg/m^3 lower than that of the older trunk. Ash contents of subfossil stem wood and knot wood were 0.34–0.54% and 0.35–0.57%, respectively. The *AC* increased in the stem wood with age but decreased in the knot wood. Compared to recently grown wood, the *AC* of subfossil wood was higher.

Table 2. Physical properties of subfossil wood in the two sample trunks.

Variable	Sample	*N*	Mean	Minimum	Maximum	Std. Deviation
ϱ_y (kg/m^3)	Older stem wood	21	361.54	324.72	426.30	28.81
	Younger stem wood	10	330.70	310.72	374.42	16.95
	Older knot wood	6	632.21	596.68	683.68	32.43
	Younger knot wood	2	546.69	525.69	567.69	-
	Reference stem wood [49]		381–427			
HB (MPa)	Older stem wood	26	7.36	5.13	11.23	1.51
	Younger stem wood	24	7.14	6.04	8.45	0.76
	Older knot wood	10	21.15	10.47	48.64	11.29
	Younger knot wood	10	19.03	7.96	35.90	9.18
	Reference stem wood [49]		13–24			
E_w (GPa)	Older stem wood	42	5.43	4.37	6.59	0.65
	Younger stem wood	14	5.36	4.12	6.42	0.58
	Reference stem wood [49]		10.6–12.7			
σ_b (MPa)	Older stem wood	21	50.0	38.7	56.7	5.1
	Younger stem wood	7	42.6	28.9	56.6	10.3
	Reference stem wood [49]		51–98			
AC (%)	Older stem wood	9	0.43	0.38	0.54	0.05
	Younger stem wood	6	0.39	0.34	0.44	0.04
	Older knot wood	9	0.42	0.35	0.52	0.06
	Younger knot wood	6	0.47	0.40	0.57	0.07
	Reference stem wood [49]		0.30–0.40			
MC (%)	Older stem wood	5	206.8	168.2	230.9	23.3
	Younger stem wood	5	234.9	208.5	274.7	27.5
	Older knot wood	5	90.8	62.5	110.7	18.6
	Younger knot wood	5	102.3	73.7	173.8	41.2
	Reference stem wood [50,51]		50–95			

3.2. Modulus of Elasticity, Modulus of Rupture, and Brinell Hardness

Both the modulus of elasticity and the modulus of rupture had lower mean values in the stem wood of the younger trunk than in the stem wood of the older trunk, but only the difference in MOR values was statistically significant (*t*-test: p(MOE) = 0.34; p(MOR) = 0.01). The MOR of the stem wood was 15% higher in the older trunk (Table 2). The Brinell hardness mean values showed a similar trend of the increasing hardness of wood with the age, but the differences between the trunks were insignificant. The hardness of the knot wood differed between the trunks more than that of stem wood. Brinell hardness of knot wood was higher than that of the stem wood in both trunks.

3.3. Colour

Based on the *t*-test, the stem wood colour of the two subfossil trunks differed, where the younger trunk had a lighter (p = 0.000) and less red (p = 0.000) colour of wood than the older one (Figure 3). The yellowness of stem wood did not differ between the trunks (p = 0.078). The lightness of the colour of subfossil wood had lower values and the redness had higher values than those of recently grown wood, while the yellowness values were on the same level. The overall colour difference of subfossil wood to that of recently grown wood was greater in the older trunk than in the younger trunk. The internal colour variation of subfossil wood was large, consisting of, e.g., darker and redder stripes and spots, which can be seen in Figure 2.

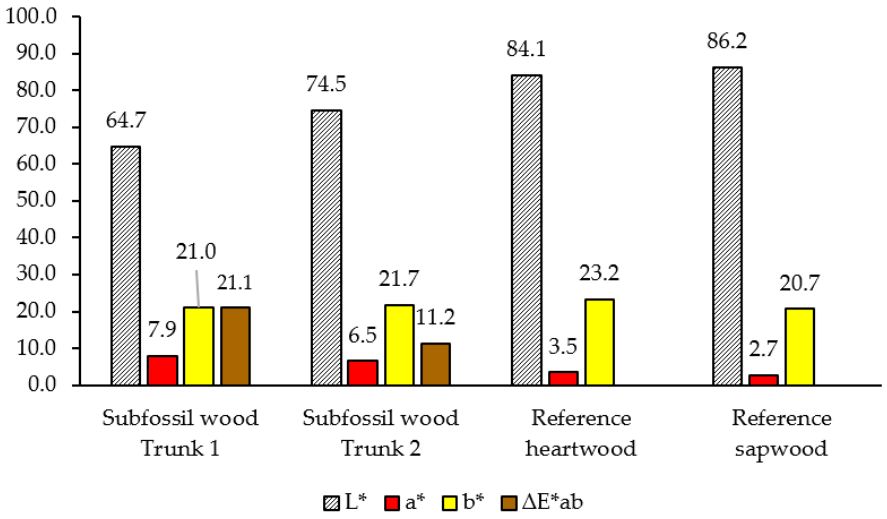


Figure 3. Lightness (L*), redness (a*), and yellowness (b*) values of air-dried subfossil and recently grown (reference) Scots pine heartwood and sapwood [46], and the colour difference of wood (ΔE^*_{ab}) between subfossil and recently grown Scots pine.

3.4. Chemical Properties

3.4.1. Structural Compounds

The composition of structural cell wall compounds from subfossil Scots pine wood reveals some differences in carbohydrates constituents compared to the reference (recently grown) wood (Table 3).

