Chemical Characterization of Lignin and Lipid Fractions in Industrial Hemp Bast Fibers Used for Manufacturing High-Quality Paper Pulps

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The chemical composition of lignin and lipids of bast fibers from industrial hemp (*Cannabis sativa*) used for high-quality paper pulp production was studied. Pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) of fibers showed a lignin with a *p*-hydroxyphenyl:guaiacyl:syringyl unit (H:G:S) molar proportion of 13:53:34 (S/G ratio of 0.64). *p*-Hydroxycinnamic acids, namely, *p*-coumaric and ferulic acids, were found in only trace amounts. Among the lipids, the main compounds identified by GC/MS of the hemp fibers extracts were series of *n*-alkanes, free and esterified sterols and triterpenols, waxes, and long-chain *n*-fatty acids. Other compounds such as *n*-aldehydes, *n*-fatty alcohols, steroid hydrocarbons, and steroid and triterpenoid ketones as well as steryl glycosides were also found.

KEYWORDS: Industrial hemp; *Cannabis sativa*; bast fibers; paper pulp, lipids; lignin; steroids; pyrolysis

INTRODUCTION

Nonwood plants are the common fiber source for paper pulp production in developing countries where wood fibers are not available. In the developed world, although wood is still by far the main raw material for paper pulp manufacture, a market exists for high value-added papers from these fibers (*1*). Hemp (*Cannabis sativa*) is native to central Asia and has been cultivated in Asia and Europe for many years. In Europe, the cultivation of hemp declined in the 19th century but recently interest has been renewed, for example, in Germany, France, The Netherlands, the United Kingdom, Spain, and Italy (*2*). Uses for industrial hemp fibers in the paper industry mainly include specialty papers, that is, cigarette papers, Bible papers, and condenser papers (*1*).

Studies on the chemical composition of hemp bast fibers are important for optimizing the pulping and bleaching processes of this raw material. Among the several parameters that may affect pulp production are the composition of lignin and lipids in fibers. In general, the efficiency of pulping is directly proportional to the amount of syringyl (S) units in the lignin (*3*, *4*). The guaiacyl (G) units have a free C-5 position available for carbon–carbon interunit 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 and cause production troubles (*5*–*8*). 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 (*9*). Moreover, such extractives might contribute to the toxicity of paper pulp effluents and products (*10*).

To the best of the authors' knowledge, studies regarding the composition of lignin and lipids from industrial hemp fibers have been scarce. In the present study we have characterized the lignin in industrial hemp bast fibers using analytical pyrolysis coupled to gas chromatography/mass spectrometry (Py-GC/MS). Py-GC/MS is a powerful analytical tool for the rapid analysis of complex polymer mixtures including lignocellulosic materials (*11*, *12*). It combines rapid thermal degradation and GC/MS analysis of marker compounds from pyrolytic breakdown. We also performed a detailed analysis of the chemical composition of lipids from industrial hemp bast fibers. These analyses were carried out by GC and GC/MS using high-temperature capillary columns of short and medium lengths, respectively (*13*). This method enables the elution and analysis of intact high molecular weight lipids such as waxes, sterol esters, and triglycerides.

MATERIALS AND METHODS

Samples. Industrial hemp (*C. sativa*) bast fibers (from Spain) were supplied by CELESA pulp mill (Tortosa, Spain). The retted hemp fibers contained 15% of core fibers. Hemp bast fibers were air-dried and subsequently milled using an Analysenmühle knife mill (Janke and Kunkel, Staufen, Germany). For the isolation of lipids, hemicellulose 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

