Wood Sci Technol (2004) 38: 245–256
DOI 10.1007/s00226-004-0241-9

ORIGINAL

Frédérique Bertaud · Bjarne Holmbom

Chemical composition of earlywood and latewood in Norway spruce heartwood, sapwood and transition zone wood

Received: 20 November 2000 / Published online: 27 May 2004

Abstract This study focused on the distribution of wood components along a cross section of a spruce stem. Thin samples of earlywood and latewood were analysed by special micro-scale analytical techniques. Heartwood contained significantly more lignin and less cellulose than sapwood. The total content of hemicelluloses was the same along the radial direction, but the distribution of sugar units differed. The amounts of arabinoglucuronoxylan and pectins were larger in the heartwood. The transition zone between heartwood and sapwood had a specific composition, with less lignin and lipophilic extractives than heartwood and sapwood. For earlywood and latewood, significant differences were found in the distribution of sugar units in hemicelluloses. Latewood contained clearly more galactoglucomannan than earlywood, and conversely less pectins. The lipophilic extractives were also less concentrated in the latewood.

Abbreviations EW or E earlywood · LW or L latewood · HW heartwood · SW sapwood · TZ transition zone wood · A.R. annual ring · AcBr Acetyl bromide · Ara arabinose · Xyl xylose · Gal galactose · Glc glucose · Man mannose · Rha rhamnose · GlcA glucuronic acid · MGlcA 4-O-methyl-glucuronic acid · GalA galacturonic acid · o.d. oven dry

Introduction

Norway spruce (*Picea abies* L.) is a predominant softwood species in the European forest and is abundantly used in the pulp and paper industry, especially for mechanical pulp production. As any wood material, spruce wood is chemically complex and its morphological, physical and chemical characteristics are not uniform. Understanding the morphological and chemical heterogeneity of wood is important in the utilisation of wood for solid wood products as well as pulp and paper. Trees develop wide, thin-wall earlywood (EW) fibres in the beginning of the growth season and, later on, narrow and thick-wall latewood (LW) fibres. According to their cell wall

F. Bertaud · B. Holmbom (✉)
Process Chemistry Centre, Laboratory of Wood and Paper Chemistry,
Åbo Akademi University, 20500 Turku/Åbo, Finland
E-mail: Bjarne.Holmbom@abo.fi · Tel.: +358-2215-4229 · Fax: +358-2215-4868

ultrastructure, EW results in flexible band-shaped fibres in pulp, whereas LW gives stiff pulp fibres (Sjöström 1993; Rudie et al. 1994; Wennerblom et al. 1996; Tyrväinen 1997; Nyakuengama et al. 1998). Considering this different behaviour, the EW/LW ratio must be considered with respect to the pulp and paper quality (Wilson and Wellwood 1965; Paavilainen 1992; Wang and Braaten 1997). Not only physical but also chemical characteristics of fibres are important for the paper quality. Due to the fibre morphology, EW contains more lignin and inversely less cellulose than LW (Fengel and Wegener 1989; Wilson and Wellwood 1965; Timell 1986; Chen 1991). The hemicellulosic polymers are not uniformly distributed in the cell wall fibres, and consequently not in wood either. It has been reported that glucomannan occurs in higher concentrations in thick-wall LW fibres than in EW fibres, whereas arabinoglucuronoxylan has an inverse distribution (Timell 1965, 1986; Wilson and Wellwood 1965; Meier 1985; Sjöström 1993).

In the cross section of the stem, heartwood (HW) and sapwood (SW) is usually clearly distinguished. At the border of HW and SW, a transition zone (TZ) can be observed by a paler color than HW and SW (Kramer and Kozlowski 1979; Hillis 1985). The physical and chemical changes associated with the transition of SW to HW have been reviewed by several authors. Generally, HW contains less cellulose and holocellulose than SW, and therefore often has a lower density than SW (Timell 1986; Fengel and Wegener 1989; Chen 1991; Shupe et al.1997). Concerning hemicelluloses, only small differences have been observed between HW and SW (Rogers and Perkins 1968; Holmbom et al. 2000). The transformation of SW to HW is also accompanied, in many species, by accumulation of extractives, which can be detrimental in pulping and papermaking and cause so-called ''pitch problems'' (Timell 1986; Fengel and Wegener 1989).

The objective of the present study was to analyse spruce wood at the micro-scale level. The chemical composition of EW and LW was investigated in a Norway spruce tree along the radial direction (HW, TZ and SW). Micro-scale techniques were implemented on a large number of samples.

