



## Lipophilic extractives from several nonwoody lignocellulosic crops (flax, hemp, sisal, abaca) and their fate during alkaline pulping and TCF/ECF bleaching

Gisela Marques, José C. del Río, Ana Gutiérrez \*

*Instituto de Recursos Naturales y Agrobiología, CSIC, P.O. Box 1052, E-41080 Seville, Spain*

### ARTICLE INFO

#### Article history:

Received 20 May 2009

Received in revised form 6 August 2009

Accepted 7 August 2009

Available online 3 September 2009

#### Keywords:

Pitch

Lipophilic extractives

Paper pulp

Nonwoody fibers

### ABSTRACT

The fate of lipophilic extractives from several nonwoody species (flax, hemp, sisal and abaca) used for the manufacturing of cellulose pulps, was studied during soda/anthraquinone (AQ) pulping and totally chlorine free (TCF) and elemental chlorine free (ECF) bleaching. With this purpose, the lipophilic extracts from the raw materials and their unbleached and bleached industrial pulps, were analyzed by gas chromatography–mass spectrometry. Aldehydes, hydroxyfatty acids and esterified compounds such as ester waxes, sterol esters and alkylferulates strongly decreased after soda/AQ pulping while alkanes, alcohols, free sterols and sterol glycosides survived the cooking process. Among the lipophilic extractives that remained in the unbleached pulps, some amounts of free sterols were still present in the TCF pulps whereas they were practically absent in the ECF pulps. Sterol glycosides were also removed after both TCF and ECF bleaching. By contrast, saturated fatty acids, fatty alcohols and alkanes were still present in both bleached pulps.

© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

Lipophilic extractives, i.e., the non-polar extractable fraction from wood and other lignocellulosic crops, include different classes of compounds, such as alkanes, fatty alcohols, fatty acids, free and conjugated sterols, terpenoids, triglycerides and waxes. These lipophilic compounds, even when present in low amounts in the raw material, may play an important role in industrial wood processing for bleached pulp and paper production since they are at the origin of the so-called pitch deposits along the pulp and paper manufacturing processes. Pitch deposition is a serious problem in the pulp and paper industry since it is responsible for reduced production levels, higher equipment maintenance costs, higher operating costs, and an increased incidence of defects in the finished products, which reduces quality and benefits (Back and Allen, 2000).

The nature and severity of pitch deposition depend not only on the raw materials used (and hence on the nature of the lipophilic compounds), but also on the industrial processes of pulping and bleaching applied at the mill. In the manufacture of alkaline pulps, a large part of the lipids originally present in the raw material is removed during the cooking and bleaching stages. However, some chemical species survive these processes and are found as pulp extractives (Bergelin and Holmbom, 2003; Freire et al., 2005, 2006; Gutiérrez et al., 2001a), suspended in process waters (Gutiérrez et al., 2001b) or forming the so-called pitch deposits

in circuits, equipments and final product (Bergelin et al., 2005; del Río et al., 1998, 2000; Gutiérrez and del Río, 2005; Silvestre et al., 1999). Growing pressure for closing water loops in pulp and paper mills leads to increasing build up of lipophilic compounds in the processes and therefore, to an increasing number of severe and costly pitch related problems.

The different classes of lipids have different behavior during pulping and bleaching. Several studies have provided information on the behavior of wood lipids, such as fatty and resin acids, triglycerides and sterols and triterpenols during pulping and bleaching (Back and Allen, 2000; Bergelin and Holmbom, 2003, 2008; Freire et al., 2005, 2006; Gutiérrez et al., 2001a; Shin and Kim, 2006). However, the chemistry of lipids from nonwoody pulps in pulping and bleaching has not been examined much so far (Gutiérrez et al., 2004; Gutiérrez and del Río, 2003a,b). Likewise, to the best of our knowledge, there is very little information available dealing with pitch problems on nonwoody pulps (Gutiérrez and del Río, 2005). In this context, the aim of this work was to identify the specific lipophilic constituents of different nonwoody fibers, which are used for the manufacturing of cellulose pulps for specialty papers, and to study their behavior during soda/anthraquinone (AQ) pulping and totally chlorine free (TCF) and elemental chlorine free (ECF) bleaching. For this, a series of pulps (crude pulps taken after soda/AQ pulping and bleached pulps taken after TCF and ECF bleaching) from different nonwoody raw materials (flax, hemp, sisal, abaca) were selected for this study. The composition of the lipophilic compounds in the fibers and their respective pulps was analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS)

\* Corresponding author. Tel.: +34 95 462 4711; fax: +34 95 462 4002.  
E-mail address: [anagu@irnase.csic.es](mailto:anagu@irnase.csic.es) (A. Gutiérrez).

using short- and medium-length high temperature capillary columns, respectively, with thin films, which enables the elution and analysis of intact high molecular weight lipids such as waxes or sterol glycosides (Gutiérrez et al., 1998; Gutiérrez and del Río, 2001). The knowledge of the behavior of lipophilic extractives during pulping and bleaching is an important step towards understanding and predicting the pitch problems and designing effective solutions for its control.

## 2. Methods

### 2.1. Samples

Two bast fibers, flax (*Linum usitatissimum*) and hemp (*Cannabis sativa*), and two leaf fibers, sisal (*Agave sisalana*) and abaca (*Musa textilis*), were selected for this study. The raw materials and their respective crude (unbleached) pulps (pulps taken after soda/AQ pulping), as well as pulp samples after TCF and ECF bleaching, were supplied by CELESA pulp mill (Tortosa, Spain). General conditions of soda/AQ pulping included the use of sodium hydroxide and anthraquinone (up to 0.05%) as cooking chemicals, and 2–4 h of cooking time at a temperature of about 160–170 °C. The TCF bleaching sequence used (QPo) included a quelating stage (Q) and a hydrogen peroxide stage under pressurized oxygen (Po). The ECF bleaching sequence used (DPo) included a chlorine dioxide stage (D) followed by a hydrogen peroxide stage under pressurized oxygen (Po).

### 2.2. Lipid extraction

Raw materials and pulps were air-dried until constant weight and the samples were Soxhlet-extracted with acetone for 8 h. All the extracts were evaporated to dryness and redissolved in chloroform for chromatographic analysis of the lipophilic fraction as described below.

