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Lipophilic Extractives in *Populus* × *euramericana* "Guariento" Stemwood and Bark

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Abstract: The lipophilic extractives in stemwood and bark from three different heights of *Populus* × *euramericana* "Guariento" were analyzed. The bark samples, especially from 4 and 8 meters height, contained much more extractives than the stemwood samples. The lipophilic extractives identified by Gas Chromatography–Mass Spectroscopy (GC-MS) were composed of five component groups (i.e. triglycerides, steryl esters, free fatty acids, sterols, and free fatty alcohols both in the stemwood and bark). Besides ferulic acid esters, α -amyrin and its esters, 4-hydroxycinnamic acid esters of fatty alcohols were also identified in the stemwood and bark. Small amounts of alkanes and oligomeric or polymeric material with higher molar mass than triglycerides were present only in the bark. Glycerides, mainly triglycerides, were the largest component group of the lipophilic extractives. The high proportion of short-chain fatty acids released after alkaline hydrolysis are beneficial when removing pitch particles or fatty acid soaps by dispersing and washing during pulping and papermaking.

Keywords: Aspen, bark, lipophilic extractives, *Populus × euramericana* "Guariento," stemwood

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INTRODUCTION

Populus \times *euramericana* "Guariento," originally from Italy, is a hybrid from *Populus deltoids* and *Populus nigra* and later on cultivated in China from 1984 onward. Nowadays, *Populus* \times *euramericana* "Guariento" is regarded as one of the most suitable aspen species grown in China, especially in North China. This fast-growing aspen has been widely planted and used in the kraft and mechanical pulp production in China in recent years.

Lipophilic extractives, often referred to as wood resin or wood pitch, are a group of minor components in wood. The chemical composition and the amount of extractives are dependent on the tree species.^[1] The extractives of softwoods, such as spruce, are ordinarily composed of fatty acids, resin acids, sterols, steryl esters, and triglycerides.^[2] Hardwood species like aspen and birch contain higher concentration of steryl esters and waxes than softwood species.^[3] Pietarinen et al.^[4] studied the chemical composition of wood resin in bigtooth and quaking aspen wood and knots. The results showed that the amount and composition of the extractives in sapwood were similar in both species. Triglycerides, short-chain fatty acids (C14 to C20), and steryl esters were predominant in the sapwood samples. However, monoglycerides, longchain fatty acids and alcohols (C22 to C28), hydroxy fatty acids, and ferulic acid esters of fatty alcohols were the major components in heartwood and knots of the two species. Rowe and Conner reviewed the extractives of several aspen species, including *P. tremuloides*, and *P. grandidentata*.^[5]

The problems of pitch deposits in aspen wood pulping and bleaching caused by lipophilic extractives have been of great concern to the pulping industry for a long time. Pitch deposition may be found in the washers, bleaching screens, cleaners, and pulp machine and may also cause higher consumption of defoamers.^[6] Fatty acids, resin acids, steryl esters, and glycerides 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.^[6] It has been estimated that the ratio of acids to unsaponifiables should be about 3:1 to achieve good deresination in kraft pulping.^[7] The ratio in fresh *P. tremuloides* sapwood is about 2:1, which can therefore explain the pitch problems occurring during kraft pulping.^[8]

Kraft pulping does not affect sterols and triterpenols in the extractives, although bleaching modifies the structures of most resin components.^[3] Even though a significant amount of sterols, triterpenols, and their corresponding esters is removed during the pulping and bleaching, a large proportion of sterols and triterpenols still remain in the bleached pulp.

In general, barks contain a much larger amount of resin than the stemwood from the same tree. The bark from fresh trembling aspen can contain more than four times as much as the rest of the wood.^[8] Barks are rich sources of many

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substances for the applications of adhesives, pharmaceuticals, and biocides.^[9] However, the use of poorly barked wood will result in higher concentrations of dissolved soaps and dispersed resin in the black liquor and white waters down stream, which will increase the rates of pitch deposition in a mill unless washing is efficient in the pulp mill and bleach plant.^[10]

In this work we analyzed the lipophilic extractives of barks and stemwood from different positions in a *Populus × euramericana* "Guariento" tree. To the best of our knowledge, this is the first time anyone has reported on the extractives from this fast-growing tree species. Our study will supply information on the lipophilic extractives in detail in order to prevent pitch problems during kraft and mechanical pulping in the pulp and paper mills using this tree species as raw material.

