

CHEMICAL CHARACTERIZATION OF FIBERS FROM HERBACEOUS PLANTS COMMONLY USED FOR MANUFACTURING OF HIGH QUALITY PAPER PULPS

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ABSTRACT

The present work aims at the chemical characterization of several non-woody fibers from herbaceous plants used for manufacturing high quality paper pulps, with especial emphasis in the composition of lignin and lipophilic compounds. Among the fibers studied are bast fibers from flax, hemp, kenaf and jute and leaf fibers from abaca and sisal. Flax and hemp showed the lowest lignin content (< 5%). However, they present a very low lignin S/G ratio (0.3 and 0.6, respectively) that makes them difficult to be delignified. On the other hand, kenaf, jute, sisal and abaca present higher lignin content, but the S/G ratio is higher (from 2.7 to 5.8) which would make them more easily delignifiable. With respect to the lipophilic extractives, flax, hemp, kenaf and jute are characterized by a high content of waxes, hemp having also a high content of sterols and triterpenols. Sisal and abaca are characterized by series of *p*-hydroxycinnamic acids esterified with long chain fatty alcohols and ω -hydroxyfatty acids.

I. INTRODUCTION

Current estimates of world paper production attribute 7% to all nonwood fibers. In developing countries, these fibers are used for manufacturing of high-quality pulps for specialty papers (such as tea bags, filters, bank notes, security papers, cigarette papers or condenser papers). Papermaking methods for non-woody materials differ from those used for wood because of differences in fiber morphology and chemical composition. Therefore, studies on the composition of the organic constituents of fibers is important for optimizing the pulping and bleaching processes.

The composition of lignin and lipids in fibers can strongly influence pulping and bleaching processes. Thus, it is known that the efficiency of pulping is directly proportional to the amount of syringyl units in lignin, since the guaiacyl units have a free C-5 position available for carbon-carbon inter-unit bonds, which make them fairly resistant to lignin depolymerization in pulping. On the other hand, it is well known that lipophilic compounds present in raw materials cause significant environmental and technical problems in the manufacturing of paper pulp. During pulping, lipids are released from the fibers forming colloidal pitch, which can deposit in either pulp or machinery causing production troubles. In the manufacture of alkaline pulps, a large part of the lipids originally present in the raw material is removed during the cooking. However, some chemical species survive these processes and are found as pulp extractives, suspended in process waters or forming the so-called pitch deposits in circuits, equipment and final product. Moreover, such extractives might contribute to the toxicity of paper pulp effluents and products.

The present work aims at the chemical characterization of several non-woody fibers from herbaceous plants commonly used for manufacturing high quality paper pulps, with especial emphasis in the composition of lignin and lipophilic compounds. The fibers studied include bast fibers from flax, hemp, kenaf and jute and leaf fibers from abaca and sisal.

II. EXPERIMENTAL

Samples. Bast fibers from flax (*Linum usitatissimum*), hemp (*Cannabis sativa*), kenaf (*Hibiscus cannabinus*), and jute (*Corchorus capsularis*), and leaf fibers from sisal (*Agave sisalana*) and abaca (*Musa textilis*) were supplied by CELESA pulp mill (Tortosa, Spain). The fibers were air-dried and subsequently milled using an Analysenmühle knife mill. For the isolation of lipids, hemicelluloses analysis and Klason lignin content estimation, the milled samples were successively extracted with acetone (8 h in a Soxhlet apparatus), and hot water (3 h at 100 °C). Klason lignin was estimated as the residue after sulfuric acid hydrolysis of the pre-extracted material, and neutral sugars from polysaccharide hydrolysis were analyzed as alditol acetates by GC according to Tappi rules T222 om-88 and T249 om85 (Tappi Methods, 2004), respectively. Ash content was estimated as the residue after 6 h at 575 °C. The composition of the metals and other elements in the fibers was analyzed by Inductively Coupled Plasma Spectrophotometry (ICP-OES) after oxidation with concentrated HNO₃ under pressure in a microwave digester. The acetone extracts were evaporated to dryness, and redissolved in chloroform for chromatographic analysis of the lipophilic fraction.

GC and GC/MS analyses. An HP 5890 gas chromatograph equipped with a split-splitless injector and a flame ionization detector (FID) was used for GC analyses of the lipophilic compounds. The injector and the detector temperatures were set at 300 °C and 350 °C respectively. Samples were injected in the splitless mode.