Experimental

Materials

A 49 year old healthy Norway spruce tree (*Picea abies* L.) grown in southern Finland was felled in December 1998. A 20-mm thick disk of the trunk was sawn out at the height of 1.5 m. The disk was symmetrical and visibly free of reaction wood, and did not contain knotwood. The HW zone was localised by visual inspection of the frozen disk. A 10-mm broad zone between HW and SW was considered as the transition zone. One stem section (section A, Fig. 1) was used for composite HW, TZ and SW samples. After freeze drying, the samples were ground in a Cyclo-Tec mill (Tecator Inc.) equipped with a screen of 0.5 mm. From another stem section (section B, Fig. 1), T-shaped pieces in each zone of the stem (HW, TZ and SW) were cut out as illustrated in Fig. 1. From these, EW and LW shavings were cut using a microtome (Leitz, Wetzlar) equipped with a stainless steel blade (Treichert, Austria). Three T-shaped pieces were microtomed to obtain enough sample for analysis (5–10 mg). The thin

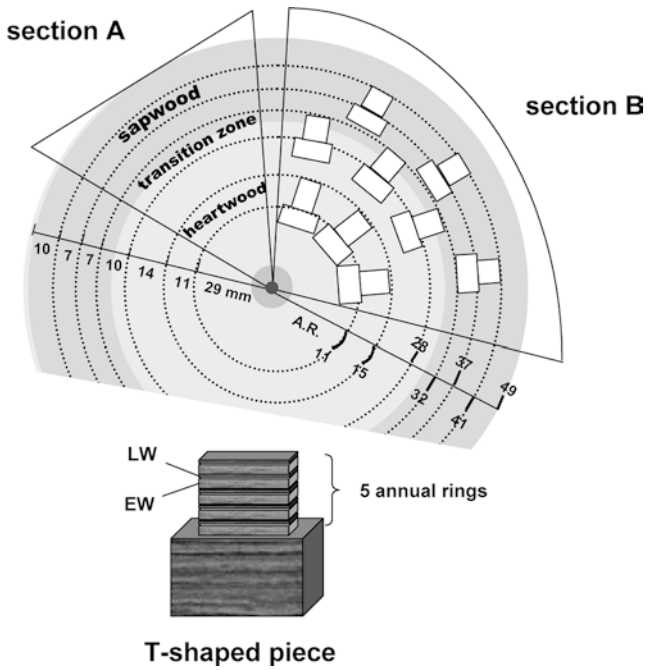

Fig. 1 Transversal section of the spruce tree disk (*Picea abies* L., 49 years old). Section A was used to prepare HW, TZ and SW samples containing five annual rings. In section B, three T-shaped pieces were cut from each zone for microtoming of EW and LW samples

shavings of EW and LW (10 mm×10 mm, 50–80 μm thickness) were freeze dried and stored at −24°C.

Analysis of wood components

The microtomed wood shavings were analysed by special micro-scale analytical techniques. Both traditional and micro-scale analytical methods were used for milled composite wood samples (HW, TZ and SW).

Hemicelluloses and pectins and their sugar composition were determined by acid methanolysis and GC analysis (Sundberg et al. 1996; Bertaud et al. 2002). 2 mL of a 2-M solution of HCl in anhydrous methanol was added to the sample (2 mg) and the sample was kept at 100°C (oven) for 5 h. A calibration solution containing the neutral and acid sugar monomers (D(-)Ara, D(+)Man, D(+)Xyl, D(+)Glc, D(+)Gal, L(+)Rha, D(+)GalA, D(+)GlcA in MeOH at 0.1 mg/mL) was methanolysed at the same conditions as the samples to obtain correction factors for losses of sugar residues during methanolysis. The methanolysed samples were silylated before the GC analysis. GC/MS was used for identification and verification of some sugar components.

Milled samples of HW, TZ and SW (300 mg) were extracted in a micro-Soxhlet apparatus with 30 mL of acetone. After 2 h of extraction and cooling, the volume of acetone was adjusted to 50 mL. A 4-mL aliquot was taken out and 2 mL of a standard solution (heneicosanoic acid, betulinol, cholesteryl heptadecanoate and 1,3-dipalmitoyl-2-oleylglycerol) in methyl *tert*.-butyl ether

containing 0.02 mg/mL of each standard component was added. After drying, the sample was silylated and 0.4 μL of the silylated sample was analysed by GC as described by Örså and Holmbom (1994) and Holmbom (1999).

Small samples (EW and LW shavings) and HW, TZ and SW milled wood (2–5 mg) were submitted to ultrasonic treatment in 25 mL acetone for 2 min using a titanium probe fit with a 13 mm tip (Sonic & Materials Vibra cell, 600 W, 20 kHz, amplitude 25%). After cooling, 1.6 mL of the above described standard solution diluted to 0.005 mg/mL was added. The solution was evaporated (evaporation temperature water bath≈40°C) to a final volume of 2–5 mL for further drying. After silylation, 2 μL of the sample was analysed by GC as above.

