Lipophilic Extractives from *Eucalyptus globulus* Pulp during Kraft Cooking Followed by TCF and ECF Bleaching

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Summary

The chemical composition of lipophilic extractives in paper pulps from *Eucalyptus globulus* wood during kraft cooking followed by TCF ("totally chlorine free") and ECF ("elemental chlorine free") bleaching sequences has been determined by gas chromatography and gas chromatography-mass spectrometry. The chemical analyses revealed that the composition of the lipophilic extractives in pulp after kraft cooking and TCF bleaching with hydrogen peroxide was similar to that of *E. globulus* wood extractives, sitosterol and sitosterol esters being the predominant compounds. In contrast, the presence of these compounds was almost negligible in pulp after ECF bleaching with chlorine dioxide and only the saturated sterol stigmasterol, in both free and esterified forms, survived the bleaching.

Introduction

Wood resin, which consists of complex mixtures of different lipophilic wood extractives including fatty acids, resin acids, waxes, sterols, sterol esters and glycerides, causes significant technical and economic troubles during pulp and paper manufacturing (Sjöström 1993). During wood pulping and refining of pulp, extractives in the resin canals and ray parenchyma cells can be released forming colloidal pitch. Pitch particles, which can be small in size, then coalesce into larger droplets which deposit on the surface of fibers or equipment being responsible for production troubles and an increased incidence of quality defects (Hillis and Sumimoto 1989).

In the production of bleached kraft pulp, a large part of the resin originally present in wood is removed in the kraft cooking. However, the wood extractives remaining in the brownstock pulp will be carried over to the bleach plant where they will react with the bleaching chemicals to various degrees depending on their chemical structure and on the bleaching agent used (Jansson et al. 1995). The species that survive the bleaching processes can be found as pulp extractives and are detrimental for product quality. The new trends to use environmentally-sound bleaching processes such as "totally chlorine free" (TCF) in place of "elemental chlorine free" (ECF) sequences, are increasing the severity of pitch problems during kraft pulping of some types of wood.

Traditionally, pitch deposits in pulping and paper manufacture have been reduced by debarking and seasoning logs and wood chips and by adding physicochemical control agents (Allen 1988; Dreisbach and Michalopoulos 1989; Allen et al. 1991). However, the cost is high and often the results are far from satisfactory. As an alternative to the

above, biological removal of wood extractives by treatment with enzymes (Fischer and Messner 1992; Fujita et al. 1992; Fischer et al. 1993) or microorganisms (Farrell et al. 1993; Fischer et al. 1994; Gao et al. 1994; Behrendt and Blanchette 1997) has been suggested in recent years for pitch control. The biotechnological preparations commercially available are not effective for pitch control during pulping of eucalypt wood, which is extensively used as pulp raw material in Spain, Portugal, Brazil and other countries. This is because they are based on enzymes (such as lipase commercialized by Novo Nordisk as ResinaseTM) or organisms (such as *Ophiostoma piliferum* strains commercialized by Clariant as CartapipTM) that mainly hydrolyze triglycerides, which only represent a minor fraction of extractives from *Eucalyptus globulus* (Gutiérrez et al. 1999). Moreover, TCF and ECF *E. globulus* pulps are obtained by kraft cooking, which saponifies triglycerides from pulpwoods (Sjöström 1993).

Designing effective biotechnological solutions for extractive removal requires the characterization of the compounds responsible for pitch deposition. In this context the aim of this work was to identify the specific constituents of *E. globulus* pulp resin during kraft pulping and bleaching compared with extractives present in wood. A thorough chemical characterization of extractives at different stages of pulp production will provide insights into the extent of their removal along the cooking and bleaching processes. Pulp samples from both TCF and ECF bleaching processes were selected for this study. The acetone extracts from these samples were analyzed by a gas chromatographic procedure previously described for the rapid analysis of wood extractives and pitch deposits, in which high temperature short and medium capillary columns are used (Gutiérrez et al. 1998).