The cellulose content in younger subfossil stem wood (41.0%) was slightly higher than in the older stem wood (39.8%) but was substantially low compared to the recently grown Scots pine wood (44%) based on literature data [52]. However, the lowest cellulose content was determined in knot wood from both subfossil Scots pine samples, i.e., 36.0% and 36.4% in older and younger knot wood, respectively.

The hemicellulose and cellulose content patterns in stem wood were similar. The content of hemicelluloses was lower both in the older and younger stem wood samples (22.7% and 24.2%, respectively) compared to the recently grown wood (26%). The hemicelluloses content in older and younger knot wood was higher than in the corresponding stem wood samples, i.e., 26.5% and 26.6% in older and younger knot wood, respectively.

According to the literature, the Klason lignin content in recently grown Scots pine wood was found in the range of 26–28% [52–54]. The content of Klason lignin in older and younger subfossil stem wood was a bit higher than in recently grown Scots pine wood (28.9% and 29.0%, respectively). In both older and younger knot wood samples, the Klason lignin was almost the same, and amounted to 31.3–31.2%, respectively.

Mannose was the principal sugar unit determined in subfossil stem wood with acid methanolysis and GC. Less mannose was found in older (8.70%) than in younger stem wood (9.9%) (Table 4). Mannose also dominated in both older and younger knot wood samples, amounting to 9.1% and 9.6%, respectively.

Xylose was the second most abundant non-cellulosic sugar unit in all the analysed samples. In older and younger stem wood, its content (5.1% and 5.0%, respectively) was slightly lower than in the corresponding older and younger knot wood samples (6.0% and 5.8%, respectively).

Table 3. Content of structural compounds (% dw) of subfossil stem wood and knot wood with reference values presented in the literature [52] for recently grown stem wood.

Compound	Sample	*N*	Mean	Minimum	Maximum	Std. Deviation
Klason lignin	Older stem wood	5	28.87	27.21	30.95	1.46
	Younger stem wood	5	28.99	27.16	32.04	1.84
	Older knot wood	5	31.27	29.22	32.70	1.47
	Younger knot wood	5	31.24	30.20	32.73	0.94
	Reference		26			
AS lignin	Older stem wood	5	0.18	0.16	0.21	0.02
	Younger stem wood	5	0.20	0.16	0.23	0.03
	Older knot wood	5	0.23	0.20	0.26	0.02
	Younger knot wood	5	0.22	0.20	0.24	0.02
	Reference		-			
Hemicelluloses	Older stem wood	5	23.70	22.55	24.41	0.94
	Younger stem wood	5	24.15	23.83	24.94	0.45
	Older knot wood	5	26.49	25.73	27.22	0.57
	Younger knot wood	5	26.56	24.58	27.63	1.16
	Reference		26			
Cellulose	Older stem wood	5	39.75	37.23	41.57	1.59
	Younger stem wood	5	40.99	38.30	42.85	1.65
	Older knot wood	5	36.00	34.19	37.09	1.21
	Younger knot wood	5	36.39	35.15	37.41	0.92
	Reference		44			
Total	Older stem wood	5	92.51	90.83	94.55	1.57
	Younger stem wood	5	94.33	93.50	95.02	0.56
	Older knot wood	5	93.99	93.06	95.76	1.14
	Younger knot wood	5	94.40	93.22	95.76	0.96
	Reference		96			

The third most abundant non-cellulosic sugar unit in all the samples was galactose. Again, older and younger stem wood contained slightly less galactose than the corresponding knot wood, i.e., 3.4–2.2% and 4.2–3.5%, respectively. The glucose content in all the analysed samples was close to that of galactose. In older and younger stem wood, as well as in older and younger knot wood, its content was 3.0–3.4% and 3.3–3.5%, respectively.

The arabinose content in the analysed older and younger stem wood samples was in the range of 0.9–1.2%, respectively. However, the corresponding knot wood samples indicated a slightly higher value, i.e., 1.2–1.4%, respectively. The rhamnose content in the analysed samples was low: 0.22–0.23% in older and younger stem wood, and 0.24–0.26% in older and younger knot wood, respectively.

Among uronic acids, galacturonic acid was the most abundant. Its content in older and younger stem wood was in the range of 1.3–1.4%, respectively, and in older and younger knot wood, it was in the same range as above. The content of 4-O-methylglucuronic acid was lower in both older and younger stem wood samples (1.0–0.9%, respectively) compared to the older and younger knot wood samples (about 1.1% for both samples). Glucuronic acid was detected in all the samples in trace amounts in the range of 0.03–0.04%.

Table 4. Content of hemicelluloses and pectins (% dw) of subfossil stem wood and knot wood.

