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Chemical Characterization of Lignin and Lipophilic Fractions from Leaf Fibers of Curaua (*Ananas erectifolius*)

GISELA MARQUES, ANA GUTIÉRREZ, AND JOSÉ C. DEL RÍO*

Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, P.O. Box 1052, 41080 Seville, Spain

The chemical composition of leaf fibers of curaua (*Ananas erectifolius*), an herbaceous plant native of Amazonia, was studied. Special attention was paid to the content and composition of lignin and lipophilic compounds. The analysis of lignin in the curaua fibers was performed in situ by pyrolysis−gas chromatography/mass spectrometry (Py-GC/MS) and showed a lignin composition with a *p*-hydroxyphenyl:guaiacyl:syringyl units (H:G:S) molar proportion of 30:29:41 (S/G molar ratio of 1.4). The presence of *p*-hydroxycinnamic acids (*p*-coumaric and ferulic acids) in curaua fibers was revealed upon pyrolysis in the presence of tetramethylammonium hydroxide. On the other hand, the main lipophilic compounds, analyzed by GC/MS, were series of long-chain *n*-fatty acids, *n*-fatty alcohols, α- and ω-hydroxyacids, monoglycerides, sterols, and waxes. Other compounds, such as ω-hydroxy monoesters and ω-hydroxy acylesters of glycerol, were also found in this fiber in high amounts.

KEYWORDS: Curaua; *Ananas erectifolius*; lipids; lignin; pyrolysis; hydroxy monoesters; glyceryl esters; paper pulp

INTRODUCTION

An alternative to wood raw materials for pulp and paper production in developing countries is the use of nonwoody fibers from herbaceous field crops. In developed countries, nonwoody fibers are mainly used for the production of specialty papers, i.e., tea bags, filter papers, bank notes, etc. The main sources of nonwoody raw materials are agricultural residues from monocotyledons, including cereal straw and bagasse. Bamboo, reeds, and some other grass plants such as flax, hemp, kenaf, jute, sisal, or abaca are also grown or collected for the pulp industry, but increased attention has been paid in recent years to find new nonwood raw materials for pulp production.

Curaua (*Ananas erectifolius*), an herbaceous plant native of the Amazonian region and a member of the bromeliad family, has been recognized since pre-Columbian days for its valuable fibers (*1*−*4*). In the past decade, it has gained commercial recognition as a material for composites for the automotive industry (*2*, *4*). The curaua fiber has also been promoted for paper pulp in Brazil, and it is now being investigated as an alternative lignocellulosic material for the production of chemical pulps.

Studies on the chemical composition of curaua fibers are important to evaluate this fiber as a potential raw material for pulp and papermaking; however, only limited studies have been performed so far on this interesting fiber (*1*, *3*, *5*). In this work, we have performed a chemical characterization of curaua fibers, paying special attention to the content and composition of the lipophilic compounds and the structural characterization of lignin, since these two organic fractions are of high importance during pulping and papermaking. It is known that the efficiency of pulping is directly proportional to the amount of syringyl (S) units in lignin (*6*, *7*). This is because the S-lignin is mainly linked by more labile ether bonds, is relatively unbranched, and has a lower condensation degree than G-lignin (*8*, *9*). Indeed, the S-lignin has a higher reactivity in alkaline systems than G-lignin (*10*). On the other hand, the 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 (*11*−*13*). Moreover, such extractives might also contribute to the toxicity of paper pulp effluents and products (*14*, *15*).

In the present study, the lignin in curaua fibers was characterized in situ by using analytical pyrolysis coupled to gas chromatography/mass spectrometry (Py-GC/MS), which is a powerful analytical tool for the rapid analysis of complex polymer mixtures, including lignocellulosic materials (*16*, *17*). Pyrolysis in the presence of a methylating reagent, tetramethylammonium hydroxide (TMAH), was used for the analysis of *p*-hydroxicinnamic acids (*p*-coumaric and ferulic acids). On the other hand, the lipid composition in curaua fibers was analyzed by GC and GC/MS, using short- and medium-length high-temperature capillary columns, respectively (*18*), which enable the elution and analysis of intact high molecular weight lipids such as waxes, sterol esters, and triglycerides.

MATERIALS AND METHODS

Samples. Curaua (*A. erectifolius*) fibers were supplied by CELESA pulp mill (Tortosa, Spain). The dried samples were milled using a knife mill (Janke and Kunkel, Analyzenmühle). For the isolation of lipids, the milled samples were extracted with acetone in a Soxhlet apparatus

* To whom correspondence should be addressed. Tel: +34 95 462 4711. Fax: +34 95 462 4002. E-mail: delrio@irnase.csic.es.