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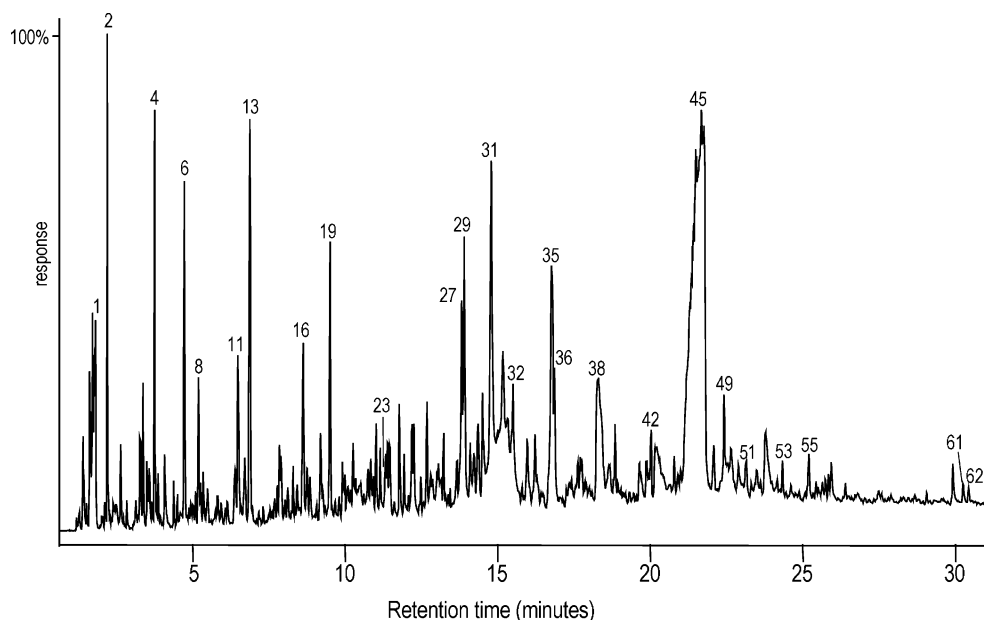
Figure 1. Py-GC/MS chromatogram of industrial hemp bast fibers. The identities and relative molar abundances of the compounds are listed in **Table 1**.
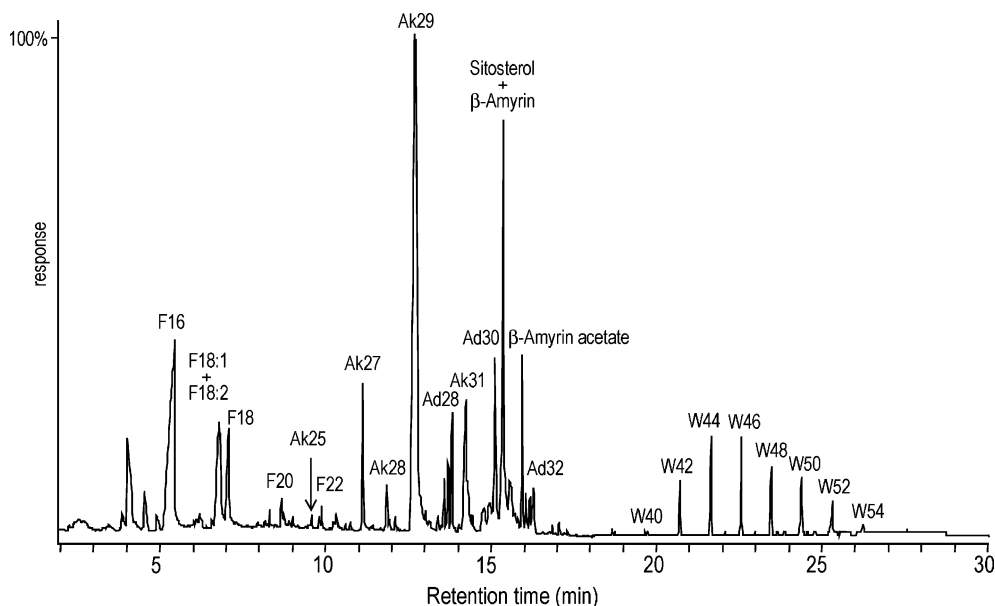

Figure 2. GC/MS chromatogram of the underivatized lipid extracts from industrial hemp bast fibers. F(*n*), *n*-fatty acid series; Ak(*n*), *n*-alkane series; Ad(*n*), *n*-aldehyde series; W(*n*), wax series; *n* denotes the total carbon atom number.

sugars from polysaccharide hydrolysis were analyzed as alditol acetates by GC according to Tappi rules T222 om-88 and T249 om85 (*14*), respectively. Ash content was estimated as the residue after 6 h at 575 °C. Two replicates were used for each sample. The composition (as percent of whole bast fiber) was as follows: ash, 2.0%; acetone extractives, 0.5%; water-soluble extract, 1.2%; Klason lignin, 4.6%; acid-soluble lignin, 1.5%. The composition of neutral monosaccharides (as percent of total neutral carbohydrates) included rhamnose, 0.4%; arabinose, 0.6%; xylose, 1.0%; mannose, 9.9%; galactose, 1.6%; and glucose, 86.4%. No uronic acid determination was performed in this study. The composition of metals and other elements in the hemp fiber was analyzed by inductively coupled plasma spectrophotometry (ICP-OES) after oxidation with concentrated HNO_3 under pressure in a microwave digestor, with the following results: Ca, 5330 ppm; K, 2103 ppm; P, 667 ppm; Mg, 480 ppm; S, 372 ppm; Al, 241 ppm; Mn, 47 ppm; Na, 26 ppm; Si, 19 ppm; Sr, 17 ppm; Ba, 7 ppm; B, 7 ppm; Zn, 4 ppm. This study does not include nitrogen analysis. 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 (Hewlett-Packard, Hoofddorp, The Netherlands) 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 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 × 0.25 mm i.d., 0.1 *μ*m, high-temperature, polyimide-coated fused silica tubing DB-5HT from J&W Scientific (Folsom, CA), especially processed for use at 400 °C. After a 1 min hold at 100 °C, the oven was temperature-programmed from 100 to 350 °C at 15 °C/min, followed by a 3 min hold at 350 °C. Peaks were quantified by area, and a mixture of standards (octadecane, palmitic acid, sitosterol, cholesteryl oleate, and campesteryl, stigmas-teryl, and sitosteryl 3-*β*-D-glucopyranosides) was used to produce calibration curves. The data from the two replicates were averaged. In all cases the standard deviations from replicates were below 10% of the mean values.