MATERIAL AND METHODS

The *Populus* × *euramericana* "Guariento" tree planted in 2001 was felled in June 2006 in Jinan, China. Stemwood sectors were cut out at three different heights. The top part with a diameter of 11.2 cm was taken at the height of 8.3 m, the middle part with a diameter of 15.7 cm was taken at the height of 4.3 m, and the bottom part with a diameter of 25.0 cm was taken at the height of 0.3 m. The top, middle, and bottom parts were then sampled from both bark and stemwood of the tree, which had a total height of 14 m. 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.

Sequential extraction of the dried samples was carried out in 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 μ m 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 \times 0.53 mm i.d. column coated with cross-linked methyl polysiloxane (HP-1)

with a film thickness of 0.15 μ m according to Örså and Holmbom^[1] and Willför et al.^[11] Cholesteryl heptadecanoate (for ferulic acid and steryl esters and diglycerides) and 1,3-dipal-mitoyl-2-oleyl glycerol (for triglycerides) were used as internal standards. No FID correction factors were used.

To analyze the total fatty acids, fatty alcohols and sterols, alkaline hydrolysis was carried out using 0.5 N KOH solution in 90% aqueous EtOH. The extracts containing approximately 0.5 mg of the extractives were evaporated to dryness followed by addition of the KOH solution. The extracts were then allowed to stand for 5 h at 70°C. Afterward, 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.

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 earlier.

The molar-mass distribution of extractives was determined by highperformance 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 μ L.

RESULTS AND DISCUSSION

Compared to other hardwood species, such as *Acacia mangium* and *Acacia crassicarpa*^[14] and *P. grandidentata* and *P. tremuloides*^[4], *Populus* × *euramericana* "Guariento" contained larger amounts of extractives. The gravimetric amounts of lipophilic extractives from the top, middle, and bottom stemwood samples of *Populus* × *euramericana* "Guariento" were 14.7 mg/g, 10.1 mg/g and 14.1 mg/g, respectively. The bark samples, especially in top (43.4 mg/g) and middle positions (46.7 mg/g), contained much larger amounts of extractives than the stemwood samples.

The results in Table 1 show that 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 of *Populus* × *euramericana* "Guariento"). In addition, ferulic acid esters, 4-hydroxycinnamic acid esters, α -amyrin, and its esters were also identified in the stemwood and bark, and small amounts of alkanes were only found in the bark samples.

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Table 1. Lipophilic extractives in *Populus × euramericana* "Guariento" given in mg/g dry wood

	Up	Up stem	Middle	Middle	Down	Down	Up	Up	Middle	Middle	Down	Down
	stem	AH^{1}	stem	stem AH	stem	stem AH	bark	bark AH	bark	bark AH	bark	bark AH
Fatty acids												
16:0 acid	0.07	0.98	0.06	0.73	0.05	0.76	0.86	3.04	0.16	3.06	0.20	2.52
18:2 acid	0.34	9.96	0.30	6.87	0.27	7.75	3.89	26.28	0.36	27.32	0.45	16.62
18:3 acid	0.04	0.55	0.03	0.43	0.03	0.50	0.87	3.79	0.12	3.20	0.15	2.73
9-18:1 acid	0.02	0.40	0.02	0.22	0.02	0.32	0.23	0.65	0.04	0.78	0.08	0.46
18:00 acid	0.02	0.20	0.01	0.11	0.01	0.11	0.15	0.63	0.05	0.71	0.05	0.38
20:00 acid	0.01	0.08	0.01	0.05	0.01	0.06	0.07	0.30	0.03	0.34	0.03	0.23
20:1 acid		0.10		0.06		0.07		0.17		0.20		0.09
22:0 acid	0.02	0.08	0.02	0.07	0.03	0.11	0.13	0.45	0.09	0.43	0.16	0.52
24:0 acid	0.03	0.11	0.04	0.11	0.05	0.24	0.15	0.37	0.16	0.41	0.27	0.52
26:0 acid	0.02	0.10	0.02	0.10	0.02	0.19	0.38	0.46	0.29	0.45	0.42	0.58
27:0 acid								0.16		0.15		0.13
28:0 acid	0.01	0.07	0.01	0.07	0.02	0.08	0.46	0.89	0.60	0.81	0.49	0.60
30:0 acid	0.13	0.09	0.14	0.09	0.10	0.12	0.03	0.26	0.16	0.22	0.01	0.11
Others ²	0.04	0.16	0.05	0.18	0.02	0.20	0.24	0.47	0.13	0.51	0.09	0.54
Sum FAs	0.60	12.89	0.57	9.10	0.53	10.51	7.43	37.93	2.11	38.60	2.39	26.02
Short chain FAs	0.50	12.37	0.45	8.58	0.41	9.68	6.27	35.13	0.81	35.91	1.02	23.30
Long chain FAs	0.10	0.53	0.12	0.52	0.12	0.83	1.16	2.80	1.30	2.68	1.37	2.72
										(Continu	u uo pə	ext page)

