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Chemical composition of lipophilic extractives from sisal (*Agave sisalana*) fibers

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ABSTRACT

The chemical composition of lipophilic extractives from sisal (*Agave sisalana*) fibers, which are used for high-quality paper pulp production, was studied. The lipophilic extract, which accounted for 0.5% of total sisal fiber weight, was analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) using short- and medium-length high temperature capillary columns, respectively. For a more detailed characterization, the extract was fractionated by solid-phase extraction and the fractions obtained were analyzed by GC and GC/MS. The most predominant compounds identified were fatty acids (30% of total lipids) including α- and ω-hydroxyfatty acids, fatty alcohols (20%), free sterols (11%), alkanes (11%) and a series of ferulic acid esters of long chain alcohols and ω-hydroxyfatty acids (10%). Additionally, steroid hydrocarbons and ketones, monoglycerides, aldehydes, waxes, and sterol glycosides were also found together with minor amounts of diglycerides, and sterol esters.

1. 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 (van Dam et al., 1994; Moore, 1996).

Sisal (*Agave sisalana*) is an herbaceous monocotyledonous plant from the Agavaceae family. Originally from Central America and Mexico, sisal grows in many tropical countries, with Tanzania and Brazil being currently the two main producers (Chand et al., 1998). Sisal fibers, which are obtained from the leaves of the plant, are widely used for many applications including ropes for the marine and agriculture industry, as well as composites (Li et al., 2000; Agopyan et al., 2005). Likewise, sisal fiber has received increasing interest as raw material for the pulp and paper industry. The main characteristic of paper pulp obtained from sisal is its high porosity, making it an excellent raw material for papers such as dielectric, plug wrap, laminating substrate, vacuum bag, tea bag and filtration papers.

Studies on the chemical composition of sisal fibers are important for improving the pulping and bleaching processes of this raw material. Existing knowledge mainly includes general features of macromolecular components and the mechanical and physical properties of sisal fiber for composites application (Li et al., 2000) as well as few studies on the chemical composition of lignin (del Río et al., 2004a,b, 2007). To our knowledge, no studies about the chemical composition of sisal lipophilic extractives have been performed until now. In the present study, we report the detailed chemical composition of lipophilic compounds from sisal fibers with the aim

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of providing knowledge of interest for pulp and paper manufacture using this fiber as raw material. As it is well known, lipophilic compounds present in raw materials cause the so-called pitch problems in the manufacturing of pulp and paper (Hillis and Sumimoto, 1989; Back and Allen, 2000). The knowledge of the composition of the lipophilic extractives present in this fiber may help to predict and control pitch problems in the manufacturing of sisal pulp.

2. Materials and methods

2.1. Sample

Sisal (*A. sisalana*) leaf fibers (from Africa) were supplied by CELESA pulp mill (Tortosa, Spain) that produces high-quality soda/antraquinone paper pulps from nonwoody plants. The plant fibers were air-dried, milled using a knife mill (Janke and Kunkel, Analysenmühle), and extracted with acetone in a Soxhlet apparatus for 8 h. The acetone extracts were evaporated to dryness, and subsequently dissolved in chloroform for chromatographic analysis of the lipophilic fraction. Two replicates were used for each sample.

2.2. Fractionation by solid-phase extraction (SPE)

The SPE fractionation was used for a more detailed characterization of some compounds that eluted close together or were present in very minor amounts. The lipid extracts were fractionated by a SPE procedure previously developed by Gutiérrez et al. (1998, 2004a) using aminopropyl-phase cartridges (500 mg) from Waters (Division of Millipore). In the SPE method described here, the lipophilic compounds are retained in the column and elute from the column in order of increasing polarity. The cartridge was loaded and eluted by gravity. The procedure for the fractionation of sisal lipophilic extractives was as follows. First, the aminopropyl column was conditioned with hexane (4 ml). Next, the dried cloroform extract containing sisal lipophilic extractives was taken up in a minimal volume (<0.5 ml) of hexane:chloroform (4:1) and loaded into the cartridge column, leaving the entire lipid mixture in the column. Next, the column was first eluted with 8 ml of hexane (fraction A) and subsequently with 6 ml of hexane:chloroform (5:1) (fraction B), then with 10 ml of chloroform (fraction C) and finally with 10 ml of diethyl ether:acetic acid (98:2) (fraction D). Each isolated fraction was dried under nitrogen and subsequently dissolved in chloroform and analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).