The GC/MS analyses were performed on a model GC 8000 Top gas chromatograph (Thermo Finnigan, San Jose, CA) coupled to a

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Voyager quadrupole mass spectrometer detector (ThermoQuest Finnigan) equipped with a 15 m × 0.25 mm i.d., 0.1 μm DB-5HT fused silica capillary column (J&W). After an initial hold for 1 min at 120 °C, the oven was heated from 120 to 380 °C at 10 °C/min, followed by a 5 min hold at 380 °C. The injector and transfer line temperatures were set at 300 and 350 °C, respectively. Helium was used as the carrier gas, and the injection was performed in splitless mode. Bis(trimethylsilyl)trifluoroacetamide (BSTFA) silylation was used when required. Compounds were identified by comparing their mass spectra with mass spectra in the Wiley and NIST libraries, by mass fragmentography, and, when possible, by comparison with authentic standards.

Py-GC/MS. The pyrolysis of hemp fibers was performed in duplicate with a Curie-point pyrolyzer (Horizon Instruments Ltd., Heathfield, Sussex, U.K.) coupled to a Varian Saturn 2000 GC/MS, using a 30 m × 0.25 mm i.d., 0.25 μm DB-5 column. Approximately 100 μg of finely divided sample was deposited on a ferromagnetic wire and then inserted into the glass liner and immediately placed in the pyrolyzer. The pyrolysis was carried out at 610 °C for 4 s. After a 1 min hold at 40 °C, the chromatograph was programmed from 40 to 300 °C at a rate of 6 °C/min. The final temperature was held for 20 min. The injector, equipped with a liquid carbon dioxide cryogenic unit, was programmed from −30 °C (1 min) to 300 °C at 200 °C/min while the GC/MS interface was kept at 300 °C. For the pyrolysis in the presence of tetramethylammonium hydroxide (TMAH), to analyze *p*-hydroxycinnamic acids, ∼100 μg of sample was mixed with 0.5 μL of 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. The compounds were identified by comparing the mass spectra obtained with those of the Wiley and NIST computer libraries and that reported in the literature (*11*, *12*). Relative peak molar areas were calculated for carbohydrate and lignin pyrolysis products. The summed molar areas of the relevant peaks were normalized to 100%, and the data for two repetitive pyrolysis experiments were averaged. The relative standard deviation for the pyrolysis data was <10%. No attempt was made to calculate the response factor for every single compound released. However, for most of the lignin-derived phenols, the response factors are nearly identical (*15*), with the exception of vanillin, but this is a minor peak here.

RESULTS AND DISCUSSION

The hemp fiber was characterized by its low lignin content, estimated as Klason lignin, which accounted for 4.6% of the total fiber. This value is lower than those of other nonwood bast fibers such as kenaf but similar to that of flax (*16*, *17*). The lipid content, ∼0.5%, is also low and similar to that of kenaf but lower than those of other nonwood materials used for papermaking, such as flax (*18*, *19*). On the other hand, the hemicellulose fraction was mainly constituted by mannose. Finally, the ash content, 2%, is also low, and the composition of the different metals and other elements in the hemp fibers revealed a predominance of Ca and K and very low contents of other elements. It is important to note the low amounts of silica found in the hemp fiber compared to those of other nonwood fibers used for papermaking, such as wheat straw.

Lignin Composition. The low lignin content of the hemp fibers is, in principle, advantageous for its use in paper pulp manufacturing as it would require fewer chemicals and less drastic conditions during pulping. However, it is known that the lignin composition also strongly affects pulping (*3*, *4*). To analyze in situ the chemical composition of lignin, the hemp bast fibers were subjected to Py-GC/MS. The Py-GC/MS chromatogram is shown in **Figure 1**, and the identities and relative abundances of the released compounds are listed in **Table 1**. The Py-GC/MS analysis of the hemp fibers released predominantly compounds arising from carbohydrates and very minor amounts of lignin-derived phenols, in agreement with the relatively low lignin content estimated as Klason lignin. As

Table 1. Identification and Relative Molar Abundance of Compounds Released after Py-GC/MS of Industrial Hemp Bast Fibers[a]

