FATE OF LIPOPHILIC EXTRACTIVES FROM SEVERAL NON-WOOD SPECIES DURING ALKALINE PULPING AND TCF/ECF BLEACHING

Marques, G., del Río, J.C., Gutiérrez, A.*

Instituto de Recursos Naturales y Agrobiología, CSIC, PO Box 1052, E-41080 Seville, Spain

ABSTRACT

The chemical composition of lipophilic extractives from several nonwoody fibers such as flax, hemp, sisal and abaca, which are used in the manufacture of high-quality paper pulps, was thoroughly studied by gas chromatography and gas chromatography-mass spectrometry. The main compounds identified included series of long chain *n*-fatty alcohols, *n*-fatty acids, *n*-aldehydes, *n*-alkanes, free and conjugated sterols, and waxes. On the other hand, the fate of these lipophilic compounds was investigated during soda/anthraquinone (AQ) pulping followed by totally chorine free (TCF) and elementary chlorine free (ECF) bleaching, by analysing unbleached and bleached pulps. The amount of most lipophilic compounds present in the raw materials strongly decreased after soda/AQ pulping although other compounds survived cooking. Among the lipophilic extractives that remained in the unbleached pulps after soda/AQ pulping, unsaturated sterols survived TCF bleaching but were removed by ECF bleaching. On the other hand, saturated fatty acids, fatty alcohols and alkanes were still present in both bleached pulps.

BACKGROUND

An alternative to wood raw materials for pulp and paper production in developing countries is the use of nonwoody raw materials. Moreover, nonwoody fibers are also used in developed countries for the production of pulps for specialty papers. The main sources of nonwoody raw materials are agricultural residues from monocotyledons, including cereal straw and bagasse. Bamboo, reeds, and some other grass plants such as flax, hemp, kenaf, jute, sisal, or abaca are also grown or collected for the pulp industry.

The composition of lipophilic compounds from raw materials is important for pulp and paper production since they form the so-called pitch deposits, which are responsible of reduced product quality and higher operating costs due to production stops for cleaning the equipment [1, 2]. The different classes of lipids have different behavior during cooking and bleaching. The lipids can be classified into two principal groups, namely fatty acids and neutral components, the latter including long chain *n*-fatty alcohols, alkanes and steroids and triterpenoids. The behavior of the fatty acids in an aqueous environment is quite different from that of the neutrals. In alkaline pulping, the acids dissociate and can dissolve in water to quite a high extent, forming fatty acid soaps. The neutrals, however, have a very low solubility in water and survive the cooking process and remain in the pulp being at the origin of the pitch deposits. The increasing trend in recirculating water in pulp mills to accomplish environmental demands is aggravating these problems. Existing knowledge on the behavior of lipophilic extractives during pulping and bleaching mainly refers to wood pulps [2-5]. In contrast, the studies on nonwood pulps are still scarce [6-8]. The present work aims at the characterization of lipophilic extractives from several nonwoody fibers during soda/AQ pulping followed by TCF and ECF bleaching. This knowledge will help to predict and control pitch problems during the manufacturing of high quality paper pulps from these raw materials.

EXPERIMENTAL

Samples. Flax (*Linum usitatissimum*) and hemp (*Cannabis sativa*) bast fibers, sisal (*Agave sisalana*) and abaca (*Musa textilis*) leaf fibers as well as their unbleached, TCF and ECF bleached soda/AQ pulps were supplied by CELESA mill (Tortosa, Spain) that produce high-quality paper pulps for specialty papers.

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

GC and GC-MS analyses. The GC analyses of lipids from raw materials and pulps were performed in an Agilent 6890N Network GC system using a short fused-silica DB-5HT capillary column (5 m x 0.25 mm internal diameter, 0.1 μm film thickness) from J&W Scientific, enabling simultaneous elution of the different lipid classes [9]. 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°C and 350°C, respectively. Helium (5 ml/min) was used as carrier gas, and the injection was performed in splitless mode. Peaks were quantified by area.

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. Compounds were identified by mass fragmentography, and by comparing their mass spectra with those of the Wiley and NIST libraries and standards. Trimethylsilyldiazomethane methylation, and bis(trimethylsilyl)trifluoroacetamide (BSTFA) silylation in the presence of pyridine, was used to produce the appropriate derivatives.

