Available online at www.sciencedirect.com
ScienceDirect
J. Anal. Appl. Pyrolysis 79 (2007) 39–46
JOURNAL of ANALYTICAL and APPLIED PYROLYSIS
www.elsevier.com/locate/jaap

Composition of non-woody plant lignins and cinnamic acids by Py-GC/MS, Py/TMAH and FT-IR

José C. del Río [a,*], Ana Gutiérrez [a], Isabel M. Rodríguez [a], David Ibarra [b], Ángel T. Martínez [b]

[a] *Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, P.O. Box 1052, E-41080-Seville, Spain*
[b] *Centro de Investigaciones Biológicas, CSIC, Ramiro de Maeztu 9, E-28040-Madrid, Spain*

Received 9 March 2006; accepted 14 September 2006
Available online 18 October 2006

Abstract

Lignins from different non-woody plants such as hemp (*Cannabis sativa*), flax (*Linum usitatissimum*), jute (*Corchorus capsularis*), sisal (*Agave sisalana*) and abaca (*Musa textilis*), commonly used for manufacturing specialty papers, were analyzed by pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS) in the absence and in the presence of tetramethylammonium hydroxide (TMAH) and by Fourier-transform infrared (FTIR) spectroscopy, after alkaline isolation. Hemp and flax lignins showed a predominance of guaiacyl (1-hydroxy-2-methoxyphenyl) units, while jute, sisal and abaca lignins contained predominantly syringyl (1-hydroxy-2,6-dimethoxyphenyl) units. *p*-Hydroxycinnamic acids, namely *p*-coumaric and ferulic acids, were also found in the isolated lignins, linked by alkali-resistant ether bonds, especially in abaca and sisal lignins. The presence of the latter compounds in the isolated lignins, as well as in their respective whole fibers, was shown by pyrolysis in the presence of tetramethylammonium hydroxide (Py/TMAH), *p*-coumaric acid being especially abundant in abaca.

Keywords: Alkalilignins; Non-woody plants; Fibers; Py-GC/MS; Syringyl/guaiacyl ratio; Tetramethylammonium hydroxide; Ferulic acid; *p*-Coumaric acid

1. Introduction

Wood is the main raw material for the pulp and paper industry in developed countries while non-wood cellulosic fibers occupy small niche markets providing special properties to a range of high added value products. However, where wood-based fibers are not available, as in the developing world, nonwood fibers are a major fiber source for the pulp and paper industry [1].

Hemp, flax, jute, sisal and abaca are among the non-wood 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). However, the processing procedures from wood to paper products are not developed for non-woody plants and have to be adapted. While the chemical structure of wood lignin is much better known and structural models for softwood and hardwood lignins were available in the 1970s [2,3] and improved later [4], studies on non-wood lignin structure are comparatively scarce [5]. Knowledge of lignin composition in non-wood fibers are important for optimizing the pulping and bleaching processes of these raw materials.

Analytical pyrolysis has been found to be useful for the characterization of complex macromolecules including wood [6–9] and non-wood lignocellulosic materials [10–13], and isolated lignins [14–16]. Characteristic features of representative lignins, including their composition in terms of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, have been established based upon chemical degradation, as well as using analytical pyrolysis [17]. Due to their composition in H, G and S units, grass lignins have been justified as HGS-lignins, which are known to be different from those of softwoods (G-lignins) or hardwoods (GS-lignins) and the corresponding compression wood lignins (which are comparatively enriched in H units). Lignin composition is an important parameter that affects pulp production. In general, the efficiency of pulping is directly proportional to the amount of syringyl (S) units in lignin [9]. The G units have a free C-5 position available for

* Corresponding author. Tel.: +34 95 462 4711; fax: +34 95 462 4002.
E-mail address: delrio@irnase.csic.es (J.C. del Río).

0165-2370/$ – see front matter
doi:10.1016/j.jaap.2006.09.003

carbon–carbon inter-unit bonds, which make them fairly resistant to lignin depolymerization in pulping, while the S lignin is relatively unbranched and has a lower condensation degree and therefore is easier to delignify.

p-Hydroxycinnamic acids, *p*-coumaric and ferulic acids, as well as different diferulates [18], are abundant in non-woody plants forming cross-linkages between lignin and polysaccharides that have been especially investigated in grasses [19–24]. The presence of these phenylpropanoid compounds constitutes a complication for lignin analysis by analytical pyrolysis since they yield products similar to those of corresponding lignin units. This problem can be solved by using pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) [25], that releases intact *p*-hydroxycinnamic acids (as methylated derivatives). Pyrolysis in the presence of TMAH (Py/TMAH; also called thermochemolysis or simultaneous pyrolysis methylation) has been also used to characterize a variety of natural polymers, including lignin [25–30].

The present study centered on the analysis of lignin and cinnamic acids in a series of non-woody plants (hemp, flax, jute, sisal and abaca) using analytical pyrolysis (both in the absence and presence of TMAH) and Fourier-transform infrared (FTIR) spectroscopy.

2. Materials and methods

2.1. Lignin preparations

Non-woody plant materials were supplied by CELESA paper-pulp mill (Tortosa, Spain), and consisted of stalk bast fibers, and leaf fibers. Among the bast fibers, hemp, flax and jute were selected, while sisal and abaca were selected among the leaf fibers. Alkalilignins were extracted from the above non-woody plants under alkaline conditions using 0.2 M NaOH (at 120 °C), precipitated at acid pH, and washed with acidulated water before analysis.

