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Lipids from Flax Fibers and Their Fate in Alkaline Pulping

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The chemical composition of lipids from bast fibers of flax (*Linum usitatissimum*), which are commonly used for high-quality paper pulp production, was thoroughly studied by gas chromatography−mass spectrometry. The main compounds identified were waxes, series of long chain *n*-fatty alcohols, *n*-aldehydes, *n*-fatty acids, and *n*-alkanes. Free and esterified sterols and triterpenols, steroid hydrocarbons, steroid and triterpenoid ketones, as well as sterol glycosides were also found in the flax bast fibers. On the other hand, the fate of these lipophilic compounds in alkaline pulping of flax fibers was investigated by analyzing two pulps obtained under distinct industrial cooking conditions. The results revealed that while waxes could be efficiently hydrolyzed during pulping depending on the alkali charge, most of the other lipophilic compounds present in flax fibers survived cooking and were present in the unbleached pulps.

KEYWORDS: Flax; *Linum usitatissimum*; bast fibers; nonwood; lipids; waxes; pulps; pitch; alkaline pulping

INTRODUCTION

Although wood is still by far the main raw material for paper pulp manufacturing in developed countries, a market exists for high-value added papers from nonwood fibers. Indeed, their prices are higher as compared to wood kraft pulp. Moreover, where wood-based fibers are not available, as in the developing world, nonwood plants are the dominant fiber source for papermaking. On the other hand, there is a growing need within Europe to consider alternative agricultural strategies that move an agricultural industry purely focused on food production to one that also supplies the needs of other industrial sectors, such as paper and textiles. Nonwood fibers, therefore, could become an important crop in this transformation (*1*, *2*). One source of industrial fiber is agricultural crops, in either the form of residues or plants grown specifically for fiber. Flax, hemp, abaca, kenaf, jute, and sisal are among the nonwood fibers used in the manufacturing of high-quality pulps for specialty papers (such as tea bags, filters, bank notes, security papers, cigarette papers, or condenser papers).

Flax (*Linum usitatissimum*) is an annual plant from the family Linaceae, one of the oldest cultivated textile fibers known. It is a commercially important crop in Europe and other parts of the world, and considerable interest exists now in the U.S. for production of flax fiber for use in textiles and a variety of high-value products (*3*). The flax plant has two regions in the stem, an outer portion formed by long bast fibers and a core containing short fibers. The bast fibers, which are freed from the core and epidermis/cuticle by a process called retting, are traditionally used by the textile industry and are also excellent raw materials for manufacturing specialty papers.

Although several studies on the characterization of flax fibers have been published (*4*−*8*), only few papers include the detailed composition of lipids from these bast fibers (*3*). Moreover, to our knowledge, little information is available on the behavior of the different lipids during processing of flax fibers for paper pulp production. It is well-known that lipophilic compounds present in raw materials cause significant technical and environmental problems in the manufacturing of paper pulp. During pulping, these compounds are released from the fibers forming colloidal pitch, which can deposit causing production troubles. In the manufacture of alkaline pulps, a large part of the lipids originally present in raw material is removed during the cooking. However, some chemical species survive this process and are found as pulp extractives, suspended in process waters or forming the so-called pitch deposits in circuits, equipment, and final product that are responsible for reduced production levels, higher operating costs, and increased incidence of quality defects (*9*, *10*). The increasing trend in recirculating water in pulp mills to meet environmental demands is aggravating these problems. On the other hand, some of these naturally occurring extractives are potential pollutants and their toxicity is not restricted to the aquatic ecosystem alone, as these compounds, if not removed from the pulp, will be present in paper products such as coffee filters, tea bags, cigarette papers, etc. (*11*).

To maximize the exploitation of flax fibers for paper pulp production, a more complete understanding of its chemistry is required. In the present study, we report the chemical composition of lipophilic compounds from bast fibers of flax used in paper pulp manufacture. On the other hand, the behavior of these lipophilic compounds during pulping has also been investigated

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by analyzing the lipid extracts from two pulps after different alkaline cooking conditions.

MATERIALS AND METHODS

Samples. Flax (*L. usitatissimum*) bast fibers and two alkaline pulps with different kappa numbers (28 and 6) were supplied by CELESA mill (Tortosa, Spain). The retted flax fibers contained less than 20% of core fibers. The pulps were obtained by soda anthraquinone cooking using two different alkali concentrations. Flax fibers were air-dried while the pulp samples were dried in an oven at 50 °C. The dried samples were milled using a knife mill (Janke and Kunkel, Analyzenmühle) and extracted with acetone in a Soxhlet apparatus for 8 h. The extracts were evaporated to dryness and resuspended in chloroform for chromatographic analysis of the lipophilic fraction. Two replicates were used for each sample, and all of them were subjected to gas chromatography (GC) and GC-mass spectrometry (MS) analyses.