### 2.3. GC and GC–MS analyses

The GC analyses of the lipids from the raw materials and pulps were performed in an Agilent 6890N Network GC system using a short fused-silica DB-5HT capillary column (5 m × 0.25 mm internal diameter, 0.1 µm film thickness) from J&W Scientific, enabling simultaneous elution of the different lipid classes (Gutiérrez et al., 1998). The temperature program was started at 100 °C with 1 min hold, and then raised to 350 °C at 15 °C/min, and held for 3 min. The injector and flame-ionization detector (FID) temperatures were set at 300 and 350 °C, respectively. Helium (5 ml/min) was used as carrier gas, and the injection was performed in splitless mode.

The GC–MS analyses were performed with a Varian 3800 chromatograph coupled to an ion-trap detector (Varian 4000) using a medium-length (12 m) capillary column of the same characteristics described above for GC/FID. The oven was heated from 120 °C (1 min) to 380 °C at 10 °C/min, and held for 5 min. The transfer line was kept at 300 °C, the injector was programmed from 120 °C (0.1 min) to 380 °C at 200 °C/min and held until the end of the analysis, and helium was used as carrier gas at a rate of 2 ml/min. The compounds were identified by mass fragmentography, and by comparing their mass spectra with those of the Wiley and NIST libraries and standards.

Both underivatized and derivatized samples were analyzed by GC and GC–MS. Two derivatized samples, silylated samples and methylated and silylated samples, were analyzed. The silylation was performed using bis(trimethylsilyl)trifluoroacetamide (BSTFA) in the presence of pyridine at 80 °C for 90 min (Gutiérrez and del

Río, 2001). Trimethylsilyl-diazomethane methylation, in the presence of methanol (at room temperature for 10 min) followed by BSTFA silylation, in the presence of pyridine, were also performed. Fatty alcohols, fatty acids and sterol glycosides were determined as silylated derivatives in the derivatized samples. Hydroxyfatty acids were determined in the samples after methylation followed by silylation. The rest of compounds were determined in the underivatized samples. Peaks were quantified by area and a mixture of standards (octadecane, palmitic acid, sitosterol, cholesteryl oleate, and sitosteryl 3β-D-glucopyranoside) with a concentration range between 0.1 and 1 mg/ml was used to elaborate calibration curves. The data from two replicates were averaged.

## 3. Results and discussion

The lipid content of the nonwoody fibers used in this study and their corresponding crude and TCF and ECF bleached pulps is shown in Table 1. Flax fibers have the highest content on lipophilic extractives followed by hemp, sisal and abaca fibers. Regardless the higher lipid content of flax fibers, the content of lipophilic extractives of its crude pulp was similar or even lower than in the other fibers. On the other hand, the lipid content of the pulps decreased further after TCF or ECF bleaching, ranging from 0.03% to 0.18%. The differences observed in the lipid content among the different crude and bleached pulps of the nonwoody fibers is related to the behavior of lipophilic extractives present in the raw materials in alkaline pulping and to their reactivity towards the bleaching agents used as described below.

### 3.1. Composition of lipophilic extractives in the nonwoody fibers selected for this study

With the aim of studying the fate of the different lipophilic extractives during soda/AQ pulping, the lipid extracts from the different nonwoody fibers selected for this study were analyzed by GC and GC–MS and then compared with those in the crude pulps. The composition of the lipophilic extractives of the selected raw materials is listed in Table 2 and the chemical structures of the main compounds identified are represented in Fig. 1.

The main lipid classes present in the nonwoody fibers selected for this study were series of alkanes (I), fatty alcohols (II), aldehydes (III), fatty acids (IV), steroids, including free (V) and conjugated sterols (VI–VII), triterpenoids (VIII) and ester waxes (IX). The detailed composition of the lipophilic compounds present in these fibers have been previously addressed (del Río et al., 2004; del Río and Gutiérrez, 2006; Gutiérrez et al., 2006b, 2008; Gutiérrez and del Río, 2003a,b).

In the case of flax bast fibers the predominant lipophilic compounds present were series of fatty acids and aldehydes, accounting for 34% and 23% of total extract, respectively, followed by ester waxes (18%), and fatty alcohols (13%). Fatty acids were also the predominant compounds (27% of total extract) in hemp bast fibers, followed by alkanes (15%), free sterols (12%) and steroid hydrocarbons (12%). Among the selected leaf fibers, free sterols predominated in both sisal (20%) and abaca (45%), followed by alkanes

**Table 1**  
Lipophilic extractives content (%) in the selected nonwoody raw materials and pulps.

	Flax	Hemp	Sisal	Abaca
Fiber	1.70	0.88	0.68	0.51
Crude pulp	0.21	0.26	0.30	0.20
TCF pulp	0.05	0.18	0.09	0.04
ECF pulp	0.13	0.18	0.14	0.03

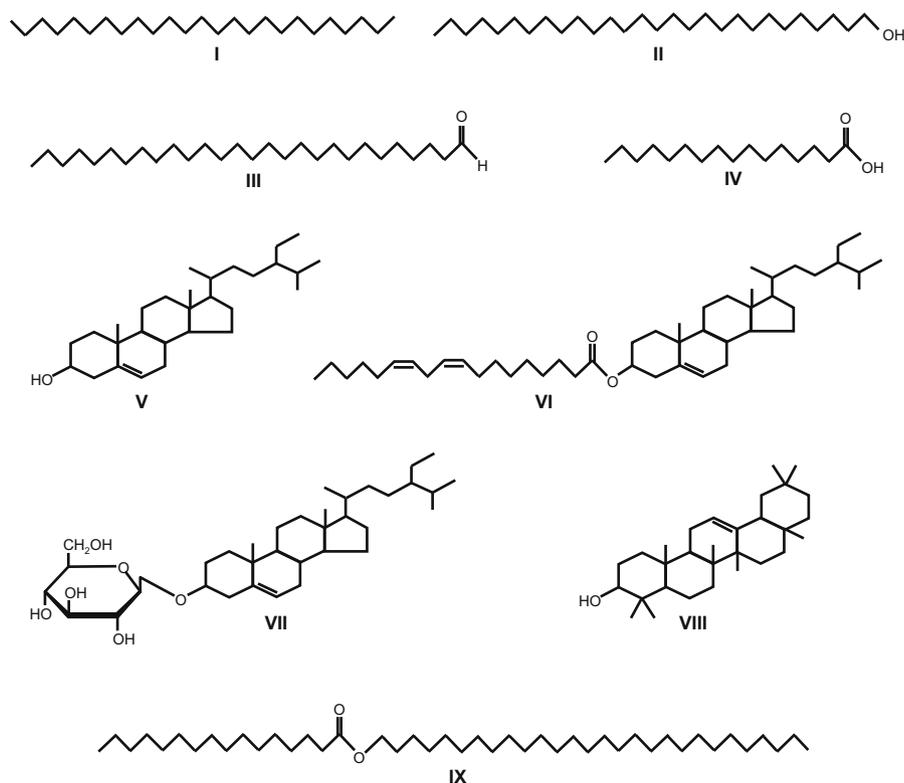
**Table 2**  
Composition of lipophilic extractives (mg/100 g) in nonwoody raw materials (M) and crude (C), TCF (T) and ECF (E) pulps.