2.2. Py-GC/MS and Py/TMAH

The pyrolyses were performed with a Curie-point flash pyrolyser coupled to a Varian Saturn 2000 GC/MS using a 30 m × 0.25 mm DB-5 column (film thickness 0.25 μm). Approximately 100 μg of finely divided sample was deposited on a ferromagnetic wire then inserted into the glass liner and placed immediately in the pyrolyser. The pyrolysis was carried out into the glass liner for 4 s. The chromatograph was programmed from 40 °C (1 min) to 300 °C at a rate of 6 °C/min. The final temperature was held for 20 min. The injector temperature was kept at 280 °C while the GC/MS interface was kept at 300 °C. For Py/TMAH, 100 μg of sample were mixed with approximately 0.5 μL TMAH (25%, w/w, aqueous solution). The wire was then inserted into the glass liner, which was placed in the pyrolyser. The pyrolysis was carried out as described above. The compounds were identified by comparison with those reported in the literature [31,32] and in the Wiley and NIST computer libraries. Relative peak molar areas (obtained by dividing the peak area by the molecular weight) were calculated for each 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.

2.3. FTIR

Spectra were obtained with a Bruker IF-28 spectrometer using 1 mg of lignin in 300 mg of KBr. A total of 50 interpherograms were accumulated, and the spectra were corrected by baseline subtraction between valleys *ca.* 1850 and 900 cm^{-1}. For S/G ratio estimation the intensities of the bands around 1327 cm^{-1} (S units) and 1271 cm^{-1} (G units) were estimated, after resolution enhancement (subtraction of ×1000 s derivative), moving-average smoothing (×100) and baseline correction between valleys *ca.* 1401 and 1172 cm^{-1} [33].

3. Results and discussion

The pyrograms of the alkalilignins from the different non-woody plants are shown in Fig. 1. The identification and relative molar abundances of the released lignin breakdown products are shown in Table 1. No carbohydrate-derived compounds were present in the pyrolyzates of the lignin samples. Relative peak areas were calculated for pyrolysis products from phenylpropanoid compounds (including lignin and *p*-hydroxycinnamic acids), and the summed areas of the peaks were normalized to 100%. The non-woody lignins comprised H, G and S moieties, which released different diagnostic compounds identified respectively as phenol (peak 1), guaiacol (peak 4), syringol (peak 14), and their 4-methyl (peaks 7,20), 4-ethyl (peaks 5,11,25), 4-vinyl (peaks 9,13,27), 4-allyl (peaks 29) and 4-propenyl (peaks 22,34) derivatives. Several oxidized phenols, such as vanillin (peak 18), syringaldehyde (peak 32), acetosyringone (peak 35) and syringylacetone (peak 36) were also identified. Clearly visible differences in the Py-GC/MS patterns were found among the different lignin samples (Fig. 1). Hemp and flax lignins released predominantly compounds with guaiacyl structure (peak 4: guaiacol; peak 7: 4-methylguaiacol; peak 13: 4-vinylguaiacol; peak 18: vanillin; peak 22: *trans*-isoeugenol; peak 24: acetoguaiacone), while jute, sisal and abaca released predominantly compounds with syringyl structure (peak 14: syringol; peak 20: 4-methylsyringol; peak 27: 4-vinylsyringol; peak 32: syringaldehyde; peak 34: *trans*-4-propenylsyringol; peak 35: acetosyringone). An important peak of 4-vinylphenol (peak 9) was also characteristic of the abaca lignin. The composition of the different non-woody lignins in terms of total H, G and S units, as well as the S/G ratio, were calculated and are shown in Table 2 (as relative molar areas). The S/G ratio revealed the presence of a G-type lignin in hemp and flax (low S/G ratio of 0.8 and 0.4, respectively). In contrast, jute, sisal and abaca lignins showed higher S/G ratios (1.7, 3.4 and 2.9, respectively) typical for hardwoods [8,9,15].