GC and GC-MS Analyses. An HP 5890 gas chromatograph (Hewlett-Packard, Hoofddorp, Netherlands) equipped with a split-splitless injector and a flame ionization detector (FID) was used for GC analyses. 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 high temperature, polyimide-coated fused silica tubing DB5-HT (5 m × 0.25 mm i.d., 0.1 μm film thickness) from J&W Scientific (Folsom, CA), especially processed for use at 400 °C. The oven was temperature-programmed from 100 (1 min) to 350 °C (3 min) at 15 °C min^{-1}. Peaks were quantified by area, and a mixture of standards was used to elaborate 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 quadrupole mass spectrometer detector (ThermoQuest Finnigan, model Voyager) equipped with a fused silica capillary column (DB-5HT, J&W; 15 m × 0.25 mm i.d., 0.1 μm film thickness). The oven was heated from 120 (1 min) to 380 °C (5 min) at 10 °C min^{-1}. 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 where 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.

RESULTS AND DISCUSSION

The lipid extracts from flax fibers accounted for 1.8% of total fibers. The underivatized and silylated 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 (*12*). This method enables the elution and analysis of intact high molecular weight lipids such as waxes, sterol esters, and triglycerides. The GC-MS chromatogram of the underivatized lipid extract from flax fibers is shown in **Figure 1**, and the identities and abundances of the main lipophilic compounds are summarized in **Table 1**. The most predominant lipids in flax fibers were waxes (47%), which are constituted by long-chain *n*-fatty acids esterified with long-chain *n*-fatty alcohols. Additionally, significant amounts of series of long-chain *n*-aldehydes (17%), *n*-fatty acids (12%), *n*-alkanes (10%), and *n*-fatty alcohols (9%) were found. Minor amounts of steroids and triterpenoids were also present in these fibers, but triglycerides were not detected. The distribution of the different aliphatic series is shown in **Figure 2**.

Waxes were found in the range from C_{46} to C_{60} with a strong even-over-odd carbon atom predominance, and the C_{50}, C_{52}, and C_{54} analogues were the most abundant. Each chromatographic peak consisted of a complex mixture of different long-chain

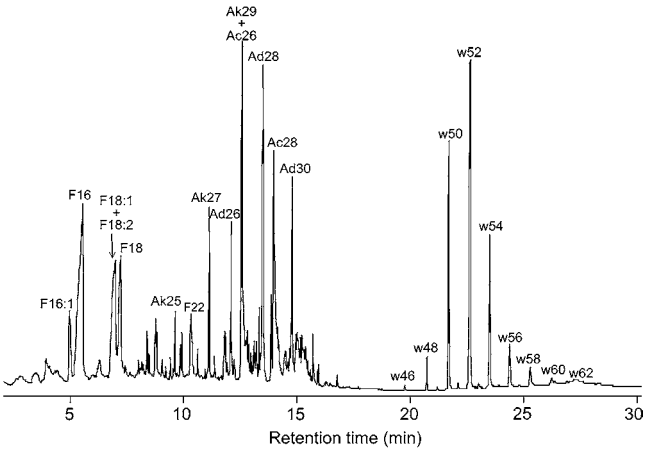

Figure 1. GC-MS chromatogram of the underivatized lipid extract from flax (*L. usitatissimum*) fibers. F(*n*), *n*-fatty acid series; Ak(*n*), *n*-alkane series; Ad(*n*), *n*-aldehyde series; Ac(*n*), *n*-alcohol series; and w(*n*), waxes series. *n* denotes the total carbon atom number.

fatty acids esterified to different long-chain fatty alcohols. The identification and quantitation of the individual long-chain esters in each chromatographic peak were based on the mass spectra of the peaks. **Figure 3** shows the mass spectra of the chromatographic peaks corresponding to waxes C_{50}, C_{52}, and C_{54}. 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 (*13*). The fragments at *m*/*z* 257, 285, 313, and 341 correspond to protonated hexadecanoic, octadecanoic, eicosanoic, and docosanoic acids, respectively. 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 integration of areas of the chromatographic profiles of the characteristic ions for the acidic moiety. A detailed structural characterization of the high molecular weight waxes in the flax fibers is shown in **Table 2**, and the distribution of the individual esterified fatty acids and fatty alcohols is shown in **Figure 2**. The esterified fatty acids ranged from C_{16} to C_{30}, and the esterified fatty alcohols ranged from C_{20} to C_{38}. The acid moiety of the waxes was exclusively constituted by saturated fatty acids with even carbon numbers. Among these, the most predominant ones were octadecanoic (C_{18}) and hexadecanoic (C_{16}) acids followed by eicosanoic (C_{20}) and docosanoic (C_{22}) acids. Among the alcohol moiety, the most predominant was tetratriacontanol (C_{34}) followed by hexatriacontanol (C_{36}) and dotriacontanol (C_{32}). The predominant wax was C_{52}, mostly constituted by octadecanoic acid (C_{18}) esterified to tetratriacontanol (C_{34}), followed by wax C_{50}, mostly constituted by hexadecanoic acid (C_{16}) esterified to tetratriacontanol (C_{34}) and by wax C_{54} mostly constituted by octadecanoic acid (C_{18}) esterified to hexatriacontanol (C_{36}).

