ANALYSIS OF LIPOPHILIC EXTRACTIVES IN POPULUS×EURAMERICANA 'NEVA'

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Lipophilic extractives in the stemwood and bark of *Populus*×*euramericana* 'Neva' were analyzed by GC, GC-MS, and high-performance size exclusion chromatography (HPSEC). The top stemwood and bark contained much larger amounts of lipophilic extractives than the corresponding bottom ones. The lipophilic extractives identified were composed of five component groups, i.e. glycerides, steryl esters, free fatty acids, sterols and free fatty alcohols, both in the stemwood and bark. 4-Hydroxycinnamic acid esters of fatty alcohols were identified in a small amount in this wood species. Glycerides, mainly triglycerides, were the largest component group of the lipophilic extractives, and linoleic (18:2) acid was the major fatty acid in triglycerides. The low ratio of acids to unsaponifiables of this aspen wood, especially in the bottom stemwood, could probably have a negative effect on pitch problems. Small amounts of oligomeric or polymeric material with higher molar mass than the triglycerides were present only in bark.

Keywords: lipophilic extractives, *Populus*×*euramericana* 'Neva', stemwood, bark, wood resin, pitch control

INTRODUCTION

Paper production in Asia, especially in China, has been growing fast in the past decade. Two fast-growing aspen species, *Populus*×*euramericana* 'Neva' and *Populus*×*euramericana* 'Guariento' (the so-called aspen 107 and 108, respectively, in China) are increasingly used in kraft or mechanical pulp production.[1] *Populus*×*euramericana* 'Neva', which is originally from Italy, is a hybrid from *Populus deltoids* and *P. nigra* and is now cultivated in China. *Populus*×*euramericana* 'Neva' is regarded as one of the most suitable aspen species grown in China, especially in North China. *Populus*×*euramericana* 'Neva' and 'Guariento' have been widely planted in North China in the recent years, and most pulp mills in North China use the two species chips to produce kraft pulp, APMP or CTMP.

It has been known for long that pitch problems during aspen kraft pulping are caused by the resin or so-called lipophilic extractives.[2] Wood extractives can cause deposit formation on pulp and paper equipment through a series of mechanisms, resulting in a negative impact on the paper machine runnability and product quality, particularly in paper mills with a high degree of white-water closure.[3-6] Fatty acids, resin acids, some steryl esters, and triglycerides form water-soluble soaps under alkaline conditions. Neutral components, such as hydrocarbons, diterpenols and diterpene aldehydes, sterols, triterpenols and certain alkali-stable steryl esters do not form soluble soaps and have a tendency to deposit and cause pitch problems.[3] It has been estimated that the ratio of acids to unsaponifiables should be about 3:1 to achieve good deresination in kraft pulping.[7] Pietarinen *et al*.[8] studied the chemical composition of wood resin in wood and knots of *P. grandidentata* (bigtooth aspen) and *P. tremuloides* (quaking aspen). The results showed that triglycerides, short-chain fatty acids (C14 to C20), and steryl esters were predominant in the sapwood samples. However, monoglycerides, long-chain fatty acids and alcohols (C22 to C28),

hydroxy fatty acids and ferulic acid esters of fatty alcohols were the major components in the heartwood and knots of the two species. Another study showed that the ratio in fresh *P. tremuloides* sapwood is about 2:1, which can therefore explain the pitch problems occurring during kraft pulping.[9] The bark contains a much larger amount of resin than the stemwood of the same tree. The bark is a rich source of many substances used for such applications as in adhesives, pharmaceuticals and biocides.[10] However, bark will cause even more severe problems, if they retain in wood chips for pulping.

In China, pitch problems often occur in the related pulp and paper mills, which use *Populus×euramericana* 'Neva' as raw material. However, no study of its extractives has been reported so far. In this work, the chemical composition of the lipophilic extractives from the stemwood and bark of this aspen species was determined. The study will supply basic and valuable information to help solve pitch problems in the pulp and paper mills using this wood species as raw material.