Compound	Flax				Hemp				Sisal				Abaca			
	M	C	T	E	M	C	T	E	M	C	T	E	M	C	T	E
Fatty acids	552	96	29	39	78	60	12	80	9	50	10	42	9	57	19	28
<i>n</i> -Hexadecanoic acid	121	27	4	18	34	15	4	29	4	24	8	27	4	20	9	10
9,12-Octadecadienoic acid	1	tr	–	–	3	1	1	–	–	–	–	–	1	3	–	–
9-Octadecenoic acid	235	39	2	1	15	1	tr	1	–	–	–	–	2	6	–	–
<i>n</i> -Octadecanoic acid	52	22	8	12	6	10	3	20	<1	6	7	16	1	21	11	16
<i>n</i> -Nonadecanoic acid	tr	3	tr	tr	tr	5	1	tr	–	–	–	–	tr	–	tr	tr
<i>n</i> -Eicosanoic acid	20	2	4	4	4	6	<1	6	tr	1	<1	2	<1	2	tr	1
<i>n</i> -Heneicosanoic acid	4	tr	tr	tr	tr	1	1	1	–	–	–	–	tr	–	–	tr
<i>n</i> -Docosanoic acid	36	2	4	2	5	7	1	8	tr	tr	1	2	<1	tr	tr	tr
<i>n</i> -Tricosanoic acid	16	tr	tr	tr	2	3	1	4	1	tr	<1	1	tr	tr	tr	tr
<i>n</i> -Tetracosanoic acid	40	1	4	2	4	7	<1	6	1	1	1	3	1	3	<1	1
<i>n</i> -Pentacosanoic acid	8	tr	tr	tr	2	1	<1	1	<1	2	tr	–	tr	–	tr	tr
<i>n</i> -Hexacosanoic acid	19	–	3	tr	3	3	tr	1	1	10	1	2	tr	2	–	1
<i>n</i> -Octacosanoic acid	–	–	–	–	–	–	tr	3	2	17	tr	tr	–	–	–	–
$\alpha$ -Hydroxyfatty acids	11	–	–	–	9	tr	–	–	7	–	–	–	1	–	–	–
2-Hydroxydocosanoic acid	3	–	–	–	–	–	–	–	1	–	–	–	–	–	–	–
2-Hydroxytricosanoic acid	2	–	–	–	–	–	–	–	1	–	–	–	–	–	–	–
2-Hydroxytetracosanoic acid	6	–	–	–	5	tr	–	–	4	–	–	–	1	–	–	–
2-Hydroxypentacosanoic acid	tr	–	–	–	4	–	–	–	1	–	–	–	tr	–	–	–
$\omega$ -Hydroxyfatty acids	–	–	–	–	–	–	–	–	6	–	–	–	1	–	–	–
22-Hydroxydocosanoic acid	–	–	–	–	–	–	–	–	1	–	–	–	1	–	–	–
26-Hydroxyhexacosanoic acid	–	–	–	–	–	–	–	–	2	–	–	–	tr	–	–	–
28-Hydroxyoctacosanoic acid	–	–	–	–	–	–	–	–	3	–	–	–	–	–	–	–
Fatty alcohols	220	68	1	52	2	44	13	59	8	74	18	51	tr	6	1	<1
<i>n</i> -Docosanol	–	–	–	–	–	4	1	4	–	5	2	3	tr	2	<1	<1
<i>n</i> -Tetracosanol	4	2	tr	–	<1	3	1	4	–	6	1	5	tr	1	<1	tr
<i>n</i> -Hexacosanol	49	15	<1	11	<1	8	2	12	2	20	5	14	tr	1	<1	tr
<i>n</i> -Octacosanol	116	38	1	29	1	21	6	28	5	35	9	25	tr	2	<1	tr
<i>n</i> -Triacosanol	51	13	<1	12	1	8	3	11	1	8	1	4	tr	<1	–	–
Alkanes	27	22	1	3	43	44	14	23	15	18	4	22	–	–	–	–
<i>n</i> -Heneicosane	–	–	–	–	–	–	–	–	2	–	–	–	–	–	–	–
<i>n</i> -Docosane	–	–	–	–	–	–	–	–	1	–	–	–	–	–	–	–
<i>n</i> -Tricosane	–	–	–	–	–	–	–	–	2	–	<1	1	–	–	–	–
<i>n</i> -Tetracosane	–	–	–	–	–	–	–	–	1	tr	–	tr	–	–	–	–
<i>n</i> -Pentacosane	2	2	<1	tr	<1	1	–	–	5	5	2	5	–	–	–	–
<i>n</i> -Hexacosane	–	–	–	–	–	–	–	–	1	tr	tr	tr	–	–	–	–
<i>n</i> -Heptacosane	5	3	<1	1	3	5	1	2	3	3	1	4	–	–	–	–
<i>n</i> -Nonacosane	20	17	<1	2	38	31	12	19	<1	10	1	12	–	–	–	–
<i>n</i> -Hentriacontane	–	–	–	–	2	7	1	2	–	tr	tr	tr	–	–	–	–
Aldehydes	371	3	<1	8	25	<1	tr	6	1	tr	tr	2	–	–	–	–
<i>n</i> -Hexacosanal	58	tr	tr	1	3	–	–	1	tr	tr	tr	–	–	–	–	–
<i>n</i> -Octacosanal	174	3	<1	5	9	<1	tr	3	1	tr	1	2	–	–	–	–
<i>n</i> -Triacontanal	139	tr	tr	2	13	tr	–	2	tr	tr	1	4	–	–	–	–
Steroid hydrocarbons	14	3	1	2	30	5	1	1	14	11	1	3	3	4	1	<1
Stigmasta-3,5,22-triene	5	3	1	2	12	4	1	1	10	11	1	3	2	3	1	<1
Stigmasta-3,5-diene	9	<1	tr	tr	18	1	<1	tr	4	tr	–	–	1	1	<1	tr
Steroid ketones	33	6	<1	tr	27	6	3	9	3	5	1	7	4	6	5	1
Cycloartenone	–	–	–	–	–	–	–	–	–	–	–	–	2	1	<1	–
$\beta$ -Amirenone	–	–	–	–	tr	1	tr	–	–	–	–	–	–	–	–	–
Stigmasta-3,5-dien-7-one	5	3	<1	tr	3	1	1	<1	2	3	1	5	1	3	3	1
Stigmast-4-en-3-one	9	1	tr	–	5	–	–	–	1	1	tr	tr	1	1	1	<1
Stigmastadienone isomer	3	1	–	–	2	<1	<1	2	<1	tr	<1	2	<1	1	1	tr
Friedelan-3-one	–	–	–	–	15	4	2	7	–	–	–	–	–	–	–	–
Ergostane-3,6-dione	6	tr	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Stigmastane-3,6-dione	10	1	–	–	2	–	–	–	<1	1	tr	–	–	–	–	–
Free sterols/triterpenols	92	33	3	–	36	78	15	6	20	107	14	14	25	20	5	<1
Campesterol	27	8	1	–	3	9	2	–	<1	9	tr	–	2	3	1	tr
Stigmasterol	23	5	<1	–	3	9	2	–	3	15	2	2	2	3	1	<1
Sitosterol	36	17	2	–	18	37	7	–	11	56	8	8	10	11	3	<1
Stigmastanol	6	3	<1	–	2	6	1	–	1	6	1	1	tr	1	<1	<1
$\beta$ -Amyrin	–	–	–	–	9	15	3	5	1	6	tr	tr	–	–	–	–
$\alpha$ -Amyrin	–	–	–	–	1	2	<1	1	tr	1	tr	tr	–	–	–	–
7-Oxositosterol	–	–	–	–	–	–	–	–	2	2	1	tr	11	2	<1	tr
Hecogenin	–	–	–	–	–	–	–	–	2	12	2	2	–	–	–	–
Sterol glycosides <sup>a</sup>	5	8	1	tr	13	16	<1	tr	2	25	2	1	2	8	<1	tr
Campesterol 3 $\beta$ -D-Glcp	tr	2	<1	tr	2	3	tr	–	tr	6	<1	tr	<1	3	<1	tr
Stigmasterol 3 $\beta$ -D-Glcp	tr	1	tr	tr	1	2	tr	–	<1	3	<1	tr	tr	1	tr	tr
Sitosterol 3 $\beta$ -D-Glcp	5	5	1	tr	10	11	<1	tr	2	16	2	1	2	4	<1	tr
Sterol/triterpenol esters	6	–	–	–	7	–	–	–	<1	–	–	–	1	–	–	–