Free fatty acids were also identified in the flax fibers ranging from C_{14} to C_{32}, with a strong even-over-odd predominance. The series were dominated by the saturated counterparts although the unsaturated $C_{18:1}$, $C_{18:2}$, and $C_{16:1}$ were also identified. Hexadecanoic acid (palmitic acid) was the most abundant, in agreement with Morrison et al. (*3*) who reported that palmitic acid was the major fatty acid found in the extracts from fibers of several flax cultivars. Stearic and oleic acids were

Table 1. Composition of Lipids (mg/100 g) from Flax (*L. usitatissimum*) Fibers and Their Alkaline Pulps

compounds	flax	flax pulps		compounds	flax	flax pulps	
		kappa 28	kappa 6			kappa 28	kappa 6
alkanes							
total	35.2	84.2	48.2	*n*-heptacosane	5.44	12.7	7.93
n-heneicosane	0.39	2.88	0.51	*n*-octacosane	1.46	5.82	4.30
n-tricosane	0.41	1.09	0.35	*n*-nonacosane	21.1	44.1	22.0
n-pentacosane	1.82	5.52	3.34	*n*-triacontane	0.52	1.94	1.48
n-hexacosane	1.32	4.43	3.23	*n*-hentriacontane	2.73	5.70	5.03
fatty acids							
total	43.0	77.0	44.1	*n*-octadecanoic acid	6.54	18.0	15.7
n-tetradecanoic acid	1.31	0.47	0.36	*n*-eicosanoic acid	1.87	2.61	1.50
n-pentadecanoic acid	0.40	0.27	0.21	*n*-docosanoic acid	2.25	2.03	0.68
9-hexadecenoic acid	0.18	0.58	0.10	*n*-tetracosanoic acid	1.49	1.94	0.72
n-hexadecanoic acid	16.8	26.5	20.7	*n*-hexacosanoic acid	0.77	1.35	0.31
n-heptadecanoic acic	0.45	0.55	0.32	*n*-octacosanoic acid	0.96	2.80	0.91
9,12-octadecadienoic acid	2.81	3.72	0.42	*n*-triacosanoic acid	0.45	0.52	0.09
9-octadecenoic acid	6.67	15.7	2.09	*n*-dotriacosanoic acid	0.05	0.00	0.00
fatty alcohols							
total	31.8	86.7	124	*n*-tetracosanol	0.44	1.04	1.97
n-hexadecanol	0.60	1.95	1.31	*n*-hexacosanol	6.49	15.4	23.5
n-octadecanol	2.48	1.82	3.44	*n*-octacosanol	14.5	48.2	70.9
n-eicosanol	1.46	2.66	4.28	*n*-triacontanol	4.10	14.2	16.1
n-docosanol	1.02	0.70	1.65	*n*-dotriacontanol	0.68	0.74	0.66
aldehydes							
total	61.9	6.91	7.93	*n*-hexacosanal	8.17	1.29	1.24
n-heneicosanal	0.64	0.00	0.00	*n*-heptacosanal	1.82	0.00	0.00
n-docosanal	1.03	0.00	0.00	*n*-octacosanal	25.4	4.13	5.42
n-tricosanal	1.90	0.00	0.06	*n*-nonacosanal	0.79	0.00	0.00
n-tetracosanal	0.87	0.15	0.11	*n*-triacontanal	19.9	1.34	1.10
n-pentacosanal	0.79	0.00	0.00	*n*-dotriacontanal	0.64	0.00	0.00
steroid hydrocarbons							
total	11.1	5.34	3.06	stigmastene	0.77	0.33	0.19
campestatriene	0.12	0.21	0.23	stigmastan-3,5,22-triene	1.49	3.41	1.47
campestadiene	0.50	0.48	0.61	stigmastan-3,5-diene	7.78	0.23	0.24
stigmastatetrane	0.44	0.68	0.32				
sterols/triterpenols							
total	2.10	5.47	2.02	stigmastanol	0.16	0.26	0.04
campesterol	0.27	0.50	0.00	β-amyrin	0.09	2.98	1.57
stigmasterol	0.15	0.04	0.00	α-amyrin	0.03	0.21	0.15
sitosterol	1.40	1.49	0.25				
α-tocopherol							
total	0.27	0.33	0.21				
steroid/triterpenoid ketones							
total	2.40	6.08	3.27	ergostan-3,6-dione	0.03	0.00	0.00
stigmastan-3-one	0.28	0.15	0.10	stigmast-4-en-3,6-dione	0.07	0.08	0.01
stigmasta-7,22-dien-3-one	0.17	0.91	0.56	stigmastane-3,6-dione	0.12	0.09	0.03
stigmasta-3,5-dien-7-one	0.15	0.84	0.27	β-amyrenone	0.23	1.60	1.21
stigmast-4-en-3-one	0.78	1.46	0.43	α-amyrenone	0.12	0.16	0.29
stigmastadienone isomer	0.46	0.78	0.36				
sterol glycosides							
total	0.43	1.10	0.41	stigmasteryl 3β-D-glucopyranoside	0.09	0.15	0.06
campesteryl 3β-D-glucopyranoside	0.08	0.18	0.06	sitosteryl 3β-D-glucopyranoside	0.26	0.77	0.29
waxes							
total	168	213	11.4	wax C_{53}	0.91	0.00	0.00
wax C_{46}	0.70	0.55	0.16	wax C_{54}	30.0	23.9	1.04
wax C_{48}	4.86	8.51	0.80	wax C_{56}	8.16	1.85	0.39
wax C_{50}	39.3	67.6	4.37	wax C_{58}	3.71	0.73	0.00
wax C_{51}	0.82	0.55	0.00	wax C_{60}	1.28	0.00	0.00
wax C_{52}	78.1	109.1	4.63				
sterol/triterpenol esters							
total	1.94	0.09	0.00	β-amyrin esters	0.54	0.06	0.00
sitosterol ester	0.08	0.03	0.00				