EXPERIMENTAL

Material

Stemwood sections were cut out at two different heights of a 5-year-old and 14.5-meter-high *Populus×euramericana* 'Neva' tree in Jinan, China, in June 2006. The top part with a diameter of 12.5 cm at the height of 8.3 m, and the bottom part with a diameter of 24.5 cm at the height of 1.3 m were then sampled from both bark and stemwood of the tree. The samples were frozen, splintered, freeze-dried, and ground in a disc mill (FFC-15, Qingdao, Shandong). The wood meal (40 to 60 mesh) was freeze-dried again to ensure practically complete removal of volatile compounds.

Methods

The dried samples were sequentially extracted with an ASE apparatus (Accelerated Solvent Extractor, Dionex Corp.) according to Willför *et al*.[11] The lipophilic extractives were extracted with *n*-hexane (solvent temperature – 90 °C, pressure – 138 MPa, two 5 min static cycles). The amount of extractives was gravimetrically determined after evaporation of the solvent. After evaporation of the extract solutions and silylation of the extractives, free fatty acids, fatty alcohols, sterols and fatty acid monoglycerides were analyzed by gas chromatography (GC) on a 25 m × 0.20 mm i.d. column coated with cross-linked methyl polysiloxane (HP-1) with a film thickness of 0.11 µm according to Ekman and Holmbom,[12] and Willför *et al*.[13] Heneicosanoic acid and betulinol were used as internal standards. No FID correction factors were used. The practical limit of quantification of each component was about 0.01 mg/g, but compounds present in smaller amounts could also be identified and reported as 'trace amount'.

Steryl esters, di- and triglycerides were quantified on a short 6 m × 0.53 mm i.d. column coated with cross-linked methyl polysiloxane (HP-1) with a film thickness of 0.15 µm, according to Örså and Holmbom[14] and Willför *et al*.[11] Cholesteryl heptadecanoate (for ferulic acid and steryl esters and diglycerides) and 1,3-dipalmitoyl-2-oleyl glycerol (for triglycerides) were used as internal standards. No FID correction factors were used.

The total fatty acids, fatty alcohols and sterols were analyzed by alkaline hydrolysis, using 0.5 N KOH solution in 90% aqueous EtOH. After the alkaline hydrolysis, the extracts were allowed to stand for 5 h at 70 °C. Afterwards, distilled water and one drop of bromocresol green solution were added. The solutions were acidified to pH 3 using 0.5 M HCl. The acidic and neutral components were extracted three times with methyl tert-butyl ether. The extracted fractions were combined, evaporated, silylated and analyzed by GC on a long column. All results were calculated on a dry wood basis.

The identification of individual components was performed by GC-MS analysis of the silylated components with an HP 6890-5973 GC-quadrupole-MSD instrument, using a similar GC column as described above.

The molar-mass distribution of extractives was determined by high-performance size exclusion chromatography (HPSEC) on a system of TSH G3000, TSK G2500 and TSK G1500 HXL columns with a guard column and a Pharmacia LKB 2142 differential refractometric detector. Tetrahydrofuran was used as eluent with a flow rate of 1 mL/min. The concentration of each sample was adjusted to a concentration of 1.5 mg/mL of extractives for all samples. The injection volume was 100 µL.

RESULTS AND DISCUSSION

The gravimetric amounts of lipophilic extractives from top stemwood (6.9 mg/g) and

bark (20.6 mg/g) of *Populus×euramericana* 'Neva' were much larger than those from bottom stemwood (4.3 mg/g) and bark (9.6 mg/g), respectively. The bark obviously contained much larger amounts of extractives than the corresponding stemwood. Compared with other aspen species, this wood species has less extractives. For example, the extractives amounts of this wood species, whether the top stemwood or bottom stemwood are lower than the average amounts of sapwood and heartwood extractives in *P. grandidentata* (16 mg/g and 3.7 mg/g) and *P. tremuloides* (17 mg/g and 6.4 mg/g).[8]

As shown in Table 1, the lipophilic extractives identified by GC were composed of five main component groups, i.e. glycerides, steryl esters, free fatty acids, sterols and free fatty alcohols, both in the stemwood and bark. In addition, ferulic acid esters, 4-hydroxycinnamic acid esters, hydroxy-fatty acid esters, alkanes, α-amyrin and its esters were also identified in the stemwood and bark. The results also show that the chemical composition of lipophilic extractives of this wood species is quite similar with the other two aspen species, indicating that different aspen species have a similar chemical composition of the extractives, although they have different extractive amounts.