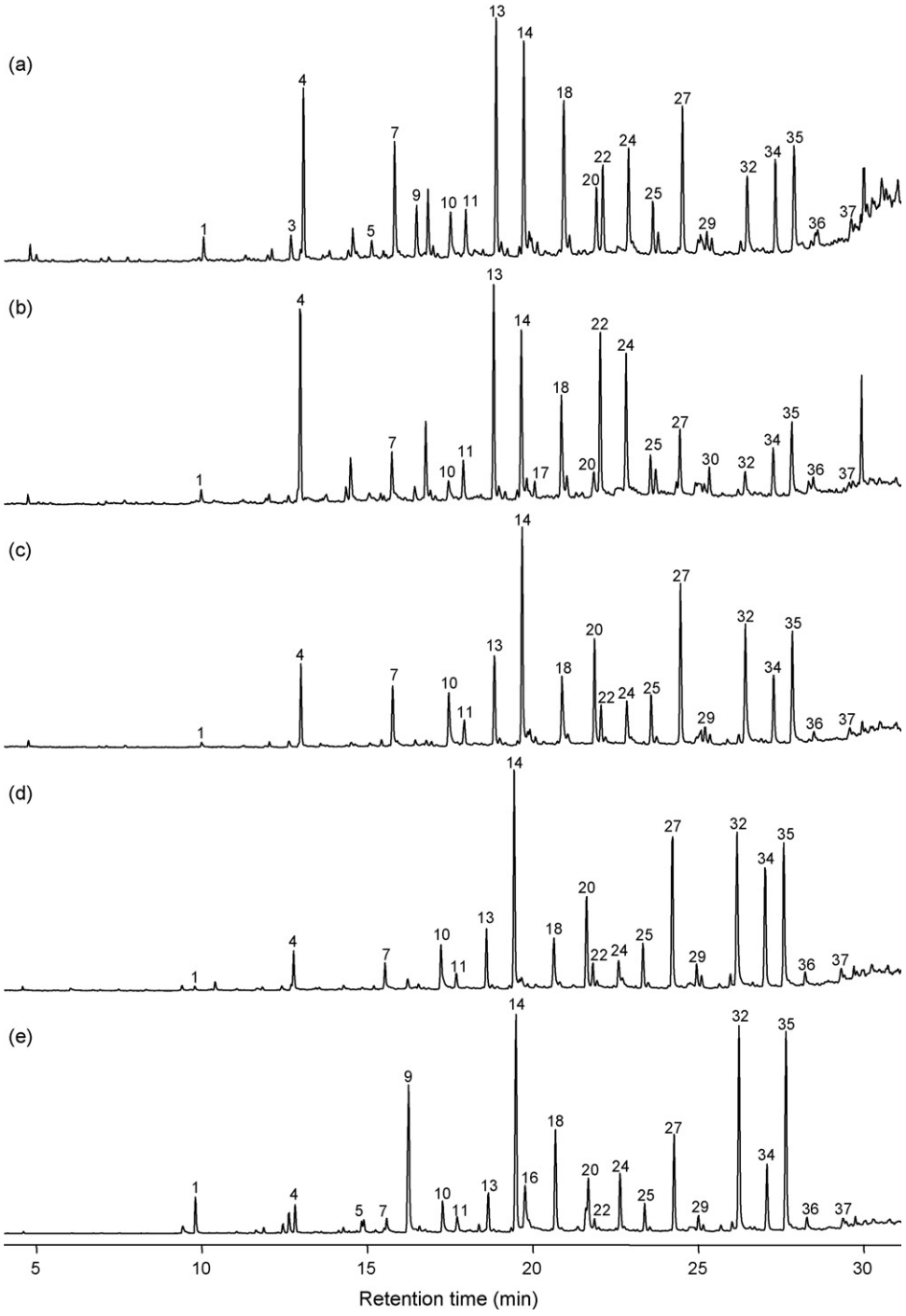

Fig. 1. Py-GC/MS analysis of lignins isolated from different non-wood cellulosic fibers selected for this study: (a) hemp, (b) flax, (c) jute, (d) sisal and (e) abaca. For peak identification refer to Table 1.

The higher reactivity of the S-lignin with respect to the G lignin in alkaline systems is known [34]. Therefore, the efficiency of pulping is directly proportional to the amounts of S-units in lignin. The G-units have a C-5 aromatic position available for very strong carbon–carbon bonds, which make them fairly resistant to the pulping depolymerization. Therefore, the low S/G ratio of hemp and flax lignins may make them more difficult to delignify (and bleach) because of the higher condensation degree of the lignin. By contrats, the high S-lignin content observed in jute, sisal and abaca lignins is advantageous for delignification during pulping because the S lignin is relatively unbranched and has lower condensation degree than the G lignin.

Sinapyl and coniferyl alcohol acetates (with the acetyl group attached at the Cγ of the lignin side-chain) have been recently identified in small amounts in the Py-GC/MS of whole fibers from jute, sisal and abaca [13]. However, these acetyl linkages are easily cleaved during alkaline extraction and

Table 1
Identity and relative molar abundances of the compounds released after Py-GC/MS of the different non-woody lignins

No.	Compound	Hemp	Flax	Jute	Sisal	Abaca
1	Phenol	1.8	1.1	0.5	0.5	3.4
2	*o*-Cresol	0.5	0.6	0.5	0.2	0.5
3	*m*-, *p*-Cresol	2.0	0.6	0.7	0.4	0.8
4	Guaiacol	9.5	16.0	7.1	3.8	1.9
5	4-Ethylphenol	0.9	0.6	0.2	0.2	1.6
6	3-Methylguaiacol	0.3	0.5	0.4	0.2	0.1
7	4-Methylguaiacol	5.0	2.8	4.3	2.2	1.2
8	Catechol	1.0	0.2	0.2	0.2	0.1
9	4-Vinylphenol	3.4	1.2	0.4	0.9	14.1
10	3-Methoxycatechol	3.3	2.0	5.2	5.0	2.5
11	4-Ethylguaiacol	2.4	2.5	1.9	1.3	1.2
12	4-Methylcatechol	0.2	0.1	0.1	0.1	0.1
13	4-Vinylguaiacol	11.3	12.8	6.7	4.4	2.6
14	Syringol	10.4	10.4	15.6	16.4	14.8
15	Eugenol	0.5	0.6	0.2	0.1	0.1
16	4-Hydroxybenzaldehyde	–	–	–	–	3.9
17	4-Propylguaiacol	0.6	0.8	0.3	0.3	0.1
18	Vanillin	8.7	7.3	5.6	4.5	6.6
19	*cis*-Isoeugenol	0.6	1.1	0.5	0.3	0.1
20	4-Methylsyringol	3.3	1.7	6.9	6.8	1.6
21	4-Hydroxyacetophenone	–	0.1	–	–	3.6
22	*trans*-Isoeugenol	4.2	9.8	2.4	1.7	0.5
23	Homovanillin	0.1	0.1	0.3	0.4	0.1
24	Acetoguaiacone	4.6	8.4	3.1	1.7	3.4
25	4-Ethylsyringol	2.3	2.1	3.0	2.9	1.4
26	Guaiacylacetone	0.9	1.6	0.4	0.4	0.2
27	4-Vinylsyringol	6.3	3.3	9.9	10.7	5.1
28	Propiovanillone	0.2	0.4	0.1	0.1	0.1
29	4-Allylsyringol	0.7	0.4	0.9	1.3	0.8
30	4-Propylsyringol	0.5	1.2	0.4	0.5	0.3
31	*cis*-4-Propenylsyringol	0.5	0.2	0.5	0.8	0.4
32	Syringaldehyde	3.9	1.5	8.8	11.8	12.0
33	4-Propynesyringol	0.1	–	0.1	0.2	0.1
34	*trans*-4-Propenylsyringol	4.3	2.7	4.3	8.5	3.6
35	Acetosyringone	4.8	4.4	7.4	10.0	10.2
36	Syringylacetone	0.2	0.5	0.6	0.9	0.6
37	Propiosyringone	0.7	0.3	0.5	0.7	0.4
38	*trans*-Sinapaldehyde	0.1	0.1	0.1	0.1	0.1