* Author for correspondence. E-mail: anagu@irnase.csic.es

RESULTS AND DISCUSSION

The lipid content of the nonwood fibers used in this study and their corresponding crude and TCF and ECF bleached pulps are shown in Table 1.

TABLE 1: LIPOPHILIC EXTRACTIVES CONTENT (%) OF NONWOODY FIBERS

	Flax	Hemp	Sisal	Abaca
Raw material	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

It can be observed that flax fibers have the highest extractive content followed by hemp, sisal and abaca. Regardless the higher lipid content of flax raw material, the lipid extract of its crude pulp was similar or even lower than most of the other pulps. On the other hand, similar lipid contents (0.04-0.09) were observed in TCF pulps with the exception of hemp (0.18%). The lipid content of ECF pulps ranged from 0.03% (abaca) to 0.18 (hemp). The fact that ECF pulps show higher lipid content than TCF pulps could be due to the less clear washing waters used in the ECF bleaching process.

It is known that the different classes of lipids show a different behavior during pulping and bleaching [2]. With the aim of studying the fate of different lipophilic extractives during soda/AQ pulping and TCF and ECF bleaching, the lipid extracts from the nonwood fibers and the unbleached and TCF and ECF bleached pulps were analyzed by GC and GC-MS. The composition of the lipophilic extractives is shown in Table 2.

TABLE 2: MAIN LIPOPHILIC EXTRACTIVES (mg/100 g) FROM NONWOODY FIBERS

Compounds	Flax	Hemp	Sisal	Abaca
***n*-alkanes**	28	43	14	-
***n*-aldehydes**	371	25	2	-
***n*-alcohols**	219	3	9	<1
fatty acids	552	76	11	9
α-hydroxyfatty acids	10	8	7	2
ω-hydroxyfatty acids	-	-	5	1
steroid hydrocarbons	14	33	14	3
sterols/triterpenols	93	33	20	25
steroid ketones	33	28	3	5
sterol glycosides	5	12	2	2
sterol/triterpenols esters	6	7	<1	2
n-alkyl ferulates	-	-	5	-
***ω*-carboxyalkylferulates**	-	-	1	-
waxes	293	17	1	-
monoglycerides	-	-	4	6
diglycerides	-	-	4	<1

It can be observed that main lipid classes such as alkanes, fatty alcohols, aldehydes, fatty acids, free and conjugated sterols, steroid hydrocarbons, ketones and waxes are present, with the exception of abaca that lacks alkanes, aldehydes and waxes. Alkyl ferulates are only present in sisal, and glycerides are only present in sisal and abaca.The fate of these lipophilic extractives during soda/AQ pulping and TCF and ECF bleaching are exemplified in Figs. 1 and 2 for flax and abaca fibers, respectively. The composition of main lipid classes present in unbleached and bleached pulps from flax and abaca is shown in Table 3.