Compound	Sample	*N*	Mean	Minimum	Maximum	Std. Deviation
Arabinose	Older stem wood	5	0.934	0.774	1.194	0.172
	Younger stem wood	5	1.223	1.091	1.320	0.086
	Older knot wood	5	1.158	0.964	1.567	0.240
	Younger knot wood	5	1.394	1.285	1.518	0.097
Rhamnose	Older stem wood	5	0.220	0.198	0.249	0.019
	Younger stem wood	5	0.227	0.216	0.235	0.008
	Older knot wood	5	0.244	0.228	0.263	0.013
	Younger knot wood	5	0.259	0.240	0.284	0.019
Xylose	Older stem wood	5	5.122	4.708	5.558	0.388
	Younger stem wood	5	4.950	4.390	5.235	0.342
	Older knot wood	5	6.029	5.450	6.390	0.385
	Younger knot wood	5	5.805	5.565	6.180	0.235
Mannose	Older stem wood	5	8.706	7.243	9.847	1.011
	Younger stem wood	5	9.845	9.172	10.377	0.432
	Older knot wood	5	9.132	7.565	10.437	1.085
	Younger knot wood	5	9.577	8.334	10.357	0.795
Galactose	Older stem wood	5	3.414	1.790	6.235	2.161
	Younger stem wood	5	2.236	1.883	3.292	0.595
	Older knot wood	5	4.225	2.963	5.375	0.877
	Younger knot wood	5	3.538	3.022	4.238	0.461
Glucose	Older stem wood	5	3.030	2.779	3.396	0.235
	Younger stem wood	5	3.350	3.316	3.394	0.032
	Older knot wood	5	3.283	2.799	3.679	0.353
	Younger knot wood	5	3.455	3.109	3.845	0.352
Glucuronic acid	Older stem wood	5	0.026	0.022	0.032	0.004
	Younger stem wood	5	0.035	0.033	0.038	0.002
	Older knot wood	5	0.030	0.027	0.035	0.003
	Younger knot wood	5	0.039	0.036	0.044	0.004
4-O-methyl-glucuronic acid	Older stem wood	5	0.999	0.891	1.119	0.104
	Younger stem wood	5	0.921	0.780	1.008	0.087
	Older knot wood	5	1.115	0.959	1.257	0.123
	Younger knot wood	5	1.068	1.029	1.158	0.054
Galacturonic acid	Older stem wood	5	1.254	1.194	1.332	0.054
	Younger stem wood	5	1.363	1.309	1.420	0.045
	Older knot wood	5	1.273	1.166	1.439	0.111
	Younger knot wood	5	1.421	1.332	1.498	0.075
Total	Older stem wood	45	23.705	22.550	24.405	0.941
	Younger stem wood	45	24.152	23.831	24.944	0.451
	Older knot wood	45	26.490	25.731	27.218	0.573
	Younger knot wood	45	26.557	24.581	27.628	1.158

3.4.2. Extractives

The total amount of extractives in the stem wood samples was very variable (Appendix A Table A1). The total amount of extractives isolated from older stem wood was about 5 times higher than from younger stem wood, i.e., 47,975.3 μg/g (4.8%) vs. 9077.9 μg/g (0.9%), respectively. However, the highest total amount of extractives was found in both knot wood samples: 98,156.4 μg/g (9.8 %) and 81,400 μg/g (8.1%) in older and younger knot wood, respectively.

Resin acids were the most abundant group of extractives in all the analysed subfossil wood samples, except those from younger stem wood. It was found that both knot wood samples contained extremely high amounts of resin acids. Thus, the GC analysis of older and younger knot wood extracts showed 5.9% and 7.0% of resin acids, respectively. The

resin acids content in the corresponding older and younger stem wood samples was lower, and amounted to 1.9% and 0.2%, respectively. Tetrahydroabietic and dehydroabietic acids were found to be the dominant compounds in the group of resin acids for both stem wood samples, i.e., 11,163.6 and 5637.3 μg/g in older, and 1368.9 and 547.8 μg/g in younger stem wood, respectively. The qualitative composition of resin acids in both knot wood samples was similar to that in the stem wood samples; however, the quantitative distribution of those compounds was quite different. For instance, large amounts of tetrahydroabietic (15,413.4 and 8322.5 μg/g), dehydroabietic (10,974.3 and 14,706.8 μg/g), dihydroabietic (11,909.9 and 11,045.9 μg/g), abietic (5384.0 and 16,235.9 μg/g), pimaric (7008.8 and 6722.2 μg/g), palustric (2282.2 and 4784.9 μg/g), iso-pimaric (2188.4 and 2589.6 μg/g), neoabietic (1394.4 and 2527.7 μg/g), and sandaracopimaric (1034.0 and 1065.7 μg/g) acids were found in the extracts from older and younger knot wood, respectively.

Terpenes were the second most abundant group of extractives in all the analysed subfossil wood samples, with the exception of younger stem wood. Altogether, 22,926.4 and 530.5 μg/g of terpenes were determined in the extracts from older and younger stem wood, respectively. Their content in the knot wood extracts was even higher, amounting to 25,013.0 and 2728.9 μg/g for older and younger knot wood, respectively. In the extracts from older stem wood, the dominating terpenes were 18-norabietane (17,579.4 μg/g), 18-norabieta-8,11,13-triene (4433.0 μg/g), and 18-norabietene (826.8 μg/g). In contrast, younger stem wood contained only small amounts of 18-norabieta-8,11,13-triene (264.4 μg/g) and 18-norabietane (180.8 μg/g).

Similar to the resin acid distribution in wood samples, large amounts of terpenes were accumulated in the corresponding older and younger knot wood samples. 18-norabietane (12,760.3 μg/g), 18-norabieta-8,11,13-triene (9527.9 μg/g), and norabietene (2042.7 μg/g) were found in the extracts from older knot wood. The most abundant terpene in younger knot wood was 18-norabieta-8,11,13-triene (1748.9 μg/g).