 Table 1. (Continued)

	Up	Up stem	Middle	Middle	Down	Down	Up	Up	Middle	Middle	Down	Down
	stem	AH^{1}	stem	stem AH	stem	stem AH	bark	bark AH	bark	bark AH	bark	bark AH
Fatty alcohols												
24:0 alcohol	0.01	0.02	0.01	0.01	0.02	0.06	0.08	0.10	0.01	0.09	0.05	0.13
26:0 alcohol	0.04		0.02		0.07		0.12		0.10		0.19	
28:0 alcohol	0.10	0.12	0.07	0.10	0.09	0.11	0.25	0.86	0.26	0.74	0.21	0.37
30:0 alcohol		0.07		0.06		0.09		0.17		0.18		0.09
Others ³		0.03	0.01	0.01	0.01	0.03	0.02	0.08	0.01	0.07	0.09	0.11
Sum FAIs	0.15	0.24	0.11	0.18	0.19	0.29	0.47	1.21	0.39	1.08	0.53	0.70
ferulic acid		0.06		0.04		0.07		0.04		0.03		0.03
4-hydroxycinnamic acid		0.03		0.03		0.03		0.05		0.07		0.07
Hydroxy-fatty acids												
16-Hydroxy-16:0 acid		0.05		0.03		0.03		0.16		0.16		0.12
1.22 dioic-22:0 acid	0.02	0.02	0.02	0.02	0.02	0.04	0.11	0.13	0.11	0.11	0.14	0.12
others ⁴		0.11		0.07		0.19		0.46		0.51		0.82
Sum hydroxy-FAs	0.02	0.18	0.02	0.12	0.02	0.26	0.11	0.75	0.11	0.79	0.14	1.06
Glycerides												
2-Monolinoleylglycerol	0.01		0.01		0.01		0.05		0.02		+	
1-Monolinoleylglycerol	0.04		0.03		0.03		0.29		0.04		0.06	
24:0-monoglyceride	0.01		0.01		0.04		0.04		ı		ı	
26:0-monoglyceride	0.03		0.03		0.07		0.02		ı		ı	
Diglycerides	0.46		0.36		0.41		1.83		0.75		0.96	
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Triglycerides	8.45		5.10		6.13		17.08		23.22		15.83	
Sum glycerides Sterols	00.6		5.54		6.70		19.31		24.03		16.86	
Sitosterol	0.26	1.80	0.26	2.16	0.21	0.74	0.15	1.71	0.56	1.89	0.55	2.15
Sitostanol	0.02	+7	0.02	+	0.02	+	+	+	0.03	+	0.02	+
Campestanol	0.01	0.02	0.01	0.02	0.01	0.01	+	+	+	0.05	+	+
Lupeol	0.02	+	0.02	0.01	0.01	+	+	0.32	0.01	0.29	0.01	0.29
Citrostadienol		0.20		0.20		0.08		0.24		0.26		0.20
Others ⁵	0.03	0.17	0.02	0.19	0.02	0.09	0.24	0.39	0.60	0.49	0.25	0.41
Sum sterols	0.34	2.19	0.33	2.57	0.28	0.92	0.49	2.71	3.20	3.02	2.34	3.12
α -Amyrin	0.03	0.19	0.03	0.20	0.03	0.10	0.02	0.18	0.03	0.21	0.01	0.22
Sterol esters	1.15		0.92		1.02		1.89		2.99		3.34	
Sum alkanes ⁶							1.00	0.95	2.54	0.48	2.05	0.23
Total	11.41	15.7 9	7.66	12.25	8.86	12.18	30.75	43.76	35.48	44.23	27.65	31.37

 $^{1}AH = After alkaline hydrolysis.$

²Fatty acids 14:0, 15:0, 16:1, 17:0, 11-18:1, 20:3, 23:0, 25:0.