therefore they could not found in the lignin pyrograms shown in Fig. 1.

On the other hand, relatively high amounts of Cα-carbonyl compounds such as vanillin (peak 18), acetoguaiacone (peak 24) and their respective syringaldehyde (peak 32) and acetosyringone (peak 35) were present in the pyrograms of all the isolated lignins. The high yields of 4-vinylguaiacol (peak 13) and *trans*-isoeugenol (peak 22) and/or their respective 4-vinylsyringol (peak 27) and *trans*-4-propenylsyringol (peak 34) can be interpreted as indication of the presence of β-O-4 linkages with a hydroxyl group at the α-position, from which water is split easily during pyrolysis [35].

A significant amount of H-type compounds was found in hemp and, especially, abaca lignins, where they amount up to 26% of total pyrolysis products (Table 1). The high amounts of 4-vinylphenol (peak 9) may be due to the presence of *p*-coumaric acid, since it is known that under pyrolytic conditions *p*-coumaric acid decarboxylates to produce 4-vinylphenol [25]. The presence of ferulic acid in lignin may also be biased upon Py-GC/MS since it will yield 4-vinylguaiacol as the main pyrolysis product. Therefore, it is clear that the presence of *p*-hydroxycinnamic acids, which form lignin-carbohydrate bridges in herbaceous plants [19–24], cannot be evaluated properly by conventional pyrolysis.

However, the presence of the above *p*-hydroxycinnamic acids in the isolated lignins (as well as in the whole fibers) can be analyzed by Py/TMAH, as shown in Fig. 2a for the abaca lignin. The Py/TMAH of the whole abaca fiber is also shown for comparison (Fig. 2b). The identity of the compounds released and their relative molar abundances in the different lignin samples are listed in Table 2. It is known that Py/TMAH induces cleavage of β-O-4 ether bonds in lignin and released products similar to those obtained upon CuO alkaline degradation, including methylated aldehydes (peaks 8, 16 and 26), ketones (peaks 11, 22 and 31) and acids (peaks 13, 24 and 34) [26–29]. Moreover, Py/TMAH also induces high temperature saponification of esters of *p*-hydroxycinnamic acids, and breakdown of ether linkages at C_4, with subsequent methylation of the formed free carboxyl and hydroxyl groups [25]. Py/TMAH of the abaca lignin released high amounts (over 20% of total peak area) of the methyl derivative of *p*-coumaric acid, that is *trans*-3-(4-methoxyphenyl)-propenoic acid methyl ester (peak 32), as well as lower amounts (near 5% of total peak area) of the methyl derivative of ferulic acid, that is the *trans*-3-(3,4-dimethoxyphenyl)-propenoic acid methyl ester (peak 42). Even higher abundances of *p*-coumaric acid (over 60% of total peak area), together with ferulic acid (2.5% of total peak area), were found after Py/TMAH of the whole abaca fiber. In addition to the *trans* forms of methylated *p*-hydroxycinnamic acids, minor amounts of the *cis* isomers (peaks 25 and 38) were also identified (peak 34). The methyl derivatives of *p*-hydroxycinnamic acids were also detected in the other non-wood fibers and isolated lignins analyzed, although their abundance was much lower than that found in abaca.

Table 3 shows the ratio of *p*-hydroxycinnamic acids to lignin-derived compounds and also the *p*-coumaric/ferulic acids ratio in the different alkalilignins and their respective whole fibers, estimated after Py/TMAH. Except in abaca, where they are very abundant, and sisal where they amount 10% of isolated lignin and whole fibers, *p*-hydroxycinnamic acids are present in low amounts in the rest of the lignins studied here. This agrees with the literature data that generally reports the presence of higher amount of these compounds in monocotyledons (such as sisal and abaca) than in dicotyledons (such as hemp, flax and jute). However, the *p*-coumaric acid content in abaca fibers and lignins can be considered as exceptionally high [24]. While *p*-coumaric acid is very abundant in abaca, and in flax and hemp *p*-coumaric acid slightly predominates over ferulic acid, ferulic acid showed slightly higher abundance than *p*-coumaric acid in jute and sisal. Some of these results are also new in the literature that generally reports higher amount of ferulic than *p*-coumaric acid in monocotyledons [36], as well as in some dicotyledons although with lower amounts of both compounds [37].