also found in significant amounts. It is interesting to note that although unsaturated fatty acids are present in free form in flax fibers, they were not found esterified with fatty alcohols forming waxes. A series of *n*-alkanes (from C_{21} to C_{31}) were also identified in the flax fibers with a strong odd-over-even carbon atom number predominance; nonacosane (C_{29}) was the most abundant. *n*-Alkanes with even carbon atom numbers (C_{26}, C_{28}, and C_{30}) were also identified albeit in lower amounts. *n*-Fatty alcohols ranging from C_{16} to C_{32} were present in the fiber extracts with strong even-over-odd carbon atom predominance; octacosanol (C_{28}) was the most abundant. Octacosanol was also the major fatty alcohol found in the flax fibers by Morrison et

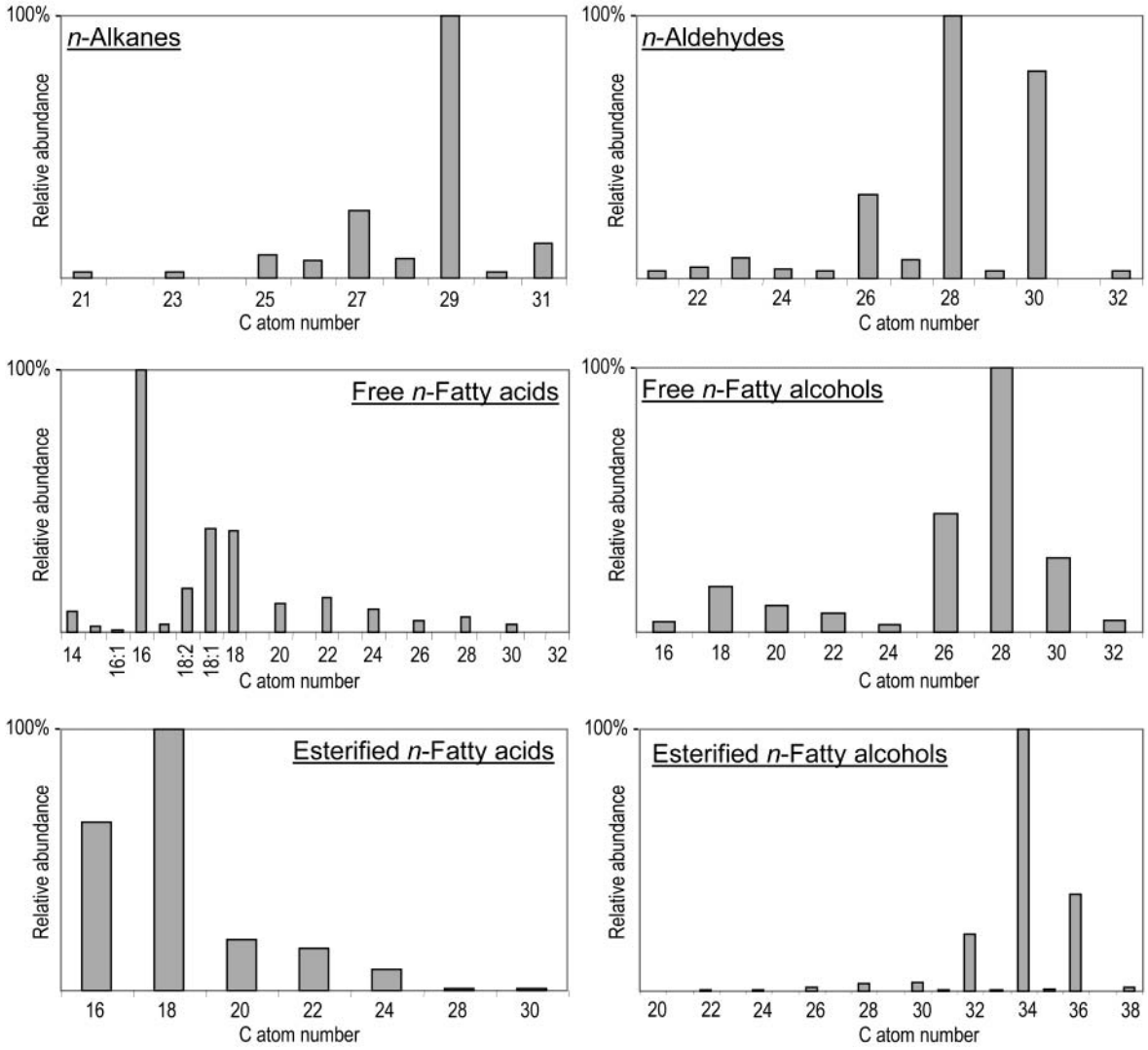

Figure 2. Distribution of the main aliphatic series identified in the extracts of flax (*L. usitatissimum*) fibers. The histograms are scaled up to the abundance of the major peak in the series.

al. (*3*). Interestingly, the series of free fatty alcohols do not parallel the series of esterified fatty alcohols. Moreover, a series of fatty alcohols with odd carbon number (C_{27}, C_{29}, C_{31}, C_{33}, C_{35}, and C_{37}) were found esterified with long-chain fatty acids but were not found in free form. Free alcohol composition is often different from that of esterified alcohols (*14*); therefore, the analysis of saponified extracts does not give reliable information about the composition of esters of fatty alcohols. A series of *n*-aldehydes ranging from C_{21} to C_{32} were identified in the flax fibers with strong even carbon atom predominance with 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 from fatty acids (*14, 15*).