Fatty acids were the third most abundant group of extractives in the subfossil wood samples. A slightly higher amounts of fatty acids were found in the stem wood compared to the knot wood. The total fatty acids content in older stem wood (2502.7 μg/g) and younger stem wood (4234.6 μg/g) was slightly higher than in the corresponding older knot wood (1542.8 μg/g) and younger knot wood (2055.1 μg/g). Saturated C16:0 acid was the most abundant in stem wood, i.e., 1200.7 and 2917.8 μg/g in older and younger stem wood, respectively. Older and younger knot wood contained two fatty acids with substantial amounts: C16:0 (466.3 and 465.1 μg/g) and C18:2 (399.4 and 792.2 μg/g) acids, respectively.

Sterols were the next abundant group of extractives determined in the subfossil wood samples, with sitosterol as the major compound. The ratio of sterols:sitosterol content in the analysed wood samples was as follows: 811.4:586.6 μg/g and 365.3:270.7 μg/g in older and younger stem wood, as well as 760.8:556.7 μg/g and 768.0:564.8 μg/g in older and younger knot wood, respectively.

Steryl esters were also found in small amounts in all wood samples, i.e., 435.8 and 1061.5 μg/g in older and younger stem wood, respectively. Their content in older and younger knot wood was about the same: 465.3 and 820.8 μg/g, respectively.

Free sugars and glycerides were among the smallest groups of extractives determined in the subfossil wood samples. Free sugars were represented mostly with hexoses, and their most notable amount was determined in the extracts from the younger knot wood sample: 1367.6 μg/g free sugars with 1365.2 μg/g of hexoses. The amount of glycerides (di- and tri-glycerides) in all the samples was in the range of 139–320 μg/g.

3.5. SWOT Analysis

Strengths. The uniqueness of subfossil wood as a raw material enables the production of exceptionally high value-added products. The low density allows the lightness of the products in artefacts. The arctic Scots pine has narrow growth rings, which means excellent dimensional stability and high quality of defect-free wooden items. The variety of colour and the interesting visual appearance of the wood could be utilised in large surfaces made of thin panels.

Weaknesses. High procurement costs lead to high prices for raw materials and products. The size or quality of the purchased raw material is not predictable or even controllable. Mud and soil on the surface of trunks may blunt the tools, e.g., in veneering processes. Furthermore, the impurities may hide the true quality of the trunks until processing. The raw material is prone to additional defects and colour changes during drying and further processing. There is no existing information on product markets, or the market does not exist. Thus, creating the market may require considerable investments and time. No information is available on the long-term behaviour, surface treatability, woodworking techniques, and processing parameters of this wood material or whether they happen to differ from the regular wood material.

Opportunities. The uniqueness enables storifying the material by creating links with the arctic environment thousands of years ago. It enables the branding of products through the images of the era. The one-of-a-kind character of the material provides the marketing, productization, commercialisation, and brand management professionals with an exceptionally interesting case.

Threats. In the case of Finland, the subfossil wood raw materials are located mostly in state-owned areas in Lapland, which may limit its commercial use. The subfossil wood is a practically non-renewable raw material in the Arctic regions, where no new, large-dimension trunks are growing. This is associated with an image risk of greedy exploitation of the ancient wood remnants. There are also risks of fake materials coming into the market, which requires the chain-of-custody certificate to ensure the originality of the subfossil wood. This is a particularly challenging task, because the potential subfossil wood supply is dispersed in many Arctic region countries, not only in Finland or Scandinavia.

4. Discussion

4.1. Physical and Mechanical Properties

The lower density of the younger subfossil stem wood compared to the older stem wood was inconsistent with previous studies in the literature. Factors that influence molecular decay leading to a decrease in density include input material composition and preservation conditions [55]. Subfossil stems of this study may have differed, for example, in the proportions of heartwood and sapwood that could no longer be reliably distinguished from the material studied. It is well-known that the heartwood of most tree species is more resistant to decay than the sapwood. In addition, ambient conditions that promote decomposition (e.g., temperature, pH, and oxygen content) may have differed in the vicinity of the trunks, in locations where they lay at the bottom of the lake. Events prior to the submergence of trunks may also have contributed to the underwater decomposition [28].

In the study by Babiński et al. [56], the basic density of 12,500-year-old subfossil Scots pine wood was 254–305 kg/m^3, which is comparable to the result of this study (331–362 kg/m^3) when the age difference is taken into account. Guyette and Stambaugh [28] found with oak wood that much of the change in density is associated with reductions in cell wall thickness of secondary cell wall layers high in cellulose and hemicellulose content (the layers S2 and S3). On average, the basic density of subfossil wood was 50–60 kg/m^3 lower than the basic density provided in the literature for the recently grown Scots pine wood [49,57].

The ash content of both subfossil trunks was higher than that reported in the literature for the recently grown Scots pine wood (0.30–0.40%) [58,59].

The modulus of elasticity of subfossil Scots pine wood was 55–58% lower and the modulus of rupture was 42–50% lower than those of recently grown Scots pine wood [60,61]. An even greater decrease was observed in the Brinell hardness, which decreased by approximately 70% compared with the recently grown wood [62]. Additionally, Endo et al. [63] found that all mechanical properties of waterlogged wood deteriorated decisively for applications requiring strength and durability.

The increased pore volume due to degradation and leaching of wood components increased the moisture content of fresh subfossil wood, as was also observed by Babiński et al. [56]. The maximum moisture content (231–275%) corresponds to the maximum theoretical water content that can be achieved with the measured wood density values [64] and is clearly different from the maximum water content of recently grown Scots pine wood.

The basic density was higher and the moisture content was lower in knot wood than in stem wood. Differences in physical and mechanical properties between stem wood and knot wood can be explained by differences in extractive content, durability, and anatomical structure.

