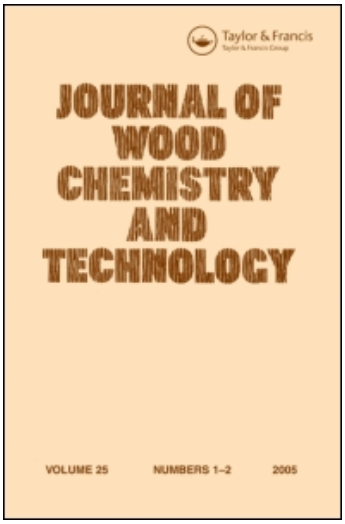

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Lipophilic Extractives in *Eucalyptus globulus* Kraft Pulps. Behavior during ECF Bleaching

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Abstract: The composition of *E. globulus* kraft pulp lipophilic extractives and their behaviour during an ECF (DEDED) bleaching sequence were investigated. Sterols; fatty acids, including several α- and ω-hydroxyfatty acids; and long-chain aliphatic alcohols are the major lipophilic extractives of the unbleached pulp. During the bleaching, about 80% of the aliphatic extractives are removed from pulp (*ca.* 70% of the sterols, 70% of the fatty acids, and 90% of the long-chain aliphatic alcohols). The decrease of sterols is mainly due to the degradation of β-sitosterol by chlorine dioxide, while the decrease of fatty acids and alcohols is essentially assigned to their extraction and elimination with the alkaline filtrates. The major chemical transformations in pulp extractives composition and structure occur in the last bleaching stages.

Keywords: Eucalyptus kraft pulp, ECF bleaching, lipophilic extractives, sterols, fatty acids, long-chain aliphatic alcohols, β-sitosterol

INTRODUCTION

Hardwood lipophilic extractives consist of a complex mixture of compounds such as long-chain aliphatic acids and alcohols, sterols, waxes, sterol esters,

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and glycerides.[1] The amount and composition of wood extractives is dependent on factors such as wood species, age, and location of growth. These wood components, when liberated during the processing of wood for pulp and paper production, may cause problems such as the formation of deposits in machinery and dark spots in bleached pulp, known as *pitch*,[2–4] as well as some increase in chemical consumption during pulping and bleaching.[5] Furthermore, extractives or their derivatives may play a key role in effluent toxicity.[6,7] The analysis of lipophilic wood extractives in pulps at different stages of pulp production is therefore extremely important because it can provide insights into the extent of their removal and degradation during pulping and bleaching processes and therefore contribute to the resolution of the problems referred to earlier.

Eucalyptus globulus is the most important fiber source for pulp and paper production in the Iberian Peninsula, where kraft pulping and ECF bleaching are the dominant production technologies. As far as the composition and fate of extractives of this species during pulping and bleaching is concerned, only a few studies on the composition of unbleached and bleached kraft pulp extractives have been published.[2,8–10] Considering its importance, we have been studying the lipophilic extractives of this wood species, and we have reported the identification of a considerable number of new compounds.[11] Based on these findings in the extractives composition, we devoted our attention to the investigation of such compounds during the pulping and bleaching processes. The present article reports a detailed GC-MS study on the behavior and fate of the lipophilic wood extractives during ECF ($D_0E_1D_1E_2D_2$) bleaching of *E. globulus* kraft pulps.

EXPERIMENTAL

Samples

An industrial unbleached *E. globulus* kraft pulp, kappa number 16.7, washed to neutral pH of the filtrates (supplied by RAIZ), was submitted to a conventional ECF bleaching sequence ($D_0E_1D_1E_2D_2$). The bleaching conditions (optimized to achieve 90% brightness) were as follows: D_0—2.2% ClO_2; 10% consistency; pH 3.0; 50°C; 25 min; E_1—2.1% NaOH; 10% consistency, pH 13.0, 70°C, 2 h; D_1—1.9% ClO_2; 10% consistency; pH 4.0; 70°C; 3 h; E_2—0.6% NaOH; 10% consistency, pH 12.0, 70°C; 2 h; D_2—0.6% ClO_2; 10% consistency; pH 4.0; 70°C; 3 h. All filtrates were collected after bleaching, purged with nitrogen and kept at 5°C until solvent extraction.