2.3. GC and GC/MS analyses

The lipophilic extractives from sisal fibers were analyzed by GC and GC/MS using short- and medium-length high temperature capillary columns with thin films, respectively, as described below. This method enables the elution and analysis of intact high molecular mass lipids.

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 °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 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, USA), especially processed for use at 400 °C. The oven was temperature-programmed from 100 °C (1 min) to 350 °C (3 min) at 15 °C min^{-1}. Peaks were quantified by area, and a mixture of standards (octadecane, palmitic acid, sitosterol, cholesteryl oleate, and campesteryl, stigmasteryl and sitosteryl 3β-D-glucopyranosides) 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 Varian Saturn 2000 (Varian, Walnut Creek, CA, USA) with an ion trap detector, 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 °C (1 min) to 380 °C (5 min) at 10 °C min^{-1}. The injector and transfer line temperatures were set at 300 °C and 350 °C, respectively. Helium was used as the carrier gas and the injection was performed in splitless mode. Trimethylsilyl-diazomethane methylation and bis(trimethylsilyl)trifluoroacetamide (BSTFA) silylation, in the presence of pyridine, were used when required. Compounds were identified by comparing their mass spectra with mass spectra in the Wiley and NIST libraries and with those reported in the literature, by mass fragmentography and, when possible, by comparison with authentic standards.

3. Results and discussion

The lipid content of sisal fibers accounted to 0.5% of total fiber weight. This value is similar to other nonwood fibers used for papermaking such as kenaf, hemp and abaca, and lower than flax (Gutiérrez and del Río, 2003a,b; Gutiérrez et al., 2004b, 2006; del Río and Gutiérrez, 2006). The underivatized, methylated and/or 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 (Gutiérrez et al., 1998, 2004a). 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 sisal fibers is shown in Fig. 1 and the identities and abundances of the main lipophilic compounds are detailed in Table 1. For a better characterization of the compounds present, the total extract of the sisal fibers was subjected to SPE fractionation, according to the method previously developed (Gutiérrez et al., 1998, 2004a). In this SPE method, the lipophilic compounds are retained in the column and elute in order of increasing polarity. The chromatograms of the different SPE fractions obtained (A–D) are shown in Fig. 2. The first fraction (A), eluted with hexane, was enriched in alkanes, waxes and sterol esters. The second fraction (B), eluted with hexane:chloroform (5:1), contained alkyldioxolane series arising from the side-reaction of monoglycerides and acetone. The third fraction (C), eluted with chloroform, con-

