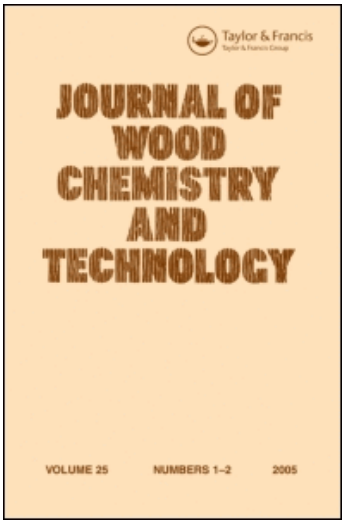

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NEW LIPOPHILIC COMPONENTS OF PITCH DEPOSITS FROM AN *EUCALYPTUS GLOBULUS* ECF BLEACHED KRAFT PULP MILL

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ABSTRACT

The chemical composition of three pitch samples coming from an *Eucalyptus globulus* ECF bleached kraft pulp mill was studied by GC-MS. All samples are rich in fatty acids, including several ω- and α-hydroxyfatty acids and several oxidation products of β-sitosterol, such as 5,6-epoxy-24-ethylcholestane-3-ol and 24-ethylcholestane-3,5,6-triol. One oxidation product of oleic acid, namely 9,10-dihydroxyoctadecanoic acid was also identified. The α-hydroxyfatty acids, the sterols oxidation products and 9,10-dihydroxyoctadecanoic acid are reported here for the first time as components of pitch issued from ECF bleached kraft pulp mills.

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Key Words: *Eucalyptus globulus*; Chlorine dioxide; Kraft pulp bleaching; Pitch; Oxidized sterols; α-Hydroxyfatty acids; ω-Hydroxyfatty acids

INTRODUCTION

Wood extractives, even when present in small amounts in wood, play an important role in the efficiency of wood processing for pulp and paper production. The lipophilic fraction, in particular, can be responsible for the formation of sticky deposits in machinery and dark spots in bleached pulp and paper, commonly known as pitch.[1]

The composition of the organic fraction of pitch deposits is directly related with the nature of the extractives of the wood species used in the mill[1] and also with the pulping and bleaching processes employed in each mill, since they can induce different chemical transformations in naturally occurring wood extractives.[2]

Several studies have been published concerning the composition of pitch deposits in bleached kraft pulp mills using *Eucalyptus globulus* wood.[3–6] The major components found in such deposits are issued from the lipophilic fraction of *E. globulus* wood extractives, and products resulting from their chemical transformation during pulping and bleaching.[3,7–10] It has been also demonstrated that pitch problems related to *E. globulus* wood extractives can be reduced by seasoning[11] and fungal wood treatments.[12–14]

In a precedent paper[5] we have reported the identification of several ω-hydroxyfatty acids in pitch deposits from an ECF bleaching plant using *E. globulus* kraft pulp. The origin of such components was, at the time, unknown. This has prompted us to carry out a more detailed study on the chemical composition of the lipophilic components of *E. globulus* wood. Such study allowed us to identify the above referred fatty acids as wood components; furthermore, several other new wood components, namely several α-hydroxyfatty acids, have been reported.[7] The identification of such new wood components leaded us to follow their behaviour during kraft pulping and ClO_2 bleaching.[18] This study confirmed that a significant fraction of such α- and ω-hydroxy fatty acids remain in pulps after bleaching and can be responsible for pitch deposition. Additionally, several oxidation products of lipophilic wood components were also identified in ClO_2 bleached pulp.

In the present study, the analysis of three pitch deposits from an *E. globulus* ECF bleached kraft pulp mill is reported. The identification of several products resulting from the oxidation of wood components, as well

as some of the above referred newly identified *E. globulus* wood components is discussed.

EXPERIMENTAL

Samples

The pitch deposits studied in the present work were obtained from a Portuguese ECF *Eucalyptus globulus* bleached kraft pulp mill, and were collected at different points of the pulp sheet-forming machine.

Sample Extraction

Pitch samples (**P1**–**P3**) were submitted to sohxlet extraction with ethyl ether for 16 h**.** The solvent was evaporated to dryness and the extracts were weighed. The results were expressed in percent of dry pitch.

For NMR analysis of unidentified oxidized sterols, 30 mg of ethyl ether extract were fractionated by thin layer chromatography on silica gel, eluting with ethyl acetate : light petroleum (2 : 8). NMR spectra of purified fractions were recorded on a Bruker AMX 300 spectrometer.