Helium was used as the carrier gas. The capillary column used was a 5 m x 0.25 mm i.d., 0.1 μ m, high temperature, polyimide coated fused silica tubing DB-5HT. After a 1 min hold at 100 $^{\circ}$ C, the oven was temperature-programmed from 100 $^{\circ}$ C to 350 $^{\circ}$ C at 15 $^{\circ}$ C/min, followed by a 3 min hold at 350 $^{\circ}$ C. Peaks were quantified by area, and a mixture of standards (octadecane, palmitic acid, sitosterol, cholesteryl oleate, and campesterol, stigmasterol and sitosterol 3- β -D-glucopyranosides) was used to produce calibration curves.

The GC/MS analyses were performed on a Model GC 8000 Top gas chromatograph coupled to a Voyager quadrupole mass spectrometer detector equipped with a 15 m x 0.25 mm i.d., 0.1 μ m DB-5HT fused silica capillary column. After an initial hold for 1 min at 120 $^{\circ}$ C, the oven was heated from 120 $^{\circ}$ C to 380 $^{\circ}$ C at 10 $^{\circ}$ C/min, followed by a 5 min hold at 380 $^{\circ}$ C. The injector and transfer line temperatures were set at 300 $^{\circ}$ C and 350 $^{\circ}$ C respectively. Helium was used as the carrier gas and the injection was performed in splitless mode.

Pyrolysis-gas chromatography/mass spectrometry. The pyrolysis of the fibers was performed with a Curie-point pyrolyzer coupled to a Varian Saturn 2000 GC/MS, using a 30 m x 0.25 mm i.d., 0.25 μ m DB-5 column. Approximately 100 μ g of finely divided sample was deposited on a ferromagnetic wire, then inserted into the glass liner and immediately placed in the pyrolyzer. The pyrolysis was carried out at 610 $^{\circ}$ C for 4 s. After a 1 min hold at 40 $^{\circ}$ C, the chromatograph was programmed from 40 $^{\circ}$ C to 300 $^{\circ}$ C at a rate of 6 $^{\circ}$ C/min. The final temperature was held for 20 min. The injector, equipped with a liquid carbon dioxide cryogenic unit was programmed from -30 $^{\circ}$ C (1 min) to 300 $^{\circ}$ C at 200 $^{\circ}$ C/min, while the GC/MS interface was kept at 300 $^{\circ}$ C. For the pyrolysis in the presence of tetramethylammonium hydroxide (TMAH), to analyze *p*-hydroxycinnamic acids, approximately 100 μ g of sample was mixed with 0.5 μ L 25% TMAH. The wire was then inserted into the glass liner, which was subsequently placed in the pyrolyzer. The pyrolysis was carried out as described above.

III. RESULTS AND DISCUSSION

General composition of the selected herbaceous fibers

The general composition of the selected herbaceous plant fibers is shown in **Table 1**. These fibers are characterized by a high content on holocellulose and a low content on lignin (< 16%), lipophilic extractives (< 0.7%) and ash (< 2.0%), which makes them appropriate for papermaking. Among them, flax and hemp fibers present the lowest lignin content (< 5%). Moreover, all of the selected fibers are characterized by a low silica content, in contrast to other nonwoody fibers used for papermaking, such as rice straw and wheat straw, that present big problems due to the high abundance of silica.

Table 1. General composition (%) of the main components in the selected herbaceous fibers.

Fibers	Holocelullose	Water-solubles	Klason Lignin	Acid-soluble Lignin	Lipophilic extractives	Ash
flax	92.0	1.3	2.9	1.6	0.7	1.5
hemp	90.3	1.2	4.6	1.5	0.5	2.0
kenaf	81.9	1.1	12.2	3.0	0.5	1.5
jute	81.6	1.0	13.3	2.8	0.4	1.0
sisal	85.0	0.5	10.8	3.0	0.5	0.2
abaca	85.6	0.3	11.8	1.4	0.4	0.5

Lipid composition of the selected herbaceous fibers

The fibers extracts were analyzed by GC and GC/MS using short and medium length high temperature capillary columns, respectively, with thin films, according to the method previously described (Gutiérrez *et al.*, 1998). The chromatograms of the underivatized lipid extracts from the different fibers are shown in **Figure 1** and the abundances of the main lipophilic compounds are detailed in **Table 2**. The main lipophilic compounds identified in the fibers include *n*-alkanes, *n*-fatty acids, *n*-fatty alcohols, *n*-aldehydes, sterols/triterpenols and waxes. Waxes are especially abundant in the bast fibers (flax, hemp, kenaf, jute), and are almost absent in the leaf fibers (sisal and abaca). Leaf fibers, on the other hand, are characterized by the presence of *p*-hydroxycinnamic acids (*p*-coumaric and ferulic acids) esterified to long chain *n*-fatty alcohols and ω -hydroxyfatty acids. Sterols and triterpenols are especially abundant in hemp fibers, with a predominance of sitosterol and β -amyrin derivatives. Kenaf shows the presence of two distinct triterpenols, namely motiol and glutinol. Jute presents also two distinct triterpenoid ketones, namely bauerenone and isomultiflorenone, and a epoxydammarane compound, which are not present in the rest of the fibers.