Neither the colour of subfossil Scots pine wood nor the colour change compared to recently grown wood have been reported in the previous literature. Colour has been studied in waterlogged oak wood [65,66], in which the colour is characterised by the reaction of ferric compounds from water with wood-tanning agents [67]. The change of colour of subfossil wood is dependent on the time at which the wood has been under submerged conditions, as well as the characteristics of the surrounding sediments [65]. In this study, the colour variation of subfossil wood was found to be larger than that of modern wood, with variation of bright, almost original-coloured wood with stripes, spots, and darker and redder areas.

4.2. Chemical Properties

The composition of both subfossil stem wood samples was close to that reported for the recently grown Scots pine wood [52–54]. The main differences between the subfossil and the recently grown Scots pine wood were in their carbohydrates, i.e., in the cellulose and hemicelluloses content. The amounts of cellulose and hemicelluloses in younger stem wood were 3.5% and 2.1% lower than in the recently grown Scots pine. In the older stem wood, this reduction was a bit deeper and amounted to 6.5% and 3.6%, respectively. In contrast to the carbohydrates, the content of the lignin in both stem wood samples was increased by 1–3% compared to that in recently grown wood. In the literature, it was reported that relatively short ageing of 180 years causes no significant changes in the chemical composition of Norway spruce wood, whereas results found for 300–800-year-old softwood were similar to our results, i.e., a decrease in cellulose content with age and a simultaneous increase in lignin [68]. In the case of Eocene and Palaeocene (66 million to 23 million years ago) gymnosperm wood species, their carbohydrates were even more dramatically degraded: hemicelluloses were almost removed, the residual carbohydrate was mainly crystalline cellulose, and the content of lignin may increase up to 80 [69]. Based on the above, it can be concluded that the amorphous hemicelluloses, as well as the amorphous part of cellulose, are the most sensitive moieties affected during anaerobic ageing. The older subfossil stem wood contained notably less arabinose, mannose, glucose, and galacturonic acid, and barely less rhamnose and glucuronic acid than that in younger subfossil stem wood. This may indicate that galactoglucomannan containing mannose and glucose units as well as pectins containing galacturonic acid and rhamnose units were the most degradable components. It is known that a certain part of arabinose units in softwood is usually assigned to arabinoglucuronoxylan, and its decrease in the older subfossil stem wood could be due to splitting from the above hemicelluloses [54]. In contrast to that phenomenon, the amount of another pentose, i.e., xylose, was slightly increased in the

older subfossil wood (Table 4). It can be supposed that after the removal of acetyl groups and sidechain-bonded arabinose units, the less-branched (arabino)glucuronoxylan will tend to form crystalline adducts with cellulose matrix, and thus resist ageing-induced reactions. However, over an extended period of time of ageing, even the less-branched (arabino)glucuronoxylan will degrade anyway and, most probably, at a higher rate than the extremely well-ordered crystalline cellulose.

It is a common belief that under anaerobic conditions in water, the accessibility of cell wall components is a key factor of wood degradation, which occurs mainly by hydrolysis [1]. After water penetrates inside the lumen and the cell wall swells, the slow hydrolysis of amorphous hemicelluloses begins towards the compound middle lamella. Obviously, the high extractives content in both samples of knot wood results in the low accessibility of the structural components of the cell wall, and thus prevents their fast degradation (Tables 3 and 4) [70]. Indeed, the differences in the knot wood composition, including the patterns for hemicelluloses and pectins, between older and younger subfossil knot wood were less pronounced than those in the corresponding stem wood samples. The analysed knot wood contained substantially less cellulose than the stem wood, which is in agreement with the earlier findings for recently grown spruce [70].

Galactose most probably originated from galactan, and its high amount in comparison to the stem wood may indicate that both knot wood samples were enriched with compression wood (Table 4) [71].

It is known that typical Scots pine heartwood contains more extractives than sapwood [72]. As the volume of heartwood increases with the age of the tree, the amount of extractives in the trunk increases, too. In our case, higher amounts of extractives both for stem wood and knot wood were obtained from the older subfossil trunk than from the younger trunk. This difference can be attributed to the individual tree properties, particularly the age of the tree at the time of its felling, as well as the differences between growth rates.

A very high content of extractives in coniferous knot wood vs. stem wood is also a well-known phenomenon well-described in the literature [73]. However, the final amounts of extractives in different morphological parts in a subfossil trunk vary to a high degree, not only between individual trees but it is also affected by many factors, from the conditions in which the tree grew to the fossilisation conditions.

Wood extractives are usually not stable in aerobic conditions, and they are rapidly altered in a fallen tree due to the accumulative action of de-watering, oxygen, enzymes, microorganisms, and atmospheric conditions [1]. However, in anaerobic conditions, in contrast to structural cell wall constituents, extractives can survive for millions of years. Thus, it is not surprising to find that bulk extractives in all the subfossil wood samples were of nearly the same amount as in the freshly harvested tree [1,74]. In addition to applicability in wood taxonomy, the composition of wood extractives can be a reliable tool for assessing the age of the subfossil wood samples. This is especially true for compounds which are related to terpenes families, i.e., most abundant groups of extractives, including resin acids and terpenes (Appendix A Table A1). In this respect, it is of particular interest to focus on the proportion between natively occurring abietic acid and related derivatives formed during wood diagenesis. Reunanen et al., in the late 1980s, reported that the amount of abietic acid derived from pine tar and tar-impregnated rope, twine, and wood parts from the 200-year-old shipwrecks was decreased, whereas the amount of dehydro- and tetrahydroabietic acids was increased [75,76]. They also observed the formation of some other structurally corresponding derivatives, i.e., more stable norabietane and norabietatriene. Later, Staccioli et al. detected those abietane-related terpenes in the fossil samples of Scots pine obtained from the 18,000-year-old terrestrial fossil [77]. According to the proposed scheme, the abietane-type terpenes transformation in the fossil samples starts with the disproportionation reaction of abietic acid to form dehydroabietic and tetrahydroabietic acids [78]. Dehydro- and tetrahydro-abietic acids can be considered as intermediate compounds and precursors for more stable derivatives. Stable derivatives