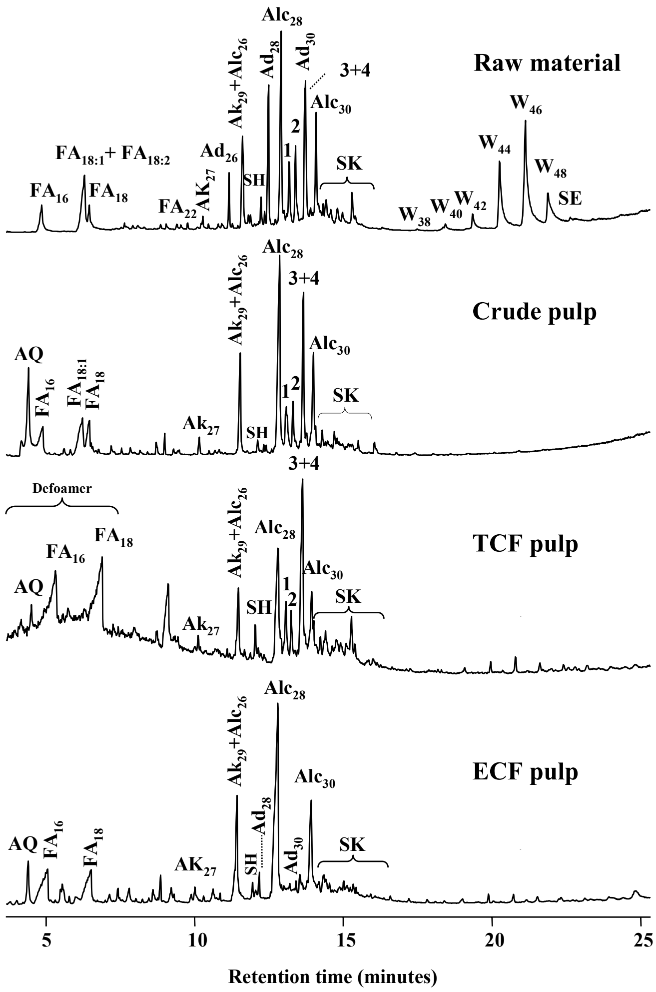

Figure 1. GC-MS chromatograms of underivatized lipophilic extractives from flax fibers (raw material), and crude, TCF and ECF pulps. Peak identification, 1: campesterol, 2: stigmasterol, 3: sitosterol, 4: stigmastanol, SH: steroid hydrocarbons, SK: steroid ketones, SE: sterol esters, AQ: anthraquinone, FA(n): fatty acids, Ak(n): alkanes, Ad(n): aldehydes, Alc(n): fatty alcohols, and W(n): waxes; n denotes the total carbon atom number.

The predominant compounds in flax bast fibers were fatty acids and aldehydes, accounting in each case for 34% and 23% of total extract, followed by waxes (18%), fatty alcohols (13%) and free sterols (6%). Minor amounts of other compounds included steroid ketones and alkanes. It can be observed that after soda/AQ pulping the content of waxes and aldehydes strongly decreased. The decrease of waxes is due to the hydrolysis of esters during alkaline cooking. The content in fatty acids (especially the unsaturated ones) also decreased significantly after cooking. This is because in alkaline pulping the acids dissociate and form fatty acid soaps and can thus dissolve in water to quite a high extent, forming fatty acid soaps, which are effective solubilizing agents facilitating the removal from pulp of sparingly soluble neutral substances.

The main compounds present in flax unbleached pulp were saturated fatty acids, fatty alcohols and alkanes. These compounds also survived TCF and ECF bleaching and were predominant in both bleached pulps. These compounds were the main compounds present in pitch deposits formed during manufacturing of hemp pulps [10]. Other compounds such as sterols that were also present in flax fibers decreased after pulping although were still present in TCF pulp. In contrast, they completely disappeared after ECF bleaching.

TABLE 3: MAIN LIPOPHILIC EXTRACTIVES (mg/100 g) FROM FLAX AND ABACA PULPS

Compounds	Flax			Abaca		
	CP	TCF	ECF	CP	TCF	ECF
n-alkanes	21	1	3	-	-	-
n-aldehydes	3	<1	8	-	-	-
n-alcohols	68	2	51	6	<1	<1
fatty acids	96	29	40	55	20	27
α-hydroxyfatty acids	-	-	-	-	-	-
ω-hydroxyfatty acids	-	-	-	tr	-	-
steroid hydrocarbons	3	1	2	4	1	1
sterols/triterpenols	33	4	-	20	5	1
steroid ketones	5	<1	tr	5	4	1
sterol glycosides	8	1	tr	7	1	tr
sterol/triterpenols esters	-	-	-	-	-	-
waxes	<1	1	1	-	-	-
monoglycerides	-	-	-	13	tr	tr
diglycerides	-	-	-	13	tr	tr

The predominant compounds in abaca leaf fibers were sterols accounting 45% of total extract. Additionally, significant amounts of fatty acids (16%), monoglycerides (11%) and steroid ketones (9%) were also found, as well as minor amounts of α-hydroxyfatty and ω-hydroxyfatty acids, alcohols, steroid hydrocarbons, sterol esters, sterol glycosides and diglycerides. The main compounds present in abaca unbleached pulp were saturated fatty acids, sterols, glycerides, sterol glycosides and alcohols. Sterols decreased after pulping, were still present in TCF pulp and in ECF pulp in very minor amounts.