⁴Hydroxy-fatty acids 1,9-dioic-9:0 acid, 9-hydroxyl-9:0 acid, 1,10-dioic-2hydroxyl-10:0 acid, x-hydroxy-18:2 acid, 1,16-dioic-16:0 acid, 18-³ 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. hydroxy-18:0, 22-hydroxy-22:0 acid, 26-hydroxy-26:0 acid, 24-hydroxyl-24:0 acid, 2-hydroxyl-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, betulaprenol-8, cycloartenol, campestanol in the samples after alkaline hydrolysis.

⁶Alkanes 1-hexacosanal, 1-octacosanal, heptacosane, nonacosane.

Trace amount

Glycerides including mono-, di-, and triglycerides were the largest component group of the lipophilic extractives, with 70% to 80% of all GC-eluted compounds in the stemwood and 60% to 70% in the bark (Table 1). The amount of glycerides in the stemwood of *Populus* × *euramericana* "Guariento" was close to that of *P. grandidentata* sapwood, but much more than that of *P. tremuloides* sapwood.^[4] The content of glycerides in the middle stemwood sample was slightly lower than that in the top and bottom samples; however, the content in the middle bark was much higher than that in the top and bottom bark samples. Among the glycerides, more than 90% were triglycerides in the stemwood. 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, diglycerides, and monoglycerides of fatty acids 24:0, 26:0, and 18:2 acid were also observed in small amounts.

Steryl esters were the second most abundant compounds in the extractives, with 10% to 15% of the total detactable lipophilic extractives in stemwood, and 5% to 15% of the total detactable lipophilic extractives in bark (Table 1). The amounts of steryl esters were on the same level in the three stemwood samples. However, the top bark contained a smaller amount of steryl esters than the middle and bottom barks. Alkaline hydrolysis could lead to much higher concentration of sitosterol, which meant that sitosterol was the major sterol in the steryl ester.

Some sterols, such as sitosterol, sitostanol, campestanol, and lupeol, were also present in free form in small amounts (Table 1). The bark contained much larger amounts of sterols in free form than the stemwood. The amount of sterols was the smallest in top bark and the largest in the middle bark. Sitosterol was the predominant sterol in the stemwood and bark.

After alkaline hydrolysis, the amount of sterols clearly increased in all samples, indicating that sterols existed mainly as esterified compounds (Table 1). Citrostadienol was only observed in the alkaline hydrolysis products. The triterpenol α -amyrin was observed both before and after hydrolysis. Much higher concentration of α -amyrin after hydrolysis indicated the presence of α -amyrin esters of fatty acids in stemwood and bark of *Populus × euramericana* "Guariento" (Figure 1).

Small amounts of free fatty acids were identified both in the stemwood and bark samples (Table 1). There was a slight trend that the amount of free fatty acids slightly increased with an increase in the height in the tree. The short-chain fatty acids (16 to 20 C atoms) dominated over the long-chain ones (22 to 30 C atoms) in the stemwood. Among the short-chain fatty acids, fatty acid 18:2 dominated in the stemwood over the other ones. The bark contained much larger amounts of free fatty acids than the stemwood. The amounts of free fatty acids significantly increased with an increase in height, from 2.39 mg/g in the bottom bark to 7.43 mg/g in the top bark. In the barks, only the top bark contained much larger amounts of short-chain



Figure 1. Structures of some lipophilic compounds identified in *Populus × euramericana* "Guariento."

free fatty acids than the long-chain ones. The amounts of long-chain free fatty acids were slightly larger than short-chain ones in the middle and bottom bark samples. Among the short-chain free fatty acids in bark, the fatty acid 18:2 also dominated over the others. Fatty acids 26:0 and 28:0 were present as the major components in the long-chain free fatty acids in the bark samples. After alkaline hydrolysis, the amount of fatty acids, especially fatty acid 18:2, was increased sharply (Table 1). For examples, the fatty acid 18:2 was increased by 20 to 30 times in stemwood samples 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. Different from free fatty acids, the short-chain fatty acids dominated over the long-chain ones in the barks after hydrolysis. The total amount of fatty acids in bark was 2 to 5 times higher than that in stemwood.