no.	compound	mass fragments (*m/z*)	origin	abundance (%)
1	hydroxyacetaldehyde	42/60	C	8.1
2	3-hydroxypropanal	73/74	C	4.2
3	(3*H*)-furan-2-one	55/84	C	0.5
4	2,3-butanedione	56/57/86	C	4.1
5	(2*H*)-furan-3-one	55/84	C	0.9
6	2-furaldehyde	67/95/96	C	3.0
7	2-methylfuran	53/81/82	C	0.5
8	2-(hydroxymethyl)furan	43/70/81/98	C	1.5
9	cyclopent-1-ene-3,4-dione	54/68/96	C	0.4
10	4-methyltetrahydrofuran-3-one	43/72	C	0.2
11	(5*H*)-furan-2-one	55/84	C	2.3
12	acetylfuran	43/95/110	C	0.2
13	2,3-dihydro-5-methylfuran-2-one	55/69/98	C	6.0
14	5-methyl-2-furfuraldehyde	53/109/110	C	1.0
15	phenol	65/66/94	LH	0.4
16	5,6-dihydropyran-2,5-dione	68/98	C	2.4
17	4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one	58/85/114	C	0.5
18	3-hydroxy-2-methyl-2-cyclopenten-1-one	55/84/112	C	0.9
19	2-hydroxy-3-methyl-2-cyclopenten-1-one	55/84/112	C	2.7
20	2,3-dimethylcyclopenten-1-one	67/95/110	C	0.2
21	4-methylphenol	77/107/108	LH	0.4
22	2-furoic acid, methyl ester	67/95/126	C	0.8
23	guaiacol	81/109/124	LG	0.5
24	4-ethylphenol	77/107/122	LH	0.1
25	3,4-dihydroxybenzaldehyde	81/109/137/138	LM	0.4
26	3,5-dihydroxy-2-methyl-(4*H*)-pyran-4-one	70/98/126	C	0.3
27	5-hydroxymethyl-2-tetrahydro-furaldehyde-3-one	43/57/69/70/85	C	1.5
28	4-methylguaiacol	95/123/138	LG	0.3
29	catechol	64/81/92/110	LM/C	3.9
30	5-hydroxymethyl-2-furaldehyde (isomer)	69/97/109/126	C	0.5
31	5-hydroxymethyl-2-furaldehyde	69/97/109/126	C	5.1
32	3-methoxycatechol	79/97/125/140	LM	0.9
33	4-ethylguaiacol	122/137/152	LG	0.2
34	4-methylcatechol	78/107/123/124	LM	0.5
35	1,4-dideoxy-D-glycerohex-1-ene-pyrenone-3-ulose	43/73/87/113/144	C	3.4
36	4-vinylguaiacol	107/135/150	LG	1.3
37	syringol	111/139/154	LS	0.2
38	pyrogallol	52/80/97/108/126	LM	4.8
39	1,6-anhydrogalactopyranose	57/60/73/98	C	0.3
40	vanillin	109/151/152	LG	0.6
41	4-methylsyringol	125/153/168	LS	0.1
42	*trans*-isoeugenol	131/149/164	LG	0.4
43	homovanillin	122/137/166	LG	0.2
44	1,6-anhydromannopyranose	57/60/73/98	C	0.9
45	1,6-anhydroglucopyranose (levoglucosan)	57/60/73/98	C	28.7
46	4-ethylsyringol	167/182	LS	0.5
47	guaiacylacetone	122/137/180	LG	0.2
48	1,6-anhydro-β-D-glucofuranose	73/85/115	C	0.4
49	4-vinylsyringol	137/165/180	LS	0.6
50	guaiacyl vinyl ketone	123/151/178	LG	0.2
51	4-allylsyringol	167/179/194	LS	0.3
52	*cis*-4-propenylsyringol	167/179/194	LS	0.1
53	syringaldehyde	167/181/182	LS	0.2
54	*cis*-coniferyl alcohol	124/137/151/180	LG	0.1
55	*trans*-4-propenylsyringol	167/179/194	LS	0.4
56	acetosyringone	153/181/196	LS	0.1
57	*trans*-coniferaldehyde	107/135/147/178	LG	0.1
58	*trans*-coniferyl alcohol	124/137/151/180	LG	0.3
59	syringylacetone	123/167/210	LS	0.1
60	*cis*-sinapyl alcohol	154/167/210	LS	0.1
61	*trans*-sinapaldehyde	137/165/180/208	LS	0.1
62	*trans*-sinapyl alcohol	154/167/210	LS	0.1
	%H			12.8
	%G			53.0
	%S			34.2
	S/G			0.64

[a] C, carbohydrates; LM, modified lignin; LH, *p*-hydroxyphenyl lignin units, H; LG, guaiacyl lignin units, G; LS, syringyl lignin units, S. Underlined mass fragments indicate base peaks.

Table 2. Composition and Abundance of Lipids from Industrial Hemp Bast Fibers (Main Mass Fragments Are Included)