Among sterols, sitosterol predominated in both free and esterified form. Minor amounts of other free sterols, such as campesterol, stigmastanol, and stigmasterol, were also found in flax fibers. Triterpenols such as β- and α-amyrins were present in free form, and β-amyrin was also present in esterified form, although in low amounts. On the other hand, several steroid hydrocarbons (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, and β- and α- amyrenones) were identified. Finally, minor amounts of several sterol glycosides, such as campesteryl, stigmasteryl, and sitosteryl β-D-glucopyranosides, were also identified in flax fibers, with the latter being the most predominant. The identification of sterol glycosides was accomplished (after BSTFA derivatization of the lipid extract) by comparison with the mass spectra and relative retention times of authentic standards (*16*).

The different classes of lipids have different behaviors during cooking. Therefore, to investigate the fate of the different flax lipids during cooking, the lipid composition of two alkaline flax pulps with different kappa numbers was studied. The lipid extracts of the flax pulps (kappa 28, with 4.2% lignin content, and kappa 6, with 0.9% lignin content) accounted for 1.3 and 0.8%, respectively. The chromatograms of the underivatized lipid extracts from the two flax pulps (kappa 28 and kappa 6) are shown in **Figure 4**, and the composition is listed in **Table 1**. The lipid composition of the alkaline pulp of kappa 28 was very similar to that originally present in the flax fibers, with a predominance of waxes (44%) and the presence of a series of *n*-fatty alcohols (18%), *n*-alkanes (17%), and *n*-fatty acids (16%). The main difference on the lipid composition of pulp of kappa 28 with respect to flax fibers concerns the amount of aldehydes, which in the flax pulp of kappa 28 decreased noticeably while the amounts of the corresponding homologue alcohols showed a parallel increase. The same trend can be