The amount of free fatty acids was notably smaller in the stemwood than that in the bark (Table 1). The top stemwood and especially the top bark contained a much larger amount of free fatty acids than the corresponding bottom parts. The short-chain fatty acids (16 to 20 C atoms) dominated over the long-chain ones (22 to 30 C atoms) in the stemwood. It is interesting that the top bark contained much more long-chain fatty acids (2.16 mg/g) than the short-chain ones (0.38 mg/g). Among the short-chain free fatty acids in bark, the fatty acid 18:2 dominated over the others (Figure 1). Fatty acid 26:0 was present as the major components in the long-chain free fatty acids in the top bark.

After alkaline hydrolysis, the amount of fatty acids was increased sharply (Table 1). For example, the fatty acid 18:2 was increased about 10 times in stemwood after alkaline hydrolysis. Fatty acid 20:1 was not present in free form in the extractives from stemwood, but was released after hydrolysis. The short-chain fatty acids still dominated over the long-chain ones in the stemwood after hydrolysis. In the extractives from bark, the amounts of fatty acids 16:0 and 18:3 increased significantly as well after hydrolysis. However, 18:2 was still the dominant fatty acid. The results also showed that the amount of the total fatty acids in the top bark was 3.3 times larger than that in the bottom bark.

In addition, some hydroxy fatty acids, such as 1,22 dioic-22:0 acid in free form (Figure 1) and 16-hydroxy-16:0 acid in esterified form were also observed in the stemwood and bark (Table 1).

Glycerides, including mono-, di- and triglycerides, were the largest component group of the lipophilic extractives, with 43% to 63% of all GC-eluted compounds both in the stemwood and bark (Table 1). Similarly to the free fatty acids, the glycerides were also increased with an increase in the tree height, from 1.32 mg/g in the bottom stemwood to 3.63 mg/g in the top one. The bark contained almost 1.8 times larger glycerides than the corresponding stemwood. Triglycerides dominated in all wood samples over the mono- and diglycerides. The results of alkaline hydrolysis showed that all the glycerides disappeared, and fatty acid 18:2 was the predominant fatty acid, indicating that linoleic (18:2) acid was the major fatty acid in the triglycerides. In addition, monoglycerides of fatty acids 24:0, 26:0, and 18:2 acid were also observed in small amounts.

Steryl esters, the second most abundant compounds in the extractives contained 18% to 30% of the total lipophilic extractives in stemwood, and about 10% of the total lipophilic extractives in bark (Table 1). The amounts of steryl esters were on the same level in the stemwood. However, the top bark contained a larger amount of steryl esters than the bottom one. Alkaline hydrolysis could lead to a much higher concentration of sitosterol, which meant that sitosterol was the major sterol in the steryl ester (Figure 1).

The amount of sterols was on the same level in the whole stemwood or in the whole bark. Sitosterol was the major sterol component present in all the samples and released 3 to 7 times more after alkaline hydrolysis, indicating that sterols existed mainly as esterified compounds (Table 1). Small amounts of lupeol and sitostanol were also identified in stemwood and bark. Citrostadienol was only observed after alkaline hydrolysis. A much higher concentration of α-amyrin after hydrolysis indicated the presence of α-amyrin esters of fatty acids in stemwood and bark. The results also showed that steryl esters disappeared after the alkaline hydrolysis, indicating that the

hydrolysis conditions could result in the complete hydrolysis of steryl esters.