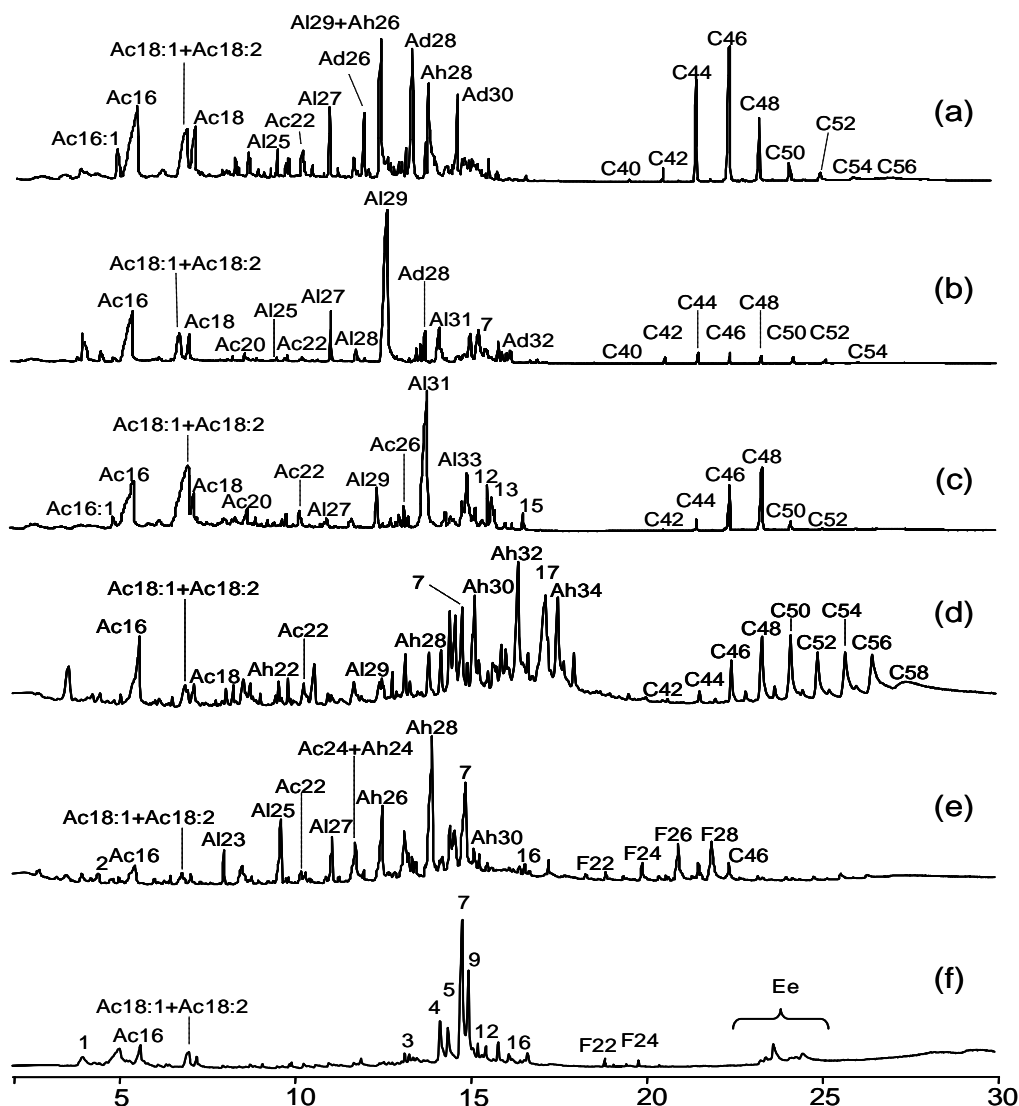


Figure 1. GC/MS of the lipophilic extracts from the different fibers: flax (a), hemp (b), kenaf (c), jute (d), sisal (e) and abaca (f). Ac(*n*): *n*-fatty acids, Al(*n*): *n*-alkanes, Ah(*n*): *n*-alcohols, Ad(*n*): *n*-aldehydes, C(*n*): waxes, F(*n*): ferulic acid esters; Ee: Sterol esters; *n*: carbon atom number; 1: *p*-coumaric acid, 2: ferulic acid, 3: stigmastan-3,5,7-triene, 4: campesterol, 5: stigmasterol, 7: sitosterol, 9: cycloartenone, 12: stigmast-4-en-3-one, 13: glutinol, 15: stigmastane-3,6-dione, 16: 7-oxositosterol; 17: epoxidammarane.