Studies on maize [38], wheat [39] and other grasses including bamboo [40] revealed that *p*-coumaric acid is esterified at the

Table 2
Identity and relative molar abundances of the compounds released after Py/TMAH of the different non-woody lignins

No.	Compound	Hemp	Flax	Jute	Sisal	Abaca
1	4-Methoxytoluene	2.4	0.5	0.1	0.2	0.6
2	4-Ethyl-1-methoxybenzene	0.6	0.3	0.1	0.1	1.0
3	1,2-Dimethoxybenzene	3.7	2.9	2.0	1.0	0.8
4	4-Methoxystyrene	3.5	0.4	0.2	0.5	6.0
5	2,3-Dimethoxytoluene	1.4	0.9	1.2	0.1	0.1
6	3,4-Dimethoxytoluene	5.0	7.8	2.8	1.1	0.5
7	(4-Methoxyphenyl)-1-methoxyethane	0.5	0.1	–	–	2.8
8	4-Methoxybenzaldehyde	0.1	–	–	0.4	4.7
9	1,2,3-Trimethoxybenzene	2.8	3.1	5.8	5.0	2.5
10	4-Ethyl-1,2-dimethoxybenzene	2.5	4.0	0.8	0.5	0.5
11	4-Methoxyacetophenone	0.3	0.7	–	0.1	2.3
12	3,4-Dimethoxystyrene	5.6	8.8	2.6	1.8	1.0
13	4-Methoxybenzoic acid methyl ester	0.5	0.2	0.1	0.3	1.5
14	3,4,5-Trimethoxytoluene	2.3	1.4	3.1	2.6	1.0
15	1-(3,4-Dimethoxyphenyl)-1-methoxyethane	1.7	2.0	3.6	2.6	0.8
16	3,4-Dimethoxybenzaldehyde	10.6	12.7	2.5	5.6	3.0
17	1-(3,4-Dimethoxyphenyl)-1-propene	2.4	5.2	1.6	0.7	0.2
18	3,4,5-Trimethoxystyrene	3.7	3.4	7.2	5.8	2.5
19	1,2,3,5-Tetramethoxybenzene	1.5	0.4	1.4	1.4	1.1
20	1-(3,4,5-Trimethoxyphenyl)-1-propene	1.6	0.1	1.3	1.0	0.5
21	1-(3,4-Dimethoxyphenyl)-1-methoxypropane	0.4	1.3	0.7	0.6	0.3
22	3,4-Dimethoxyacetophenone	4.0	6.6	0.8	3.0	2.0
23	1-(3,4-Dimethoxyphenyl)-2-propanone	0.4	0.7	0.1	0.6	0.3
24	3,4-Dimethoxybenzoic acid methyl ester	8.8	9.4	9.3	4.0	1.7
25	*cis* 3-(4-Methoxyphenyl)-3-propenoic acid methyl ester	0.2	0.1	0.1	0.4	2.8
26	3,4,5-Trimethoxybenzaldehyde	7.1	4.0	5.7	17.7	9.4
27	3,4-Dimethoxybenzeneacetic acid methyl ester	1.2	0.6	0.3	0.3	0.1
28	*cis* 1-(3,4-Dimethoxyphenyl)-2-methoxyethylene	1.7	2.7	5.0	0.1	0.1
29	*trans* 1-(3,4-Dimethoxyphenyl)-2-methoxyethylene	2.0	2.0	2.9	0.1	0.1
30	*cis* 1-(3,4-Dimethoxyphenyl)-1-methoxyprop-1-ene	2.6	1.9	3.4	4.3	2.1
31	3,4,5-Trimethoxyacetophenone	2.6	2.5	2.0	13.2	9.8
32	*trans* 3-(4-Methoxyphenyl)-propenoic acid methyl ester	1.1	0.4	0.4	6.2	20.4
33	1-(3,4,5-Trimethoxyphenyl)-2-propanone	0.1	0.1	0.1	0.9	0.9
34	3,4,5-Trimethoxybenzoic acid methyl ester	6.1	3.5	13.0	9.5	6.7
35	1-(3,4,5-Trimethoxyphenyl)-2-methoxypropane	0.7	0.5	0.6	1.9	0.8
36	1,2,3-Trimethoxyphenylpropan-3-one	0.6	0.2	1.9	0.8	1.1
37	*cis* 1-(3,4,5-Trimethoxyphenyl)-2-methoxyethylene	0.6	0.5	6.9	0.8	1.3
38	*cis* 3-(3,4-Dimethoxyphenyl)-propenoic acid methyl ester	0.1	0.2	–	0.1	0.2
39	*trans* 1-(3,4,5-Trimethoxyphenyl)-2-methoxyethylene	0.4	0.2	4.4	0.6	0.9
40	*cis* 1-(3,4,5-Trimethoxyphenyl)-methoxyprop-1-ene	0.1	0.2	0.5	0.1	0.3
41	*trans* 1-(3,4,5-Trimethoxyphenyl)-methoxyprop-1-ene	0.2	0.2	0.6	0.1	0.3
42	*trans* 3-(3,4-Dimethoxyphenyl)-propenoic acid methyl ester	3.2	2.4	3.2	3.0	3.9

γ-position of lignin side-chains, and predominantly to S units [40,41]. Therefore, probably the major part of the *p*-coumaric acid in abaca fibers also attaches at the γ-position of the lignin side-chain. However, as bifunctional molecules with carboxylic and phenolic binding sites, the *p*-hydroxycinnamic acids can be involved in both ester and ether linkages to other cell wall components. Therefore, the *p*-hydroxycinnamic acids still remaining in the lignins extracted from abaca fibers are, most probably, ether-linked [19,20,24], because the ester linkages are easily cleaved under alkaline extraction [37].