**Table 2** (continued)

Compound	Flax				Hemp				Sisal				Abaca				
	M	C	T	E	M	C	T	E	M	C	T	E	M	C	T	E	
$\beta$ -Amyrin acetate	-	-	-	-	6	-	-	-	-	-	-	-	-	-	-	-	-
Sitosterol esters	6	-	-	-	1	-	-	-	-	<1	-	-	-	1	-	-	-
Ester waxes <sup>a</sup>	284	-	-	-	17	-	-	-	-	<1	-	-	-	-	-	-	-
C40	8	-	-	-	tr	-	-	-	-	-	-	-	-	-	-	-	-
C42	19	-	-	-	4	-	-	-	-	tr	-	-	-	-	-	-	-
C44	68	-	-	-	5	-	-	-	-	<1	-	-	-	-	-	-	-
C46	130	-	-	-	4	-	-	-	-	tr	-	-	-	-	-	-	-
C48	56	-	-	-	2	-	-	-	-	<1	-	-	-	-	-	-	-
C50	4	-	-	-	2	-	-	-	-	<1	-	-	-	-	-	-	-
Ferulates	-	-	-	-	-	-	-	-	-	5	-	-	-	-	-	-	-
<i>t</i> -Tetracosanil ferulate	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-	-
<i>t</i> -Hexacosanil ferulate	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-	-	-
<i>t</i> -Octacosanil ferulate	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-	-	-

<sup>a</sup> Abbreviations: Glcp, glucopyranoside; C(*n*), *n* denotes the total carbon atom number; tr: traces.



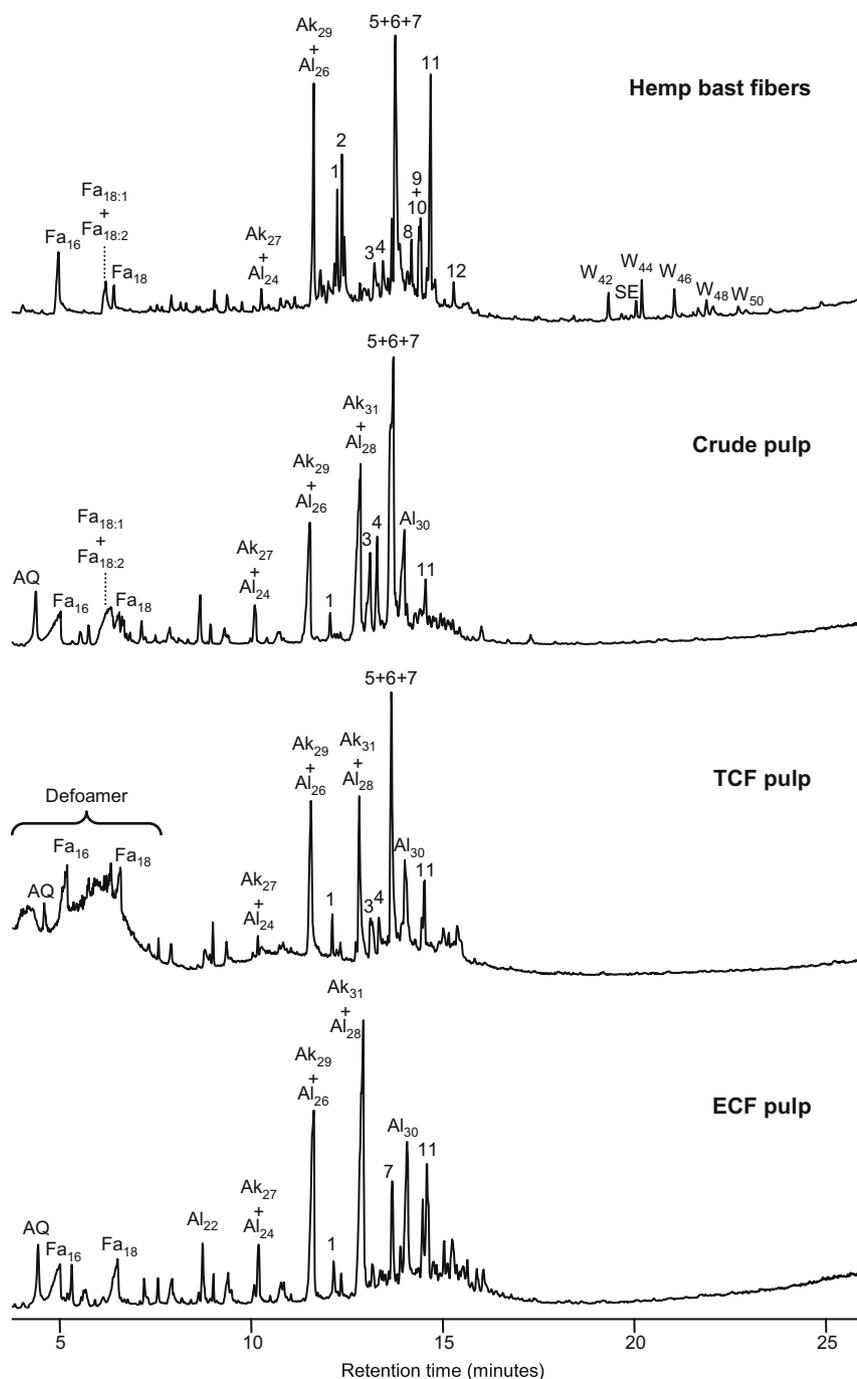
**Fig. 1.** Chemical structures of compounds representing the main classes of lipophilic extractives found in lignocellulosic fibers: (I) pentacosane; (II) octacosanol; (III) octacosanal; (IV) palmitic acid; (V) sitosterol; (VI) sitosteryl linoleate; (VII) sitosteryl 3 $\beta$ -D-glucopyranoside; (VIII)  $\beta$ -amyrin; and (IX) octacosyl hexadecanoate.