Table 2. Lipophilic composition (mg/100 g) in the different herbaceous plant fibers.

Main series of lipophilic compounds	flax	hemp	kenaf	jute	sisal	abaca
<i>n</i> -Alkanes	35.16	52.50	26.89	4.75	10.07	-
<i>n</i> -Fatty acids	43.01	21.67	33.35	13.03	18.95	12.99
α -Hydroxyfatty acids	0.70	0.45	0.60	10.28	2.28	0.82
ω -Hydroxyfatty acids	-	-	-	3.45	9.12	3.30
<i>n</i> -Fatty alcohols	31.77	6.00	13.00	12.69	18.37	2.22
<i>n</i> -Fatty aldehydes	61.96	7.90	0.65	-	1.97	-
Sterols/Triterpenols	2.37	33.21	5.57	10.77	10.66	13.60
Steroid/Triterpenoid ketones	2.40	8.29	3.97	2.43	1.17	5.75
Sterol glycosides	0.43	1.80	0.38	0.84	0.97	1.48
<i>p</i> -Hydroxycinnamic acid esters	-	-	-	-	9.40	2.63
Sterol/Triterpenol esters	1.94	26.53	0.63	-	0.21	1.75
Waxes	167.71	21.34	29.31	18.06	1.81	-

Lignin composition of the selected herbaceous fibers

The lignins in the fibers were analyzed *in situ* by Py-GC/MS, in the absence and in the presence of TMAH. The composition in terms of H, G and S units, including the S/G ratio, are shown in **Table 3**. Hemp and flax lignins showed a predominance of G-lignin units, while jute, sisal and abaca lignins contained predominantly S-lignin units. In general, the efficiency of pulping is directly proportional to the amounts of S-units in lignin. The G-units have a C-5 aromatic position available for very strong carbon-carbon bonds, which make them fairly resistant to the pulping depolymerization. Therefore, the high S/G ratio of kenaf, jute, sisal and abaca makes them easier to be delignified because of the lower condensation degree of lignin, despite having the highest content on Klason lignin.

Table 3. Lignin and *p*-hydroxycinnamic acid composition in the fibers estimated after Py-GC/MS and Py/TMAH

Py-GC/MS	Flax	Hemp	kenaf	jute	sisal	abaca
%H	57	13	1	2	1	64
%G	33	53	16	32	20	6
%S	11	34	82	66	79	30
S/G	0.3	0.6	5.1	2.1	4.0	4.5
Py/TMAH						
Cinnamic acids/lignin	0.03	0.03	0.02	0.03	0.07	2.64
<i>p</i> -Coumaric/ferulic	1.4	1.9	0.5	0.6	0.7	27.9

On the other hand, *p*-hydroxycinnamic acids, namely *p*-coumaric and ferulic acids, were also found in the fibers, linked by ester and/or ether bonds, and are especially abundant in abaca and sisal lignins. The presence of the latter compounds in the isolated lignins, as well as in their respective whole fibers, was shown by Py/TMAH, *p*-coumaric acid being especially abundant in abaca. Moreover, it is interesting to note the presence of sinapyl and coniferyl acetates among the pyrolyzates of the fibers from kenaf, jute, sisal and abaca, with a predominance of the *trans* over the *cis* form, similar to that of the respective non-acetylated sinapyl alcohols. Previous NMR and degradative studies (Ralph, 1996) have shown that lignin in kenaf is acetylated at the γ -position of the side-chain and that this acetylation occurred predominantly on S-lignin units. Moreover, it has recently been demonstrated that sinapyl acetate is a true lignin precursor in kenaf (Lu and Ralph, 2002; del Río *et al.*, 2004) involved in the polymerization of lignin along with the normal coniferyl and sinapyl alcohols. Therefore, it is also possible that sinapyl and coniferyl alcohol acetates are also lignin precursors in the case of the rest of the lignins from jute, sisal and abaca.

IV. CONCLUSIONS

The present work reports a thorough chemical characterization of the fibers of different herbaceous plants used for paper pulp manufacturing, with especial emphasis in the composition of lignin and lipophilic extractives. The knowledge of chemical composition of main components of these fibers will be useful for a better utilization of these nonwoody plants.

V. ACKNOWLEDGEMENTS

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