GC-MS Analyses

Prior to GC-MS analysis, nearly 10 mg of each dried ethyl ether extract were methylated with diazomethane and then converted to TMS derivatives (15).

GC-MS analyses were performed using an Hewlett-Packard gas chromatograph 5890 equipped with a mass selective detector MDS series II, using helium as carrier gas (35 cm/s), equipped with a DB-1 J&W capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The chromatographic conditions were as follows: initial temperature: 80°C, temperature rate: 4°C/min, final temperature: 285°C, injector temperature: 290°C, transferline temperature: 290°C, split ratio: 1 : 100.

In order to verify the presence of esterified structures such as steryl esters, the extracts were also analysed by GC-MS using short length columns (15 m). These GC-MS analyses were performed using a Trace gas chromatograph 2000 Series equipped with a Finnigan Trace MS mass spectrometer, using helium as carrier gas (35 cm/s), and a DB-1 J&W capillary column (15 m × 0.32 mm i.d., 0.25 μm film thickness). The chromatographic

conditions were as follows:[9] initial temperature: 100°C for 3 min; temperature rate: 5°C/min; final temperature: 340°C for 12 min; injector temperature: 320°C; transfer-line temperature: 290°C; split ratio: 1 : 100.

Components of the extracts were identified as TMS and/or methylated derivatives by comparing their mass spectra with the equipment mass spectral library and with data from the literature.

RESULTS AND DISCUSSION

The ethyl ether extractives yields of the three pitch samples studied are similar, they account for 23.4% (w/w, on dry pitch base) of **P1**, 28.5% of **P2** and 21.8% of **P3**. These values are within the ranges of extractives yields reported;[3–6] the remaining fraction of pitch deposits is normally attributed to inorganic components[4,5] and to polymeric organic materials.[5,16,17]

The qualitative composition of the ethyl ether extracts of these pitch samples is very similar as can be seen from Table 1; however, sample **P2** presents a higher content of lipophilic extractives identified by GC-MS than **P1** and **P3**. Figure 1 illustrates the typical GC-MS chromatogram of the derivatized ethyl ether extract of **P1**. The major components of the ethyl ether extracts of the pitch samples studied (Table 1, Figure 1) are β-sitostanol, several oxidation products of β-sitosterol and fatty acids. Minor amounts of long chain aliphatic alcohols were also detected.

β-Sitosterol, the major component of the lipophilic extractives of *E. globulus* wood,[3,7–9] was found in all samples in lower amounts than β-sitossitostanol, as previously reported for other pitch samples from *E. globulus* mills using ECF bleaching sequences.[4,5] Chlorine dioxide oxidizes unsaturated lipophilic extractives, such as β-sitosterol, whereas the saturated extractives are in general very resistant.[2]

Among the major components of the extracts two oxidation products of β-sitosterol were identified (Figure 2): 5,6-epoxy-24-ethylcholestane-3-ol and 24-ethylcholestane-3,5,6-triol (the major component of the extract of samples **P1** and **P2**). Minor amounts of 24-ethyl-6-cholestene-3,5-diol, 24-ethyl-5-cholestene-3,7-diol, and 24-ethyl-3,5-cholestediene-7-one were also identified (Figure 2). The last one has been already reported to occur in pitch deposits from *E. globulus* mills.[4,6] The other oxidation products were recently reported to occur in ClO_2 bleached *E. globulus* kraft pulps[18] and are referred here for the first time as pitch components.

Other components, (Table 1, peaks 51–54, 57, 58, 60 and 61) show fragmentation patterns characteristic of sterol TMS derivatives. However, their unambiguous identification could not be achieved based only on the

Table 1. Lipophilic Components of the Pitch Deposits Studied. The Peak Numbers Refer to the Chromatogram in Figure 1. Values Are Expressed in mg Compound/g of the Ethyl Ether Extract, and, into Brackets, as Percentage of the Identified Amount