(14%) and fatty acids (10%) in sisal, and by fatty acids (16%) in abaca fibers.

These lipophilic compounds can be classified into two principal groups, namely organic acids and neutral components. Organic acids include fatty acids, and the neutrals include alkanes, aldehydes, fatty alcohols, and free sterols as well as esterified and conjugated compounds such as ester waxes, sterol esters, alkylferulates and sterol glycosides. Organic acids and neutral compounds, the latter including saponifiable and unsaponifiable compounds, present different behavior during alkaline pulping, as shown below.

### 3.2. Fate of lipophilic extractives during soda/AQ pulping

The fate of the different lipophilic extractives during soda/AQ pulping was studied by analyzing the respective crude pulps. This is exemplified in Figs. 2 and 3 for the hemp bast fibers and the sisal leaf fibers, respectively. The composition of main lipids present in the crude pulps of the studied fibers is listed in Table 2. It can be observed that the lipophilic compounds from the raw materials are modified to a different extent during alkaline (soda/AQ) pulping depending of their chemical nature. Fatty acids, which are among the main lipophilic extractives predominating in all these

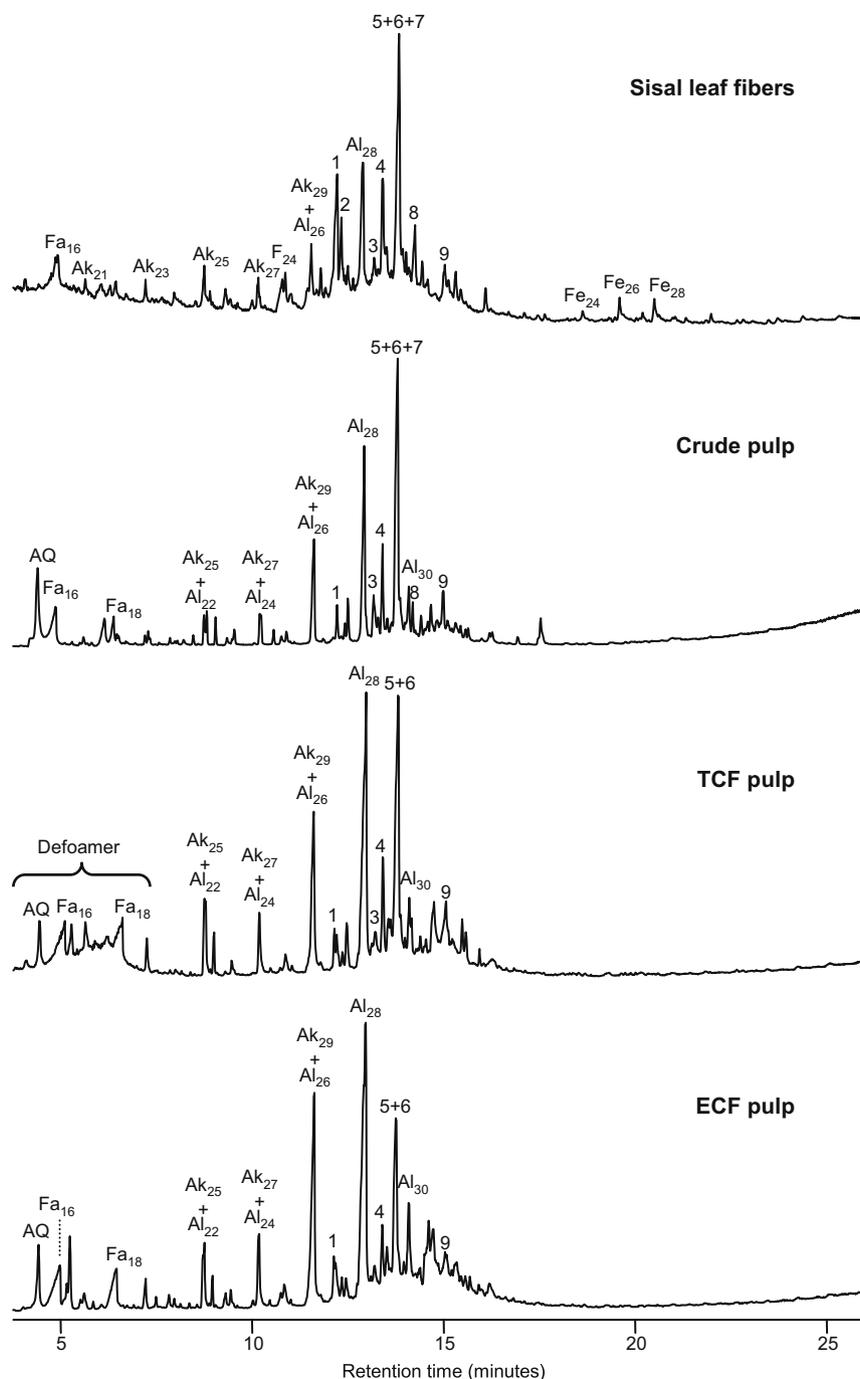


**Fig. 2.** GC–MS chromatograms of underivatized lipophilic extractives from hemp fibers (raw material), and their crude, TCF and ECF pulps. Peak identification, 1: stigmasta-3,5,22-triene; 2: stigmasta-3,5-diene; 3: campesterol; 4: stigmasterol; 5: sitosterol; 6: stigmastanol; 7:  $\beta$ -amyirin; 8: stigmasta-3,5-dien-7-one; 9:  $\beta$ -amyirin acetate; 10: stigmast-4-en-3-one; 11: friedelan-3-one; 12: stigmastane-3,6-dione; AQ: anthraquinone; Fa(*n*): fatty acids; Ak(*n*): alkanes; Al(*n*): fatty alcohols; SE: sterol esters; W(*n*): ester waxes; *n* denotes the total carbon atom number.

fibers, were also present in significant amounts in the crude pulps. The content of fatty acids decreased significantly after soda/AQ pulping of flax fibers whereas an increase in fatty acids content was produced after pulping of the other fibers, being especially evident in the case of sisal and abaca. In contrast,  $\alpha$ -hydroxyfatty acids present in all the fibers, and  $\omega$ -hydroxyfatty acids present in sisal and abaca, were completely absent in crude pulps.

On the other hand, esterified compounds such as ester waxes, sterols esters and ferulic acid esters, were completely hydrolyzed during soda/AQ pulping. This is especially evident in the case of flax fibers where ester waxes predominate. In contrast, other con-

jugated compounds, namely sterol glycosides, which are present in all nonwoody fibers studied here, resisted the alkaline cooking conditions and were present intact in the crude pulps, as already reported in the pulping of woody (Gutiérrez and del Río, 2001; Nilvebrant and Byström, 1995) and nonwoody plants (Gutiérrez and del Río, 2003a,b; Gutiérrez et al., 2004). The importance of the presence of sterol glycosides after alkaline pulping is due to their high hydrophilic–lipophilic balance, high melting point and very low solubility in water, alkali and the usual organic solvents (Hillis and Sumimoto, 1989). Due to these properties, sterol glycosides constitute a part of protecting layers that prevent the cooking