can be formed by means of decarboxylation/reduction reactions, for instance, 18-norabieta-8,11,13-triene from dehydroabietic acid and abietane, followed by 18-norabietane from tetrahydroabietic acid (Table A1). One can also assume that the ratio between the stable and the intermediate terpenes, for instance, 18-norabietane/tetrahydroabietic acid and/or 18-norabieta-8,11,13-triene/dehydroabietic acid, could be a valuable tool to validate the age of the subfossil wood sample.

Fatty acids are another group of lipophilic compounds which survived in the analysed subfossil wood samples. However, in contrast to the large portion of unsaturated fatty acids typical for lipophilic extractives from recently grown Scots pine, they mainly consist of more stable saturated fatty acids [74]. Probably, such differences in the composition of fatty acids can also be considered as a marker for the subfossil wood samples [69].

4.3. SWOT Analysis

The SWOT analysis presented a variety of views to be considered in subfossil wood utilisation. Consultation with the environmental permit authorities would be the first step when considering logging and the use of the material. There are many practical challenges associated with utilising subfossil wood. The procurement of subfossil wood raw materials is very expensive due to the limited availability of raw materials and their location in remote areas. Furthermore, the procurement involves searching and manually collecting individual logs. This causes a considerable economic risk, i.e., a considerable investment of time and resources in raw material procurement and logistics.

High procurement costs raise the raw material price and thus severely restrict the eligible market only for certain niche applications. However, similar raw materials, i.e., underwater logged or swamp wood, have been successfully commercialised. It could be possible to make works of art, such as ancient jewellery or replicas of stringed (horsehair) instruments, which are very simple but represent the ancient cultures. The unique story of the age and origin of the raw material and the culture that prevailed during that time creates images that enable the branding of high value-added products.

5. Conclusions

The chemical composition of two subfossil Scots pine trunks retrieved from a lake in Finnish Lapland, dated to 404–486 CE and to 1318–1444 CE, exhibited the main signs of the original wood. However, all the values of the physico-mechanical properties were different from typical values of recently grown Scots pine wood. It seems that in anaerobic conditions of lake water, the Scots pine trunk underwent hydrolytic reactions, affecting mostly structural carbohydrate compounds of the cell wall and middle lamellae, i.e., cellulose and hemicellulose.

Compared to the younger trunk, in the older trunk after an additional 1000 years of ageing, even deeper degradation of the polymeric carbohydrates developed. Obviously, the degradation of structural cell wall constituents directly influenced the physico-mechanical properties of the stem wood. However, the older age and longer submergence time in this study did not result in lower density and strength, as those values of the younger trunk were lower than those of the older one.

Based on the results of this study, the physical and mechanical properties of subfossil wood are dependent on not only the time the trunk has been in the subsurface conditions, but also the intrinsic properties of the wood, such as the ratio of heartwood to sapwood, as well as on surrounding subsurface conditions and events prior to the submergence of trees.

On the other hand, the large amounts of extractives in the knot wood substantially decreased the accessibility of the cell wall structure towards hydrolytic reactions. The extractives are also responsible for the high density and hardness of knot wood.

Bulk amounts of extractives in both stem wood and knot wood samples were in the range of those from the recently grown Scots pine wood. However, abietic acid and other terpenes, as well as fatty acids, underwent a transformation, resulting in the formation of more stable compounds.

Our results indicate that the subfossil Scots pine wood has a high potential for high value-added decorative products or specialty interior applications depicting the regional culture, because it is light but still strong enough to be machined and bonded to other materials. A profitable business requires a very high unit value for the products because the raw material procurement is extremely laborious and expensive. Successful branding may, however, create niche markets that enable profitable business.

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Appendix A

Table A1. Content of extractives (µg/g dw) of subfossil stem wood and knot wood.