The wood residue after the ultrasonic extraction was transferred into a screw-capped test tube and subjected to lignin determination by the acetyl bromide (AcBr) procedure according to Johnson et al. (1961), and later modified by Iiyama and Wallis (1988). 5 mL of 20% (v/v) AcBr in acetic acid and 0.1 mL of perchloric acid (70%) were added to the wood residue. The sample was kept in an oven at 50°C for 3 h with regular shaking to promote dissolution of the sample. After treatment, the mixture was cooled down and transferred to a 50-mL volumetric flask containing 10 mL of 2-M sodium hydroxide and 12 mL of acetic acid. The solution was diluted to 50 mL with acetic acid. Its UV absorption was measured against a blank which was prepared in parallel with the sample. The lignin content of the sample was calculated from the absorbance at 280 nm and compared with a calibration curve obtained from an acetic acid lignin isolated from the pre-extracted spruce sample (Nikandrov et al. 1998).

The AcBr technique, applicable to very small samples, was compared to the classical Klason procedure on pre-extracted milled HW, TZ and SW samples. Lignin determination was performed according to the standard procedure (Tappi 222 om-98). The acid-soluble lignin in the liquor was estimated by the UV absorbance at 280 nm (absorption coefficient equal to 110 L g^{-1} cm^{-1}) (Dence 1992; Brunow et al. 1999).

Results and discussion

Heartwood, sapwood and transition zone wood

Main component groups

HW, TZ and SW samples from section A (Fig. 1) were analysed by both classical and micro-scale analytical techniques to determine the main components (Table 1).

The cellulose content increased along the cross section from HW to SW, corresponding to the decrease in lignin, as previously noticed (Timell 1986; Fengel and Wegener 1989; Chen 1991; Shupe et al. 1997). The total amount of hemicelluloses was almost the same along the cross section of the tree, as also noted by Sundberg et al. (1996) and Holmbom et al. (2000). In TZ, the lignin content was significantly lower than in the other parts. The AcBr procedure, applicable to very small samples, gave slightly higher lignin content than the Klason method, and had a lower accuracy ($\pm$5%). The sampling and the

analytical procedure could explain these observations (Iiayama and Wallis 1988). The calibration curve at 280 nm, and consequently the absorption coefficient obtained, is dependent upon the used lignin reference (Rodrigues et al. 1999). The acetic acid lignin reference, isolated from the spruce wood, had an absorption coefficient of 19.5 ± 0.2 L g^{-1} cm^{-1}, well in the range of literature values (Johnson et al. 1961; Marton 1967; Iiayama and Wallis 1988; Fengel and Wegener 1989; Dence 1992; Sjöström and Westermark, 1999). The absorptivity based on Klason lignin was higher than for the isolated lignin, as also reported by Rodrigues et al. (1999). The amounts of lipophilic extractives were below 1% (w/w o.d. wood) in all three wood zones. Both methods used, micro-soxhlet and ultra-sonic extraction, gave similar results. SW contained more lipophilic extractives than HW, in agreement with previous results (Ekman 1979a). TZ had the lowest amount of lipophilic compounds, as also noted by Higuchi et al. (1969), Ekman (1979b) and Hillis (1985). This can be due to the special cellular activities during growth within the transition zone of a tree (Bamber 1976; Kramer and Kozlowski 1979).

Carbohydrate composition of hemicelluloses and pectins in the different wood zones

The sugar composition of hemicelluloses and pectins in the HW, TZ and SW samples are presented in Fig. 2. The predominant hemicellulose type in spruce is galactoglucomannan (15–20% in softwood) (Sjöström and Westermark 1999), here noticed by the large amounts of mannose (Man) and glucose (Glc). The glucose and mannose contents were rather similar in the different wood zones (53 ± 2 and 100 ± 2 mg/g respectively for Glc and Man). Galactose (Gal), also occurring in galactans, was slightly larger in HW. Another major hemicellulose in spruce is arabinoglucuronoxylan (5–10%) (Sjöström and Westermark 1999), here represented by xylose (Xyl), arabinose (Ara) and 4-O-methylglucuronic acid (MGlcA). HW contained clearly more glucuronoxylan than SW with 25–30% more Xyl, Ara and MGlcA. These differences were also noted by Sjöström et al. (1965) and Luukko et al. (1999). The amount of pectins, represented by galacturonic acid (GalA) and rhamnose (Rha) was also highest in HW. The distribution of pectins between HW, SW and TZ has not been

Table 1 Main component groups in the different wood zones, in % (w/w) of o.d. wood

Component (Technique)	Heartwood HW	Transition zone wood TZ	Sapwood SW
Lignin			
(Acetyl bromide, UV)	32.4 ± 1.6[1]	29.5 ± 0.5	30.9 ± 0.8
(Klason)[2]	28.3 ± 0.3	27.3 ± 0.2	27.7 ± 0.1
Hemicelluloses			
(Methanolysis, GC)	25.7 ± 1.4	25.3 ± 1.4	24.3 ± 1.4
Lipophilic extractives			
(Micro-Soxhlet, GC)	0.51 ± 0.03	0.44 ± 0.05	0.88 ± 0.05
(Ultrasonic, GC)	0.57 ± 0.8	0.45 ± 0.6	0.91 ± 0.7
Cellulose[3]			
(By difference)	45.5 ± 1.7	46.9 ± 1.4	47.1 ± 1.6

[1] standard deviation for three determinations;
[2] including the acid-soluble part, only 0.7% of wood;
[3] (100 - Klason lignin—hemicelluloses—lipophilics)

determined previously. The composition of hemicelluloses in TZ was between HW and SW. However, the glucuronic acid content (GlcA) was lower in TZ than in HW and SW.