This work is part of a wider project aimed at the evaluation of the viability of biotechnological solutions for eliminating problematic lipophilic compounds from both eucalypt wood and pulp by treatment with fungi and enzymes. The characterization of lipophilic extractives from *E. globulus* pulp will greatly assist the development of these environmentally-sound biotechnological approaches.

Material and Methods

Pulp samples

Samples of kraft pulps from the ENCE mills at Pontevedra and Huelva (Spain), were selected at different points of the TCF and ECF bleaching processes, respectively. The locations where the pulps were collected are shown in Table 1. Samples representative of a TCF process were collected after kraft cooking and several washes (W1, W2), an oxygen delignification stage (O), a post-oxygen press (press), a chelating stage (Q) and after the bleaching with hydrogen peroxide (P). One pulp sample representative of the ECF process was collected after bleaching of oxygen-delignified kraft pulp with chlorine dioxide (D).

Extraction

The dried pulps (10 g) were Soxhlet-extracted with acetone (Panreac, Barcelona, Spain) for 6 hours. The acetone extracts were evaporated to dryness and redissolved in chloroform for the analysis of the lipophilic fraction by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

GC and GC-MS

A Hewlett Packard HP 5890 gas chromatograph equipped with a split-splitless injector and a flame ionization detector (FID) was used for GC analyses (Hewlett Packard, Hoofddorp, Netherlands). The injector and the detector temperatures were set at 300 °C and 350 °C respectively. Samples (1 µl) were injected in the splitless mode. Helium was used as the carrier gas at a rate of 2 ml min⁻¹. The capillary column used was a high temperature, polyimide coated fused silica tubing DB5-HT (5 m × 0.25 mm I.D., 0.1 µm film thickness) from J&W Scientific (Folsom, CA, USA), especially processed for use at 400 °C. The oven was temperature-programmed from 100 °C (1 min) to 350 °C (3 min) at 15 °C min⁻¹. A mixture of standard compounds (palmitic acid, sitosterol, cholesteryl oleate and triheptadecanoin) supplied by Sigma Chemical Co. (St. Louis, MO, USA) was used to prepare a calibration curve for the quantitation of wood extractives with a concentration range between 0.1 and 1 mg ml⁻¹. All peaks were quantified by area. The correlation coefficient was higher than 0.99 in all cases.

Table 1. Location and extractive content of the pulp samples selected for this study

Label	Location	Acetone extract (%)
W1	First washing filter after kraft cooking	0.23
W2	Last washing filter before oxygen stage	0.14
O	Washing filter from inter-oxygen stage	0.11
Press	Post-oxygen press	0.11
Q	Filter from chelating stage	0.09
P	Peroxide filter	0.07
D	Chlorine dioxide filter	0.07

The GC-MS analyses were performed on a Varian Star 3400 gas chromatograph (Varian, Walnut Creek, CA, USA) with an ion trap detector (Varian Saturn 2000) using a high temperature capillary column (DB-5HT, 15 m × 0.25 mm I.D., 0.1 µm film thickness; J & W Scientific). Helium was used as the carrier gas. The samples (1 µl) were injected with an autoinjector (Varian 8200) directly onto the column using a SPI (Septum-equipped Programmable Injector) system. The temperature of the injector during the injection was 120 °C, and 0.1 min after the injection was programmed to 380 °C at a rate of 200 °C min⁻¹ and held 10 min. The oven was temperature-programmed from 120 °C (1 min) to 380 °C (5 min) at 10 °C min⁻¹. The temperatures of the ion trap and the transfer line were set at 200 °C and 300 °C respectively. Compounds were identified by comparison of the mass spectra with those in the Wiley and Nist libraries, by mass fragmentography and, when possible, by comparison with standard compounds.

Results and Discussion

As a preliminary step in the development of biotechnological treatments to overcome some of the drawbacks in the manufacturing of high quality kraft pulps from *E. globulus* wood, the chemical characterization of pulp resin throughout the production processes was performed. Representative pulp samples were collected at different points along the kraft cooking and TCF and ECF bleaching processes. Table 1 shows the amount of acetone extract in each sample.