Small or trace amounts of free fatty alcohols 24:0, 26:0, and 28:0 were also observed in free form in stemwood and bark, and the top bark contained a much higher concentration of free fatty alcohols, especially fatty alcohols 26:0 and 28:0 (Table 1).

Table 1
Lipophilic extractives in *Populus*×*euramericana* 'Neva' by GC amounts given in mg/g dry wood

	Top stemwood	Top stemwood AH[1]	Bottom stemwood	Bottom stemwood AH	Top bark	Top bark AH	Bottom bark	Bottom bark AH
Fatty acids								
16:0	0.07	0.53	0.05	0.34	0.10	0.97	0.09	0.29
18:2	0.26	2.73	0.12	1.34	0.15	5.62	0.19	1.03
18:3	0.06	0.43	0.04	0.31	0.05	1.31	0.07	0.28
9-18:1	0.01	0.09	0.01	0.04	0.02	0.17	0.02	0.07
18:0	0.01	0.07	0.01	0.04	0.02	0.17	0.02	0.06
20:0	0.01	0.02	+[7]	0.01	0.01	0.09	0.01	0.03
20:1		0.01		0.01		0.04		0.01
22:0	0.02	0.06	0.02	0.03	0.18	0.41	0.05	0.12
24:0	0.02	0.05	0.02	0.04	0.49	1.04	0.05	0.23
26:0	+	0.05	0.01	0.03	1.03	1.51	0.10	0.25
27:0		+		+		0.04		0.02
28:0	+	0.04	0.01	0.02	0.37	0.56	0.06	0.13
30:0	0.18	0.15	0.07	0.07	0.09	0.07	0.06	0.06
others[2]	0.04	0.12	0.04	0.10	0.03	0.20	0.04	0.11
Sum FAs	0.68	4.35	0.40	2.38	2.54	12.20	0.76	2.69
Short chain FAs	0.46	4.00	0.27	2.19	0.38	8.57	0.44	1.88
Long chain FAs	0.22	0.35	0.13	0.19	2.16	3.63	0.32	0.81
Fatty alcohols								
24:0	+	+	+	+	0.07	0.11	0.01	0.06
26:0	+	+	+	+	0.77	0.81	0.09	0.09
28:0	0.02	0.04	0.01	0.01	0.72	0.98	0.15	0.47
30:0		0.07		0.11		0.06		0.02
others[3]	+	0.01	+	+	0.03	0.15	0.02	0.29
Sum FAls	0.03	0.12	0.01	0.13	1.59	2.11	0.27	0.93
Ferulic acid		0.03		0.01		0.11		0.18
4-Hydroxycinnamic acid		0.02		0.02		0.17		0.20
Hydroxy-fatty acids								
16-hydroxy-16:0 acid		0.02		0.01		0.14		0.08
1,22 dioic-22:0 acid	0.01	0.02	0.01	0.01	0.05	0.05	0.03	0.03
others[4]		0.06		0.04		0.31		0.20
Sum hydroxy-FAs	0.01	0.10	0.01	0.06	0.05	0.50	0.03	0.31
Glycerides								
1-monolinoleylglycerol	0.03		0.01		0.01		0.02	
24:0-monoglyceride	+		0.01		0.01		0.01	
26:0-monoglyceride	0.01		0.01		0.02		0.04	
diglycerides	0.27		0.14		0.98		0.85	
triglycerides	3.32		1.15		5.22		1.54	
Sum glycerides	3.63		1.32		6.24		2.46	
Sterols								
sitosterol	0.29	1.15	0.27	0.77	0.37	1.32	0.24	1.69
sitostanol	0.03	+	0.03	+	0.01	+	0.01	+
lupeol	0.02	0.01	+	+	+	0.05	+	0.09
citrostadienol		0.12		0.06		0.08		0.01
others[5]	0.03	0.10	0.02	0.05	0.08	0.11	0.08	0.15
Sum sterols	0.37	1.38	0.32	0.88	0.46	1.56	0.33	1.94
α-Amyrin	0.04	0.19	0.05	0.22	0.02	0.12	0.01	0.08
Steryl esters	1.02		0.91		1.13		0.56	
Sum alkanes[6]	0.01	0.01	+	+	0.29	0.32	0.39	0.38
Total	5.79	6.20	3.02	3.70	12.32	17.09	4.81	6.71