Lipophilic extractives

SW contained more lipophilic extractives than HW and TZ (Table 2), as noted previously by Ekman (1979a). This was due mainly to the larger amount of triglycerides. Triglycerides, as well as steryl esters, occur in living parenchyma cells. When HW is formed and the parenchyma cells die, the triglycerides are hydrolysed by lipase enzymes. The amount of free fatty acids was slightly higher in the HW, as previously reported (Ekman1979b; Fengel and Wegener 1989), but most of the fatty acids had obviously been metabolised. Also, the amount of steryl esters was slightly smaller in HW. The amount of free sterols was larger, thus indicating some hydrolysis of steryl esters during HW formation. TZ contained more triglycerides than HW, but contained less of all the other groups. Lignans were detected in small amounts in HW but not in SW and TZ.

Both extraction methods gave similar results. However, it seems that triglycerides were hydrolysed to some extent during ultrasonic extraction. There is a risk for oxidation of extractives during ultrasonic treatment, especially if water is present, since hydroxyl radicals can be formed.

Earlywood and latewood

Main components

Samples of EW and LW from five successive annual rings were analysed for each wood part using the micro-scale techniques: AcBr method for lignin, methanolysis and GC for hemicelluloses and pectins, and ultrasonic extraction and GC for lipophilic extractives. The amounts of the main component groups of EW and LW in HW, SW and TZ are presented in Tables 3, 4 and 5, respectively.

All EW samples contained significantly more lignin than LW in the same annual ring, already noticed by many researchers. The amounts of hemicelluloses and pectins followed the opposite trend, with higher levels in LW. The

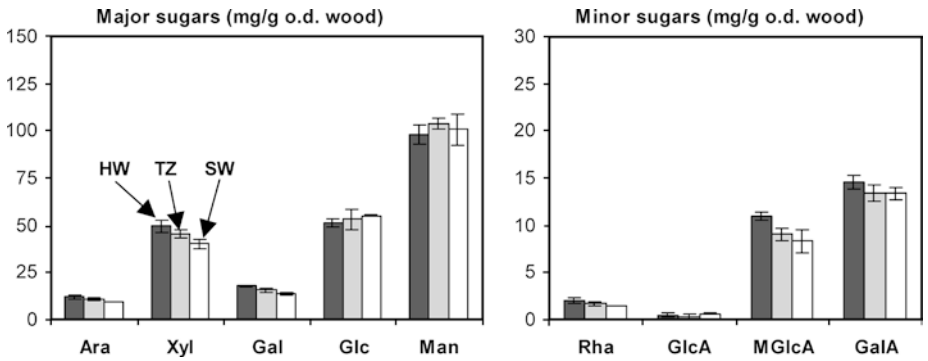

Fig. 2 Sugar composition of hemicelluloses and pectins in heartwood (HW), transition zone wood (TZ) and sapwood (SW). The standard deviation for the three determinations are pointed out

Table 2 Lipophilic extractives in the different wood zones determined by extraction and GC analysis, in mg/g of o.d. wood

Sample	Technique	Free fatty acids	Sterols	Steryl esters	Triglycerides	Resin acids	Total
Heartwood	Micro-Soxhlet	1.1 ± 0.1	0.167 ± 0.001	1.10 ± 0.04	0.68 ± 0.03	1.9 ± 0.1	5.1 ± 0.3
	Ultrasonic	1.3 ± 0.2	0.17 ± 0.02	1.0 ± 0.1	0.688 ± 0.001	2.4 ± 0.4	5.7 ± 0.8
Transition Zone wood	Micro-Soxhlet	0.4 ± 0.1	0.10 ± 0.01	0.8 ± 0.1	1.74 ± 0.016	1.1 ± 0.1	4.4 ± 0.5
	Ultrasonic	0.8 ± 0.1	0.10 ± 0.01	0.7 ± 0.1	1.58 ± 0.03	1.1 ± 0.4	4.5 ± 0.6
Sapwood	Micro-Soxhlet	0.6 ± 0.1	0.062 ± 0.003	1.4 ± 0.1	4.48 ± 0.12	2.2 ± 0.1	8.8 ± 0.5
	Ultrasonic	0.7 ± 0.2	0.062 ± 0.006	1.3 ± 0.1	4.13 ± 0.03	2.5 ± 0.3	9.1 ± 0.7

amount of cellulose, calculated as the rest, was slightly larger in most LW samples. No clear differences could be observed between the five annual rings. A predominant incorporation of lipophilic extractives in EW was also mentioned by Lloyd (1978). Resin canals, usually more numerous in EW, would influence the amounts of extractives.