The analysis of lipophilic extractives in the pulp samples was carried out by GC and GC-MS using short and medium length high temperature capillary columns, respectively, which allow the elution and separation of high-molecular-mass lipids such as waxes, sterol esters and triglycerides (Wakeham and Frew 1982; Lusby *et al.* 1984; Evershed *et al.* 1989; Sitholé *et al.* 1992; Örså and Holmbom 1994). The composition of lipophilic extractives in these pulps was compared with that of *E. globulus* wood resin which consisted mainly of steroids (hydrocarbons, sterols, sterol esters and ketones), fatty acids and triglycerides (Fig. 1). A detailed study on the composition of lipophilic extractives from *E. globulus* wood has already been published (Gutiérrez *et al.* 1999). The chromatograms of the extracts from different representative pulp samples are shown in Figure 2

Fig. 1. Total Ion Chromatogram of lipophilic extractives from *E. globulus* wood. The identity of major compounds is shown in the chromatogram.

and the composition of the lipophilic extractives in the pulp samples after the kraft cooking and throughout the bleaching sequences is outlined in Table 2. The major lipophilic components in the eucalypt pulp sample after kraft cooking (W1) were sterols and sterol esters. Minor amounts of steroid hydrocarbons and ketones, squalene and fatty acids, were also identified. Sitosterol was found to be the dominating sterol in the pulp sample. Furthermore, it contained fucosterol, citrostadienol, cycloartenol, 24-methylenecycloartanol and stigmastanol. Sterol esters were mostly composed of sitosterol and other sterol esters (including mainly cycloartenol and 24-methylenecycloartanol esters), with minor amounts of stigmastanol esters. Steroid ketones (stigmastan-3-one, stigmasta-3,5-dien-7-one, stigmast-4-en-3-one and stigmasta-3,6-dione) and steroid hydrocarbons (the main compound being tentatively identified as stigmasta-3,5-diene), were also identified in W1. The above compounds were already found in *E. globulus* wood extractives (Gutiérrez *et al.* 1999).

The main difference observed between the composition of resin from *E. globulus* wood and the pulp after cooking was the total absence of glycerol esters and the lower

amount of fatty acids. This is due to the fact that during kraft cooking glycerol esters are hydrolyzed and the fatty acids dissolved as sodium salts in the cooking liquor (Hillis and Sumimoto 1989). However, sterol esters, which are not extensively hydrolyzed, and sterols do not form soluble soaps under the alkaline conditions used in kraft pulping and therefore, have a tendency to deposit and cause pitch problems (Swan 1967; Affleck and Ryan 1969; Leone and Breuil 1998). The fatty acid soaps are effective solubilizing agents facilitating the removal from pulp of sparingly soluble neutral substances such as sterols. When the content of fatty acids is low compared to that of unsaponifiable substances as in eucalypt wood, the fatty acid soaps formed during the cooking do not possess sufficient micellar-forming properties to carry the less polar compounds into solution. So, an unbleached pulp with high proportion of resin is produced (Swan 1967). The high concentration of unsaponifiable compounds with respect to the saponifiable extractives is the main cause for pitch problems in the kraft pulping of some hardwoods used by the pulp and paper industry, such as aspen or eucalypt (Swan 1967; Allen 1988; Allen *et al.* 1991; Dunlop-Jones *et al.* 1991; Sitholé *et al.* 1992; Chen *et al.* 1995; Leone and Breuil 1998). Another remarkable difference between the composition of resin from *E. globulus* wood (Gutiérrez *et al.* 1999) and brown pulp was the higher relative proportion in the latter of cycloartenol and 24-methylenecycloartanol esters with respect to sitosterol esters. This may be due to the presence of two methyl groups in the C4 of cycloartenol and 24-methylenecycloartanol which makes the hydrolysis of the ester linkage more difficult.