compound	mass fragments	abundance (mg/100 g)	compound	mass fragments	abundance (mg/100 g)
***n*-alkanes**		**52.50**	**triterpenoid/steroid ketones**		**8.28**
n-heneicosane	57/71/85/296	0.16	β-amyrenone	189/203/218/409/424	1.91
n-tricosane	57/71/85/324	0.12	α-amyrenone	189/203/218/409/424	0.38
n-pentacosane	57/71/85/352	0.31	stigmastan-3-one	231/232/414	0.84
n-hexacosane	57/71/85/366	0.19	stigmasta-7,22-dien-3-one	55/269/298/367/410	0.61
n-heptacosane	57/71/85/380	4.71	stigmasta-3,5-dien-7-one	174/269/410	0.15
n-octacosane	57/71/85/394	1.25	stigmast-4-en-3-one	124/229/412	2.52
n-nonacosane	57/71/85/408	39.03	stigmastadienone isomer	57/136/174/269/410	0.64
n-triacontane	57/71/85/422	0.92	ergostane-3,6-dione	137/245/414	0.09
n-hentriacontane	57/71/85/436	4.72	stigmast-4-en-3,6-dione	137/398/408/411/426	0.03
n-tritriacontane	57/71/85/464	1.09	stigmastane-3,6-dione	245/287/428	1.11
fatty acids		**21.66**	**waxes**		**21.34**
n-tetradecanoic acid	60/73/129/228	0.25	wax C_{40}	57/257/285/313/592	0.10
n-pentadecanoic acid	60/73/129/242	0.29	wax C_{42}	57/313/341/353/620	1.95
9-hexadecenoic acid	55/69/236/254	0.05	wax C_{44}	57/257/313/341/369/648	4.23
n-hexadecanoic acid	60/73/129/256	11.15	wax C_{45}	57/313/355/369/662	0.12
9,12-octadecadienoic acid	67/81/280	3.82	wax C_{46}	57/257/313/341/369/676	4.47
9-octadecenoic acid	75569/264	2.27	wax C_{47}	57/313/341/369/383/690	0.09
n-octadecanoic acid	60/73/129/284	2.10	wax C_{48}	57/313/341/369/397/704	3.25
n-eicosanoic acid	60/73/129/312	0.78	wax C_{49}	57/313/327/341/369/718	0.13
n-docosanoic acid	60/73/129/340	0.48	wax C_{50}	57/341/369/437/453/760	3.66
n-tetracosanoic acid	60/73/129/368	0.23	wax C_{51}	57/341/369/397/746	0.14
n-hexacosanoic acid	60/73/129/396	0.07	wax C_{52}	57/341/369/437/435/760	2.61
n-octacosanoic acid	60/73/129/424	0.08	wax C_{54}	57/369/397/425/788	0.59
n-triacontanoic acid	60/73/129/452	0.09	**sterol/triterpenol esters**		**26.50**
α-hydroxy fatty acids		**0.43**	β-amyrin acetate	189/203/218/468	17.68
2-hydroxyhexadecanoic acid	73/299/343[a]	0.31	α-amyrin acetate	189/203/218/468	4.43
2-hydroxydocosanoic acid	73/383/427[a]	0.03	taraxerol acetate	204/218/426	0.80
2-hydroxytricosanoic acid	73/397/441[a]	0.03	lupeol acetate	43/189/218/468	2.64
2-hydroxytetracosanoic acid	73/411/455[a]	0.05	sitosterol hexadecanoate	147/381/396	0.04
2-hydroxypentacosanoic acid	73/425/469[a]	0.01	sitosterol octadecanoate	147/381/396	0.01
fatty alcohols		**6.01**	β-amyrin tetradecanoate	189/203/218	0.04
n-octadecanol	75/103/327[b]	0.19	β-amyrin pentadecanoate	189/203/218	0.05
n-eicosanol	75/103/355[b]	0.33	β-amyrin hexadecanoate	189/203/218	0.15
n-docosanol	75/103/383[b]	1.04	β-amyrin octadecanoate	189/203/218	0.03
n-tetracosanol	75/103/411[b]	0.33	β-amyrin eicosanoate	189/203/218	0.06
n-hexacosanol	75/103/439[b]	0.59	β-amyrin docosanoate	189/203/218	0.10
n-octacosanol	75/103/467[b]	1.57	β-amyrin tetracosanoate	189/203/218	0.20
n-triacontanol	75/103/495[b]	1.63	β-amyrin hexacosanoate	189/203/218	0.10
n-dotriacontanol	75/103/523[b]	0.33	β-amyrin octacosanoate	189/203/218	0.04
aldehydes		**7.91**	β-amyrin triacontanoate	189/203/218	0.01
n-heneicosanal	82/96/292	0.09	α-amyrin tetradecanoate	189/203/218	<0.01
n-docosanal	82/96/306	0.11	α-amyrin hexadecanoate	189/203/218	0.02
n-tricosanal	82/96/320	0.18	α-amyrin octadecanoate	189/203/218	0.01
n-tetracosanal	82/96/334	0.08	α-amyrin eicosanoate	189/203/218	0.02
n-pentacosanal	82/96/348	0.05	α-amyrin docosanoate	189/203/218	0.02
n-hexacosanal	82/96/362	0.39	α-amyrin tetracosanoate	189/203/218	0.02
n-octacosanal	82/96/390	2.51	α-amyrin hexacosanoate	189/203/218	0.02
n-nonacosanal	82/96/404	0.15	α-amyrin octacosanoate	189/203/218	<0.01
n-triacontanal	82/96/418	3.72	α-amyrin triacontanoate	189/203/218	<0.01
n-dotriacontanal	82/96/446	0.63	**steryl glycosides**		**1.80**
steroid hydrocarbons		**2.84**	campesteryl 3-β-D-gluco-pyranoside	204/217/361/383[b]	0.15
stigmasta-3,5,22-triene	135/143/394	1.46	stigmasteryl 3-β-D-gluco-pyranoside	204/217/361/395[b]	0.14
stigmasta-3,5-diene	81/147/381/396	1.38	sitosteryl 3-β-D-gluco-pyranoside	204/217/361/397[b]	1.51
free sterols/triterpenols		**31.81**			
campesterol	55/145/213/382/400	1.70			
stigmasterol	55/83/255/394/412	1.85			
sitosterol	145/213/396/414	13.93			
stigmastanol	215/416	3.78			
β-amyrin	203/218/426	9.47			
α-amyrin	203/218/426	1.08			
α-tocopherol	165/205/430	**1.40**			