Peak	Compound	P1		P2		P3	
1	Glycerol	0.409	(0.1)	1.26	(0.2)	3.42	(1.2)
2	Tetradecanoic acid	0.322	(0.1)	0.41	(0.1)	0.563	(0.2)
3	Pentadecanoic acid	0.898	(0.3)	0.66	(0.1)	1.10	(0.4)
4	6,10,14-Trimethyl-2-pentadecanone	0.156	(0.1)	0.67	(0.1)	0.842	(0.3)
5	Hexadecanoic acid	10.0	(3.5)	9.00	(1.8)	12.0	(4.2)
6	1-Hexadecanol	0.197	(0.1)	1.01	(0.2)	1.16	(0.4)
7	Heptadecanoic acid	0.943	(0.3)	1.04	(0.2)	0.937	(0.3)
8	Hexadecanoic acid (TMS)	0.555	(0.2)	0.56	(0.1)	1.57	(0.6)
9	Linoleic acid	0.477	(0.2)	2.22	(0.4)	0.88	(0.3)
10	Oleic acid	0.665	(0.2)	2.17	(0.4)	1.53	(0.5)
11	Octadecanoic acid	2.67	(0.9)	3.28	(0.6)	1.75	(0.6)
12	2-Hydroxyhexadecanoic acid	1.96	(0.7)	3.50	(0.7)	1.68	(0.6)
13	1-Octadecanol	0.675	(0.2)	2.41	(0.5)	1.82	(0.6)
14	Nonadecanoic acid	1.25	(0.4)	3.87	(0.8)	0.711	(0.3)
15	Eicosanoic acid	4.69	(1.6)	13.05	(2.5)	10.3	(3.6)
16	1-Eicosanol	0.63	(0.2)	2.84	(0.6)	1.12	(0.4)
17	Heneicosanoic acid	3.90	(1.4)	3.58	(0.7)	2.28	(0.8)
18	9,10-Di-hydroxyoctadecanoic acid	3.99	(1.4)	6.10	(1.2)	5.35	(1.9)
19	Isomer of 18	1.39	(0.5)	4.55	(0.9)	3.62	(1.3)
20	Isomer of 18	2.33	(0.8)	4.38	(0.9)	6.85	(2.4)
21	Docosanoic acid	10.3	(3.6)	9.95	(1.9)	6.05	(2.1)
22	1-Docosanol	2.35	(0.8)	8.30	(1.6)	4.50	(1.6)
23	Tricosanoic acid	8.85	(3.1)	7.85	(1.5)	3.08	(1.1)
24	1-Tricosanol	0.793	(0.3)	4.15	(0.8)	0.741	(0.3)
25	Tetracosanoic acid and 2-hydroxydocosanoic acid	16.6	(5.8)	12.45	(2.4)	5.32	(1.9)
26	1-Tetracosanol	2.32	(0.8)	9.25	(1.8)	2.17	(0.8)
27	2-Hydroxytricosanoic acid and pentacosanoic acid	7.01	(2.4)	6.30	(1.2)	2.76	(1.0)
28	22-Hydroxydocosanoic acid	5.91	(2.1)	2.62	(0.5)	0.861	(0.3)
29	2-Hydroxytetracosanoic acid	6.30	(2.2)	5.30	(1.0)	1.96	(0.7)
30	Hexacosanoic acid	13.1	(4.5)	8.05	(1.6)	3.01	(1.1)
31	1-Hexacosanol	2.48	(0.9)	5.80	(1.1)	1.50	(0.5)
32	23-Hydroxytricosanoic acid	1.15	(0.4)	2.43	(0.5)	Tr	—
33	2-Hydroxypentacosanoic acid	2.11	(0.7)	2.26	(0.4)	0.721	(0.3)
34	Heptacosanoic acid	1.62	(0.6)	1.88	(0.4)	0.841	(0.3)
35	n.i.	2.43	(0.8)	1.78	(0.3)	Tr	—
36	24-Hydroxytetracosanoic acid	15.4	(5.3)	3.97	(0.8)	1.28	(0.5)

(*continued*)