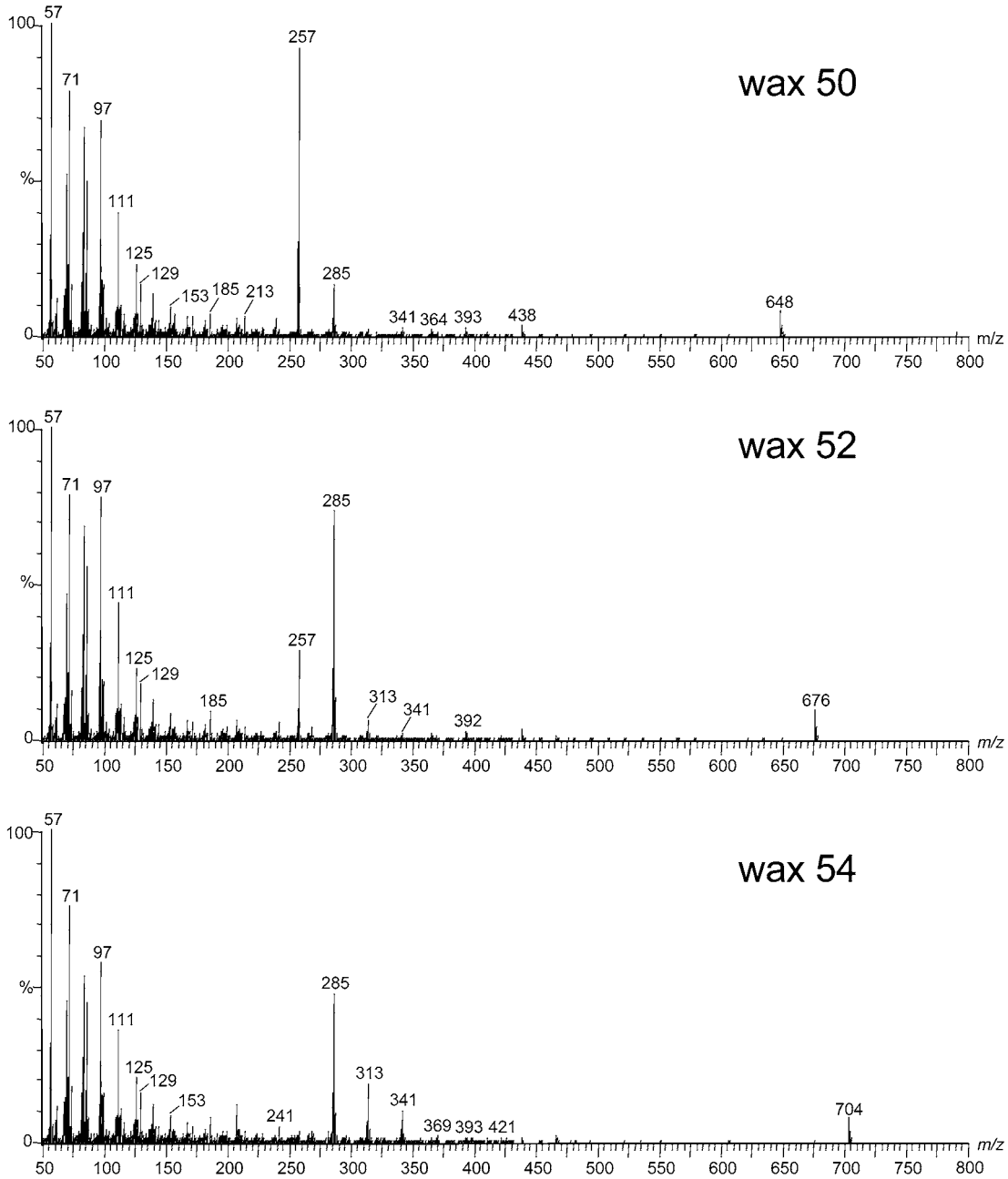

Figure 3. Mass spectra of the chromatographic peaks corresponding to wax C_{50}, wax C_{52}, and wax C_{54}.

observed in the flax pulp of kappa 6. On the other hand, the amount of waxes in flax pulp of kappa 6 showed a strong decrease, accounting for only 5% of the total identified lipids. The low wax content in the pulp of kappa 6 is due to the alkali concentration used to obtain this pulp that produced the extensive hydrolysis of wax esters. In this pulp sample, the lipophilic compounds are dominated by fatty alcohols (50%), alkanes (20%), and fatty acids (18%) with minor amounts of aldehydes, steroids, and triterpenoids. It is important to note that although waxes have been almost completely hydrolyzed in the pulp with kappa 6, the released alcohols (which have a maximum at C_{34}) were not detected among the lipophilic compounds present in this pulp and the profile of the alcohol series was similar to that of flax fibers. Probably, these fatty alcohols were removed with the cooking liquor or in the subsequent washing stage.