After separation of the liquid fraction (carryover or bleaching filtrate), the unbleached and DEDED bleached pulps were washed to neutrality. The unbleached pulp was then submitted to a mechanical (beating) treatment (2000 rotations) in a PFI mill, in order to increase the accessibility of the

extractives on the fiber structure. Pulps were then air-dried before solvent extraction.

Extraction Procedures

Liquid filtrates (3 aliquots of 100 mL) were acidified to pH 2 with 5% HCl and then sequentially extracted with dichloromethane (3×, 100 mL) and ethyl acetate (3×, 100 mL).

Three aliquots of ca. 20 g of each pulp were extracted in a Soxhlet apparatus with dichloromethane (750 mL) for 16 h, followed by ethyl acetate (750 mL) for 16 h. The solvents were evaporated to dryness and the extracts were quantified gravimetrically. The results were expressed as percent of the dry weight of the pulp. The unbleached pulp was previously submitted to a beating treatment (2000 rotations) in a PFI mill before solvent extraction, in order to increase the extractives accessibility and thus the extraction yield (confirmed by results on extraction yields before and after beating). The beating treatment has not influenced the extraction yield of bleached or partially bleached pulps.

The extraction procedure using dichloromethane and ethyl acetate was adopted taking into consideration the need of extracting aqueous solutions. Although acetone is normally used for pulps extraction, the same solvent sequence was used for pulps, in order to facilitate the comparison of results. Dichloromethane together with ethyl acetate gives lipophilic extractives contents quite similar to those obtained by acetone extraction, as confirmed by preliminary results on our pulps, in good agreement with results obtained for other species.[12] Additionally, the chromatograms from the extracts obtained in the dichloromethane followed by ethyl acetate extraction are simpler and easier to analyze than those obtained from the single extraction with acetone.

Alkaline Hydrolysis

In order to verify the presence of esterified components, 20 mg of each extract were dissolved in 10 mL of a solution of 1 mol/L potassium hydroxide in 10% aqueous methanol. The mixture was heated at 100°C under a nitrogen atmosphere, for one hour. The reaction mixture was cooled, acidified with 1 mol/L HCl, and then extracted three times with dichloromethane or ethyl acetate. The solvent was evaporated to dryness.

GC-MS Analyses

Before GC-MS analysis, approximately 20 mg of each dried extract were trimethylsilylated as previously described.[11] 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), 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; transfer-line temperature, 290°C; and split ratio, 1:100.

In order to further verify the presence of esterified structures such as triglycerides and sterol esters, the extracts were also analyzed by GC-MS using short length columns. 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:[11] 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.

Compounds were identified as TMS derivatives by comparing their mass spectra with the GC-MS spectral library, with data from the literature, and in some cases by injection of standards. For quantitative analysis, the GC-MS was calibrated with pure reference compounds, representative of the major lipophilic extractives components. Hexadecanoic acid, 1-nonadecanol, stigmasterol, 16-hydroxyhexadecanoic and 2-hydroxyoctadecanoic acids were analyzed relative to the internal standards, pentanedioic acid (IS1) and 1-eicosanol (IS2). The respective multiplication factors needed to obtain correct quantification of the peak areas were calculated as an average of 4 GC-MS runs.

Chemicals

16-Hydroxyhexadecanoic acid (97% purity), 1-nonadecanol (98% purity), 1-eicosanol (98% purity), and β-sitosterol (99% purity) were purchased from Fluka Chemie (Madrid, Spain); stigmasterol (95% purity) was supplied by Sigma Chemicals Co. (Madrid, Spain); 2-hydroxyoctadecanoic acid was provided by Dr. Les West from Kraft Foods-USA. 5,6-Epoxy-24-ethylcholestane-3-ol (5,6-epoxy-β-sitosterol) was prepared by reaction of β-sitosterol with *m*-chloroperbenzoic acid, whereas 24-ethylcholestane-3,5,6-triol was obtained by cleavage of 5,6-epoxy-β-sitosterol with 30% perchloric acid in THF.[13]

RESULTS AND DISCUSSION

The extractive yields found for *E. globulus* unbleached and $D_0E_1D_1E_2D_2$ bleached kraft pulps and for the resulting bleaching filtrates are shown in Table 1. When comparing the extraction yields of unbleached and bleached