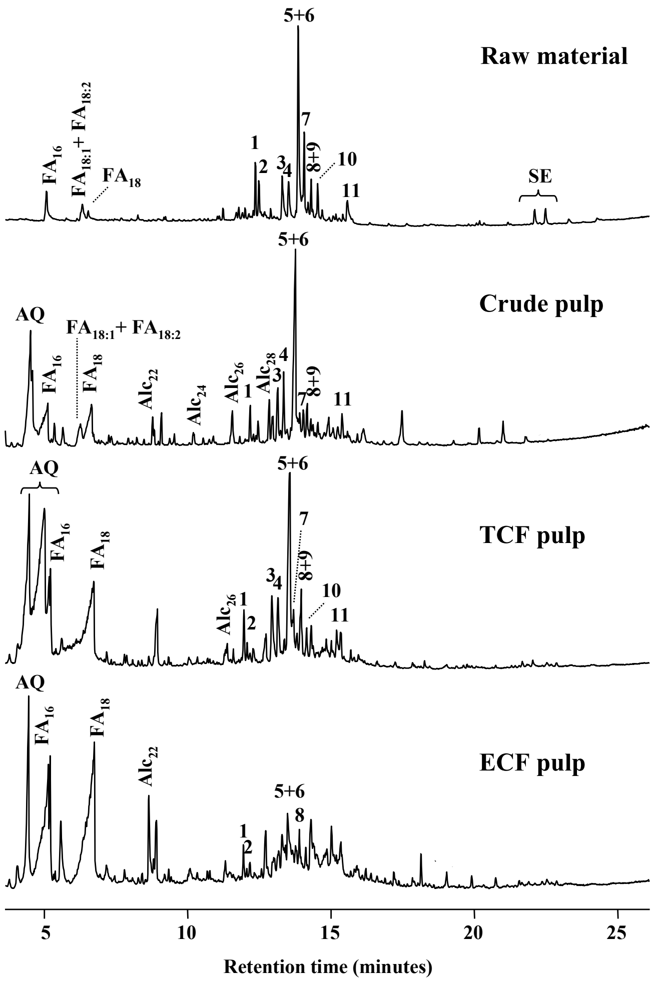

Figure 2. GC-MS chromatograms of underivatized lipophilic extractives from abaca fibers (raw material), and crude, TCF and ECF pulps. Peak identification, 1: stigmasta-3,5,22-triene, 2: stigmasta-3,5-diene, 3: campesterol, 4: stigmasterol, 5: sitosterol, 6: stigmastanol, 7: cycloartenone, 8: stigmasta-3,5-dien-7-one, 9: 24-methylencycloartenone, 10: stigmast-4-en-3-one, 11: 7-oxositosterol, AQ: anthraquinone, FA(n): fatty acids, Ak(n): alkanes, Alc(n): fatty alcohols, SE: sterol esters and W(n): waxes; n denotes the total carbon atom number.

In general, the fate of lipophilic extractives in the other nonwood fibers during soda/AQ pulping and TCF and ECF bleaching was similar to that described for lipids from flax and abaca fibers. In addition to waxes and sterol esters present in flax pulps, other esters such as alkyl ferulates present in sisal fibers were completely hydrolyzed after soda/AQ pulping.

CONCLUSIONS

The composition of lipophilic extractives from several nonwood fibers, such as flax, hemp, sisal and abaca during soda/anthraquinone (AQ) pulping followed TCF and ECF bleaching has been analyzed by GC and GC-MS. It was observed that the amount of most lipophilic compounds decreased after soda/AQ pulping and esterified compounds were strongly hydrolyzed. Among the lipophilic extractives that remained in the unbleached pulps after soda/AQ pulping, unsaturated sterols survive TCF bleaching but were removed by ECF bleaching. On the other hand, saturated fatty acids, fatty alcohols and alkanes were still present in both TCF and ECF bleached pulps. This knowledge will help to predict and control pitch problems during the manufacturing of high quality pulps from these raw materials.

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