[a] As methyl ester and TMS ether derivatives. [b] As TMS ether derivatives. Underlined mass fragments indicate base peaks.

a result, carbohydrate pyrolysis products represented 81% on average and phenols from lignin represented 19% of the total identified compounds from hemp fibers. The main carbohydrate-derived compounds were hydroxyacetaldehyde (**1**), 3-hydroxypropanal (**2**), 2-furaldehyde (**6**), 2,3-dihydro-5-methylfuran-2-one (**13**), 2-hydroxy-3-methyl-2-cyclopenten-1-one (**19**), 5-hydroxymethyl-2-furaldehyde (**31**), 1,4-dideoxy-D-glycerohex-1-enopyranone-3-ulose (**35**), and levoglucosan (**45**), the latter being the most prominent peak in the pyrogram. Among the lignin-derived compounds, the pyrogram of hemp bast fibers showed compounds derived from *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) lignin units, with a predominance of the G units. The main lignin-derived compound identified was 4-vinylguaiacol (**36**). Other guaiacyl counterparts including

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Table 3. Composition and Abundance of the Different Individual Esters Identified among the Waxes Identified in Industrial Hemp Fibers

waxes	fatty acid: fatty alcohol	abundance (mg/100 g)
wax C_{40}		
tetradecanoic acid, hexacosyl ester	C_{14}:C_{26}	0.02
hexadecanoic acid, tetracosyl ester	C_{16}:C_{24}	0.02
octadecanoic acid, docosyl ester	C_{18}:C_{22}	0.06
wax C_{42}		
hexadecanoic acid, hexacosyl ester	C_{16}:C_{26}	0.11
octadecanoic acid, tetracosyl ester	C_{18}:C_{24}	0.04
eicosanoic acid, docosyl ester	C_{20}:C_{22}	1.44
docosanoic acid, eicosyl ester	C_{22}:C_{20}	0.33
tetracosanoic acid, octadecyl ester	C_{24}:C_{18}	0.03
wax C_{44}		
hexadecanoic acid, octacosyl ester	C_{16}:C_{28}	0.28
octadecanoic acid, hexacosyl ester	C_{18}:C_{26}	0.09
eicosanoic acid, tetracosyl ester	C_{20}:C_{24}	0.98
docosanoic acid, docosyl ester	C_{22}:C_{22}	2.40
tetracosanoic acid, eicosyl ester	C_{24}:C_{20}	0.45
hexacosanoic acid, octadecyl ester	C_{26}:C_{18}	0.03
wax C_{45}		
hexadecanoic acid, nonacosyl ester	C_{16}:C_{29}	0.01
eicosanoic acid, pentacosyl ester	C_{20}:C_{25}	0.05
docosanoic acid, tricosyl ester	C_{22}:C_{23}	0.03
tetracosanoic acid, heneicosyl ester	C_{24}:C_{21}	0.03
wax C_{46}		
hexadecanoic acid, triacontyl ester	C_{16}:C_{30}	0.54
octadecanoic acid, octacosyl ester	C_{18}:C_{28}	0.24
eicosanoic acid, hexacosyl ester	C_{20}:C_{26}	1.75
docosanoic acid, tetracosyl ester	C_{22}:C_{24}	1.50
tetracosanoic acid, docosyl ester	C_{24}:C_{22}	0.28
hexacosanoic acid, eicosyl ester	C_{26}:C_{20}	0.14
octacosanoic acid, octadecyl ester	C_{28}:C_{18}	0.02
wax C_{47}		
hexadecanoic acid, hentriacontyl ester	C_{16}:C_{31}	0.01
eicosanoic acid, heptacosyl ester	C_{20}:C_{27}	0.03
docosanoic acid, pentacosyl ester	C_{22}:C_{25}	0.05
wax C_{48}		
hexadecanoic acid, dotriacontyl ester	C_{16}:C_{32}	0.11
octadecanoic acid, triacontyl ester	C_{18}:C_{30}	0.13
eicosanoic acid, octacosyl ester	C_{20}:C_{28}	1.18
docosanoic acid, hexacosyl ester	C_{22}:C_{26}	0.87
tetracosanoic acid, tetracosyl ester	C_{24}:C_{24}	0.49
hexacosanoic acid, docosyl ester	C_{26}:C_{22}	0.39
octacosanoic acid, eicosyl ester	C_{28}:C_{20}	0.06
triacontanoic acid, octadecyl ester	C_{30}:C_{18}	0.02
wax C_{49}		
eicosanoic acid, nonacosyl ester	C_{20}:C_{29}	0.13
wax C_{50}		
hexadecanoic acid, tetratriacontyl ester	C_{16}:C_{34}	0.06
octadecanoic acid, dotriacontyl ester	C_{18}:C_{32}	0.07
eicosanoic acid, triacontyl ester	C_{20}:C_{30}	1.27
docosanoic acid, octacosyl ester	C_{22}:C_{28}	1.36
tetracosanoic acid, hexacosyl ester	C_{24}:C_{26}	0.53
hexacosanoic acid, tetracosyl ester	C_{26}:C_{24}	0.09
octacosanoic acid, docosyl ester	C_{28}:C_{22}	0.20
triacontanoic acid, eicosyl ester	C_{30}:C_{20}	0.08
wax C_{51}		
eicosanoic acid, hentriacontyl ester	C_{20}:C_{31}	0.04
docosanoic acid, nonacosyl ester	C_{22}:C_{29}	0.08
tetracosanoic acid, heptacosyl ester	C_{24}:C_{27}	0.02
wax C_{52}		
hexadecanoic acid, hexatriacontyl ester	C_{16}:C_{36}	0.05
octadecanoic acid, tetratriacontyl ester	C_{18}:C_{34}	0.03
eicosanoic acid, dotriacontyl ester	C_{20}:C_{32}	0.33
docosanoic acid, triacontyl ester	C_{22}:C_{30}	1.17
tetracosanoic acid, octacosyl ester	C_{24}:C_{28}	0.71
hexacosanoic acid, hexacosyl ester	C_{26}:C_{26}	0.05
octacosanoic acid, tetracosyl ester	C_{28}:C_{24}	0.03
triacontanoic acid, docosyl ester	C_{30}:C_{22}	0.24
wax C_{54}		
hexadecanoic acid, octatriacontyl ester	C_{16}:C_{38}	0.01
eicosanoic acid, tetratriacontyl ester	C_{20}:C_{34}	0.03
docosanoic acid, dotriacontyl ester	C_{22}:C_{32}	0.14
tetracosanoic acid, triacontyl ester	C_{24}:C_{30}	0.30
hexacosanoic acid, octacosyl ester	C_{26}:C_{28}	0.08
octacosanoic acid, hexacosyl ester	C_{28}:C_{26}	0.02
triacontanoic acid, tetracosyl ester	C_{30}:C_{24}	0.01