[1] AH = After alkaline hydrolysis;
[2] = Fatty acids 14:0, 15:0, 16:1, 17:0, 11-18:1, 20:3, 23:0, 25:0
[3] = Fatty alcohols 22:0, 25:0, 27:0 in the samples before alkaline hydrolysis, or 20:0, 22:0, 25:0, 26:1 in the samples after alkaline hydrolysis
[4] = Hydroxy-fatty acids 1,9-dioic-9:0 acid, 9-hydroxy-9:0 acid, 1,10-dioic-2-hydroxy-10:0 acid, x-hydroxy-18:2 acid, 1,16-dioic-16:0 acid, 18-hydroxy-18:0, 22-hydroxy-22:0 acid, 26-hydroxy-26:0 acid, 24-hydroxy-24:0 acid, 2-hydroxy-26:0 in samples after alkaline hydrolysis
[5] = Stigmasta-3, alpha-tocopherol, campestanol in the samples before alkaline hydrolysis, or methylene cycloartanol, 7-oxositosterol, citrostadienol, urs-12-ene-3,28-diol, syringaresinol, betulaprenol-8, cycloartenol, campestanol in the samples after alkaline hydrolysis
[6] = Alkanes, including 1-hexacosanal, 1-octacosanal, heptacosane and nonacosane
[7] = trace amount

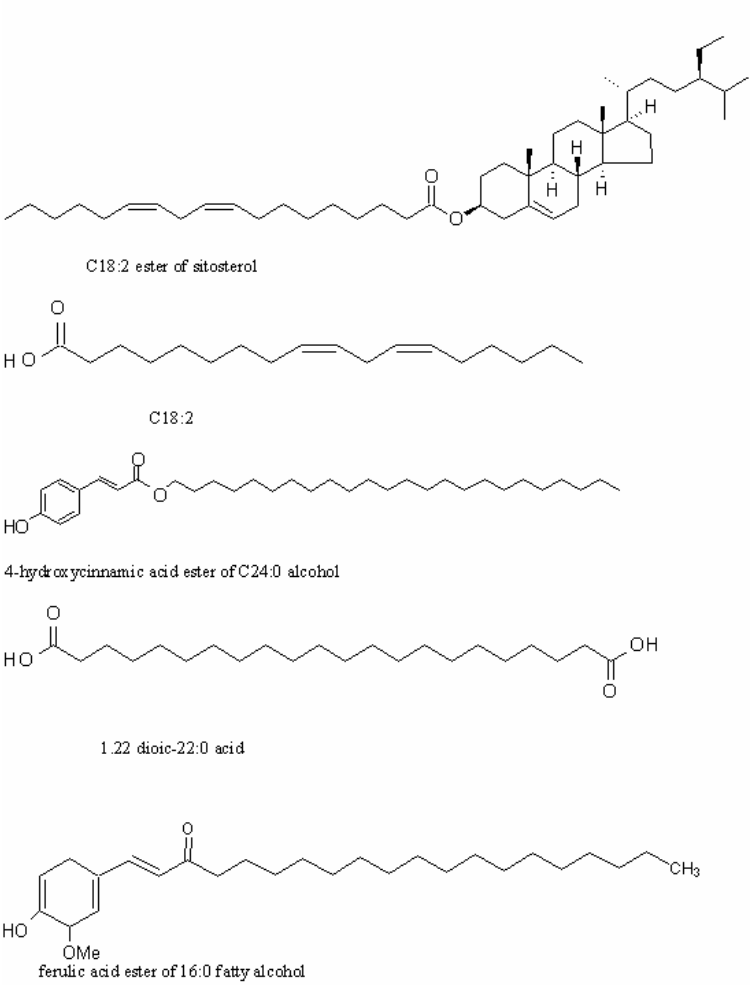

Figure 1: Structures of some lipophilic compounds identified in *Populus×euramericana* 'Neva'