The relative composition of *p*-hydroxycinnamic acids (*p*-coumaric/ferulic acids ratio) present in the lignins and their respective fibers, estimated by Py/TMAH (Table 3), reveals additional features. Interestingly, this ratio is lower, except for sisal, in all the extracted lignins (where ester linkages have been cleaved) when comparing with the whole fiber (with intact ester linkages). This means that most of the *p*-coumaric acid has been extensively attached through ester bonds to lignin side chains (and carbohydrates) in the fibers cell walls while ferulic acid was linked to lignin predominantly by ether bonds, which is in agreement with previous works [24,38–41]. Similar results have been reported by other authors in abaca fiber, where it was found that most *p*-coumaric acid was esterified to lignin, while the major part of ferulic acid was etherified to lignin [42]. In sisal, however, it seems to occur the contrary, ferulic acid is predominantly linked to lignin through ester bonds and *p*-coumaric acid through ether bonds.

The results from analytical pyrolysis were confirmed by FTIR. The spectra of the different lignins (Fig. 3) show typical lignin patterns [43,44], although significant differences in the

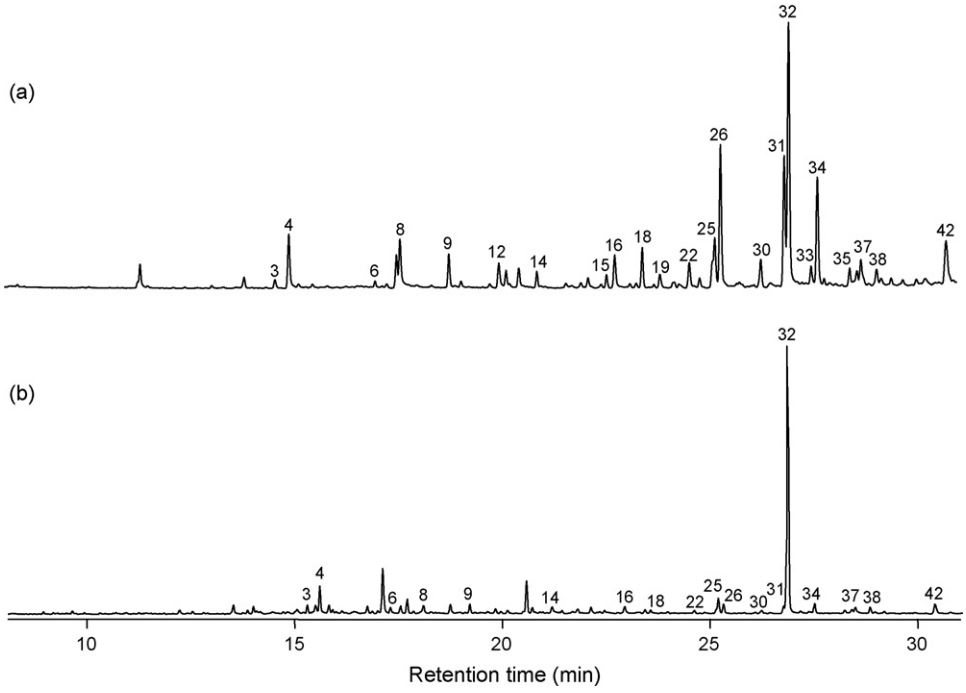

Fig. 2. Py/TMAH analysis of abaca lignin (a) compared with abaca whole fiber (b). For peak identification refer to Table 2.

intensities of some of the bands were observed. The sisal, abaca and jute spectra were very similar, whereas flax and hemp showed the most different band patterns. Differences between FTIR spectra of flax and sisal lignins were already reported [45]. The intensities of peaks around 1327 and 1271 cm^{-1} (ring breathing of S and G units, respectively) after resolution enhancement were used to estimate the S and G contents. The 1327 cm^{-1} band was clearly visible in the spectra of sisal, abaca and jute, that at 1271 cm^{-1} was visible in the flax lignins, and both bands were evident in the hemp lignins. Other S-type bands, *e.g.* at 1128 and 834 cm^{-1} (in plane and out of plane C-H bending respectively) were also evident in the flax lignin spectrum, together with G bands (1271 and 853 cm^{-1}). On the other hand, no differences in the intensities of the typical lignin triplet at 1515, 1462-4 and 1425-7 cm^{-1} were observed, and a strong band at 1218 cm^{-1} was found in all the spectra. The S/G values calculated upon FT-IR are in agreement with those calculated upon Py-GC/MS, and revealed the presence of a G-type lignin in flax (low S/G ratio of 0.4). In contrast, jute, sisal and abaca lignins were of the S-type (S/G ratios of 1.4, 3.4 and 1.9, respectively). In the case of the hemp lignin, however, the ratio calculated upon FTIR (S/G 2.0) was different from that calculated upon Py-GC/MS. Finally, the absence of the band at 1169 cm^{-1}, characteristic of ester-linked *p*-hydroxycinnamic acids [24], in the spectra of the different alkalilignins, and particularly in abaca lignin where *p*-hydroxycinnamic acids are more abundant as seen by Py/TMAH, indicates that the *p*-coumaric

Table 3
H, G and S molar contents from Py-GC/MS of the alkalilignins, and cinnamic content and composition from Py/TMAH of alkalilignins and whole fibres (molar abundances)

	Hemp	Flax	Jute	Sisal	Abaca
Lignins					
H (%)[a]	9	4	2	2	26
G (%)[a]	51	67	36	22	19
S (%)[a]	40	29	62	76	55
S/G ratio[a]	0.8	0.4	1.7	3.4	2.9
p-Hydroxycinnamic acids/lignin ratio[b]	0.05	0.03	0.04	0.11	0.39
p-Coumaric/ferulic ratio[b]	0.4	0.2	0.1	2.1	5.7
Whole fibers					
p-Hydroxycinnamic acids/lignin ratio[b]	0.03	0.03	0.02	0.07	2.64
p-Coumaric/ferulic ratio[b]	1.9	1.4	0.6	0.7	27.9

[a] From molar areas of peaks in Table 1.
[b] From molar areas of peaks in Table 2.