The lipids present in the flax fibers can be classified into two principal groups, namely fatty acids and neutral components, the latter including waxes, long-chain *n*-fatty alcohols, alkanes, aldehydes, and steroids and triterpenoids. The behavior of the fatty acids in an aqueous environment is quite different from that of the neutrals. At sufficiently high pH (as 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. Among these, waxes as well as some sterol and triterpenol esters, can be difficult to hydrolyze even in strongly alkaline pulping processes. When they are not extensively hydrolyzed during cooking, as occurs in the pulp with kappa 28, they tend to remain in the pulps as neutral esters that can be difficult to remove even in the washing and bleaching stages (*17*). Likewise, free sterols and triterpenols do not form soluble soaps under the alkaline pulping conditions and, therefore, have a tendency to deposit and cause pitch problems (*18*). Other sterol derivatives such as sterol glycosides could also have a role in the formation of pitch deposits since they survive the cooking conditions and are found intact in the

Table 2. Composition of the Different Waxes (mg/100 g) Identified in Flax (*L. usitatissimum*) Fibers and Their Alkaline Pulps

waxes fatty acid: fatty alcohol	flax	flax pulp	
		kappa 28	kappa 6
wax C_{46}	0.70	0.55	0.16
C_{16}:C_{30}	0.26	0.26	0.12
C_{18}:C_{28}	0.07	0.04	0.04
C_{20}:C_{26}	0.24	0.18	0.00
C_{22}:C_{24}	0.13	0.07	0.00
wax C_{48}	4.86	8.51	0.80
C_{16}:C_{32}	3.37	7.18	0.72
C_{18}:C_{30}	0.34	0.69	0.08
C_{20}:C_{28}	0.42	0.17	0.00
C_{22}:C_{26}	0.59	0.44	0.00
C_{24}:C_{24}	0.13	0.03	0.00
C_{26}:C_{22}	0.02	0.01	0.00
wax C_{50}	39.3	67.6	4.37
C_{16}:C_{34}	30.1	54.1	3.23
C_{18}:C_{32}	6.82	12.4	1.04
C_{20}:C_{30}	0.67	0.44	0.04
C_{22}:C_{28}	1.14	0.40	0.04
C_{24}:C_{26}	0.35	0.07	0.00
C_{26}:C_{24}	0.03	0.06	0.00
C_{28}:C_{22}	0.06	0.04	0.00
C_{30}:C_{20}	0.07	0.07	0.00
wax C_{51}	0.82	0.55	0.00
C_{16}:C_{35}	0.32	0.22	0.00
C_{18}:C_{33}	0.33	0.33	0.00
C_{20}:C_{31}	0.05	0.00	0.00
C_{22}:C_{29}	0.10	0.00	0.00
C_{24}:C_{27}	0.03	0.00	0.00
wax C_{52}	78.1	109	4.63
C_{16}:C_{36}	15.8	18.0	0.88
C_{18}:C_{34}	55.1	85.4	3.39
C_{20}:C_{32}	4.69	4.34	0.24
C_{22}:C_{30}	1.17	0.80	0.12
C_{24}:C_{28}	0.96	0.18	0.00
C_{26}:C_{26}	0.08	0.07	0.00
C_{28}:C_{24}	0.15	0.07	0.00
C_{30}:C_{22}	0.16	0.22	0.00
wax C_{53}	0.91	0.00	0.00
C_{16}:C_{37}	0.12	0.00	0.00
C_{18}:C_{35}	0.48	0.00	0.00
C_{20}:C_{33}	0.16	0.00	0.00
C_{22}:C_{31}	0.14	0.00	0.00
wax C_{54}	30.0	23.9	1.04
C_{16}:C_{38}	0.63	1.24	0.00
C_{18}:C_{36}	16.6	15.0	0.48
C_{20}:C_{34}	7.13	5.03	0.28
C_{22}:C_{32}	4.59	2.40	0.28
C_{24}:C_{30}	0.58	0.15	0.00
C_{26}:C_{28}	0.16	0.04	0.00
C_{28}:C_{26}	0.17	0.04	0.00
C_{30}:C_{24}	0.08	0.01	0.00
wax C_{56}	8.16	1.85	0.39
C_{18}:C_{38}	0.41	0.29	0.00
C_{20}:C_{36}	1.85	0.44	0.02
C_{22}:C_{34}	4.12	0.95	0.37
C_{24}:C_{32}	1.54	0.11	0.00
C_{26}:C_{30}	0.07	0.07	0.00
C_{28}:C_{28}	0.11	0.00	0.00
C_{30}:C_{26}	0.05	0.00	0.00
wax C_{58}	3.71	0.73	0.00
C_{20}:C_{38}	0.20	0.00	0.00
C_{22}:C_{36}	1.02	0.26	0.00
C_{24}:C_{34}	2.05	0.47	0.00
C_{26}:C_{32}	0.34	0.00	0.00
C_{28}:C_{30}	0.04	0.00	0.00
C_{30}:C_{28}	0.05	0.00	0.00
wax C_{60}	1.28	0.00	0.00
C_{22}:C_{38}	0.16	0.00	0.00
C_{24}:C_{36}	1.11	0.00	0.00