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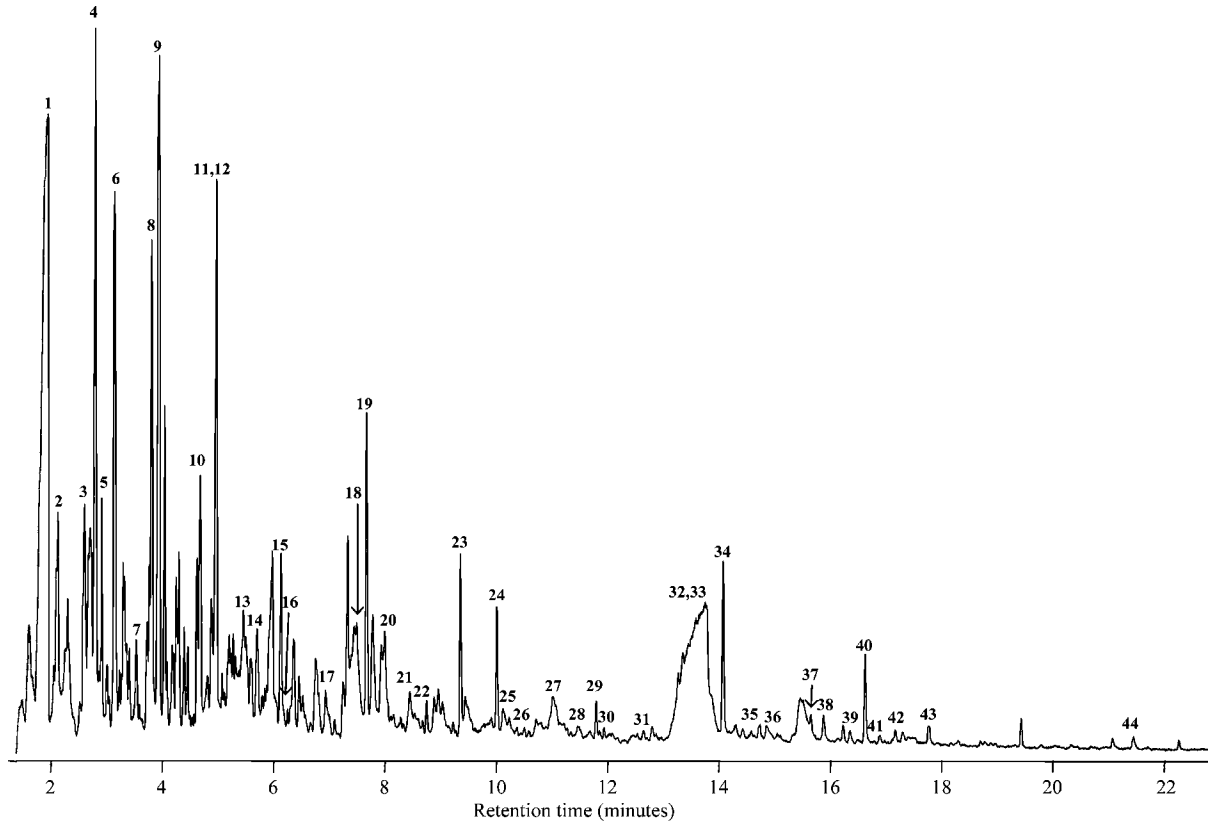

Figure 1. Py-GC/MS chromatogram of curaua fibers. The identities and relative molar abundances of the compounds are listed in **Table 1**.

for 8 h. The acetone extracts were evaporated to dryness and weighted. Then, the extracts were resuspended in chloroform for chromatographic analysis of the lipophilic fraction. Two replicates were used for each sample, and all samples were subjected to GC and GC/MS analyses. For carbohydrate analysis and estimation of the Klason lignin content, the acetone-extracted samples were subsequently extracted with hot water (3 h at 100 °C) to remove the water-soluble material. Holocellulose was isolated from the pre-extracted fibers by delignification for 4 h using the acid chlorite method (*19*). The α-cellulose content was determined by removing the hemicelluloses from the holocellulose by alkali extraction (*19*). Klason lignin was estimated as the residue after sulfuric acid hydrolysis of the pre-extracted material according to Tappi rule T222 om-88 (*20*). The acid-soluble lignin was determined, after the insoluble lignin was filtered off, by spectrophotometric determination at 205 nm wavelength. Neutral sugars from polysaccharide hydrolysis were analyzed as alditol acetates by GC according to Tappi rule T249 om85 (*20*). The ash content was estimated as the residue after 6 h at 575 °C. The general composition (as percent of whole fiber) was as follows: holocellulose, 92.5%; α-cellulose, 66.4%; ash, 1.3%; acetone extractives, 5.3%; water-soluble extract, 5.1%; Klason lignin, 4.9%; and acid-soluble lignin, 1.6%. The composition of neutral monosaccharides (as percent of total neutral carbohydrates) included arabinose, 2.7%; xylose, 8.0%; mannose, 3.5%; galactose, 0.2%; and glucose, 85.6%. No uronic acid determination was performed in this study. The composition of metals and other elements was analyzed by inductively coupled plasma spectrophotometry after oxidation with concentrated HNO_3 under pressure in a microwave digestor, with the following results: K, 2770 ppm; Ca, 2025 ppm; Mg, 945 ppm; Mn, 120 ppm; Na, 95 ppm; Al, 86 ppm; Fe, 82 ppm; Sr, 10 ppm; and Zn, 4 ppm.

Solid-Phase Extraction (SPE) Fractionation. For a better characterization of the different homologous series, the lipid extracts were fractionated by a SPE procedure using aminopropyl-phase cartridges (500 mg) from Waters Division of Millipore (Mildford, MA), as already described (*18*). Briefly, the dried chloroform extracts were taken up in a minimal volume (<0.5 mL) of hexane:chloroform (4:1) and loaded into the cartridge column previously conditioned with hexane (4 mL). The cartridge was loaded and eluted by gravity. The column was first eluted with 8 mL of hexane and subsequently with 6 mL of hexane:chloroform (5:1), then with 10 mL of chloroform and finally with 10 mL of diethyl ether:acetic acid (98:2). Each isolated fraction was dried under nitrogen and analyzed by GC and GC/MS.

GC and GC/MS Analyses. The GC analyses of the extracts were performed in an Agilent 6890N Network GC system using a 5 m × 0.25 mm i.d., 0.1 μm DB-5HT fused silica capillary column from J&W Scientific (Folsom, CA). The temperature program was started at 100 °C with a 1 min hold and then raised to a final temperature of 350 °C at 15 °C/min, and held for 3 min. The injector and flame ionization detector temperatures were set at 300 and 350 °C, respectively. Helium was used as the carrier gas at a rate of 5 mL/min, and the injection was performed in splitless mode. Peaks were quantified by area, and a mixture of standards (octadecane, palmitic acid, sitosterol, and cholesteryl oleate) was used to elaborate calibration curves. The data from the two replicates were averaged. In all cases, the standard derivations from replicates were below 10% of the mean values.

The GC/MS analyses were performed with a Varian model Star 3400 GC equipped with a model Saturn 2000 ion trap detector using a medium-length (12 m) capillary column of the same characteristics described above. The oven was heated from 120 (1 min) to 380 °C at 10 °C/min and held for 5 min. The transfer line was kept at 300 °C. The injector was temperature programmed from 120 (0.1 min) to 380 °C at a rate of 200 °C/min and held until the end of the analysis. Helium was used as the carrier gas at a rate of 2 mL/min. Methylation with trimethylsilyldiazomethane and silylation with bis(trimethylsilyl)-trifluoroacetamide (BSTFA) was used when required. Compounds were identified by comparing their mass spectra with mass spectra in Wiley and NIST libraries, by mass fragmentography, and when possible, by comparison with authentic standards.