Table 1 – Composition of lipids (mg/100 g) in sisal fibers

Compounds	Mass fragments	MW	Abundance
n-Alkanes			10.07
n-Heneicosane	57/71/85/296	296	0.14
n-Docosane	57/71/85/310	310	0.06
n-Tricosane	57/71/85/324	324	1.50
n-Tetracosane	57/71/85/338	338	0.18
n-Pentacosane	57/71/85/352	352	4.58
n-Hexacosane	57/71/85/366	366	0.39
n-Heptacosane	57/71/85/380	380	2.54
n-Octacosane	57/71/85/394	394	0.10
n-Nonacosane	57/71/85/408	408	0.40
n-Triacontane	57/71/85/422	422	0.04
n-Hentriacontane	57/71/85/436	436	0.15
Fatty acids			30.35
n-Tetradecanoic acid	60/73/129/228	228	0.27
n-Pentadecanoic acid	60/73/129/242	242	0.10
9-Hexadecenoic acid	55/69/236/254	254	0.08
n-Hexadecanoic acid	60/73/129/256	256	2.25
n-Heptadecanoic acid	60/73/129/270	270	0.12
9,12-Octadecadienoic acid	67/81/280	280	0.48
9-Octadecenoic acid	55/69/264	282	1.68
n-Octadecanoic acid	60/73/129/284	284	0.71
n-Nonadecanoic acid	60/73/129/298	298	0.02
n-Eicosanoic acid	60/73/129/312	312	0.18
n-Heneicosanoic acid	60/73/129/326	326	0.11
n-Docosanoic acid	60/73/129/340	340	1.22
n-Tricosanoic acid	60/73/129/354	354	0.55
n-Tetracosanoic acid	60/73/129/368	368	2.22
n-Pentacosanoic acid	60/73/129/382	382	1.34
n-Hexacosanoic acid	60/73/129/396	396	2.47
n-Heptacosanoic acid	60/73/129/410	410	0.61
n-Octacosanoic acid	60/73/129/424	424	2.93
n-Nonacosanoic acid	60/73/129/438	438	0.44
n-Triacontanoic acid	60/73/129/452	452	1.03
n-Dotriacontanoic acid	60/73/129/480	480	0.09
n-Tetratriacontanoic acid	60/73/129/508	508	0.07
2-Hydroxytetracosanoic acid	73/411/455[a]	470[a]	2.16
2-Hydroxypentacosanoic acid	73/425/469[a]	484[a]	0.12
22-Hydroxydocosanoic acid	73/395/411/427[a]	442[a]	0.68
24-Hydroxytetracosanoic acid	73/423/439/455[a]	470[a]	0.35
26-Hydroxyhexacosanoic acid	73/451/467/483[a]	498[a]	4.04
28-Hydroxyoctacosanoic acid	73/479/485/511[a]	526[a]	4.05
Fatty alcohols			18.37
n-Docosanol	75/103/383[a]	398[a]	0.49
n-Tetracosanol	75/103/411[a]	426[a]	0.31
n-Hexacosanol	75/103/439[a]	454[a]	4.76
n-Octacosanol	75/103/467[a]	482[a]	11.99
n-Triacontanol	75/103/495[a]	510[a]	0.74
n-Dotriacontanol	75/103/523[a]	538[a]	0.08
Aldehydes			1.97
n-Heneicosanal	82/96/292	310	0.07
n-Docosanal	82/96/306	324	0.24
n-Tricosanal	82/96/320	338	0.20
n-Tetracosanal	82/96/334	352	0.11
n-Pentacosanal	82/96/348	366	0.20
n-Hexacosanal	82/96/362	380	0.36
n-Octacosanal	82/96/390	408	0.79
Steroid hydrocarbons			3.90
Ergosta-3,5,7-triene	135/143/380	380	0.04
Stigmasta-3,5,7-triene	135/143/394	394	3.26
Stigmasta-3,5-diene	81/147/381/396	396	0.64

Table 1 (*Continued*)

Compounds	Mass fragments	MW	Abundance
Free sterols			10.21
Campesterol	55/145/213/382/400	400	0.38
Stigmasterol	55/83/255/394/412	412	1.73
Sitosterol	145/213/396/414	414	7.43
Stigmastanol	215/416	416	0.22
7-Ketositosterol	135/161/395/428	428	0.45
Steroid ketones			1.17
Stigmasta-3,5-dien-7-one	174/269/410	410	0.51
Stigmast-4-en-3-one	124/229/412	412	0.34
Stigmast-4-en-3,6-dione	137/398/408/411/426	426	0.03
Stigmastane-3,6-dione	245/287/428	428	0.28
Waxes			1.81
C_{40}	57/71/257/592	592	0.03
C_{42}	57/71/257/620	620	0.15
C_{44}	57/71/257/285/648	648	0.57
C_{46}	57/71/285/313/676	676	0.72
C_{48}	57/71/313/704	704	0.19
C_{50}	57/71/313/341/752	732	0.16
Sterol esters			0.21
Sitosterol esters	147/255/381/396		0.21
Steryl glycosides			0.97
Campesteryl 3β-D-glucopyranoside	204/217/361/383[a]	850[a]	0.07
Stigmasteryl 3β-D-glucopyranoside	204/217/361/395[a]	862[a]	0.20
Sitosteryl 3β-D-glucopyranoside	204/217/361/397[a]	864[a]	0.70
Monoglycerides			2.99
2,3-Dihydroxypropylhexadecanoate	73/147/203/371/459[a]	474[a]	0.08
2,3-Dihydroxypropyloctadec-9-enoate	73/129/147/397/485[a]	500[a]	0.05
2,3-Dihydroxypropyloctadecanoate	73/147/203/399/487[a]	502[a]	0.04
2,3-Dihydroxypropylhexacosanoate	73/147/203/511/599[a]	614[a]	0.65
2,3-Dihydroxypropyloctacosanoate	73/147/203/539/627[a]	642[a]	1.59
2,3-Dihydroxypropylnonacosanoate	73/147/203/553/641[a]	656[a]	0.11
2,3-Dihydroxypropyltriacontanoate	73/147/203/567/655[a]	670[a]	0.46
Diglycerides			0.28
1,3-Dipalmitoylglycerol	73/129/313/371/625[a]	640[a]	0.12
1,3-Palmitoylstearoylglycerol	73/313/341/371/399[a]	668[a]	0.09
1,3-Distearoylglycerol	73/129/341/399/653[a]	696[a]	0.08
n-Alkyl ferulates			9.15
trans-Eicosanyl ferulate	137/177/194/474	474	<0.01
trans-Heneicosanyl ferulate	137/177/194/488	488	0.07
trans-Docosanyl ferulate	137/177/194/502	502	0.39
trans-Tricosanyl ferulate	137/177/194/516	516	0.15
trans-Tetracosanyl ferulate	137/177/194/530	530	0.91
trans-Pentacosanyl ferulate	137/177/194/544	544	0.20
trans-Hexacosanyl ferulate	137/177/194/558	558	3.11
trans-Heptacosanyl ferulate	137/177/194/572	572	0.11
trans-Octacosanyl ferulate	137/177/194/586	586	4.17
trans-Nonacosanyl ferulate	137/177/194/600	600	<0.01
trans-Triacontanyl ferulate	137/177/194/614	614	0.05
ω-Carboxyalkylferulates			0.25
trans-Feruloyloxydocosanoic acid	177/470/486/514	532	<0.01
trans-Feruloyloxytetracosanoic acid	177/498/514/542	560	0.04
trans-Feruloyloxyhexacosanoic acid	177/526/542/570	588	0.10
trans-Feruloyloxyoctacosanoic acid	177/554/570/598	616	0.11
trans-Feruloyloxytriacontanoic acid	177/554/570/598	616	<0.01