Table 1. Extraction yields for pulps (% w/w) and filtrates (% w/v). Values in parentheses refer to the fraction (%) of extract analysed by GC-MS

	DCM + ethyl acetate (%)	
Sample	Ave.[a]	SD[b]
Unbleached pulp (kappa number 16.7)	0.312 (23.4)	0.026
$D_0E_1D_1E_2D_2$ Bleached pulp	0.247 (6.7)	0.016
D_0 filtrate	0.229 (40.8)	0.002
E_1 filtrate	0.237 (24.6)	0.005
D_1 filtrate	0.122 (58.2)	0.002
E_2 filtrate	0.172 (22.4)	0.002
D_2 filtrate	0.051 (40.5)	0.001

[a]Average of three values.
[b]Standard deviation.

pulps, it could be concluded that the $D_0E_1D_1E_2D_2$ bleaching sequence promotes a decrease of only around 20% of the lipophilic extractives initially present in the unbleached pulp. However, because the fraction of pulp extractives detected by GC-MS decreases considerably after the bleaching (Table 1), the decrease observed for the amount of compounds detected by GC-MS, such as sterols, fatty acids, and long-chain aliphatic alcohols, is much higher than 20%, as will be discussed later.

Unbleached Pulp Lipophilic Extractives

The lipophilic extractives of *E. globulus* unbleached kraft pulp (Table 2) are mainly composed of sterols and long-chain aliphatic acids and alcohols. The major components identified are β-sitosterol and β-sitostanol followed by hexadecanoic, docosanoic, tetracosanoic, hexacosanoic, 22-hydroxydocosanoic, 24-hydroxytetracosanoic acids and the alcohols 1-hexadecanol and Z-9-octadecen-1-ol. Two α-hydroxy fatty acids, namely 2-hydroxydocosanoic and 2-hydroxytetracosanoic acids were also detected, however, in lower amounts. These results are in general consistent with the chemical composition of lipophilic extracts of *E. globulus* wood and pulps reported elsewhere.[8,11,14,15]

After kraft pulping, the relative proportion of sterols, when compared with the other families of extractives, and especially with fatty acids, increased considerably, probably due to the partial hydrolysis of steryl esters and also because sterols are largely resistant to kraft pulping,

Table 2. Lipophilic components of the *E. globulus* unbleached kraft pulp (sum of dichloromethane and ethyl acetate extracts)

Compound	Ave.[a] mg/kg pulp	SD[b]
1-Hexadecanol	37.0	0.9
Hexadecanoic acid	8.9	0.15
Z-9-Octadecen-1-ol	117.2	0.7
Heptadecanoic acid	4.3	0.135
1-Octadecanol	25.4	0.5
Linoleic acid	8.1	0.01
Oleic acid	7.2	0.01
Octadecanoic acid	1.4	0.05
Eicosanoic acid	3.0	0.11
Heneicosanoic acid	1.9	0.06
1-Docosanol	8.9	0.18
Docosanoic acid	12.7	0.3
Tricosanoic acid	4.2	0.11
1-Tetracosanol	2.2	0.04
2-Hydroxydocosanoic acid	2.1	0.02
Tetracosanoic acid	25.4	0.5
2-Hydroxytricosanoic acid	1.7	0.03
Pentacosanoic acid	5.0	0.03
22-Hydroxydocosanoic acid	15.2	0.4
2-Hydroxytetracosanoic acid	5.7	0.2
Hexacosanoic acid	37.9	0.1
2-Hydroxypentacosanoic acid	3.9	0.03
1-Octacosanol	16.4	0.23
24-Hydroxytetracosanoic acid	27.3	0.7
2-Hydroxyhexacosanoic acid	2.2	0.003
Octacosanoic acid	9.9	0.2
24-Ethyl-6-cholestene-3,5-diol	2.1	0.10
β-Sitosterol	260.6	15.6
β-Sitostanol	29.2	5.2
1-Triacontanol	11.4	0.05
Cycloartenol	2.7	0.20
26-Hydroxyhexacosanoic acid	20.2	0.5
24-Ethyl-5-cholestene-3,7-diol	1.9	0.09
Triacontanoic acid	3.2	0.08
24-Methylenecycloartanol	2.1	0.04
Citoestradienol	3.1	0.31
Total	731.5	