guaiacol (**23**), 4-methylguaiacol (**28**), 4-ethylguaiacol (**3**), and *trans*-4-propenylguaiacol (**55**) were also detected, although in lower amounts. Moreover, several oxidized phenols, such as vanillin (**40**), guaiacylacetone (**47**), guaiacyl vinyl ketone (**50**), and *trans*-coniferylaldehyde (**57**) were also identified, together with the lignin precursor *trans*-coniferyl alcohol (**58**). The *p*-hydroxyphenyl and syringyl counterparts were also detected, although in lower amounts. The relative molar distribution of the different lignin units H:G:S was 13:53:34 with a S/G molar ratio of 0.64. No sinapyl or coniferyl acetates have been detected in hemp fibers. These acetylated lignin units have been detected by Py-GC/MS in nonwood fibers (*16*, *20*) with syringyl-rich lignins such as kenaf, yute, sisal, and abaca but were not detected in other fibers with guaiacyl-rich lignin such as flax (*20*). In the present work, the presence of cinnamic acids in the hemp fibers were analyzed using Py-GC/MS in the presence of TMAH. The methyl derivatives of *p*-coumaric and ferulic acids (4-methoxycinnamic acid and 3,4-dimethoxycinnamic acid methyl esters, respectively) were found in only trace amounts (cinnamic acids/lignin molar ratio of 0.04), with a predominance of ferulic acid over *p*-coumaric acid.

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 (and H units both C-3 and C-5) available for very strong carbon−carbon bonds, which make them fairly resistant to the pulping depolymerization. Therefore, the low S/G ratio of hemp fibers may make them more difficult to delignify (and bleach) because of the higher condensation degree of the lignin, despite having a very low lignin content. In fact, the difficulty in delignifying (and bleaching) hemp soda/anthraquinone pulp has been revealed by the pulp mill using these fibers (personal communication).

Lipid Composition. The total lipid extract of the industrial hemp bast fibers accounted for 0.5% of the total fiber. The underivatized and silylated extracts were analyzed by GC and GC/MS. The GC/MS chromatogram of the underivatized hemp lipids is shown in **Figure 2**, and the detailed list with the identities and abundances of the main compounds present in the hemp extracts is summarized in **Table 2**. The most predominant lipid classes in hemp fibers were series of *n*-alkanes (29%), free (17%) and esterified (15%) sterols and triterpenols, *n*-fatty acids (12%), and waxes (12%). Minor amounts of *n*-aldehydes, *n*-fatty alcohols, and steroid and triterpenoid hydrocarbons and ketones were also present in these fibers. The series of *n*-alkanes were identified in the range from C_{21} to C_{33} with a strong odd-over-even carbon atom number predominance, nonacosane (C_{29}) being the most predominant. *n*-Alkanes with even carbon atom numbers (C_{26}, C_{28}, and C_{30}) were also identified.