Main mass fragments and molecular weight (MW) are included.

[a] as TMS ether derivatives. Underlined mass fragments indicate base peaks.

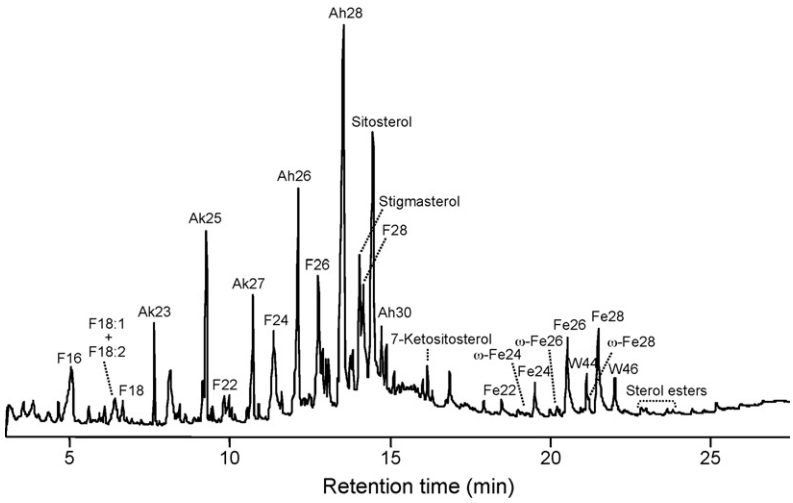

Fig. 1 – GC/MS chromatogram of the underivatized lipid extract of sisal fibers. Labeling for the different peaks are: F(*n*): *n*-fatty acids series; Ak(*n*): *n*-alkanes series; Ah(*n*): *n*-alcohols series; Fe(*n*): *n*-alkylferulates series; ω-Fe(*n*): ω-carboxyalkylferulates series; W(*n*): waxes series; *n* denotes the total carbon atom number.

tained fatty alcohols, sterols and *n*-alkyl ferulates. A final fraction (D) enriched in free fatty acids and esters of ferulic acid with ω-hydroxyfatty acids was eluted with diethyl ether–acetic acid (98:2).

The most predominant lipid classes present in sisal fibers were series of fatty acids (30% of total lipids) including α- and ω-hydroxyfatty acids, fatty alcohols (20%), alkanes (11%), free sterols (11%) and a series of ferulic acid esterified with long chain alcohols or with ω-hydroxyfatty acids (10%). Additionally, steroid hydrocarbons, monoglycerides, aldehydes, waxes, ketones and sterol glycosides were also found together with minor amounts of diglycerides, ferulic acids esterified and sterol esters.