[a]Average; [b]Standard deviation.

being retained in the pulp,[2,8] whereas fatty acids are in part solubilized during kraft pulping, being removed with the black liquor, as previously observed.[16,17]

The hydrolysis of esterified structures during kraft pulping also explains the considerable amounts of fatty acids with more than twenty carbon atoms found in unbleached pulp, as well as the presence of ω- and α-hydroxy fatty acids because these compounds are present in wood mainly in esterified form.[11]

The triglycerides present in wood[4,11,15] were completely hydrolyzed during kraft pulping, although steryl esters were still detected in small amounts in the pulp after cooking. This was confirmed by GC-MS analysis of the dichloromethane extract with short length columns as well as by the slight increase in the sterol fraction found after alkaline hydrolysis of the extract (results not shown). The resistance of some steryl esters to hydrolysis during kraft pulping of *E. globulus* wood has been previously reported.[8] The analyses by GC-MS using short columns also detected one steryl glycoside, namely sitosteryl 3-β-*D*-glucopyranoside, known to be present in *E. globulus* wood and kraft pulp.[18,19]

Aromatic compounds such as ferulic acid esters identified in *E. globulus* wood[11] were not detected in the kraft pulp probably because these compounds are completely hydrolyzed during kraft pulping. In addition, ferulic acid resulting from the hydrolysis of ferulates, and other aromatic compounds identified in *E. globulus* wood[11] were also not identified in kraft pulp, possibly due to their degradation or removal with the black liquor during kraft pulping.[16,17]

Among the minor components, two hydroxylated derivatives from β-sitosterol, identified as 24-ethyl-6-cholestene-3,5-diol and 24-ethyl-5-cholestene-3,7-diol, were detected (Figure 1). These components were not found in *E. globulus* wood extractives[8,11,15] and should therefore be formed during pulping.

Bleached Pulp Extractives

The lipophilic extract of the *E. globulus* $D_0E_1D_1E_2D_2$ bleached pulp (Table 3) is composed mainly of long-chain aliphatic components, with docosanoic, tetracosanoic, 24-hydroxytetracosanoic, and hexacosanoic acids as the major components, and of sterols, mainly β-sitostanol and 24-ethylcholestane-3,5,6-triol (Figure 1). Several long-chain aliphatic alcohols were also detected, but in lower amounts. Removal of approximately 80% of these families of lipophilic compounds was achieved when compared with the kraft pulp.

It is noteworthy that the relative abundance of aliphatic acids/alcohols and sterols changed significantly when compared to the unbleached pulp extractives (Figure 2), where β-sitosterol was the major component. This significant decrease in the amount of β-sitosterol, which in this extract is even less abundant than β-sitostanol (Table 3), is mainly due to its degradation during ClO_2 bleaching, and to a lesser extent due to its elimination with the bleaching filtrates. The identification of high amounts of

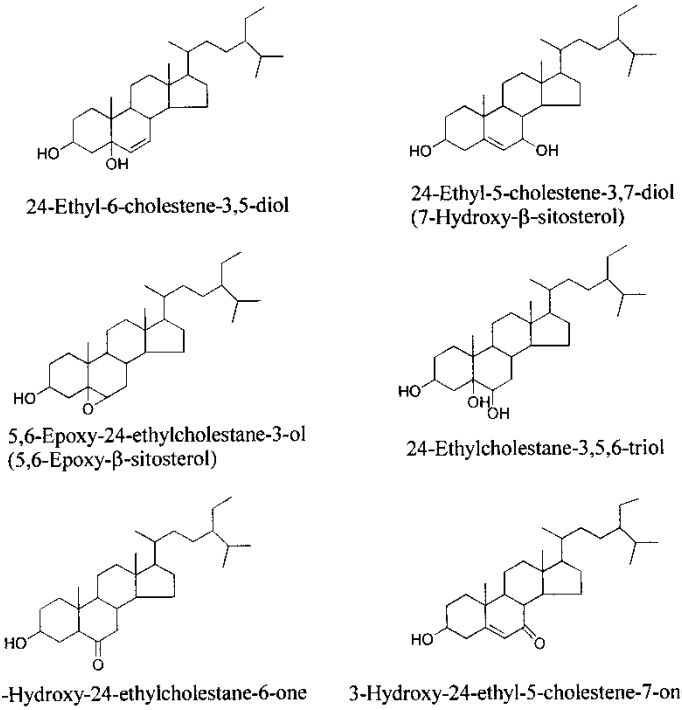

Figure 1. Structures of the main oxidized sterol derivatives identified in kraft and ECF bleached pulps and bleaching filtrates.