Table 1. Continued

Peak	Compound	P1	P2	P3
37	2-Hydroxyhexacosanoic acid	1.69 (0.6)	2.25 (0.4)	0.569 (0.2)
38	Octacosanoic acid	6.83 (2.4)	3.79 (0.7)	1.12 (0.4)
39	1-Octacosanol	1.88 (0.7)	4.84 (0.9)	0.936 (0.3)
40	25-Hydroxypentacosanoic acid	2.30 (0.8)	2.92 (0.6)	Tr –
41	2-Hydroxyheptacosanoic acid	1.52 (0.5)	3.61 (0.7)	1.79 (0.6)
42	Nonacosanoic acid	1.12 (0.4)	1.09 (0.2)	Tr –
43	n.i.	3.19 (1.1)	3.67 (0.7)	1.81 (0.6)
44	26-Hydroxyhexacosanoic acid	13.0 (4.5)	5.30 (1.0)	2.09 (0.7)
45	24-Ethyl-6-cholestene-3,5-diol	3.08 (1.1)	10.15 (2.0)	3.68 (1.3)
46	β-Sitosterol	6.71 (2.3)	25.45 (5.0)	8.53 (3.0)
47	β-Sitostanol	20.0 (6.9)	63.5 (12.4)	43.2 (15.3)
48	24-Ethyl-3,5-cholestediene-7-one	1.37 (0.5)	Tr —	3.29 (1.2)
49	27-Hydroxyheptacosanoic acid	1.35 (0.5)	3.07 (0.6)	3.66 (1.3)
50	24-Ethyl-5-cholestene-3,7-diol	2.67 (0.9)	9.55 (1.9)	3.40 (1.2)
51	Oxidised sterol	4.08 (1.4)	9.15 (1.8)	2.01 (0.7)
52	Oxidised sterol	5.84 (2.0)	10.25 (2.0)	3.42 (1.2)
53	Oxidised sterol	3.89 (1.3)	10.45 (2.0)	4.19 (1.5)
54	3-Hydroxy-24-ethyl-5-cholestene-7-one	7.90 (2.7)	19.5 (3.8)	9.36 (3.3)
55	5,6-Epoxy-24-ethylcholestane-3-ol	8.60 (3.0)	21.8 (4.3)	11.4 (4.0)
56	30-Hydroxytriacontanoic acid	7.49 (2.6)	13.55 (2.6)	6.81 (2.4)
57	Oxidised sterol	5.19 (1.8)	14.05 (2.7)	9.49 (3.4)
58	Oxidised sterol	4.05 (1.4)	8.65 (1.7)	6.43 (2.3)
59	24-Ethylcholestane-3,5,6-triol	26.2 (9.1)	72.75 (14.2)	41.9 (14.8)
60	3-Hydroxy-24-ethylcholestane-6-one	4.42 (1.5)	12.85 (2.5)	7.69 (2.7)
61	Isomer of 54	7.02 (2.4)	21.15 (4.1)	11.6 (4.1)
	Total	288.2	512.4	282.7 —

mass spectra; on the other hand, the samples available did not allowed the isolation by preparative chromatography of enough amounts of each component to carry out a detailed NMR characterization using 2-D techniques. Therefore the gathered information only allowed to tentatively propose structures for these components. Compounds 54 and 61 show molecular ions ($M^{+\cdot}$) at m/z 500, 14 mass units higher than the TMS derivative of β-sitosterol; furthermore, in the ^{13}C NMR spectra (not shown) resonances characteristic of an α,β-unsaturated carbonyl group are observed. These data are consistent with structures such as 3-hydroxy-24-ethyl-5-cholestene-7-one (Figure 3) or isomers. The mass spectra of compound 60 shows the same molecular ion (m/z 502) as observed for the TMS derivative of 5,6-epoxy-24-ethylcholestane-3-ol (peak 55) but, their fragmentation profiles are quite different. In the ^{13}C NMR spectra of this compound a resonance character-

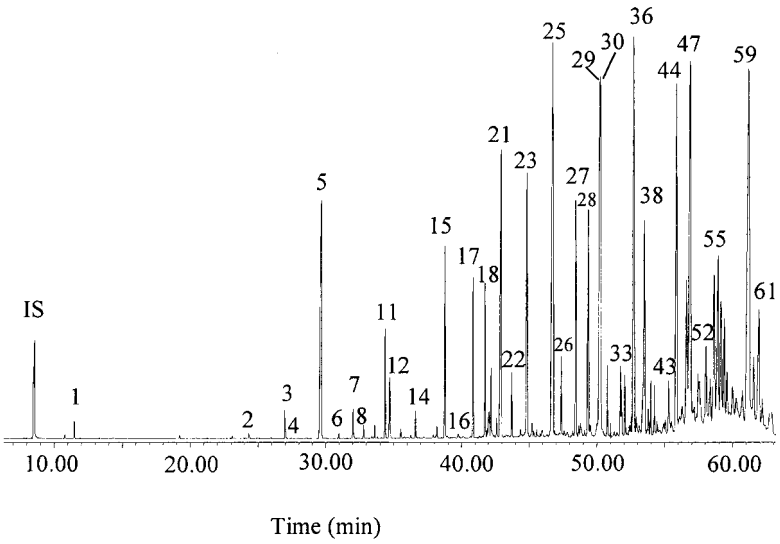

Figure 1. Total ion chromatogram of the derivatized ethyl ether extract of the pitch sample **P1**. IS internal standard: hexanedioic acid.