Py-GC/MS. The pyrolysis of curaua fibers (approximately 100 μg) was performed in duplicate with a model 2020 microfurnace pyrolyzer (Frontier Laboratories Ltd., Yoriyama, Japan) directly connected to an Agilent 6890 GC/MS system equipped with a 30 m × 0.25 mm i.d., 0.25 μm HP 5MS fused silica capillary column. The detector consisted of an Agilent 5973 mass selective detector (EI at 70 eV). The pyrolysis was performed at 500 °C. The final temperature was achieved at a rate of 20 °C/min. The GC/MS conditions were as follows: oven temper-

Table 1. Identification and Relative Molar Abundances (%) of the Compounds Released after Py-GC/MS of Curaua Fibers[a]

no.	compound	mass fragments	MW	origin	%
1	acetic acid	45/60	60	C	35.8
2	2-hydroxypropanal	43/74	74	C	3.1
3	(3*H*)-furan-2-one	55/84	84	C	3.1
4	1,3-hydroxydihydro-2-(3*H*)-furanone	58/102	102	C	6.0
5	(2*H*)-furan-3-one	55/84	84	C	1.4
6	2-furaldehyde	67/95/96	96	C	6.4
7	cyclopent-1-ene-3,4-dione	54/68/96	96	C	0.9
8	(5*H*)-furan-2-one	55/84	84	C	4.2
9	2,3-dihydro-5-methylfuran-2-one	55/69/98	98	C	8.5
10	4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one	58/85/114	114	C	2.1
11	3-hydroxy-2-methyl-2-cyclopenten-1-one	55/85/112	112	C	1.1
12	2-hydroxy-3-methyl-2-cyclopenten-1-one	55/85/112	112	C	4.8
13	4-methylphenol	77/107/108	108	LH	0.7
14	guaiacol	81/109/124	124	LG	0.5
15	2-furoic acid, methyl ester	67/95/126	126	C	1.3
16	4-methylguaiacol	95/123/138	138	LG	0.1
17	3,4-dihydroxybenzaldehyde	81/109/137/138	138	L	0.5
18	catechol	64/81/92/110	110	L/C	1.0
19	4-vinylphenol	65/91/120	120	LH/*p*CA	2.2
20	5-hydroxymethyl-2-furaldehyde	69/97/109/126	126	C	1.9
21	3-methoxycatechol	60/97/125/140	140	L	0.3
22	4-ethylguaiacol	122/137/152	152	LG	0.2
23	4-vinylguaiacol	107/135/150	150	LG	1.1
24	syringol	111/139/154	154	LS	0.7
25	eugenol	131/149/164	164	LG	0.2
26	4-propylguaiacol	122/136/166	166	LG	<0.1
27	vanillin	109/151/152	152	LG	0.3
28	*cis*-isoeugenol	131/149/164	164	LG	<0.1
29	4-methylsyringol	125/153/168	168	LS	0.2
30	*trans*-isoeugenol	131/149/164	164	LG	0.1
31	acetoguaiacone	123/151/166	166	LG	0.1
32	levoglucosane	60/98	162	C	7.7
33	4-ethylsyringol	167/182	182	LS	0.8
34	4-vinylsyringol	137/165/180	180	LS	0.9
35	4-allylsyringol	167/179/194	194	LS	0.1
36	4-propylsyringol	123/167/196	196	LS	0.1
37	*cis*-4-propenylsyringol	167/179/194	194	LS	0.2
38	syringaldehyde	167/181/182	182	LS	0.2
39	4-propinylsyringol	106/131/177/192	192	LS	0.1
40	*trans*-4-propenylsyringol	167/179/194	194	LS	0.5
41	*trans*-coniferaldehyde	107/135/147/178	178	LG	0.1
42	acetosyringone	153/181/196	196	LS	0.1
43	syringylacetone	123/167/210	210	LS	0.1
44	*trans*-sinapaldehyde	137/165/180/208	208	LS	0.1
	%H				29.8
	%G				29.1
	%S				41.1
	S/G				1.4
	%L				11.7
	%C				88.3
	L/C				0.13

[a] Mass fragments, molecular weight (MW), origin, and relative molar abundances (%) are included. C, carbohydrates; L, lignin; LH, *p*-hydroxyphenyl lignin units, H; LG, guaiacyl lignin units, G; LS, syringyl lignin units, S; and *p*CA, *p*-coumaric acid.

ature was held at 50 °C for 1 min and then increased up to 100 °C at 30 °C/min, from 100 to 300 °C at 10 °C/min, and isothermal at 300 °C for 10 min. The carrier gas used was helium with a controlled flow of 1 mL/min. For the pyrolysis in the presence of TMAH, approximately 100 μg of sample was mixed with 0.5 μL of 25% TMAH. 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 (*16*, *17*). 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 less than 5%.

RESULTS AND DISCUSSION

The curaua fiber was characterized by high holocellulose and α-cellulose contents (92.5 and 66.4, respectively) and a low lignin content (6.5% of the total fiber weight). This lignin content is similar to other nonwood fibers such as flax or hemp and lower than other nonwood fibers such as kenaf or abaca (*21*−*26*). The extractives content (5.3% of total fiber weight) is very high and much higher than other nonwood fibers, which are usually less than 1% (*21*−*26*). However, most of the acetone extract corresponds to polar compounds, while only 1.3% corresponded to lipophilic compounds, which were estimated by redissolving the acetone extracts in chloroform. On the other hand, the hemicellulose fraction was mainly constituted by xylose. Finally, the ash content (1.3% of total fiber weight) was low in comparison to cereal straw (*27*), and the composition of the different metals revealed a predominance of Ca and K and a very low content of other metals.