Compound	Older Stem Wood				Younger Stem Wood				Older Knot Wood				Younger Knot Wood			
	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
Carboxylyc acids																
Succinic acid	0.3	0.0	0.7	0.3	0.1	0.0	0.2	0.1	0.1	0.0	0.6	0.2	0.0	0.0	0.0	0.0
Fatty acids																
Acid 14:0	91.9	4.8	432.1	190.2	500.0	7.5	1330.1	617.3	43.2	4.0	131.7	51.1	91.8	5.3	136.1	50.2
Acid 15:0	202.7	10.2	425.2	159.0	14.7	3.7	29.4	13.2	222.3	8.4	662.3	285.6	23.6	0.3	53.2	21.2
Acid 16:0	1200.7	118.3	4845.0	2041.2	2917.8	64.6	6969.3	3297.5	466.3	274.6	858.0	235.0	465.1	185.1	616.3	163.5
Acid 17:0	26.0	0.3	110.0	47.1	76.4	1.1	180.1	89.4	18.3	0.0	34.9	15.5	37.7	26.9	52.6	9.8
Acid 18:0	763.5	113.6	1590.3	632.8	59.4	11.0	126.7	51.3	176.7	1.6	385.6	187.4	42.0	33.6	52.0	7.2
Acid 18:2	60.2	3.6	170.0	77.4	489.3	1.1	1485.0	666.3	399.4	43.5	679.1	314.7	792.2	150.2	1204.6	388.9
Acid 20:0	29.3	12.0	79.6	28.3	40.8	12.5	77.9	32.6	28.4	5.5	62.4	22.9	355.3	131.5	578.3	182.0
Acid 22:0	61.2	43.8	95.8	21.0	66.1	42.4	102.3	28.3	92.2	48.5	148.6	42.9	127.1	108.5	147.5	17.3
Acid 24:0	51.3	10.1	129.9	48.2	19.8	11.7	34.9	9.6	38.6	23.7	68.6	18.3	28.6	18.4	40.3	9.2
13-Hydroxystearic acid	15.8	1.5	55.5	22.7	50.4	0.7	121.0	61.3	57.4	5.8	126.8	43.9	91.7	31.7	132.1	37.6
Sum	2502.7	940.1	5933.2	1982.4	4234.6	156.8	10,412.6	4843.3	1542.8	659.1	2499.3	788.6	2055.1	1050.5	2594.8	617.3
Resin acids																
Secodehydroabietic acid	452.3	99.9	617.0	206.6	80.8	13.4	152.8	58.3	768.9	634.4	867.5	87.5	1000.0	749.9	1292.3	193.6
9,10-epoxy-18:0 acid	13.4	0.0	64.2	28.4	142.0	0.4	386.9	185.0	118.1	0.0	376.2	160.0	123.0	24.3	204.9	87.1
8,15-pimaradien-18-oic acid	18.3	0.6	72.4	31.0	10.2	0.1	39.3	16.4	116.5	71.3	220.7	63.0	137.3	104.8	162.1	22.9
Pimaric acid	547.2	43.3	2284.9	973.5	31.0	6.8	71.6	27.8	7008.8	759.2	14,801.9	6435.9	6722.2	5920.4	7957.6	749.5
Sandaracopimaric acid	137.4	11.6	587.3	251.8	3.9	0.0	12.4	5.0	1034.0	113.7	2402.5	982.2	1065.7	923.8	1275.1	136.8
Iso-pimaric acid	153.6	0.2	665.0	286.8	3.6	2.1	5.1	1.3	2188.4	106.8	5214.0	2092.4	2589.6	2161.2	2965.5	326.5
Dihydroabietic acid	665.8	41.1	2817.9	1205.5	25.9	7.8	48.6	20.8	11,909.9	210.0	36,513.1	15,352.7	11,045.9	9212.5	14,022.1	2106.8
Palustric acid	67.2	1.5	293.0	126.6	1.2	0.2	3.0	1.2	2282.2	175.7	5911.5	2351.4	4784.9	2212.4	8300.0	2377.5
Levopimaric acid	18.6	0.8	48.7	19.7	4.4	0.9	10.4	3.9	625.6	59.9	1546.5	706.6	411.6	78.4	1075.5	401.1
Dehydroabietic acid	5637.3	1012.3	21,692.8	9003.8	547.8	151.1	1162.6	438.2	10,974.3	3892.2	26,901.4	9272.9	14,706.8	10,927.7	18,906.0	3153.9
Tetrahydroabietic acid	11,163.6	1961.1	44,227.0	18,508.1	1368.9	275.2	3057.3	1024.4	15,413.4	9042.8	24,413.2	6392.6	8322.5	2128.7	15,979.0	6011.1
Abietic acid	56.4	1.7	227.4	96.1	6.4	4.0	10.9	2.8	5384.0	356.6	13,668.8	5584.3	16,235.9	4602.1	23,536.6	7295.1
Neoabietic acid	25.0	0.9	115.6	50.7	0.7	0.1	1.8	0.7	1394.4	67.2	3393.8	1364.1	2527.7	1267.9	5014.8	1510.5
x-Hydroxy-tetrahydroabietic acid	12.0	0.7	45.5	18.9	4.9	0.8	12.7	4.6	195.5	2.9	453.3	193.3	467.8	341.8	620.2	116.8
x-Hydroxy-dehydroabietic acid	7.6	3.5	12.0	3.6	4.7	2.9	6.1	1.3	72.1	16.4	208.6	80.0	319.2	128.6	650.9	203.9
Sum	18,975.6	3275.0	73,700.4	30,652.6	2236.5	468.3	4877.9	1693.0	59,486.1	17077.2	124,450.5	44,730.6	70,459.9	59,815.3	83,903.8	8615.3
Sterols																
Campesterol	36.6	7.0	52.2	17.3	15.9	3.7	30.9	11.6	32.8	25.1	45.5	7.7	33.5	27.5	40.9	6.7
Campestanol	39.4	11.2	75.3	23.9	6.9	3.9	9.9	2.8	41.6	24.7	72.2	17.9	33.9	21.4	43.2	8.3
Sitosterol	586.6	81.7	809.4	299.0	270.7	54.8	521.9	199.5	556.7	451.9	684.2	94.3	564.8	509.9	619.6	51.4
Sitostanol	96.6	25.0	139.0	44.2	55.1	9.0	117.9	44.8	60.1	40.3	74.3	13.9	72.8	55.9	110.2	21.5
Citrostadienol	10.7	3.3	17.0	5.5	5.6	1.5	11.1	3.8	20.8	15.8	26.1	3.8	17.1	12.7	19.2	2.6
Stigmasta-3,5-diene	23.5	3.7	59.9	21.9	6.8	4.3	8.7	1.6	37.6	28.4	42.1	5.5	31.0	23.9	39.9	6.3
Sitosteryl formiate	17.9	4.4	37.2	13.0	4.4	3.1	5.2	0.9	11.2	5.7	18.7	5.3	14.9	7.3	25.4	6.7
Sum	811.4	136.3	1079.0	387.8	365.3	84.9	701.2	259.8	760.8	622.3	909.7	110.1	768.0	682.4	867.6	76.2