istic of a carbonyl group was present, but no characteristic olefinic resonances were detected. These spectroscopic data are consistent with the structure of 3-hydroxy-24-ethylcholestane-6-one (Figure 3) or isomers.

Considering all the oxidized derivatives of β-sitosterol, they represent the most abundant fraction of the lipophilic extract of the pitch deposits analyzed by GC-MS. This is in close agreement with the facts that β-sitosterol is the most abundant lipophilic wood component[7] and that it is mostly oxidized during ClO_2 bleaching stages.[4,5]

Fatty acids are common pitch components.[3–6] The major fatty acids identified in samples **P1**, **P2** and **P3** are palmitic, docosanoic, tricosanoic, tetracosanoic and hexacosanoic acids. The predominance of fatty acids higher than C_{20} in pitch deposits from *E. globulus* mills has already been mentioned.[5] These aliphatic components are present mainly esterified in wood;[7] during alkaline kraft pulping the major part of these esterified structures are hydrolyzed and they are liberated and partially carried to the bleaching plant with the kraft pulp.[18]

The unsaturated linoleic and oleic acids were identified in all samples in minor amounts as previously reported for pitch deposits from *E. globulus* mills using ECF bleaching[3–5] since they are expected to promptly decompose under the oxidative bleaching conditions. One oxidation product of

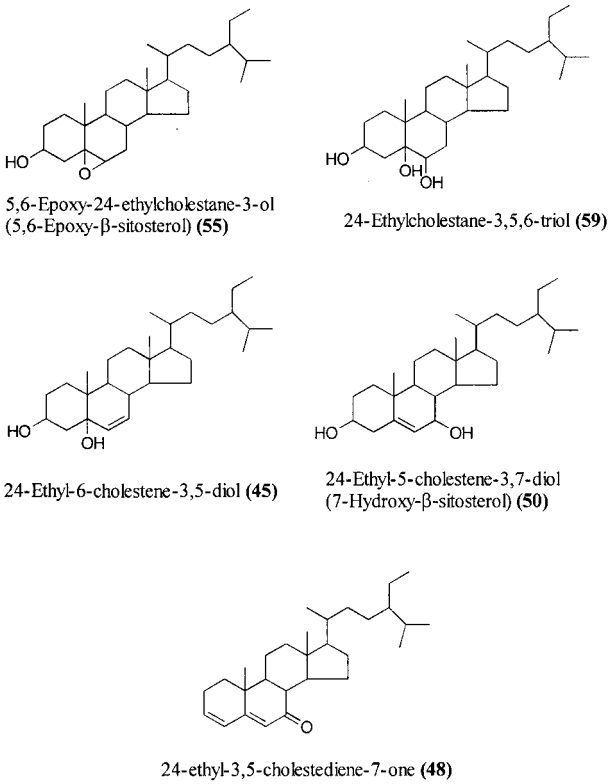

Figure 2. Structures of the oxidation products of β-sitosterol identified in the pitch samples studied.

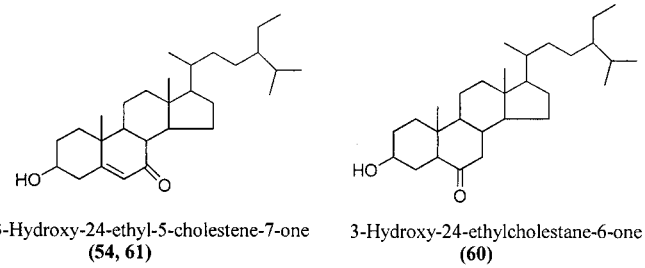

Figure 3. Structures tentatively proposed for compounds **54**, **60** and **61**.

oleic acid has been identified by GC-MS as 9,10-di-hydroxyoctadecanoic acid (as methyl ester, TMS ether derivative); its mass spectrum is characterized by the presence of two intense fragments at m/z 215 and 259 which correspond to α-cleavage between the hydroxy groups, indicating the position of the vicinal diol in the fatty acid chain.[19,20] The 9,10-di-hydroxyoctadecanoic acid is referred here for the first time as pitch component. Peaks 19 and 20 (Figure 1) show fragmentation patterns similar to that of 9,10-di-hydroxyoctadecanoic acid and therefore are expected to be isomers of this compound.