Lignin Composition. The lignin composition of curaua fibers was analyzed in situ by Py-GC/MS. The Py-GC/MS chromato-

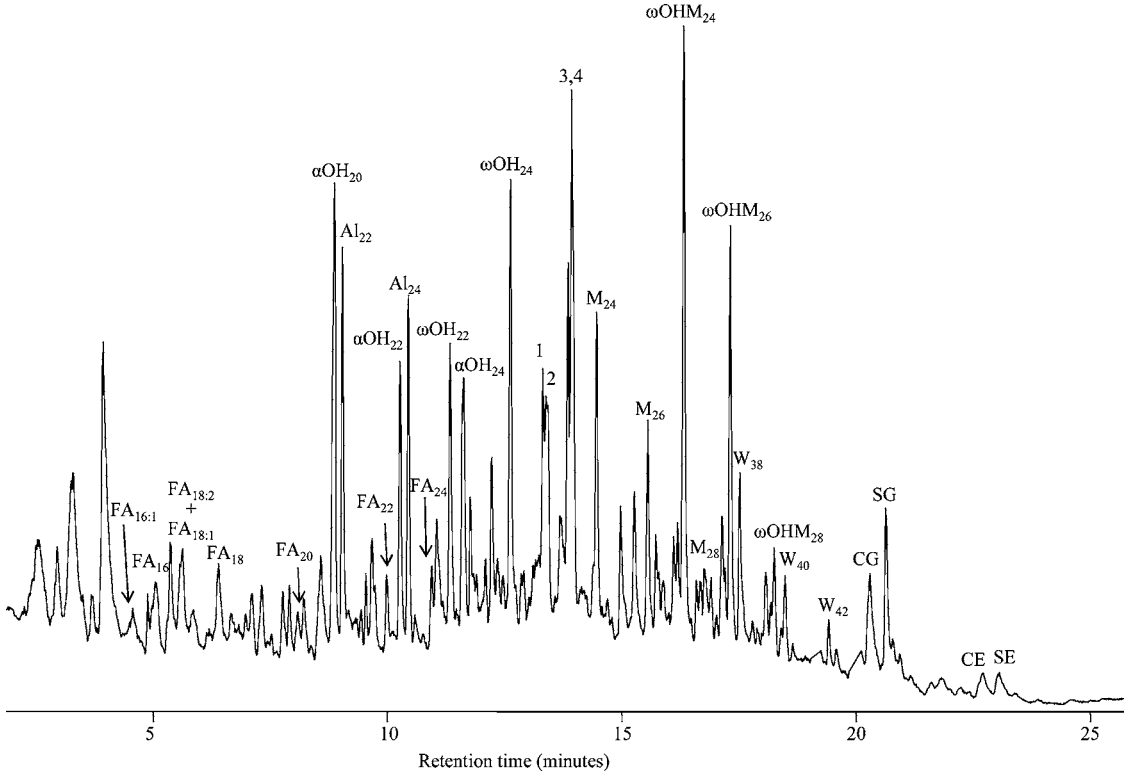

Figure 2. GC/MS chromatogram of the methyl ester and TMSi ether derivative of the lipid extract from curaua fibers. $FA_{(n)}$, *n*-fatty acid series; $Al_{(n)}$, alcohol series; $W_{(n)}$, wax series; $\alpha OH_{(n)}$ and $\omega OH_{(n)}$, α- and ω-hydroxy fatty acids series; $M_{(n)}$, monoglyceride series; $\omega OHM_{(n)}$, ω-hydroxy acylesters of glycerol series; SG, sitosteryl 3β-D-glucopyranoside; CG, campesteryl 3β-D-glucopyranoside; 1, campesterol; 2, ergostanol; 3, sitosterol; 4, stigmastanol; CE, campesterol ester; and SE, sitosterol ester; *n* denotes the total carbon atom number.

gram of curaua fibers is shown in **Figure 1**, and the identities and relative molar abundances of the released compounds are listed in **Table 1**. The Py-GC/MS of curaua fibers released predominantly compounds arising from carbohydrates, with only minor amounts of lignin-derived phenols. Carbohydrate pyrolysis products represented 88% on average, and phenols from lignin represented only 12% of the total identified compounds, which is in agreement with the low lignin content estimated as Klason lignin. Among the lignin-derived compounds, the pyrogram of curaua fibers showed compounds derived from *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) lignin units, with a slight predominance of the S units. The main lignin-derived compounds identified were 4-methylphenol (**13**), guaiacol (**14**), 4-vinylphenol (**19**), 4-vinylguaiacol (**23**), syringol (**24**), 4-ethylsyringol (**33**), 4-vinylsyringol (**34**), and *trans*-4-propenylsyringol (**40**). The relative molar distributions of the different lignin units (H:G:S) estimated by Py-GC/MS were 30:29:41 with a S/G molar ratio of 1.4. The predominance of S-lignin observed in the curaua fiber is advantageous for delignification during pulping because the S-lignin is relatively unbranched and has a lower condensation degree than H- and G-lignins. Moreover, S-lignin is more reactive in alkaline media (*10*).

It must be noted that the relatively high abundances of 4-vinylphenol (**19**) observed in the pyrogram of curaua fibers could be due to the presence of *p*-coumaric acid, which upon pyrolysis will decarboxylate to produce 4-vinylphenol (*28*). *p*-Hydroxycinnamic acids (*p*-coumaric and ferulic acids) occur widely in the cell walls of herbaceous plants forming cross-linkages between lignin and polysaccharides (*29*−*34*). The presence of *p*-hydroxycinnamic acids constitutes a complication for lignin analyses by analytical pyrolysis since they yield pyrolysis products similar to those of corresponding lignin units. However, this problem can be solved by the use of pyrolysis in the presence of TMAH (Py/TMAH), which prevents decarboxylation and releases intact *p*-hydroxycinnamic acids (as their methyl derivatives), in addition to different lignin degradation products (*28*, *35*−*38*).

Py/TMAH of curaua fibers released significant amounts of the methyl derivative of *p*-coumaric acid (25% of the lignin and cinnamic acids released products) as well as minor amounts of the methyl derivative of ferulic acid (5% of the lignin and cinnamic acids released products). *p*-Hydroxycinnamic acids are present in curaua fiber in relatively high amounts (cinnamic acids/lignin ratio of 0.4, estimated after Py/TMAH) and agree with the relatively high content of 4-vinylphenol released by Py-GC/MS. Studies on maize (*39*), wheat (*40*), and other grasses including bamboo (*41*) revealed that *p*-coumaric acid is esterified at the γ-position of lignin side chains and predominantly to S units (*41*, *42*). Therefore, probably the major part of the *p*-coumaric acid in curaua fibers also attaches at the γ-position of the lignin side chain by ester bonds. The relatively high content of *p*-hydroxycinnamic acids in curaua fibers would also be advantageous for pulping since ester bonds are easily cleaved during cooking.