Free fatty acids were identified ranging from tetradecanoic (C_{14}) to tetratriacontanoic (C_{34}) acids, with strong even-over-odd carbon atom predominance. Octacosanoic (C_{28}), hexacosanoic (C_{26}), palmitic ($C_{16:0}$) and tetracosanoic (C_{24}) acids were the most abundant. Relatively high amounts of ω-hydroxyfatty acids (ranging from C_{22} to C_{28}) and α-hydroxyfatty acids (ranging from C_{24} to C_{25}) were also identified. *n*-Fatty alcohols were present in the sisal extracts ranging from C_{22} to C_{32} with a strong even-over-odd carbon atom predominance, octacosanol (C_{28}) being the most abundant. Interestingly, the series of free fatty alcohols parallels the distribution of the esterified fatty alcohols in waxes and in *n*-alkyl ferulates as described below. A series of *n*-alkanes ranging from C_{21} to C_{31} was also identified in the sisal fibers with a strong odd-over-even carbon atom number predominance, pentacosane (C_{25}) being the most predominant.

Sterols were also found in significant amounts among the lipids of sisal fibers. Sitosterol was the most abundant among the free sterols with the presence of minor amounts of campesterol, stigmasterol, stigmastanol and 7-ketositosterol. Low amounts of sitosterol could also be found in ester form. Steryl glycosides, such as campesteryl, stigmasteryl and sitosteryl 3β-D-glucopyranosides were identified in minor amounts, the latter 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 (Gutiérrez and del Río, 2001). Minor amounts of steroid hydrocarbons (stigmasta-3,5,7-triene and stigmasta-3,5-diene) and steroid ketones (stigmasta-3,5-dien-7-one, stigmast-4-en-3-one, stigmast-4-en-3,6-dione and stigmastane-3,6-dione) were also identified.

Series of *p*-hydroxycinnamate esters consisting of ferulic acid esterified to long chain fatty alcohols (C_{20}–C_{30}) and ω-hydroxyfatty acids (C_{22}–C_{30}) were also identified among the lipids of sisal fiber. The characterization of the individual compounds was achieved based on the mass spectra obtained by GC/MS of the underivatized and their methyl and/or TMS ether derivatives (del Río et al., 2004a,b). The series of *n*-alkyl *trans*-ferulates, concentrated in alcoholic fraction of SPE (Fig. 2C), occurred in the range from C_{20} to C_{30}, with the presence of both the even and odd carbon atom number homologues, C_{26} and C_{28} being the most prominent. The C_{26} and C_{28} also were the most abundant free fatty alcohols in sisal fiber, as described above. In contrast, in most wood and nonwoody plant species in which ferulic acid esters have been reported, C_{22} and C_{24} fatty alcohols were the dominant components esterifed to ferulic acid (Kolattukudy and Espelié, 1989; del Río et al., 2004a,b; del Río and Gutiérrez, 2006). *n*-Alkylferulates with odd-carbon number atoms have rarely been reported (Baldé et al., 1991). The series of *n*-alkyl ferulates identified occurred mostly in the *trans*-form, although some minor amounts of the *cis*-isomer were also observed at lower retention times.

On the other hand, ferulic acid was also found esterified with the hydroxyl group of ω-hydroxyfatty acids. This series of compounds was concentrated in the acidic SPE fraction (Fig. 2D). The feruloyl ester-linked ω-hydroxyfatty acids identified ranged from C_{22} to C_{30}, the C_{26} and C_{28} homologues being the most abundant. The C_{26} and C_{28} homologues also were the most abundant ω-hydroxyfatty acids present in free form. The odd members of the series were