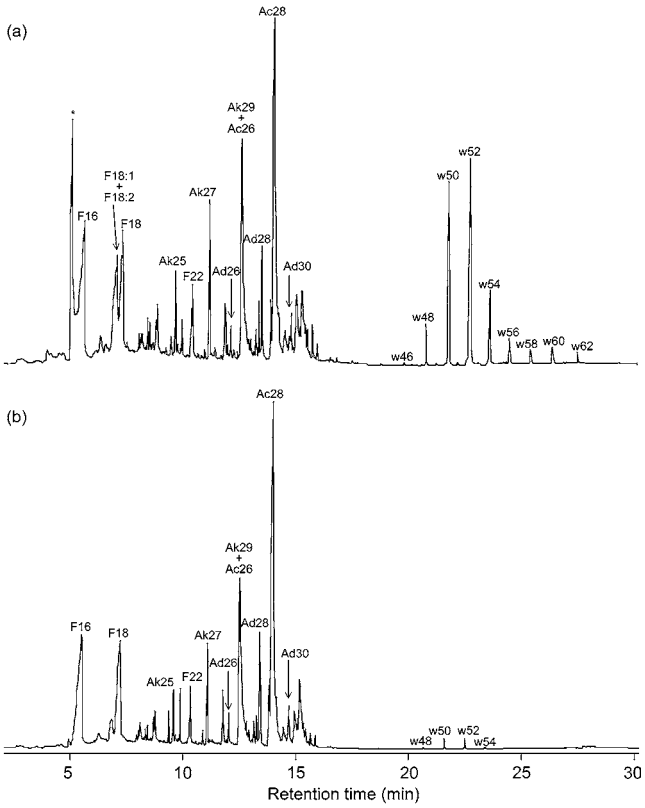

Figure 4. GC-MS chromatograms of the underivatized lipid extracts from (**a**) flax pulp with kappa number 28 and (**b**) flax pulp with kappa number 6. F(*n*), *n*-fatty acid series; Ak(*n*), *n*-alkane series; Ad(*n*), *n*-aldehyde series; Ac(*n*), *n*-alcohol series; and w(*n*), waxes series. *n* denotes the total carbon atom number. * is anthraquinone.

pulp, even at low kappa numbers, as shown in **Table 1**. Sterol glycosides have a high hydrophilic−lipophilic balance, high melting point, and very low solubility in water, alkali, and the usual organic solvents. Because of these properties, they constitute a part of protecting layers that prevent the cooking and bleaching chemicals from reaching the lipids, and thereby keep them and other compounds in the pulps (*19*). On the other hand, fatty acid soaps are effective solubilizing agents facilitating the removal from pulp of sparingly soluble neutral substances. However, in flax fibers, the content of fatty acids is low (only 12% of total lipids) as compared to that of neutral substances (88% of total lipids); therefore, the fatty acid soaps formed during the cooking may not possess sufficient micellar-forming properties to carry the less polar compounds into solution. So, an unbleached pulp with a high proportion of lipophilic compounds can be produced. The higher concentration of unsaponifiable compounds with respect to the saponifiable ones is also the main cause for pitch problems in the kraft pulping of some woods used by the pulp and paper industry, such as aspen or eucalypt (*20*−*25*). Therefore, the ratio of saponifiables to unsaponifiables has been suggested to be a better index for predicting pitch problems than the total amount of lipids (*17*).

In conclusion, it has been shown that some of the lipophilic compounds present in flax fibers survived cooking and were present in the unbleached pulps. However, waxes (the most abundant lipids in flax fibers) may be efficiently hydrolyzed during pulping at high alkali charges. The final selection of the cooking conditions (alkali charge) for minimizing lipid content in the pulps should be a compromise between the optimum in terms of lipid removal, the lowest decrease of pulp yield, and

the conservation of those pulp properties of interest for the different types of paper to be produced.

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