The alcohol 30:0 was identified after alkaline hydrolysis. *Cis*- and *trans*-ferulic acid esters of the fatty alcohols 24:0, 26:0 and 28:0 have been found in *P. grandidentata* and *P. tremuloides* heartwood and knots.[8] After alkaline hydrolysis, the released ferulic acid was found in all the stemwood and bark, indicating the presence of ferulic acid esters of the fatty alcohols in this wood species (Figure 1).

It is interesting that 4-hydroxycinnamic acid was identified after hydrolysis in small amounts both in stemwood and bark, which showed the presence of 4-hydroxycinnamic acid esters of fatty alcohols, such as 24:0, 28:0 and 30:0 (Figure 1). These hydroxycinnamic acid esters of fatty alcohols were in the same amount in the bark and stemwood at different heights of the tree. This component was not identified in other aspen species, such as *P. grandidentata* and *P. tremuloides*.[8]

The results of HPSEC analysis showed that triglycerides, steryl ester, diglycerides and fatty acids were also observed in all the stemwood and bark samples (Figure 2). A small peak was observed on the left side of triglycerides in the bark, indicating that small amounts of oligomeric or polymeric material with higher molar mass than the triglycerides were present only in the bark of this wood species.

Figure 3 simulates the situation of lipophilic extractives after kraft cooking by alkaline hydrolysis. The results show that all the glycerides and steryl esters were hydrolysed to the corresponding compounds, i.e. fatty acids and sterols. After hydrolysis the extractives were mainly composed of fatty acids, fatty alcohols and

sterols. The short-chain fatty acids were dominant in the hydrolyzed extractives both in the bark and stemwood. The short-chain fatty acids contained 60% to 65% of the total hydrolyzed extractives in the stemwood, and 28% to 50% in the bark. Long-chain fatty acids, on the other hand, only contained 5% of the total hydrolyzed extractives in the stemwood, and 12% to 21% in the bark. The ratio of short-chain fatty acids to the long-chain fatty acids was about 11.5 in the stemwood, and 2.3 in the bark. This ratio is much higher than that in *A. mangium* and *A. crassicarpa*,[15] but smaller than that in the sapwood of *P. grandidentata* and *P. tremuloides*.[8]

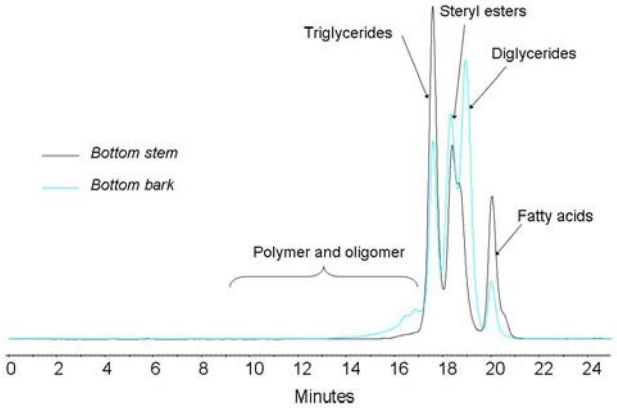

Figure 2: HPSEC chromatograms of bottom stemwood and bottom bark of *Populus×euramericana* 'Neva'