The standard deviation of the EW values were larger than the LW values, expressing the larger heterogeneity of EW, because the spring wood of annual rings was much thicker than the summer wood (Fig. 1). The contents of the main components in EW and LW samples should not be compared with the values of each wood part previously presented (Table 1). Indeed, the chemical composition of each annual ring depends on the growth conditions. Nevertheless, a special feature of TZ (Table 5) was a low lignin content in both EW and LW (Tables 3 and 4). This was in line with our previous observation (Table 1) indicating special metabolic activities in TZ (Higuchi et al. 1969).

Carbohydrate composition of hemicelluloses and pectins in earlywood and latewood

The carbohydrate composition of hemicelluloses and pectins differed notably between EW and LW. LW contained more galactoglucomannan for all three

Table 3 Main component groups in earlywood (E) and latewood (L) samples of successive annual rings of spruce heartwood (HW), in % (w/w) of o.d. wood

E or L samples Annual ring	Lignin	Hemicelluloses and Pectins	Extractives	Cellulose
E11	33.6 ± 0.9	24.3 ± 1.5	0.3 ± 0.1	41.8 ± 2.5
L11	30.0 ± 0.9	25.8 ± 1.1	0.3 ± 0.1	44.0 ± 2.0
E12	33.6 ± 1.6	23.8 ± 0.7	0.3 ± 0.1	42.3 ± 2.3
L12	31.0 ± 1.0	24.7 ± 1.5	0.2 ± 0.0	44.1 ± 2.5
E13	30.4 ± 0.7	24.9 ± 0.8	0.1 ± 0.0	44.6 ± 1.6
L13	29.1 ± 0.5	25.1 ± 1.7	0.2 ± 0.1	45.6 ± 2.3
E14	31.4 ± 0.9	22.6 ± 1.0	0.3 ± 0.1	45.7 ± 1.9
L14	29.9 ± 1.0	26.7 ± 1.6	0.2 ± 0.0	43.3 ± 2.6
E15	31.8 ± 0.2	20.7 ± 2.0	0.3 ± 0.1	47.2 ± 2.2
L15	29.4 ± 0.2	24.2 ± 1.3	0.2 ± 0.1	46.3 ± 1.5
E average	32.2 ± 1.4	23.2 ± 1.7	0.3 ± 0.1	44.3 ± 2.3
L average	29.8 ± 0.7	25.3 ± 1.0	0.2 ± 0.0	44.7 ± 1.2

Table 4 Main component groups in earlywood (E) and latewood (L) samples of successive annual rings of spruce sapwood (SW), in % (w/w) of o.d. wood

E or L samples Annual ring	Lignin	Hemicelluloses and Pectins	Extractives	Cellulose
E37	28.8 ± 1.6	22.1 ± 1.1	0.6 ± 0.0	48.5 ± 2.6
L37	27.6 ± 0.9	23.7 ± 1.4	0.4 ± 0.1	48.2 ± 2.4
E38	29.7 ± 1.0	22.3 ± 2.3	0.6 ± 0.1	47.3 ± 3.3
L38	26.7 ± 1.6	24.0 ± 1.4	0.3 ± 0.0	49.0 ± 3.0
E39	33.2 ± 0.6	21.2 ± 2.5	0.5 ± 0.1	45.1 ± 3.1
L39	26.9 ± 0.2	22.8 ± 1.7	0.4 ± 0.1	49.8 ± 1.9
E40	31.4 ± 3.3	21.2 ± 2.1	0.8 ± 0.1	46.6 ± 5.5
L40	27.2 ± 1.2	23.1 ± 1.5	0.2 ± 0.1	49.5 ± 2.7
E41	29.8 ± 0.3	20.2 ± 2.0	0.7 ± 0.1	49.4 ± 2.3
L41	29.3 ± 6.0	23.1 ± 1.4	0.5 ± 0.1	47.2 ± 7.4
E average	30.6 ± 1.7	21.4 ± 0.9	0.6 ± 0.1	47.4 ± 1.7
L average	27.5 ± 1.0	23.3 ± 0.5	0.4 ± 0.1	48.7 ± 1.1

Table 5 Main component groups in earlywood (E) and latewood (L) samples of successive annual rings of spruce transition zone wood (TZ), in % (w/w) of o.d. wood