**Fig. 3.** GC-MS chromatograms of undervivatized lipophilic extracts from sisal fibers (raw material), and their crude pulp, TCF and ECF pulps. Peak identification, 1: stigmasta-3,5,22-triene; 2: stigmasta-3,5-diene; 3: campesterol; 4: stigmasterol; 5: sitosterol; 6: stigmastanol; 7:  $\beta$ -amyrin; 8: stigmasta-3,5-dien-7-one; 9: hecogenin; AQ: anthraquinone; Fa(*n*): fatty acids; Ak(*n*): alkanes; Al(*n*): fatty alcohols; Fe(*n*): *n*-alkylferulates; *n* denotes the total carbon atom number.

and bleaching chemicals to reach the resin and thereby keep them and other extractives in the pulp. Other neutral compounds, such as aldehydes, which were present in significant amounts in flax and hemp fibers, decreased largely during pulping and therefore were practically absent in the crude pulps. The content of steroid hydrocarbons and steroid ketones also decreased after soda/AQ cooking. Finally, alkanes, fatty alcohols and free sterols and triterpenols survived the alkaline conditions and therefore were the main lipophilic constituents in crude pulps.

The behavior of the fatty acids in an aqueous environment is quite different from that of the neutrals. At alkaline pH, the acids dissociate and can dissolve in water to quite a high extent forming

fatty acid soaps that can form micelles. Fatty acid soaps are effective solubilizing agents facilitating the removal from pulp of sparingly soluble neutral substances (Back, 2000). The ratio of saponifiables-to-unsaponifiables has been suggested to be a better index for predicting pitch problems than the total amount of lipids (Back and Allen, 2000). In fact, the higher abundances of unsaponifiable compounds with respect to the saponifiable ones is the main cause for pitch problems during pulping of some woods, such as aspen or eucalypt (Chen et al., 1995; del Río et al., 1998, 2000). This fact can explain why the lipid content of crude flax pulps is similar or even lower than the other pulps regardless flax fibers had the highest extractive content. As mentioned above, fatty acids

are the predominant lipids in flax fibers and can help to solubilize other water-insoluble components such as fatty alcohols and sterols. In contrast, the lipid content of crude sisal pulp is higher than the other three pulps regardless the relatively low content of lipophilic extractives in the raw material. Sisal fibers have low fatty acid content whereas the content in neutrals such as alkanes, fatty alcohols and steroids is relatively high. Particularly, the high abundances of free sterols, which have a high propensity to form pitch deposits (del Río et al., 1998, 2000), in the crude pulps from hemp and sisal, would point to a high pitch deposition tendency of the lipophilics from these fibers.

### 3.3. Fate of lipophilic extractives during TCF and ECF bleaching

The lipophilic extractives remaining in the crude pulp are carried over to the bleach plant, where they react with the bleaching agents used (Björklund-Jansson et al., 1995; Holmbom, 2000). Pulp bleaching technology radically changed in the 1990s when the previously used chlorine was replaced by several new bleaching chemicals (Sjöström, 1993) and ECF and TCF sequences were adopted. As a consequence, new pitch problems arose due to the different reactivity of pulp lipids with the new bleaching agents. With the aim of studying the behavior of the different classes of lipophilic extractives under different bleaching conditions, both TCF and ECF bleached pulps were analyzed and compared with their respective crude pulps.