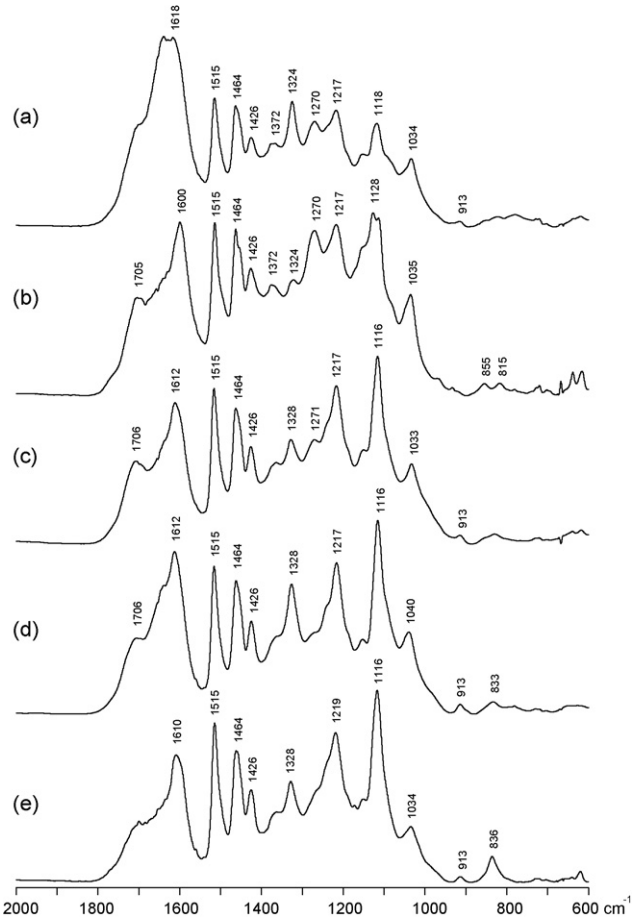

Fig. 3. FTIR spectra of the lignins isolated from the different non-wood cellulosic fibers selected for this study: (a) hemp, (b) flax, (c) jute, (d) sisal and (e) abaca. See text for band assignment.

and ferulic acids present in the lignin preparations are linked by alkali-resistant ether bonds.

4. Conclusions

Alkalilignins from a series of non-wood fibers (hemp, flax, jute, sisal and abaca), used for paper pulp manufacture, have been analyzed. Hemp and flax lignins have low S/G ratios, while jute, sisal and abaca present high S/G ratios, as revealed by Py-GC/MS and FTIR. On the other hand, *p*-hydroxycinnamic acids are biased by Py-GC/MS, however, Py/TMAH has shown to be a suitable technique for the analysis of *p*-hydroxycinnamic acids linked by ether or ester bonds to cell wall components. Thus, Py/TMAH showed a significant amount of *p*-coumaric acid in the abaca lignin (*p*-hydroxycinnamic acids/lignin ratio of 0.39) and much lower cinnamic contents in the other lignins. The analysis of whole fibers also showed very high amounts of *p*-coumaric acid in abaca (*p*-hydroxycinnamic acids/lignin ratio of 2.64). Moreover, the analysis of cinnamic acids in fibers showed that most *p*-coumaric acid is attached to cell walls through ester bonds, while ferulic acid was predominantly ether-linked. In sisal it seems to occur the contrary, ferulic acid is predominantly linked though ester bonds and *p*-coumaric acid through alkali-resistant ether bonds.

Acknowledgements

We thank Celulosa de Levante S.A. (CELESA; Tortosa, Spain) for supplying the non-woody plant fibers. This work has been supported by the project AGL2005-01748 from the Spanish MCyT.