24-ethylchlolestane-3,5,6-triol in the bleached pulp is evidence for the degradation of β-sitosterol. This compound has been reported as one of the main oxidation product formed by the reaction of pure β-sitosterol with ClO_2.[14] Minor amounts of other β-sitosterol derivatives, namely 24-ethyl-6-cholestene-3,5-diol, 24-ethyl-5-cholestene-3,7-diol, 5,6-epoxy-24-ethylcholestane-3-ol, 3-hydroxy-24-ethylcholestane-6-one (or isomer) and 3-hydroxy-24-ethyl-5-cholestene-7-one (or isomer) were also detected (Table 3, Figure 1). The *E. globulus* $D_0E_1D_1E_2D_2$ bleached pulp contains around 70% less sterols than the corresponding unbleached pulp (Figure 2). On the other hand, about 70% of the sterols remaining in the bleached pulp are oxidation products of β-sitosterol (Table 3).

Steryl esters, mainly sitosteryl esters, are also almost completely degraded during ECF bleaching of *E. globulus* kraft pulps, as previously reported by Gutiérrez et al.[10]: they were detected in trace amounts in the bleached pulp and were not detected in the bleaching filtrates. However, the steryl glycoside identified in the unbleached pulp was still detected in the pulp after chlorine dioxide bleaching, showing its resistance to hydrolysis or oxidative degradation during ECF bleaching. In fact, the resistance of steryl

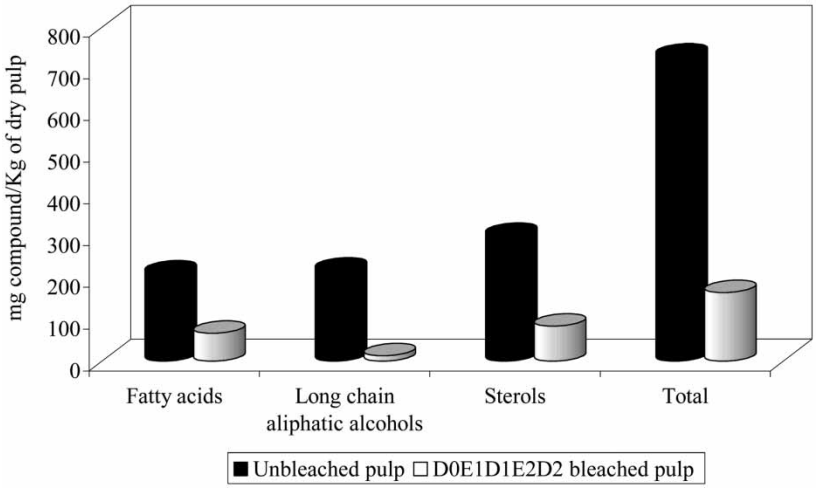

Figure 2. Major families of compounds present in the unbleached kraft pulp (kappa number 16.7, washed to neutral pH of filtrate) and DEDED bleached pulp.

glycosides to hydrolysis during D stages has been reported in bleaching experiments using model compounds.[20]

The amount of aliphatic acids and alcohols in the $D_0E_1D_1E_2D_2$ bleached pulp is also lower than in the unbleached pulp (Figure 2), the decrease observed for these families of compounds is around 70 and 90%, respectively: as expected,[14] unsaturated long-chain aliphatic acids, namely oleic and linoleic acids, are almost completely degraded during ClO_2 bleaching, whereas saturated aliphatic acids are resistant to ClO_2 bleaching conditions (Table 3), being eliminated by dissolution in the bleaching filtrates (see the later discussion).

The decrease of sterols (70%), fatty acids (70%), and alcohols (90%) in the unbleached pulp observed during the ECF bleaching sequence is significantly higher than the decrease of total extractives content calculated gravimetrically (around 20%, Table 1). This can be due in part to the accumulation of the non-volatile compounds with relatively low molecular weight in the bleached pulp, eventually formed during delignification/bleaching reactions, which are extracted by dichloromethane and ethyl acetate but are not detected by GC-MS. The nature of such fraction of the extract needs further investigation.