E or L samples Annual ring	Lignin	Hemicelluloses and Pectins	Extractives	Cellulose
E28	29.7 ± 0.5	20.7 ± 0.0	0.2 ± 0.0	49.5 ± 0.6
L28	26.7 ± 0.5	22.1 ± 0.8	0.1 ± 0.0	51.0 ± 1.4
E29	31.3 ± 0.4	21.4 ± 0.6	0.2 ± 0.0	47.1 ± 1.0
L29	27.4 ± 1.8	24.1 ± 1.0	0.3 ± 0.1	48.2 ± 2.9
E30	28.9 ± 0.9	22.6 ± 1.1	0.2 ± 0.0	48.3 ± 2.0
L30	26.4 ± 1.9	21.6 ± 0.9	0.2 ± 0.0	51.8 ± 2.8
E31	27.8 ± 0.2	22.6 ± 1.3	0.1 ± 0.0	49.5 ± 1.5
L31	26.5 ± 0.5	24.2 ± 1.2	0.3 ± 0.0	49.0 ± 1.6
E32	29.1 ± 0.6	20.9 ± 0.7	0.2 ± 0.0	49.7 ± 1.3
L32	29.6 ± 1.3	23.2 ± 1.0	0.2 ± 0.2	47.0 ± 2.4
E average	29.4 ± 1.3	21.6 ± 0.9	0.2 ± 0.1	48.8 ± 1.1
L average	27.3 ± 1.3	23.1 ± 1.2	0.2 ± 0.1	49.4 ± 2.0

studied wood parts, as also mentioned by Sjöström and Westermark (1999). For xylose (Xyl) and arabinose (Ara), only small differences were found, indicating similar amounts of arabinoxylan in LW and EW (Figs. 3, 4, and 5). Considering the thicker secondary wall in LW fibres, a higher mannan content in LW can be expected since this component is preferentially incorporated in the S_2 layer as mentioned by Timell (1965, 1986) and Sjöström (1993). Pectins, mainly represented by GalA and Rha, were more predominant in EW. This can be explained by their specific location in the compound middle lamella (Sjöström et al. 1965; Timell 1965; Meier 1985; Hafrèn 1999).

In the transition zone, the GlcA amounts were very low in both EW and LW, confirming the previous TZ analysis (Fig. 2). The LW samples of TZ contained clearly less of all hemicellulosic components than LW samples of HW and SW. Even the mannose and glucose amounts were smaller in LW than EW for TZ, contrary to results for HW and SW (Fig. 5).

Summary of results

The chemical composition of HW, TZ and SW in a Norway spruce stem section showed specific differences. The cellulose content decreased along the cross section from SW to HW, with a corresponding increase in lignin, whereas the amounts of hemicelluloses and pectins were about the same. However, HW contained more glucuronoxylan and pectins than SW. The amount of lipophilic extractives (below 1% w/w o.d. wood) was higher in SW, due mainly to a larger amount of triglycerides. In TZ, the amounts of lignin and lipophilic extractives

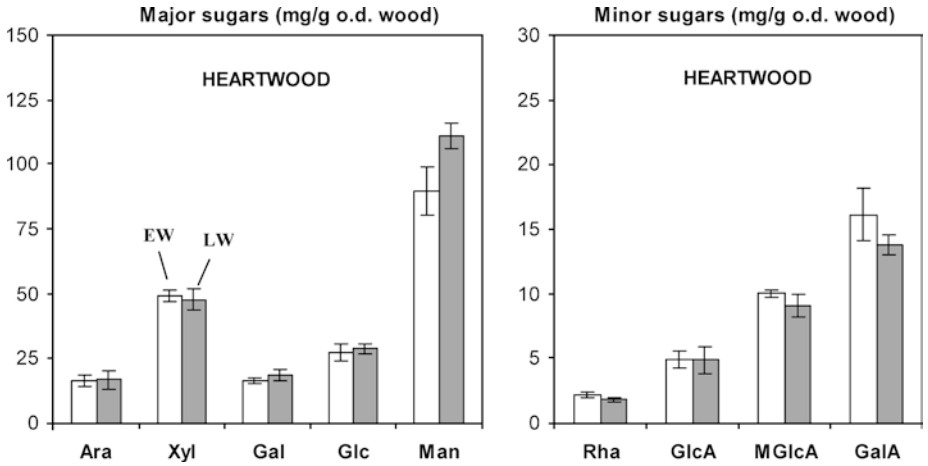

Fig. 3 Sugar composition of hemicelluloses and pectins in earlywood (EW) and latewood (LW) of spruce heartwood (HW); average of five successive annual rings