Lipid Composition. The total lipid extract of the curaua fibers accounted for 1.3% of the total fiber weight. The extracts were analyzed by GC and GC/MS according to the method developed by Gutiérrez et al. (*18*). The chromatogram of the curaua extracts (as methyl ester and TMSi ether derivatives) is shown in **Figure 2**, and the detailed list with the identities and abundances of the main compounds present is summarized in **Table 2**. The main compounds identified were series of *n*-fatty acids, *n*-fatty alcohols, α- and ω-hydroxyacids, monoglycerides, sterols, and waxes. Other series of high molecular weight compounds such as ω-hydroxy monoesters and ω-hydroxy

Table 2. Composition and Abundance (mg/kg) of Lipophilic Compounds in Curaua Fibers[a]

compound	mass fragments (*m*/*z*)	MW	abundance	compound	mass fragments (*m*/*z*)	MW	abundance
fatty acids (total abundance, 813.2)							
n-tetradecanoic acid	60/73/129/228	228	4.3	9-octadecenoic acid	55/69/264	282	91.6
n-pentadecanoic acid	60/73/129/242	242	3.3	*n*-octadecanoic acid	60/73/129/284	284	262.0
9-hexadecenoic acid	55/69/236/254	254	7.6	*n*-eicosanoic acid	60/73/129/312	312	24.2
n-hexadecanoic acid	60/73/129/256	256	162.5	*n*-docosanoic acid	60/73/129/340	340	138.2
9,12-octadecadienoic acid	67/81/280	280	23.0	*n*-tetracosanoic acid	60/73/129/368	368	96.5
ω-hydroxy fatty acids (total abundance, 1423.3)							
16-hydroxyhexadecanoic acid	311/343/359#	374#	20.2	24-hydroxytetracosanoic acid	423/455/471#	486#	367.0
18-hydroxyoctadecanoic acid	339/371/387#	402#	28.4	26-hydroxyhexacosanoic acid	451/483/499#	514#	532.5
20-hydroxyeicosanoic acid	367/399/415#	430#	30.8	28-hydroxyoctacosanoic acid	479/511/527#	542#	119.2
22-hydroxydocosanoic acid	395/427/443#	458#	235.0	30-hydroxytriacontanoic acid	507/539/555#	570#	90.2
α-hydroxy fatty acids (total abundance, 226.5)							
2-hydroxyeicosanoic acid	73/117/355*	472*	62.7	2-hydroxytetracosanoic acid	73/117/411*	528*	79.2
2-hydroxydocosanoic acid	73/117/149/383*	500*	19.9	2-hydroxyhexacosanoic acid	73/117/439*	556*	64.7
fatty alcohols (total abundance, 552.4)							
n-eicosanol	75/103/355*	370*	8.9	*n*-hexacosanol	75/103/439*	454*	44.3
n-docosanol	75/103/383*	398*	247.2	*n*-octacosanol	75/103/467*	482*	9.8
n-tetracosanol	75/103/411*	426*	242.2				
sterols (total abundance, 618.7)							
campesterol	55/145/213/382/400	400	56.9	sitosterol	145/213/396/414	414	226.4
ergostanol	215/402	402	145.7	stigmastanol	215/416	416	189.7
tocopherols (total abundance, 31.4)							
α-tocopherol	165/205/430	430	31.4				
steroid hydrocarbons (total abundance, 119.4)							
ergostatriene	135/143/380	380	23.8	stigmasta-3,5,22-triene	135/143/394	394	2.6
ergostadiene	81/147/367/382	382	14.4	stigmasta-3,5-diene	81/147/381/396	396	6.8
stigmastadiene	81/147/381/396	396	71.8				
steroid ketones (total abundance, 57.9)							
stigmasta-3,5-dien-7-one	174/269/410	410	7.7	stigmastadienone isomer	57/136/174/269/410	410	16.4
stigmast-4-en-3-one	124/229/412	412	24.4	stigmastane-3,6-dione	245/287/428	428	9.4
sterol esters (total abundance, 89.4)							
campesterol ester			49.3	sitosterol ester			40.1
steryl glycosides (total abundance, 264.9)							
campesteryl 3β-D-glucopyranoside	204/217/361/383*	850*	141.3	sitosteryl 3β-D-glucopyranoside	204/217/361/397*	864*	123.6
waxes (total abundance, 173.2)							
C_{36}	201/229/257/285/536	536	3.5	C_{41}	257/271/285/299/313/327/341/355/606	606	2.3
C_{37}	243/257/550	550	3.3	C_{42}	257/285/313/341/620	620	24.9
C_{38}	257/564	564	56.8	$C_{42:1}$	264/283/618	618	1.2
C_{39}	243/257/271/285/299/578	578	5.9	C_{43}	257/271/285/299/313/327/355/369/634	634	1.5
C_{40}	257/285/313/592	592	46.5	C_{44}	257/285/313/341/648	648	19.1
$C_{40:1}$	264/283/590	590	2.9	C_{46}	257/285/313/341/369/397/676	676	5.3
ω-hydroxy monoesters (total abundance, 369.5)							
C_{36}	73/129/237/311/609*	624*	29.1	C_{40}	73/129/237/311/339/367/395/665*	680*	95.6
C_{37}	73/129/237/311/623*	638*	3.0	C_{42}	73/129/237/311/339/367/395/693*	708*	11.7
C_{38}	73/129/237/311/339/637*	652*	229.8	C_{44}	73/129/367/395/721*	736*	0.3
monoglycerides (total abundance, 714.6)							
1-monotetradecanoylglycerol	73/103/129/147/343/431*	446*	5.1	1-monotetracosanoylglycerol	73/103/129/147/483/571*	586*	179.3
1-monohexadecanoylglycerol	73/103/129/147/371/459*	474*	5.3	1-monohexacosanoylglycerol	73/103/129/147/511/599*	614*	168.2
1-monooctadecanoylglycerol	73/103/129/147/399/487*	502*	5.3	1-monooctacosanoylglycerol	73/103/129/147/539/627*	642*	23.4
1-monoeicosanoylglycerol	73/103/129/147/427/515*	530*	31.6	1-monotriacontanoylglycerol	73/103/129/147/567/655*	670*	8.2
1-monodocosanoylglycerol	73/103/129/147/455/543*	558*	288.2				
ω-hydroxy acylesters of glycerol (total abundance, 960.8)							
1-mono(22-hydroxydocosanoyl)glycerol	73/103/129/147/203/486/543/631*	646*	116.8	1-mono(26-hydroxyhexacosanoyl)glycerol	73/103/129/147/203/542/599/687*	702*	301.7
1-mono(24-hydroxytetracosanoyl)glycerol	73/103/129/147/203/514/571/659*	674*	482.8	1-mono(28-hydroxyoctacosanoyl)glycerol	73/103/129/147/203/570/627/715*	730*	59.5

[a] Key: tr, traces; * as TMSi ether derivates; # as methyl ester and TMSi ether derivates.