Bleaching Filtrates Composition

The lipophilic extractives of the D filtrates are mainly composed of long-chain aliphatic alcohols such as Z-9-octadecen-1-ol and 1-hexadecanol (Figure 3).

Table 3. Lipophilic components of the *E. globulus* $D_0E_1D_1E_2D_2$ bleached kraft pulp (Sum of dichloromethane and ethyl acetate extracts)

Compound	Ave[a] mg/kg pulp	SD[b]
1-Hexadecanol	3.33	0.16
Hexadecanoic acid	4.0	0.19
Z-9-octadecen-1-ol	7.08	0.35
Heptadecanoic acid	1.15	0.06
1-Octadecanol	2.87	0.14
Octadecanoic acid	1.68	0.08
Docosanoic acid	6.39	0.31
Tricosanoic acid	1.43	0.07
2-Hydroxydocosanoic acid	1.22	0.06
Tetracosanoic acid	12.8	0.63
2-Hydroxytricosanoic acid	1.09	0.05
Pentacosanoic acid	1.36	0.06
22-Hydroxydocosanoic acid	1.57	0.08
2-Hydroxytetracosanoic acid	3.02	0.15
Hexacosanoic acid	16.1	0.78
24-Hydroxytetracosanoic acid	7.17	0.35
Octacosanoic acid	2.77	0.13
24-Ethy-6-cholestene-3,5-diol	1.79	0.07
β-Sitosterol	4.15	0.20
β-Sitostanol	21.4	1.05
26-Hydroxyhexacosanoic acid	5.46	0.27
24-Ethyl-5-cholestene-3,7-diol	1.48	0.06
5,6-Epoxy-24-ethylcholestane-3-ol	1.76	0.02
24-Ethylchloestane, 3,5,6-triol	34.8	1.7
3-Hydroxy-24-ethylcholestane-6-one or isomer	1.55	0.08
3-Hydroxy-24-ethyl-5-cholestene-7-one or isomer	2.21	0.06
Unidentified sterol derivative	15.1	0.74
Total	164.7	

[a]Average.
[b]Standard deviation.

Long-chain aliphatic acids and sterols were also detected but in lower amounts. Short-chain aliphatic acids, the major fraction being represented by five glucuronoxylan-derived monochlorinated carboxylic acids,[21–23] were also detected in significant amounts in the D filtrates. As previously reported,[21,23] the amount of these chlorinated compounds decreased significantly along the bleaching sequence.

The extracts of the alkaline bleaching filtrates (results not shown) are mainly composed of phenolic compounds, resulting from lignin degradation during bleaching, and aliphatic compounds, such as long-chain aliphatic

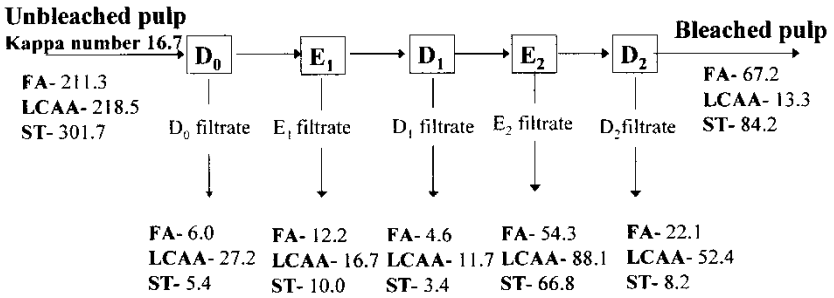

Figure 3. Amounts of lipophilic extractives (mg/kg of dry pulp) removed in the different bleaching stages along the ECF bleaching sequence. (FA—fatty acids; LCCA—long-chain aliphatic alcohols; ST—sterols).