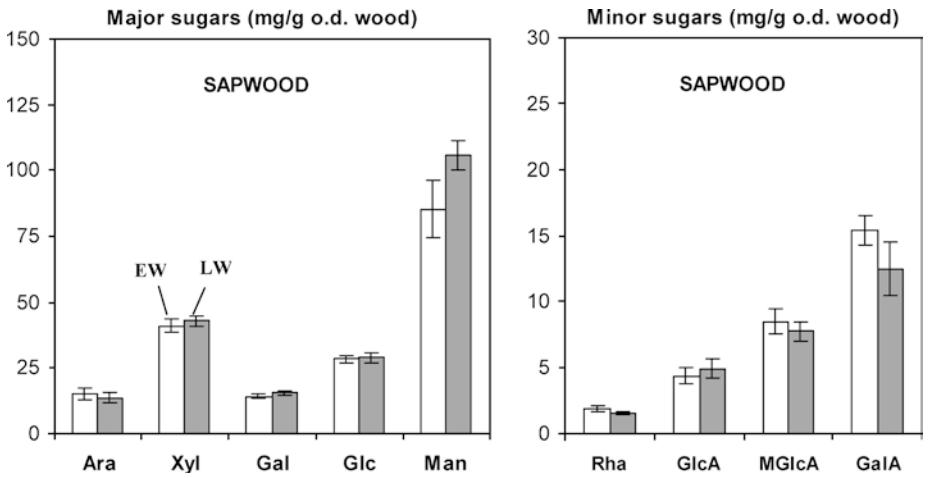

Fig. 4 Sugar composition of hemicelluloses and pectins in earlywood (EW) and latewood (LW) of spruce sapwood (SW); average of five successive annual rings

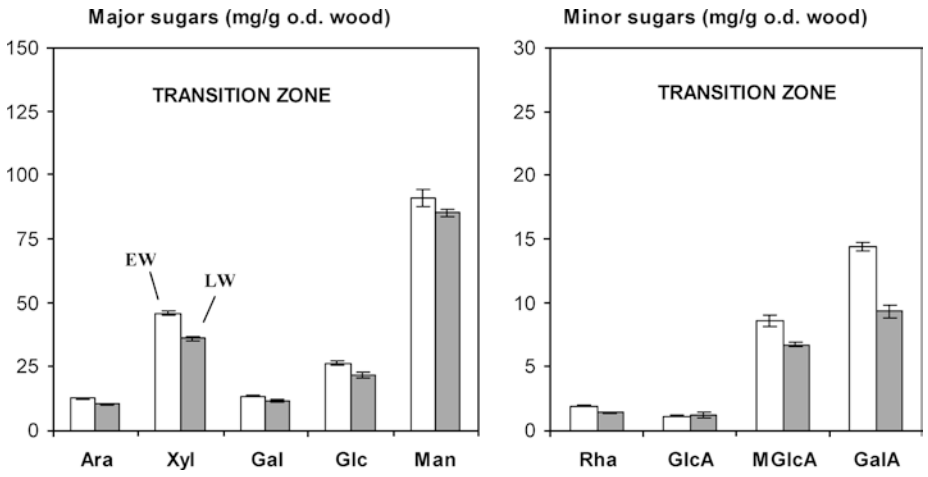

Fig. 5 Sugar composition of hemicelluloses in earlywood (EW) and latewood (LW) of spruce transition zone wood (TZ); average of five successive annual rings

were very small, probably attributed to the specific metabolic activities in this region of the wood stem.

According to the different morphology of EW and LW fibres, the thick-wall fibres of LW contained more holocelluloses (celluloses + hemicelluloses) and conversely less lignin than EW fibres. A clearly higher content of galactoglucomannan was found in LW, as mannose is preferentially incorporated in the S_2-layer of fibre walls. A larger amount of pectins (GalA, Rha) in EW may be explained by their preferential location in the middle lamella. The amount of lipophilic extractives was also larger in EW than in LW. In TZ, the differences between EW and LW were not so clear.

Acknowledgements The authors want to thank Jarl Hemming and Markku Reunanen for their valuable advice and technical support. This work was a part of the activities of the Åbo Akademi Process Chemistry Centre, a National Centre of Excellence supported by the Academy of Finland.

References

Bamber RK (1976) Heartwood, its function and formation. Wood Sci Technol 10:1–8

Brunow G, Lundquist K, Gellerstedt G (1999) Lignin. In: Sjöström E, Alén R (eds) Analytical methods in wood chemistry, pulping, and papermaking. Springer, Berlin Heidelberg New York, pp 77–125

Bertaud F, Sundberg A, Holmbom B (2002) Evaluation of acid methanolysis for analysis of wood hemicelluloses and pectins. Carbohyd Polym 48:319–324

Chen C L (1991) Lignins: occurrence in woody tissues, isolation, reactions and structure. In: Lewin M, Goldstein IS (eds) Wood structure and composition. Marcel Dekker, New York, pp 183–263

Dence CW (1992) The determination of lignin. In: Lin SY, Dence CW (eds) Methods in lignin chemistry. Springer, Berlin Heidelberg New York, pp 33–62

Ekman R (1979a) Distribution of lignans in Norway spruce. Acta Acad Abo Ser B 39(3):1–6

Ekman R (1979b) Analysis of nonvolatile extractives in Norway spruce sapwood and heartwood. Acta Acad Abo Ser B 39(4):1–20