Table A1. *Cont.*

Compound	Older Stem Wood				Younger Stem Wood				Older Knot Wood				Younger Knot Wood			
	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
Terpenes																
Pimarol	11.5	0.1	49.3	21.2	37.4	5.0	108.3	44.0	344.1	0.0	1340.3	560.2	270.9	151.3	374.3	100.1
3-hydroxylambda-8(17),13(16),14-trienoic	0.5	0.1	1.3	0.5	3.0	0.0	10.3	4.3	49.9	0.9	137.7	54.6	258.6	106.4	550.3	170.9
18-norabietane+	15.8	0.2	40.0	16.2	0.7	0.2	1.5	0.5	17.3	4.2	35.2	12.2	4.5	0.0	20.3	8.8
18-norabietene	826.8	10.7	1455.2	597.7	10.6	7.5	14.5	2.7	2042.7	195.8	5164.5	1873.2	44.9	6.9	134.2	51.8
18-norabietane	17,579.4	161.8	36,389.6	13,458.5	180.8	105.1	295.6	74.0	12,760.3	1197.3	22,942.3	9403.9	206.9	66.3	534.1	186.8
18-norabieta-8,11,13-triene	4433.0	238.1	6733.9	2630.4	264.4	61.8	636.9	219.3	9527.9	4157.4	15,646.3	5361.0	1748.9	586.7	4621.3	1649.1
Cycloartenol	52.8	24.2	68.7	17.3	27.3	8.9	41.9	13.8	255.1	190.9	378.4	76.4	173.5	164.8	178.0	5.5
Methylene cycloartanol	6.5	1.5	9.2	3.2	6.5	1.7	10.0	3.3	15.6	2.7	24.6	9.1	20.6	16.0	25.6	3.5
Sum	22926.4	489.2	43016.8	15,366.3	530.8	215.1	1035.2	303.4	25,013.0	7699.5	44,064.1	15,795.3	2728.9	1544.6	5775.9	1731.4
Free sugars																
Sugar pentose_1	7.9	0.6	24.5	9.4	0.3	0.1	0.5	0.2	2.4	0.2	8.1	3.3	1.8	0.5	3.3	1.2
Sugar hexose_1	226.1	15.6	644.2	249.7	11.1	0.4	29.6	12.6	1365.2	310.5	3533.9	1261.1	63.8	0.8	269.1	116.0
Sum	234.1	16.2	649.3	251.0	11.4	0.5	29.7	12.6	1367.6	310.7	3534.3	1260.7	65.6	2.1	271.9	116.5
Glycerides																
Diglycerides	54.2	12.2	212.5	88.6	271.6	64.0	636.1	220.4	24.3	6.4	41.5	12.9	27.1	1.6	45.9	18.4
Triglycerides	85.4	25.8	117.5	34.8	52.5	16.3	75.5	25.9	178.4	88.4	283.1	70.8	139.6	109.8	167.6	20.5
Sum	139.6	106.4	238.3	55.9	324.1	124.5	710.7	226.2	202.8	129.9	309.8	66.6	166.8	142.5	183.6	17.3
Steryl esters	435.8	128.8	1483.7	587.1	1061.5	741.6	1584.1	394.4	465.3	227.4	825.6	250.9	820.8	677.9	1219.6	225.7
Most abundant non-identified																
RT9.83	113.9	8.5	485.0	207.8	232.6	2.0	721.7	321.3	325.0	39.9	691.5	273.1	195.0	20.3	285.9	106.5
RT10.64	515.1	12.6	1067.1	423.9	10.8	8.3	16.3	3.5	882.1	62.6	1377.8	526.8	17.4	3.4	42.7	15.3
RT11.86	415.1	4.6	608.2	252.6	4.0	3.3	4.4	0.4	1255.5	221.9	2192.5	779.5	51.8	3.4	186.0	76.6
RT12.48	124.6	9.0	221.9	90.6	6.0	3.1	14.7	4.9	1338.3	447.4	2641.4	800.6	85.6	1.5	308.3	127.0
RT15.25	249.5	58.2	409.1	171.8	42.5	1.1	132.7	56.0	1091.5	52.5	2458.3	950.2	14.7	6.9	17.6	4.6
RT16.62	531.3	33.0	2263.7	970.1	17.7	6.7	40.6	14.2	4425.7	283.9	11,347.6	4314.9	3993.7	2104.1	6860.2	1767.1
Sum	1949.5	125.9	5055.0	2116.8	313.6	24.5	930.4	400.3	9318.1	1108.2	20,709.1	7645.1	4538.2	2139.6	7700.7	2097.1
Total sum, µg/g dry wood	47975.3	11,728.3	101,130.0	33,787.1	9077.9	2181.7	17,018.2	7058.1	98,156.6	66,787.2	155,927.1	37,597.0	81,423.2	75,058.5	93,625.9	7202.9

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