acids and alcohols and sterols. The major phenolic compounds are vanillin, syringaldehyde, vanillic acid, and syringic acid. The high content of long-chain aliphatic compounds and sterols in these filtrates and particularly in E_2 filtrate (Figure 3) suggests that the alkaline extraction stages are effective in the removal of lipophilic extractives from pulp. The E_2 filtrate has a content of lipophilic extractives higher than that of the E_1 filtrate, probably due to their increasing accessibility in the pulp fiber[24] along the bleaching sequence. The accessibility of extractives in pulp fiber can also explain the high content of lipophilic compounds, particularly fatty acids and alcohols, found in the D_2 filtrate (Figure 3). The α- and ω-hydroxyfatty acids, detected in the unbleached and bleached pulps, were also identified in the dichloromethane extracts of the E_1 and E_2 filtrates. 9,10-Dihydroxyoctadecanoic acid and a di(halohydrin) of linoleic acid, reported as the major products formed by the reaction of pure oleic and linoleic acids with ClO_2,[14] were also identified in the alkaline bleaching filtrates. Short-chain aliphatic hydroxyacids formed by the alkaline degradation of carbohydrates during bleaching[2] were detected in significant amounts in the E_1 and E_2 filtrates. The content of these acids decreases along the bleaching sequence. In addition to 24-ethylcholestane-3,5,6-triol, another sterol derivative identified as 5,6-epoxy-24-ethylcholestane-3-ol (Figure 1) was also identified in E_1 and E_2 filtrates. The identification of these sterol derivatives in bleaching filtrates is of enormous interest because of the concerns regarding the biological effects of plant sterols and derivatives[7] and also because of their contribution to *pitch* formation.[25]

Both β-sitosterol and oleic and linoleic acids oxidation products were identified in higher amounts in the E_2 filtrate than in the E_1 filtrate; this can indicate that the major structural transformations of unsaturated extractive compounds during ECF bleaching do not occur at the beginning of the bleaching sequence (where ClO_2 is mainly consumed in delignification reactions and extractives are less accessible), but in the later D stages.

In fact, the analysis of a D_0E_1 partially bleached pulp showed that β-sitosterol is still the major lipophilic compound and that its oxidation products are only minor components of the pulp after the first D stage (results not shown).

The identification of several oxidation products of β-sitosterol and of oleic and linoleic acids in the bleached pulp and in the alkaline extraction filtrates demonstrates that ClO_2 is effective in the conversion of unsaturated lipophilic structures into more oxidized derivatives, whereas the saturated compounds are not affected. In fact it is known that β-sitosterol, oleic acid, and linoleic acid are almost completely degraded during ECF bleaching,[9,15,17] but in most cases their oxidation products were not identified. Compounds such as ω- and α- hydroxyfatty acids as well as long-chain aliphatic alcohols are resistant to oxidation with ClO_2 and remain unchanged during bleaching, as reported for model compounds experiments.[14]

Finally, in the global balance of the lipophilic components in the bleaching sequence, around 20% of the fatty acids, 5% of the aliphatic alcohols, and 40% of the sterols originally present in the kraft pulp are missing. Such differences may be assigned to the probable conversion of some of these structures to higher oxidation state derivatives not detectable by GC-MS,[14] or difficult to extract from liquid filtrates.

CONCLUSIONS

Sterols; fatty acids, including several α- and ω-hydroxyfatty acids; and long-chain aliphatic alcohols were found to be the major lipophilic extractives of the *E. globulus* unbleached kraft pulp. The ECF bleaching sequence removes around 80% of the lipophilic components (80% of sterols, 70% of fatty acids, and 90% of long-chain aliphatic alcohols) from the unbleached kraft pulp. The significant decrease of sterols initially present in pulp is mainly due to the degradation of β-sitosterol during chlorine dioxide bleaching as confirmed by the identification of several oxidation products in the bleached pulp and in the alkaline filtrates. On the other hand, the decrease of fatty acids and long-chain aliphatic alcohols is mainly assigned to their elimination with the alkaline extraction filtrates. The major changes in extractives composition and structure as well as the higher removal efficiency with filtrates takes place in the last bleaching stages due to the increasing accessibility of extractives in the pulp fiber along the bleaching sequence. These results should be taken into account in the solution of the *pitch* problems associated with the production of *E. globulus* ECF bleached pulp because the recirculation of these last filtrates, in conventional counter-current washing systems, represents a major contribution to concentration of lipophilic components in the bleaching plant. Therefore, a partial purge of the E2 and D2 filtrates may help to reduce the accumulation of lipophilic extractives in situations of risk of *pitch* deposition.

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