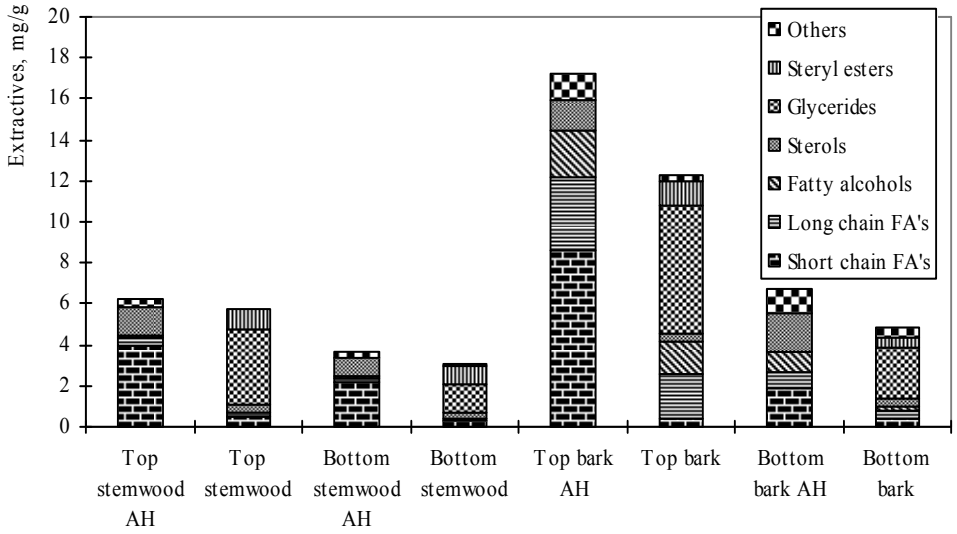

Figure 3: Lipophilic extractives in *Populus×euramericana* 'Neva' determined by GC before and after alkaline hydrolysis

On the other hand, the ratio of acids to unsaponifiables varied from 1.8 of the bottom stemwood to 2.4 of the top stemwood, and the ratio of the bottom bark was even as low as 0.7. Obviously, the high proportion of short-chain fatty acids is of benefit to the removal of pitch particles or fatty acid soaps by dispersing and washing during pulping and papermaking. Therefore, the low ratio of acids to unsaponifiables is probably a problem in kraft pulp mills using this wood species as raw material.

It should be noted that sterols, the second most abundant components in the hydrolyzed extractives, contained about 23% of the total hydrolyzed extractives in the stemwood. Because sterols have a much stronger effect on resin

viscosity than fatty acids,[16] sterols probably play a much greater role in determining resin properties, such as colloidal stability and deposition tendency.

Comparing the results obtained with those of our earlier study on *Populus×euramericana* 'Guariento',[1] it was found that the lipophilic extractives of the two species are quite similar in chemical composition. They are all composed of triglycerides, steryl esters, free fatty acids, sterols and free fatty alcohols, both in the stemwood and bark.[1] Most differences in the lipophilic extractives of the two species are in their amount. *Populus×euramericana* 'Guariento' has much higher content of triglycerides than the 'Neva', and the sterols, sterol esters and free fatty acids are present in similar amounts in the two species. Therefore, the ratio of acids to unsaponifiables in the 'Guariento' is much higher than that in the 'Neva' during the kraft pulping, which means that *Populus×euramericana* 'Neva' may create more pitch problems during kraft pulping, although it has lower amounts of extractives. Surfactants could be a choice in pitch control during the kraft pulping process in the mills using this wood species as raw material.

CONCLUSION

The lipophilic extractives identified by GC-MS are composed of five component groups, i.e. glycerides, steryl esters, free fatty acids, sterols and free fatty alcohols both in the stemwood and bark of *Populus×euramericana* 'Neva'. The top stemwood and bark contain much larger amounts of lipophilic extractives than the corresponding bottom ones. Small amounts of oligomeric or polymeric material with higher molar mass than that of triglycerides are present only in the bark. Glycerides, mainly triglycerides, are the largest component group of the lipophilic extractives, and linoleic (18:2) acid was the major fatty acid in triglycerides. The high proportion of short-chain fatty acids is of benefit to the removal of pitch or fatty acid soaps by dispersing and washing during pulping and papermaking. However, the low ratio of acids to unsaponifiables in this aspen wood, especially in the bottom stemwood, could probably have a negative effect on pitch problems in related kraft mills.

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