Sterols and triterpenols were also present among the lipids of hemp fibers. Sitosterol was the most abundant among the free sterols with the presence of minor amounts of stigmastanol, stigmasterol, and campesterol. Lower amounts of sitosterol could also be found in ester form. Several steryl glycosides, such as sitosteryl, campesteryl, and stigmasteryl 3-β-D-glucopyranosides, were also identified in minor amounts, the former being the most predominant. The identification of steryl glycosides was accomplished (after BSTFA derivatization of the lipid extract) by comparison with the mass spectra and relative retention times of authentic standards (*23*). Among triterpenols, β-amyrins predominated in both free and esterified form, and α-amyrins were also present. Significant amounts of triterpenol acetates (including β- and α-amyrin, taraxerol, and lupeol acetates) were identified in the hemp fiber extracts. Several steroid hydrocar-

bons (such as stigmasta-3,5-diene and stigmasta-3,5,22-triene) and steroid and triterpenoid ketones (such as stigmast-4-en-3-one, stigmastan-3-one, stigmasta-7,22-dien-3-one, stigmastane-3,6-dione and β- and α-amyrenones) were also identified.

Free fatty acids were present in the range from tetradecanoic (C_{14}) to dotriacontanoic (C_{32}) acids, with a strong even-over-odd carbon atom predominance. Palmitic ($C_{16:0}$) and linoleic ($C_{18:2}$) acids were the most abundant followed by oleic ($C_{18:1}$) and stearic ($C_{18:0}$) acids. α-Hydroxy fatty acids were also identified among the hemp extractives, and the series was present in the range from 2-hydroxyhexadecanoic acid to 2-hydroxypentacosanoic acid.

Waxes were also important components of the hemp fiber extracts and were found in the range from C_{40} to C_{54} with a strong predominance of the even carbon atom number homologues, the C_{44} and C_{46} analogues being the most abundant. Among the waxes, the GC/MS analysis revealed that each chromatographic peak consisted of a complex mixture of different long-chain fatty acids esterified to different long-chain fatty alcohols. The identification and quantitation of the individual long-chain esters in each chromatographic peak were resolved on the basis of the mass spectra of the peaks. The mass spectra of long-chain esters are characterized by a base peak produced by a rearrangement process involving the transfer of 2H atoms from the alcohol chain to the acid chain, giving a protonated acid ion (*24*, *25*). Therefore, the base peak gives the number of carbon atoms in the acid moiety and the molecular ion the total number of carbon atoms in the ester. It is possible then to determine the individual contribution of esters to every chromatographic peak by mass spectrometric determination of the molecular ion and the base peak. Quantitation of individual esters was accomplished by integrating areas in the chromatographic profiles of ions characteristic for the acidic moiety. The detailed structural composition and abundance of the high molecular weight waxes identified in the hemp fiber are shown in **Table 3**. The esterified fatty acids ranged from C_{16} to C_{30} and the esterified fatty alcohols from C_{16} to C_{38}. The acyl moiety of the waxes was exclusively constituted by saturated fatty acids with even carbon number, docosanoic (C_{22}) and eicosanoic (C_{20}) acids being the most predominant. Waxes with unsaturated fatty acids could not be detected, despite the high amounts of oleic and linoleic acids being present in free form. Among the esterified alcohols, the most predominant was docosanol (C_{22}), followed by octacosanol (C_{28}), hexacosanol (C_{26}), triacontanol (C_{30}), and tetracosanol (C_{24}), although they showed the presence of low amounts of the odd carbon atom number homologues, which accounted for the odd carbon atom number waxes. The predominant wax was C_{46}, mostly constituted by eicosanoic acid (C_{20}) esterified to hexacosanol (C_{26}) and by docosanoic acid (C_{22}) esterified to tetracosanol (C_{24}).

n-Fatty alcohols ranging from C_{18} to C_{32} were present in the hemp extracts with the presence of only the even carbon atom homologues, triacontanol (C_{30}) and octacosanol (C_{28}) being the most abundant. It can be observed that the series of free fatty alcohols parallels the distribution of the esterified fatty alcohols in waxes. A series of *n*-aldehydes ranging from C_{21} to C_{32} were identified in the hemp fibers with triacontanal (C_{30}) and octacosanal (C_{28}) predominating. The distribution of the aldehyde series correlates to that of free alcohols, as usually occurs in the plant kingdom, suggesting that aldehydes are intermediates in the biosynthesis of alcohols (*26*, *27*).

The different lipid classes have different behaviors during cooking. The waxes are hydrolyzed during alkaline cooking, and the fatty acids are dissolved. At sufficiently high pH (as 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. On the other hand, alkanes, fatty alcohols, sterols and triterpenols, steroid hydrocarbons and ketones, and steryl glycosides survive cooking. These compounds have a very low solubility in water and are difficult to remove and, therefore, can be at the origin of pitch problems. In conclusion, the present work reports the chemical composition of lignin and lipids of industrial hemp fibers. Knowledge of the chemical composition of the main components of hemp fibers will be useful for a better utilization of nonwood plants.

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