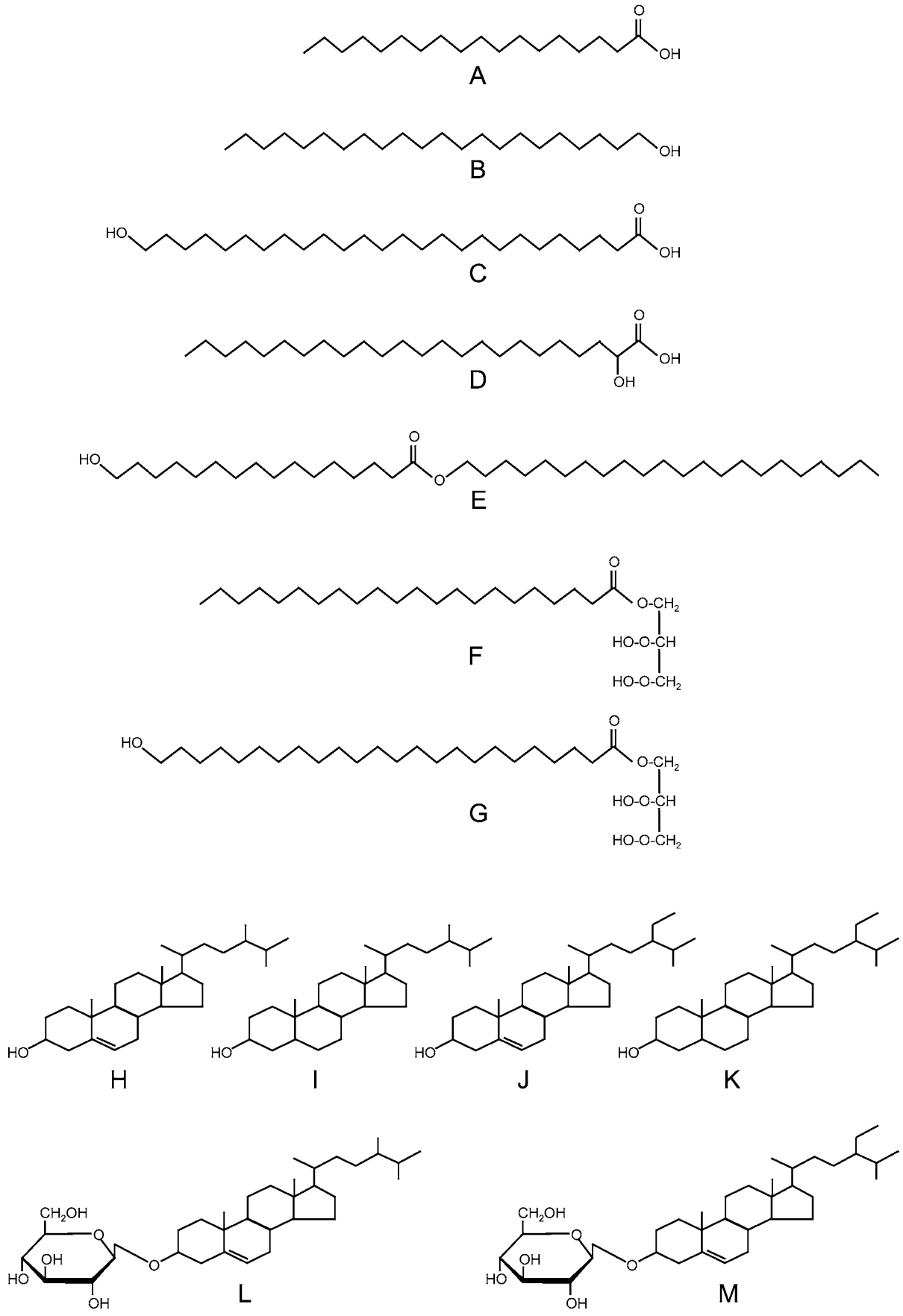

Figure 3. Structures of the main lipids present in the curaua fibers. (**A**) Stearic acid; (**B**) *n*-docosanol; (**C**) 26-hydroxyhexacosanoic acid; (**D**) 2-hydroxytetracosanoic acid; (**E**) docosanyl, 16-hydroxyhexadecanoate; (**F**) 1-monodocosanoylglycerol; (**G**) 1-mono(24-hydroxytetracosanoyl)glycerol; (**H**) campesterol; (**I**) ergostanol; (**J**) sitosterol; (**K**) stigmastanol; (**L**) campesteryl 3β-D-glucopyranoside; and (**M**) sitosteryl 3β-D-glucopyranoside.