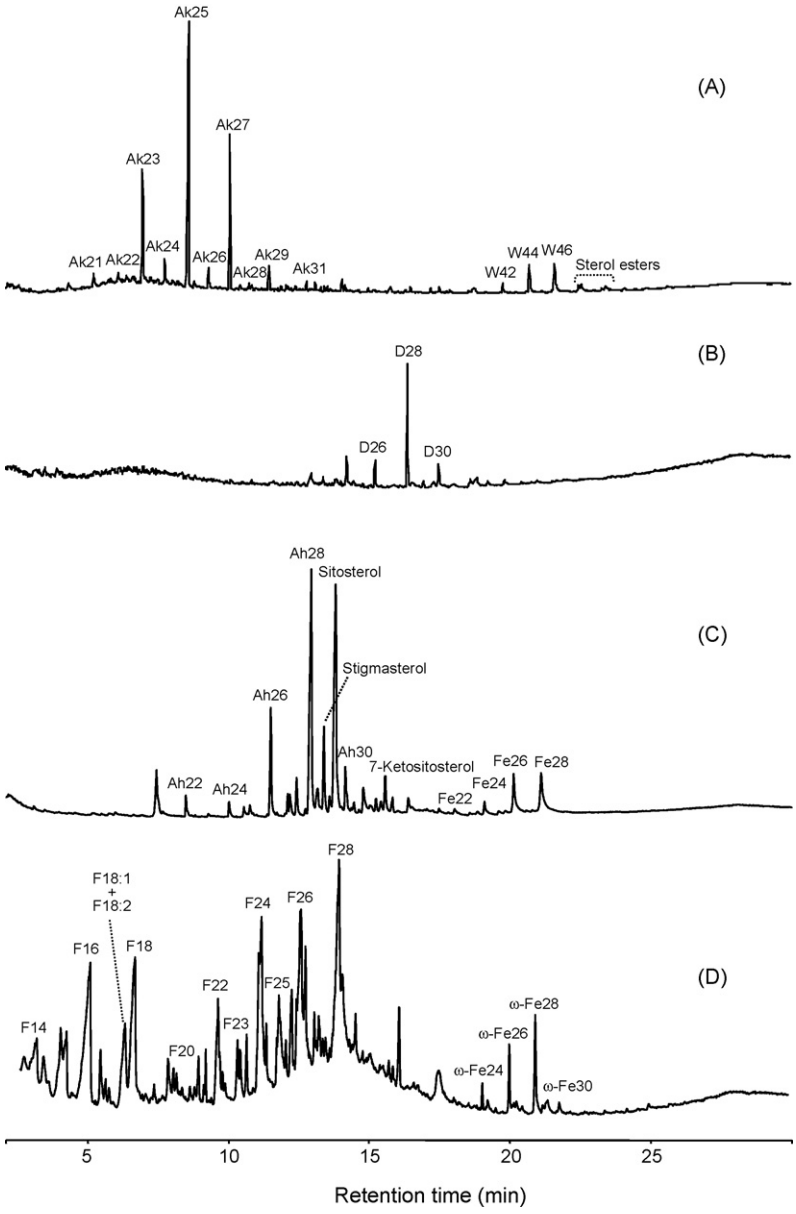

Fig. 2 – GC/MS chromatograms of the different SPE fractions isolated from sisal fibers extracts. (A) Fraction A, eluted with 8 ml of hexane; (B) fraction B, eluted with 6 ml of hexane:chloroform (5:1); (C) fraction C: eluted with 10 ml of chloroform; (D) fraction D: eluted with 10 ml of diethyl ether:acetic acid (98:2). Labeling for the different peaks are the same reflected in Fig. 1. D(*n*) denotes the alkyldioxolane series arising from the side-reaction of monoglycerides and acetone.

not present in sisal fibers. Feruloyl esters of ω-hydroxyfatty acids have been rarely reported in plants. A series of acidic esters derived from C_{22} to C_{29} ω-hydroxyfatty acids and *trans*- and *cis*-ferulic acids was reported for the first time in *Virola* species (Kawanishi and Hashimoto, 1987) and has also recently been found in other plant species, including abaca (*Musa textilis*) (del Río et al., 2004a,b; del Río and Gutiérrez, 2006) and *Eucalyptus globulus* wood (Freire et al., 2002).

Finally, minor amounts of other compounds such as series of *n*-aldehydes (ranging from C_{21} to C_{28}), mono- and diglycerides and waxes (from C_{40} to C_{50}), were also identified among the sisal fiber extracts.

The pitch problems that the lipophilic extractives present in sisal fibers could originate will depend on the pulping (i.e. mechanical and chemical) process used. Some of the main lipophilic compounds of sisal fibers, such as alkanes, fatty alcohols, some fatty acids, and steroids have been reported to be stable under alkaline (soda/antraquinone) pulping of other nonwood fibers (Gutiérrez and del Río, 2003a,b; Gutiérrez et al., 2004b). The lipophilic extractives that survive pulping will present a different behavior during bleaching depending on their chemical structure and on the bleaching agent used (Jansson et al., 1995; Gutiérrez et al., 2001; Freire et al., 2006). Finally, the compounds that survive the bleaching process can be found as pulp extractives, and become a source of prob-

lems in the paper machine. Some of the lipophilic compounds present in sisal fibers have been found in pitch deposits produced during the manufacturing of both totally chlorine free and elementary chlorine free pulps from different raw materials (del Río et al., 1998, 2000; Gutiérrez and del Río, 2005).

In conclusion, the present work reports the content and chemical composition of lipids of sisal fibers. The knowledge of the chemical composition of lipophilic extractives from these fibers will be useful for a better utilization of this interesting plant material.

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