In the subsequent steps of the process after cooking there was an important decrease in the amount of all the compounds present in the extracts. As shown in Table 2, the most important reduction in the content of lipophilic extractives was achieved in the washing stages (W1-W2). During the oxygen prebleaching (O), post-oxygen press (Press), chelating stage (Q) and hydrogen peroxide bleaching (P), the content of the different extractives continued to decrease significantly but the relative composition of the different compounds was not considerably modified. This indicates that, in general terms, the oxygen prebleaching and the hydrogen peroxide bleaching stages have minor influence on the composition of pulp extracts. In contrast, the composition of the lipophilic extract from the chlorine dioxide bleached pulp (D) was quite different from that after hydrogen peroxide bleaching. The main compounds identified in this pulp were steroid hydrocarbons, steroid ketones, sterols, and sterol esters (representing 36, 28, 26, and 8 % of the pulp extract, respectively). Of the original sterols present in *E. globulus* wood and in the unbleached and TCF bleached pulps, only the saturated sterol stigmastanol could be identified in the pulp bleached with chlorine dioxide together with traces of sitosterol. This result is in agreement with Jansson *et al.* (1995) who also found that the amount of sitosterol in softwood pulp decreased more than 99 % after bleaching with chlorine dioxide to full brightness, whereas the amount of stigmastanol only decreased about 30 %. The lower decrease of sitosterol in the hydrogen per-

Fig. 2. Total Ion Chromatograms of lipophilic extractives from *E. globulus* kraft pulps after first washing stage after cooking (W1), bleaching with hydrogen peroxide (TCF) and bleaching with chlorine dioxide (ECF).

Table 2. Chemical composition of resin from *E. globulus* kraft pulps (mg/kg pulp)

	W1	W2	O	Press	Q	P	D
Fatty acids							
Palmitic acid	12	4	1	< 1	< 1	< 1	1
Oleic + linoleic acids	3	< 1	< 1	< 1	< 1	< 1	0
Stearic acid	4	1	< 1	< 1	< 1	< 1	1
Hydrocarbons							
Squalene	12	5	3	2	2	1	< 1
Steroid hydrocarbons	55	49	47	34	25	25	30
Tocopherols							
α -Tocopherol	8	3	2	2	1	1	0
Sterols							
Sitosterol	505	234	170	155	120	90	4
Stigmastanol	97	45	42	29	25	23	18
Fucosterol	76	27	18	14	12	8	0
Cycloartenol	12	4	2	2	2	1	0
24-Methylenecycloartanol	5	5	3	3	2	2	0
Citrostadienol	26	11	8	7	7	5	0
Steroid ketones							
Stigmastan-3-one	3	3	3	3	2	1	4
Stigmasta-3,5-dien-7-one	14	12	12	10	5	5	9
Stigmast-4-en-3-one	3	3	2	2	1	2	4
Stigmasta-3,6-dione	28	16	8	4	1	5	7
Sterol esters							
Sitosterol esters	142	46	46	46	45	45	2
Stigmastanol esters	46	18	18	18	15	15	4
Other sterol esters	123	42	39	36	36	35	1

oxide bleached pulp indicates that this bleaching agent has lower capacity than chlorine dioxide to oxidize unsaturated sterols. Likewise, the series of sterol esters identified in the ECF pulp corresponded to stigmastanol esters, and only traces of sitosterol esters were identified. On the other hand, the same steroid ketones and steroid hydrocarbons present in the *E. globulus* wood and in the unbleached and hydrogen peroxide bleached pulps were also present in the chlorine dioxide bleached pulp. Finally, no chlorinated compounds were identified in the latter pulp, in agreement with Jansson *et al.* (1995) who could not identify chlorinated compounds in extracts of a chlorine dioxide bleached pulp.

Conclusions

The composition of lipophilic extractives present in the eucalypt pulps after kraft cooking and TCF and ECF bleaching processes was studied. Triglycerides were hydrolyzed during the cooking and the fatty acids dissolved. Therefore, they were not present as extractives in the pulp. The major lipophilic compounds identified in TCF pulps were sterols and sterol esters, sitosterol being the major free and esterified sterol. An important decrease of lipophilic compounds occurred throughout the bleaching process, although with the same qualitative composition. In general, the oxygen prebleaching and hydrogen peroxide bleaching stages had minor influence on the composition of eucalypt

pulp extracts. However, the composition of the extracts after chlorine dioxide bleaching was very different. Sitosterol was nearly absent and only the saturated sterol stigmastanol was present after ECF bleaching.

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