Table 3. Composition of the Different Waxes (mg/kg) Identified in Curaua Fibers[a]

wax	fatty acid:fatty alcohol	abundance
wax C_{36}		3.5
	C_{12}:C_{24}	0.2
	C_{14}:C_{22}	1.1
	C_{16}:C_{20}	2.0
	C_{18}:C_{18}	0.2
wax C_{37}		3.3
	C_{16}:C_{21}	0.9
	C_{15}:C_{22}	2.4
wax C_{38}		56.8
	C_{16}:C_{22}	56.8
wax C_{39}		5.9
	C_{15}:C_{24}	0.9
	C_{16}:C_{23}	2.6
	C_{17}:C_{22}	2.2
	C_{18}:C_{21}	0.2
	C_{19}:C_{20}	<0.1
wax C_{40}		46.5
	C_{16}:C_{24}	25.3
	C_{18}:C_{22}	15.5
	C_{20}:C_{20}	5.7
wax $C_{40:1}$		2.9
	$C_{18:1}$:C_{22}	2.9
wax C_{41}		2.3
	C_{15}:C_{26}	0.1
	C_{16}:C_{25}	0.6
	C_{17}:C_{24}	0.6
	C_{18}:C_{23}	0.4
	C_{19}:C_{22}	0.4
	C_{20}:C_{21}	0.2
	C_{21}:C_{20}	<0.1
	C_{22}:C_{19}	<0.1
	C_{23}:C_{18}	<0.1
	C_{24}:C_{16}	<0.1
wax C_{42}		32.2
	C_{16}:C_{26}	3.4
	C_{18}:C_{24}	4.0
	C_{20}:C_{22}	22.1
	C_{22}:C_{20}	2.7
wax $C_{42:1}$		1.2
	$C_{18:1}$:C_{24}	1.2
wax C_{43}		1.5
	C_{15}:C_{28}	<0.1
	C_{16}:C_{27}	<0.1
	C_{17}:C_{26}	0.1
	C_{18}:C_{25}	0.1
	C_{19}:C_{24}	0.1
	C_{20}:C_{23}	0.2
	C_{21}:C_{22}	0.7
	C_{22}:C_{21}	0.2
	C_{23}:C_{20}	0.1
	C_{24}:C_{19}	<0.1
	C_{25}:C_{18}	<0.1
wax C_{44}		19.1
	C_{16}:C_{28}	0.9
	C_{18}:C_{26}	0.5
	C_{20}:C_{24}	1.7
	C_{22}:C_{22}	16.0
wax C_{46}		5.3
	C_{16}:C_{30}	0.2
	C_{18}:C_{28}	0.2
	C_{20}:C_{26}	0.2
	C_{22}:C_{24}	1.8
	C_{24}:C_{22}	2.9

[a] tr, traces.

acylesters of glycerol, as well as sterol esters and sterol glycosides, were also present in important amounts. The structures of the main lipophilic compounds identified in the curaua extract are shown in **Figure 3**. The ω-hydroxy fatty acids both in free or in esterified form (forming esters with both fatty alcohols and glycerol) was the main series of compounds present in the extracts.

Table 4. Composition and Abundance (mg/kg) of the Different ω-Hydroxy Monoesters Identified in Curaua Fibers

ω-hydroxy monoester	ω-hydroxy fatty acid: fatty alcohol	abundance
ω-hydroxy monoester C_{36}		29.1
	ω-OHC_{16}:C_{20}	29.1
ω-hydroxy monoester C_{37}		3.0
	ω-OHC_{16}:C_{21}	3.0
ω-hydroxy monoester C_{38}		229.8
	ω-OHC_{16}:C_{22}	223.9
	ω-OHC_{18}:C_{20}	5.9
ω-hydroxy monoester C_{40}		95.6
	ω-OHC_{16}:C_{24}	59.5
	ω-OHC_{18}:C_{22}	35.2
	ω-OHC_{20}:C_{20}	0.9
ω-hydroxy monoester C_{42}		11.7
	ω-OHC_{16}:C_{26}	4.8
	ω-OHC_{18}:C_{24}	0.7
	ω-OHC_{20}:C_{22}	5.3
	ω-OHC_{22}:C_{20}	0.9
ω-hydroxy monoester C_{44}		0.3
	ω-OHC_{20}:C_{24}	0.1
	ω-OHC_{12}:C_{22}	0.2

The series of free fatty acids was present in the range from *n*-tetradecanoic (C_{14}) to *n*-tetracosanoic (C_{24}) acids, with strong even-over-odd carbon atom predominance. Stearic acid ($C_{18:0}$) and palmitic acid ($C_{16:0}$) were the most abundant fatty acids followed by *n*-docosanoic (C_{22}) and *n*-tetracosanoic (C_{24}) acids. Unsaturated fatty acids, such as palmitoleic ($C_{16:1}$), oleic ($C_{18:1}$), and linoleic ($C_{18:2}$) acids, were also present, oleic acid being especially abundant.

Hydroxy fatty acids (α- and ω-) were also identified in the curaua extracts, with a high abundance of the ω-hydroxy fatty acids and the presence of exclusively the even carbon atom number homologues. α-Hydroxyfatty acids were present in the range from 2-hydroxyeicosanoic acid (C_{20}) to 2-hydroxyhexacosanoic acid (C_{26}) with a maximum at C_{24}, whereas the ω-hydroxyfatty acids were identified in the range from 16-hydroxyhexadecanoic acid (C_{16}) to 30-hydroxytriacontanoic acid (C_{30}) with a maximum at C_{26}.

Waxes (esters of fatty acids to fatty alcohols) were also important components of the curaua fiber extracts and were found in the range from C_{36} to C_{46}. 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 quantification of the individual long chain esters in each chromatographic peak were resolved based on 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*, *43*−*45*). 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 the esters to every chromatographic peak by mass spectrometric determination of the molecular ion and the base peak. Quantification 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 curaua fiber is shown in **Table 3**. The esterified fatty acids ranged from C_{12} to C_{25}, and the

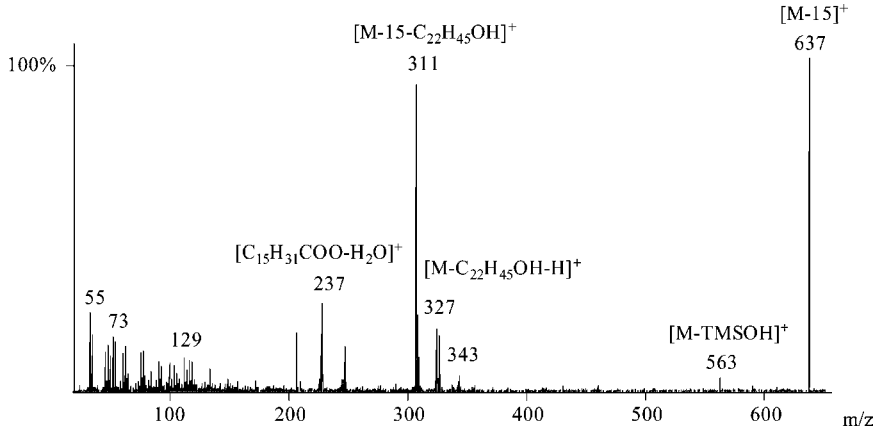

Figure 4. Mass spectrum of trimethylsilylated hydroxy monoester C_{38}.