References

[1] G. Moore, Nonwood Fibre Applications in Papermaking, Pira International, Leatherhead, Surrey, UK, 1996.
[2] H. Nimz, Angew. Chem. Int. Ed. 13 (1974) 313–321.
[3] E. Adler, Wood Sci. Technol. 11 (1977) 169–218.
[4] P. Karhunen, P. Rummakko, J. Sipila, G. Brunow, I. Kilpeläinen, Tetrahedron Lett. 36 (1995) 4501–4504.
[5] R.C. Sun, J.M. Lawther, W.B. Banks, Ind. Crop. Prod. 6 (1997) 1–8.
[6] C. Saiz-Jiménez, J.J. Boon, J.I. Hedges, J.K.C. Hessels, J.W. de Leeuw, J. Anal. Appl. Pyrolysis 11 (1987) 437–450.
[7] H. Yokoi, Y. Ishida, H. Ohtani, S. Tsuge, T. Sonoda, T. Ona, Analyst 124 (1999) 669–674.
[8] J.C. del Río, M. Speranza, A. Gutiérrez, M.J. Martínez, A.T. Martínez, J. Anal. Appl. Pyrolysis 64 (2002) 421–431.
[9] J.C. del Río, A. Gutiérrez, M. Hernando, P. Landín, J. Romero, A.T. Martínez, J. Anal. Appl. Pyrolysis 74 (2005) 110–115.
[10] W.H. Morrison, D.D. Archibald, J. Agric. Food Chem. 46 (1998) 1870–1876.
[11] K. Kuroda, T. Ozawa, T. Ueno, J. Agric. Food Chem. 49 (2001) 1840–1847.
[12] A. Gutiérrez, I.M. Rodríguez, J.C. del Río, J. Agric. Food Chem. 52 (2004) 4764–4773.
[13] J.C. del Río, A. Gutiérrez, A.T. Martínez, Rapid Commun. Mass Spectrom. 18 (2004) 1181–1185.
[14] C. Saiz-Jiménez, J.W. de Leeuw, Org. Geochem. 10 (1986) 869–876.
[15] D. Meier, O. Faix, in: S.Y. Lin, C.W. Dence (Eds.), Methods in Lignin Chemistry, Springer, Berlin, 1992 , pp. 177–199 (Chapter 4.7).
[16] S. Camarero, P. Bocchini, G.C. Galletti, A.T. Martínez, Rapid Commun. Mass Spectrom. 13 (1999) 630–636.
[17] S.Y. Lin, C.W. Dence, Methods in Lignin Chemistry, Springer-Verlag, Berlin, 1992.
[18] M. Bunzel, J. Ralph, J.M. Marita, R.D. Hatfield, H. Steinhart, J. Sci. Food Agric. 81 (2001) 653–660.
[19] A. Scalbert, B. Monties, J.-Y. Lallemand, E. Guittet, C. Rolando, Phytochemistry 24 (1985) 1359–1362.
[20] T.B.T. Lam, K. Iiyama, B.A. Stone, Phytochemistry 31 (1992) 1179–1183.
[21] T.B.T. Lam, K. Kadoya, K. Iiyama, Phytochemistry 57 (2001) 987–992.
[22] J.H. Grabber, J. Ralph, R.D. Hatfield, J. Agric. Food Chem. 48 (2000) 6106–6113.
[23] R.C. Sun, X.F. Sun, S.H. Zhang, J. Agric. Food Chem. 49 (2001) 5122–5129.
[24] R.C. Sun, X.F. Sun, S.Q. Wang, W. Zhu, X.Y. Wang, Ind. Crop. Prod. 15 (2002) 179–188.
[25] J.C. del Río, F. Martín, F.J. González-Vila, Trends Anal. Chem. 15 (1996) 70–79.
[26] J.M. Challinor, J. Anal. Appl. Pyrolysis 35 (1995) 93–107.
[27] D.J. Clifford, D.M. Carson, D.E. MacKinney, J.M. Bortiatynski, P.G. Hatcher, Org. Geochem. 23 (1995) 169–175.
[28] F. Martín, J.C. del Río, F.J. González-Vila, T. Verdejo, J. Anal. Appl. Pyrolysis 35 (1995) 1–13.
[29] J.C. del Río, D.E. McKinney, H. Knicker, M.A. Nanny, R.D. Minard, P.G. Hatcher, J. Chromatogr. A 823 (1998) 433–448.
[30] K. Kuroda, N. Nishimura, A. Izumi, D.R. Dimmel, J. Agric. Food Chem. 50 (2002) 1022–1027.
[31] O. Faix, D. Meier, I. Fortmann, Holz Roh-Werkstoff 48 (1990) 351–354.
[32] J. Ralph, R.D. Hatfield, J. Agric. Food Chem. 39 (1991) 1426–1437.
[33] R. Bechtold, A.E. González, G. Almendros, M.J. Martínez, A.T. Martínez, Holzforschung 47 (1993) 91–96.

[34] Y. Tsutsumi, R. Kondo, K. Sakai, H. Imamura, Holzforschung 49 (1995) 423–428.
[35] J.-W. Choi, O. Faix, D. Meier, Holzforschung 55 (2002) 185–192.
[36] R.J. Henry, P.J. Harris, Plant Mol. Biol. Reporter 15 (1997) 216–218.
[37] V.V. Lozovaya, T.A. Gorshkova, E.V. Yablokova, N.I. Rumyantseva, A. Valieva, A. Ulanov, J.M. Widholm, Phytochemistry 50 (1999) 395–400.
[38] J. Ralph, R.D. Hatfield, S. Quideau, R.F. Helm, J.H. Grabber, H.-J.G. Jung, J. Chem. Soc. 34 (1994) 1–12.
[39] C. Crestini, D.S. Argyropoulos, J. Agric. Food Chem. 45 (1997) 1212–1219.
[40] F.C. Lu, J. Ralph, J. Agric. Food Chem. 47 (1999) 1988–1992.
[41] J.H. Grabber, S. Quideau, J. Ralph, Phytochemistry 43 (1996) 1189–1194.
[42] R.C. Sun, J.M. Fang, A. Goodwin, J.M. Lawther, A.J. Bolton, J. Sci. Food Agric. 79 (1999) 1091–1098.
[43] O. Faix, Holzforschung 45 (1991) 21–27.
[44] G. Vázquez, G. Antorrena, J. González, S. Freire, Holzforschung 51 (1997) 158–166.
[45] G. Boeriu, D. Bravo, R.J.A. Gosselink, J.E.G. van Dam, Ind. Crops Prod. 20 (2004) 205–218.