In general terms, the qualitative composition of the lipophilic extractives from the TCF pulps was very similar to that of their respective crude pulps (Figs. 2 and 3) although the lipid content was significantly lower (Table 2). Fatty alcohols, alkanes, free sterols and triterpenols, and fatty acids were the main lipophilic compounds present in the TCF bleached pulps, although in lower amount than in their respective crude pulps. The low reactivity of most pulp lipids in TCF bleaching sequences (using hydrogen peroxide as a bleaching agent) has been reported (Freire et al., 2003; Gutiérrez et al., 2001a). The decrease in the content of these lipophilic compounds in the TCF pulps, regardless the low reactivity of hydrogen peroxide towards them, might be due to the extensive washing in alkaline conditions carried out in the industrial TCF bleaching sequences used. Moreover, it is interesting to note that sterol glycosides, which resisted soda/AQ pulping conditions, were removed to a high extent under the industrial TCF bleaching conditions used in this work. The high efficiency of hydrogen peroxide in degrading sterol glycosides was previously reported using model compounds (Nilvebrant and Byström, 1995). However, a lower extent in the removal of sterol glycosides were observed during TCF bleaching of eucalypt pulps (Gutiérrez et al., 2006a). In addition to the lipophilic extractives arising from the raw materials, several non-resolved peaks corresponding to the defoamers used in the process could also be observed in TCF pulps (Figs. 2 and 3). The excessive use of defoamers can also produce problems of pitch deposition (Allen, 2000). The presence of defoamer in pitch deposits produced during manufacturing of paper pulp from hemp fibers has been reported (Gutiérrez and del Río, 2005).

On the other hand, the composition of the lipophilic extractives from ECF pulps was somewhat different compared to that from their respective crude pulps (Figs. 2 and 3). The main difference observed was the large removal of free sterols in all the ECF pulps, although some minor amounts of free sterols still remained in sisal ECF pulp. The complete degradation of unsaturated sterols, such as sitosterol, during ECF bleaching has been previously reported in pitch deposits, pulps and in reactions with pure compounds (Freire et al., 2003; Gutiérrez et al., 2001a; Björklund-Jansson et al., 1995). On the other hand, sterol glycosides were largely removed during the ECF bleaching and were practically absent in these pulps. A less reactivity of these compounds with chlorine dioxide compared to

hydrogen peroxide has been reported (Nilvebrant and Byström, 1995). Therefore, the complete removal of sterol glycosides in the ECF pulps studied here may have been due to the use of hydrogen peroxide in the ECF sequence.

The removal of lipophilic extractives in bleaching can be mainly achieved by two mechanisms. The first one includes the dispersion and desorption of pulp lipids followed by removal with washing liquors, and the second mechanism includes the chemical degradation/modification of lipids, mainly by oxidative action of bleaching chemicals resulting in more hydrophilic compounds, which may be subsequently removed in washing (Holmbom, 2000). The decrease in the content of the lipophilic compounds in the TCF pulps studied here might be due to the first mechanism as mentioned above, taking into account the low reactivity of these lipids towards hydrogen peroxide. In contrast, the removal of unsaturated compounds during ECF bleaching was due to the second mechanism (Holmbom, 2000). The lower reactivity of pulp lipids in TCF bleaching sequences using hydrogen peroxide as a bleaching agent compared to ECF bleaching using chlorine dioxide (Back and Allen, 2000; Gutiérrez et al., 2009) may cause pitch problems to be, in principle, more severe in the former bleaching sequences. This is specially evident in the case of unsaturated sterols and triterpenoids as well as unsaturated fatty acids, which are strongly modified by chlorine dioxide but remain practically unaltered by oxygen and hydrogen peroxide (Holmbom, 2000; Bergelin and Holmbom, 2003; Freire et al., 2005, 2006; Gutiérrez et al., 2001a). However, in the nonwoody pulps studied here, the major lipophilic compounds present are saturated fatty acids, fatty alcohols and alkanes, which do not show reactivity towards chlorine dioxide, and therefore there are not great differences in the composition of the lipophilic extractives between ECF and TCF bleached pulps, with the exception of abaca pulp which lacks fatty alcohols and alkanes and where unsaturated sterols are the predominant lipophilic compounds. Therefore, both ECF and TCF bleached pulps will undergo similar pitch problems. Fatty acids, fatty alcohols and alkanes have been reported to be the compounds responsible for pitch deposits formed during pulping of nonwoody plants (Gutiérrez and del Río, 2005).

## 4. Conclusions

A thorough chemical characterization of the lipophilic extractives from different nonwoody fibers (flax, hemp, sisal and abaca) at different stages of pulp production (soda/AQ pulping and TCF/ECF bleaching) has been carried out. This study provides useful information into the extent of their removal along the cooking and bleaching processes. The soda/AQ pulping stage led to the removal of aldehydes, hydroxyfatty acids and the complete hydrolysis of esterified compounds such as ester waxes, sterol esters and alkyl ferulates. Among the bleaching processes, ECF bleaching showed high reactivity towards unsaturated sterols and both ECF and TCF bleaching were very effective in removing sterol glycosides from nonwoody pulps. In contrast, saturated fatty acids, fatty alcohols and alkanes, which are the main lipophilic compounds in most of the studied fibers, survived pulping and bleaching conditions and were the predominating compounds in both TCF and ECF bleached pulps.

## Acknowledgements

This study has been supported by the Spanish Projects BIO2007-28719-E and AGL2008-00709 and the EU Project BIORENEW (NMP2-CT-2006-026456). We thank CELESA pulp mill (Tortosa, Spain) for providing the samples. G.M. thanks the Spanish MEC for a FPI fellowship.