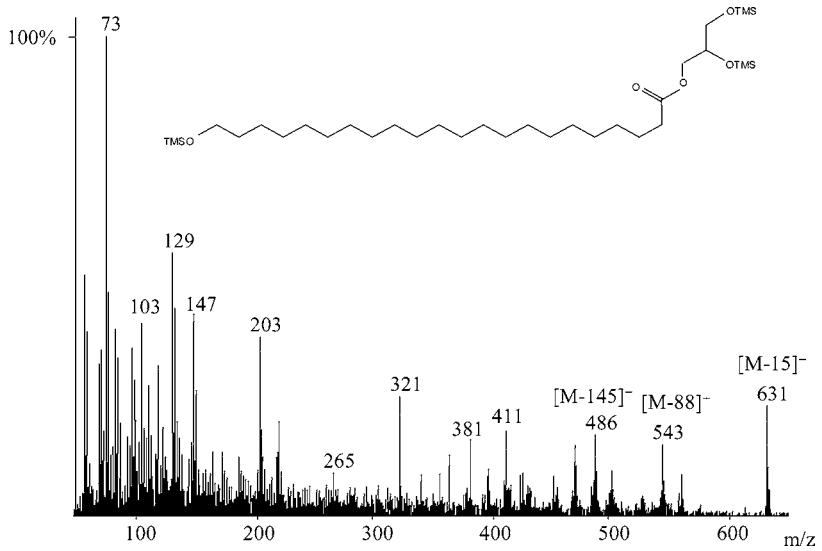

Figure 5. Mass spectrum and structure of the TMSi ether derivative of 1-mono(22-hydroxydocosanoyl)glycerol.

esterified fatty alcohols ranged from C_{16} to C_{30}. Waxes with unsaturated fatty acids ($C_{40:1}$ and $C_{42:1}$) were also found in lower amounts, the unsaturated fatty acid being in all cases oleic acid.

Other waxes, consisting of a complex mixture of different long chain ω-hydroxy fatty acids esterified to different long chain fatty alcohols, were also found in high amounts. These waxes are similar to those described among the waxes normally secreted by bees (*46*−*48*). The mass spectrum of the TMSi ether derivative of a selected ω-hydroxy monoester (C_{38}) is shown in **Figure 4**. The mass spectrum of this compound is characterized by a base peak at *m*/*z* 637 corresponding to the $[M - 15]^+$ fragment ion and a fragment formed by the loss of the fatty alcohol at *m*/*z* 311. The elimination of trimethylsilanol (TMSOH) from the molecular ions also can be observed at *m*/*z* 563 (*49*, *50*). As occurred with the esters of fatty acids with fatty alcohols, each chromatographic peak is composed of a complex mixture of compounds. Quantification of individual compounds was performed by integrating the chromatographic profiles of the characteristic ions. The detailed structural composition of the ω-hydroxy monoesters is shown in **Table 4**. The esterified ω-hydroxy fatty acids ranged from C_{16} to C_{22}, and the esterified fatty alcohols ranged from C_{20} to C_{26}.

ω-Hydroxy fatty acids esterified to glycerol were also found in high amounts in the curaua fiber. The mass spectra of the TMSi derivatives of ω-hydroxy acylesters of glycerol are characterized by the presence of an abundant fragment arising from the loss of a methyl group at $[M - 15]^+$. The cleavage between the C-2 and the C-3 carbons in the glyceryl moiety gives rise to the fragments at *m*/*z* 103 and $[M - 103]^+$. Other diagnostic ions are derived from the glyceryl moiety, i.e., at *m*/*z* 205 as a result of the cleavage between the C-2 and the C-1 (the esterified carbon) and at *m*/*z* 219 due to the loss of the acyloxy moiety. The same loss of the acyloxy group from $M^{+\bullet}$ and $M - 15^+$, but with the H rearrangement, gives rise to the ions at *m*/*z* 218 and 203, respectively. Other significant ions in the low-mass region occur at *m*/*z* 73 (the TMSi group), *m*/*z* 129 (the glycerol carbon backbone with a TMSi group [$H_2C{=}CH{-}CH{=}O^+$-$Si(CH_3)_3$]), and *m*/*z* 147 (produced by the rearrangement of two TMSi groups) (*51*). The ω-hydroxy fatty acids esterified to the glycerol range from C_{22} to C_{28}. The structure and mass spectrum of the TMSi derivative of 1-mono-(22-hydroxydocosanoyl)glycerol are shown in **Figure 5**.

n-Fatty alcohols ranging from C_{20} to C_{28} were present in the curaua extracts with the presence of only the even carbon atom homologues, docosanol (C_{22}) and tetracosanol (C_{24}) being the most abundant. Monoglycerides, accounting for 690.7 mg/kg of the fibers, were present in important amounts, from C_{14} to C_{30}, C_{22} (1-monodocosanoylglycerol) being the most prominent. Di- and triglycerides were only identified in trace amounts.

Sterols were also present among the lipids of curaua fibers in high amounts. Sitosterol was the most abundant among the free sterols with the presence of minor amounts of stigmastanol, ergostanol, and campesterol. Lower amounts of sitosterol and campesterol could also be found in ester form. Sterol glycosides,

such as sitosteryl and campesteryl 3β-D-glucopyranosides, were also identified in high 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 (*52*). Finally, other compounds identified among the curaua fiber extractives were α-tocopherol, several steroid hydrocarbons, and steroid ketones, as reflected in **Table 2**.

In conclusion, curaua fiber is characterized by a high content of holocellulose and α-cellulose and low lignin content, which would make this fiber suitable for papermaking. Moreover, the lignin composition indicates a slight predominance of S-lignin units (S/G molar ratio of 1.4). On the other hand, the high extractive content can be considered as a detrimental aspect; however, most of the acetone extracts are due to polar compounds and only 1.3% corresponds to lipophilic compounds. Indeed, most of the lipophilic compounds are easily saponifiable and, therefore, can be hydrolyzed and dissolved during alkaline cooking.

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