Fengel D, Wegener G (1989) Wood. de Gruyter, New York

Hafrén J (1999) Ultrastructure of the wood cell wall. PhD Thesis, Royal Institute of Technology, Stockholm, Sweden
Higuchi T, Onda Y, Fujimoto Y (1969) Biochemical aspects of heartwood formation with special reference to the site of biogenesis of heartwood compounds. Wood Res 48: 5–30
Hillis WE (1985) Occurrence of extractives in wood tissue. In: Higuchi T (ed) Biosynthesis and biodegradation of wood components. Academic, New York, pp 209–226
Holmbom B (1999) Extractives. In: Sjöström E, Alén R (eds) Analytical methods in wood chemistry, pulping, and papermaking. Springer, Berlin Heidelberg New York, pp 125–149
Holmbom B, Pranovich AV, Sundberg A, Buchert J (2000) Charged groups in wood and mechanical pulps. In: Kennedy JF, Phillips GO, Williams PA (eds) Pulp for papermaking. Woodhead, Cambridge, pp 109–119
Iiyama K, Wallis AFA (1988) An improved acetyl bromide procedure for determining lignin in woods and wood pulps. Wood Sci Technol 22:271–280
Johnson DB, Moore WE, Zank LC (1961) The spectrophotometric determination of lignin in small wood samples. Tappi 44(11):793–798
Kramer PJ, Kozlowski TT (1979) Physiology of woody plants. Academic, New York
Lloyd JA (1978) Distribution of extractives in *Pinus radiata* earlywood and latewood. N Zeal J For Sci 2:288–294
Luukko K, Laine J, Pere J (1999) Chemical characterization of different mechanical pulp fines. Appita 52(2):126–131
Marton J (1967) Determination of lignin in small pulp and paper samples using the acetyl bromide method. Tappi 50(7):335–337
Meier H (1985) Localization of polysaccharides in wood cell walls. In: Higuchi T (ed) Biosynthesis and biodegradation of wood components. Academic, New York, pp 43–50
Nikandrov A, Sévillano RM, Mortha G, Robert D, Zaroubin MY, Lachenal D (1998) Characterisation of residual lignins from oak kraft pulps isolated by acetic acid and $ZnCl_2$. In: Proceedings of the 5th EWLP. University of Aveiro, pp 165–169
Nyakuengama JG, Matheson C, Spencer D, Evans R, Vinden P (1998) Correlation among growth, density, fibre diameter and heartwood in radiata pine. Appita J 51(1):35–38
Örså F, Holmbom B (1994) A convenient method for the determination of wood extractives in papermaking process waters and effluents. J Pulp Pap Sci 20(12):J361–366
Paavilainen L (1992) The possibility of fractionating softwood sulfate pulp according to cell wall thickness. Appita J 45(5):319–326
Rodrigues J, Faix O, Pereira H (1999) Improvement of the acetyl bromide method for lignin determination within large scale screening programmes. Holz Roh Werkst 57:341–345
Rogers HJ, Perkins HR (1968) Cell wall and membranes. E&FN Spon, London, pp 27–45
Rudie AW, Morra J, St Laurent JM, Hickey KL (1994) The influence of wood and fiber properties in mechanical pulping. Tappi J 77(6):86–90
Shupe TF, Hse CY, Choong ET, Groom LH (1997) Differences in some chemical properties of innerwood and outerwood from five silviculturally different loblolly pine stands. Wood Fiber Sci 29(1):91–97
Sjöström E (1993) Wood chemistry, fundamentals and applications. Academic, London
Sjöström E, Janson J, Haglund P, Enström B (1965) The acidic groups in wood and pulp as measured by ion exchange. J Polym Sci 11:221–241
Sjöström E, Westermark U (1999) Chemical composition of wood and pulps: basic constituents and their distribution. In: Sjöström E, Alén R (eds) Analytical methods in wood chemistry, pulping, and papermaking. Springer, Berlin Heidelberg New York, pp 1–21
Sundberg A, Sundberg K, Lillandt C, Holmbom B (1996) Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography. Nord Pulp Pap Res J 11(4):216–219
Timell TE (1965) Wood and bark polysaccharides. In: Côte WA (ed) Cellular ultrastructure of woody plants. Part II: wood constituents—their chemistry, biosynthesis, ultrastructure, and physical characteristics. Syracuse University Press, New York, pp 127–157
Timell TE (1986) Compression wood in Gymnosperms, vol I. Springer, Berlin Heidelberg New York, pp 410–416
Tyrväinen J (1997) Newsgrade TMP from three different Norway spruce (*Picea abies*) wood assortments in mill scale. Pulp Pap-Canada 98(10):T376–385
Wang X, Braaten KR (1997) Growth rings and spruce pulpwood sorting. Nord Pulp Pap Res J 12(3):196–202
Wennerblom M, Frövi AD, Olsson AM, Salmén L (1996) Softening properties of earlywood and latewood of spruce. Nord Pulp Pap Res J 4:279–280

Wilson JW, Wellwood RW (1965) Intra-increment chemical properties of certain western Canadian coniferous species. In: Côte WA (ed) Cellular ultrastructure of woody plants. Syracuse University Press, New York, pp 551–559