Hydroxy fatty acid, 1,22 dioic-22:0 acid, in free form was also observed in all samples (Table 1). After alkaline hydrolysis, small amounts of other hydroxy fatty acids were also identified. The bark contained much larger amounts of total hydroxy fatty acids than the stemwood. Furthermore, the bottom stemwood or bark contained slightly larger amounts of total hydroxy fatty acids than the top and middle samples.

Fatty alcohols 24:0, 26:0, and 28:0 were observed in free form in all the wood samples. In addition, free fatty alcohols 22:0, 25:0, and 27:0 were also found in trace amounts. Fatty alcohol 30:0 was released after alkaline hydrolysis. The fatty alcohols increased remarkably after hydrolysis, especially in the extractives from barks, in which fatty alcohol 28:0 constituted more than 50%. *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.^[4] After alkaline hydrolysis, the released ferulic acid was found in all the stemwood and bark samples, indicating the presence of ferulic acid esters of the fatty alcohols in the wood species (Figure 1).

It is interesting that 4-hydroxycinnamic acid was identified in small amounts both in stemwood and bark of *Populus* \times *euramericana* "Guariento," 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 at the same level at different heights of the tree. However, the amounts of these esters in bark were about double to that in stemwood.

Triglycerides, steryl ester, diglycerides, and fatty acids were also observed in all the stemwood and bark samples of *Populus* \times *euramericana* "Guariento" by HPSEC analysis. Figure 2 shows the chromatograms of bottom stemwood and bottom bark of *Populus* \times *euramericana* "Guariento." A small peak was observed on the left side of triglycerides in all three bark samples, indicating that small amounts of oligomeric or polymeric material with higher molar mass than the triglycerides were present only in the bark of *Populus* \times *euramericana* "Guariento."



Figure 2. HPSEC chromatograms of bottom stemwood and bottom bark of *Populus* × *euramericana* "Guariento."





Figure 3. Lipophilic extractives in *Populus* \times *euramericana* "Guariento" determined by GC after alkaline hydrolysis.

Figure 3 shows the alkali hydrolyzed extractives, simulating the situation of lipophilic extractives after kraft cooking. The results showed that short-chain fatty acids were dominant in the hydrolyzed extractives both in the bark and stemwood samples. The short-chain fatty acids contained 70% to 80% of the total hydrolysed extractives in stemwood samples, and 75% to 80% in the bark samples. Long-chain fatty acids, on the other hand only contained 3% to 7% of the total hydrolyzed extractives in the stemwood samples, and 6% to 9% in the bark samples, which is much smaller than the proportion of long-chain fatty acids in *A. mangium* and *A. crassicarpa*,^[14] and close to that in *P. grandidentata* and *P. tremuloides*.^[4] 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. It should be noted that sterols, the second most components in the hydrolyzed extractives, have much higher viscosity than fatty acids,^[15] and could probably play an important role in pitch deposition in kraft process.

CONCLUSIONS

 $Populus \times euramericana$ "Guariento" contained larger amounts of lipophilic extractives than earlier studied aspen species such as *P. grandidentata* and *P. tremuloides*. The bark, especially in higher positions in the tree, contained much more extractives than the stemwood.

The lipophilic extractives identified by GC–MS 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). Besides ferulic acid esters, α -amyrin and its esters, 4-hydroxycinnamic acid esters of fatty alcohols were also identified in the stemwood and bark, and small amounts of alkanes were only found in the bark samples.

Glycerides including mono-, di-, and triglycerides were the largest component group of the lipophilic extractives, with 70% to 80% of all GCeluted compounds in the stemwood and 55% to 65% in the bark of the *Populus* \times *euramericana* "Guariento" samples. Linoleic (18:2) acid was the major fatty acid in triglycerides. Sterols were present mainly in their esterified forms. Sitosterol was the dominant sterol in the stemwood and bark samples.

Small amounts of oligomeric or polymeric material with higher molar mass than the triglycerides were present only in bark of *Populus* \times *euramericana* "Guariento." 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. It should be noted that sterols, the second most components in the hydrolyzed extractives, have much higher viscosity than fatty acids, and could probably play an important role in pitch deposition in kraft process.

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