## References

- Allen, L.H., 2000. Pitch control in pulp mills. In: Back, E.L., Allen, L.H. (Eds.), Pitch Control, Wood Resin and Deresination. TAPPI Press, Atlanta, pp. 265–288.
- Back, E.L., 2000. Deresination in pulping and washing. In: Back, E.L., Allen, L.H. (Eds.), Pitch Control, Wood Resin and Deresination. TAPPI Press, Atlanta, pp. 205–230.
- Back, E.L., Allen, L.H., 2000. Pitch Control, Wood Resin and Deresination. TAPPI Press, Atlanta.
- Bergelin, E., Holmbom, B., 2003. Deresination of birch kraft pulp in bleaching. J. Pulp Pap. Sci. 29, 29–34.
- Bergelin, E., Holmbom, B., 2008. Reactions and distribution of birch extractives in kraft pulp oxygen delignification. J. Wood Chem. Technol. 28, 261–269.
- Bergelin, E., Möller, R., Holmbom, B., 2005. Analysis of pitch and deposit samples in kraft pulp production. Pap. Puu-Pap. Tim. 87, 399–403.
- Björklund-Jansson, M., Wormald, P., Dahlman, O., 1995. Reactions of wood extractives during ECF and TCF bleaching of kraft pulp. Pulp Pap. Can. 96, T134–T137.
- Chen, T., Wang, Z., Zhou, Y., Breuil, C., Aschim, O.K., Yee, E., Nadeau, L., 1995. Using solid-phase extraction to assess why aspen causes more pitch problems than softwoods in kraft pulping. Tappi J. 78, 143–149.
- del Río, J.C., Gutiérrez, A., 2006. Chemical composition of abaca (*Musa textilis*) leaf fibers used for manufacturing of high quality paper pulps. J. Agric. Food Chem. 54, 4600–4610.
- del Río, J.C., Gutiérrez, A., González-Vila, F.J., Martín, F., Romero, J., 1998. Characterization of organic deposits produced in the kraft pulping of *Eucalyptus globulus* wood. J. Chromatogr. A 823, 457–465.
- del Río, J.C., Romero, J., Gutiérrez, A., 2000. Analysis of pitch deposits produced in kraft pulp mills using a totally chlorine free bleaching sequence. J. Chromatogr. A 874, 235–245.
- del Río, J.C., Rodríguez, I.M., Gutiérrez, A., 2004. Identification of intact long-chain p-hydroxycinnamate esters in leaf fibers of abaca (*Musa textilis*) using gas chromatography/mass spectrometry. Rap. Commun. Mass Spectrom. 18, 2691–2696.
- Freire, C.S.R., Silvestre, A.J.D., Neto, C.P., 2003. Oxidized derivatives of lipophilic extractives formed during hardwood kraft pulp bleaching. Holzforschung 57, 503–512.
- Freire, C.S.R., Silvestre, A.J.D., Neto, C.P., 2005. Lipophilic extractives in *Eucalyptus globulus* kraft pulps. Behavior during ECF bleaching. J. Wood Chem. Technol. 25, 67–80.
- Freire, C.S.R., Silvestre, A.J.D., Neto, C.P., Evtuguin, D.V., 2006. Effect of oxygen, ozone and hydrogen peroxide bleaching stages on the contents and composition of extractives of *Eucalyptus globulus* kraft pulps. Bioresour. Technol. 97, 420–428.
- Gutiérrez, A., del Río, J.C., 2001. Gas chromatography-mass spectrometry demonstration of steryl glycosides in eucalypt wood, kraft pulp and process liquids. Rap. Commun. Mass Spectrom. 15, 2515–2520.
- Gutiérrez, A., del Río, J.C., 2003a. Lipids from flax fibers and their fate in alkaline pulping. J. Agric. Food Chem. 51, 4965–4971.
- Gutiérrez, A., del Río, J.C., 2003b. Lipids from flax fibers and their fate in alkaline pulping (vol. 51, p. 4965, 2003). J. Agric. Food Chem. 51, 6911–6914.
- Gutiérrez, A., del Río, J.C., 2005. Chemical characterization of pitch deposits produced in the manufacturing of high-quality paper pulps from hemp fibers. Bioresour. Technol. 96, 1445–1450.
- Gutiérrez, A., del Río, J.C., González-Vila, F.J., Martín, F., 1998. Analysis of lipophilic extractives from wood and pitch deposits by solid-phase extraction and gas chromatography. J. Chromatogr. A 823, 449–455.
- Gutiérrez, A., Romero, J., del Río, J.C., 2001a. Lipophilic extractives from *Eucalyptus globulus* pulp during kraft cooking followed by TCF and ECF bleaching. Holzforschung 55, 260–264.
- Gutiérrez, A., Romero, J., del Río, J.C., 2001b. Lipophilic extractives in process waters during manufacturing of totally chlorine free kraft pulp from eucalypt wood. Chemosphere 44, 1237–1242.
- Gutiérrez, A., Rodríguez, I.M., del Río, J.C., 2004. Chemical characterization of lignin and lipid fractions in kenaf bast fibers used for manufacturing high-quality papers. J. Agric. Food Chem. 52, 4764–4773.
- Gutiérrez, A., del Río, J.C., Ibarra, D., Rencoret, J., Romero, J., Speranza, M., Camarero, S., Martínez, M.J., Martínez, A.T., 2006a. Enzymatic removal of free and conjugated sterols forming pitch deposits in environmentally sound bleaching of eucalypt paper pulp. Environ. Sci. Technol. 40, 3416–3422.
- Gutiérrez, A., Rodríguez, I.M., del Río, J.C., 2006b. Chemical characterization of lignin and lipid fractions in industrial hemp bast fibers used for manufacturing high-quality paper pulps. J. Agric. Food Chem. 54, 2138–2144.
- Gutiérrez, A., Rodríguez, I.M., del Río, J.C., 2008. Chemical composition of lipophilic extractives from sisal (*Agave sisalana*) fibers. Ind. Crop. Prod. 28, 81–87.
- Gutiérrez, A., del Río, J.C., Martínez, A.T., 2009. Microbial and enzymatic control of pitch in the pulp and paper industry. Appl. Microbiol. Biotechnol. 82, 1005–1018.
- Hillis, W.E., Sumimoto, M., 1989. Effect of extractives on pulping. In: Rowe, J.W. (Ed.), Natural Products of Woody Plants, vol. II. Springer-Verlag, Berlin, pp. 880–920.
- Holmbom, B., 2000. Resin reactions and deresination in bleaching. In: Back, E.L., Allen, L.H. (Eds.), Pitch Control, Wood Resin and Deresination. TAPPI Press, Atlanta, pp. 231–244.
- Nilvebrant, N.-O., Byström, S., 1995. Demonstration of glucosidic linked sterols in birch. In: Proceedings of Eighth International Symposium on Wood and Pulping Chemistry, Helsinki. 6–9 June 2, pp. 135–140.
- Shin, S.J., Kim, C.H., 2006. Residual extractives in unbleached aspen and pine kraft pulps and their fate on oxygen delignification. Nord. Pulp Pap. Res. J. 21, 260–263.
- Silvestre, A.J.D., Pereira, C.C.L., Neto, C.P., Evtuguin, D.V., Duarte, A.C., Cavaleiro, J.A.S., Furtado, F.P., 1999. Chemical composition of pitch deposits from ECF *Eucalyptus globulus* bleached kraft pulp mill: its relationship with wood extractives and additives in process streams. Appita J. 52, 375–382.
- Sjöström, E., 1993. Wood Chemistry. Fundamentals and Applications. Academic Press, San Diego.