The identification of several oxidation products of β-sitosterol and oleic acid demonstrates that ClO_2 is effective in the conversion of unsaturated structures into more oxidised compounds. Considerable amounts of such products were detected in the pitch deposits studied here. The increasing degree of oxidation is expected to increase the hydrophilic character of the original compounds and therefore to facilitate their removal with bleaching filtrates.

Among the major fatty acid components, several ω- and α-hydroxyfatty acids were also identified (Table 1), namely, 22-hydroxydocosanoic, 23-hydroxytricosanoic, 24-hydroxytetracosanoic, 25-hydroxypentacosanoic, 26-hydroxyhexacosanoic and 2-hydroxyhexadecanoic, 2-hydroxydocosanoic, 2-hydroxytricosanoic, 2-hydroxytetracosanoic, 2-hydroxypentacosanoic, 2-hydroxyhexacosanoic and 2-hydroxyheptacosanoic acids, respectively. The ω-hydroxyfatty acids have already been reported to occur in pitch deposits collected in *E. globulus* pulp mills.[5] However, the α-hydroxyfatty acids are referred here for the first time as pitch components. Both ω- and α-hydroxyfatty acids were identified in *E. globulus* wood only in esterified form,[7] being released during pulping as referred above for fatty acids higher than C_{20}. Some of these hydroxyfatty acids are identified as major components of *E. globulus* unbleached kraft pulps lipophilic extracts.[18]

Long chain aliphatic alcohols are minor constituents of the pitch samples studied, which is consistent with the poor content of long chain aliphatic alcohols and waxes in *E. globulus* wood.[7,8] The major components identified are 1-docosanol, 1-tricosanol, 1-tetracosanol, 1-hexacosanol and 1-octacosanol. Smaller amounts of 1-hexadecanol, 1-octadecanol and 1-eicosanol are also present. Only 1-tetracosanol and 1-hexacosanol were reported in previous studies as components of pitch deposits from *E. globulus* mills,[5] the other alcohols identified in these samples are reported here for the first time.

The identification of ω- and α-hydroxyfatty acids as well as long chain alcohols in bleached pulps[18] and also in the pitch deposits confirm that

alkyl alcohol type structures are resistant to oxidation with ClO_2 and remain unchanged during bleaching stages.

Finally, the absence of steryl esters in pitch samples **P1**–**P3** was confirmed by the analysis of the derivatized extracts by GC-MS with short columns.[9] The presence of steryl esters in pitch deposits from *E. globulus* pulps has been described by some authors;[3,4,6] however, the absence of such components in the pitch samples reported here is consistent with the very low amounts of such structures found in bleached kraft pulps,[18] as expected due to the severe alkaline conditions used during kraft pulping.

CONCLUSIONS

The qualitative composition of the ethyl ether extracts of the pitch samples issued from the pulp sheet forming machine of an *E. globulus* ECF bleached kraft pulp mill was found to be quite similar. The major components of these pitch samples are fatty acids, including several ω- and α-hydroxyfatty acids recently reported to occur in *E. globulus* wood[7] and pulps,[18] and several oxidation products of β-sitosterol, such as 5,6-epoxy-24-ethylcholestane-3-ol and 24-ethylcholestane-3,5,6-triol. 9,10-Dihydroxyoctadecanoic acid, an oxidation product of oleic acid was also identified. The α-hydroxyfatty acids along with the β-sitosterol oxidation products and the 9,10-dihydroxyoctadecanoic acid are referred here for the first time as pitch components. The results obtained show that the composition of pitch deposits is directly related to the composition of the lipophilic fraction present in the wood species used for pulp production or with their oxidation products. Furthermore, it was also shown that the unsaturated lipophilic extractives are extensively transformed during ClO_2 bleaching. The oxidised structures formed are still enough lipophilic to form pitch deposits rather than to be extensively eliminated with bleaching filtrates.

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