

# CHEMICAL COMPOSITION OF JUTE (*CORCHORUS CAPSULARIS*) FIBERS USED FOR PAPER PULP MANUFACTURING

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## ABSTRACT

The lipid and lignin composition of jute fibers has been characterized. The most predominant lipophilic compounds were high molecular weight ester waxes (24% of total extract), followed by free fatty acids (17%), free fatty alcohols (17%) and  $\alpha$ -hydroxyfatty acids (14%). Additionally, significant amounts of alkanes (6%),  $\omega$ -hydroxyfatty acids (6%), sterols (6%), steroid and triterpenoids ketones (3%) and steryl glycosides (1%) were also identified. The lignin was first analyzed “in situ” by Py-GC/MS and the isolated MWL subsequently characterized by 2D-NMR. A predominance of S over G lignin units, with only minor amounts of H units (H:G:S of 2:33:65) was found. The main inter-unit linkage present in was the  $\beta$ -O-4' aryl-ether bond (72%) followed by  $\beta$ - $\beta'$  resinol-type substructures and with lower amounts of  $\beta$ -5' phenylcoumaran and  $\beta$ -1' spirodienone substructures.

## BACKGROUND

Jute (*Corchorus capsularis*) is an herbaceous annual plant from the Tiliaceae family, mostly grown in Southeast Asian countries. Jute fiber comes from the bast or outer region of the stem and is a good source of different grades of pulp [1]. There have been previous published studies describing the characteristics of this fiber, including the content of their main organic fractions, particularly lignin and carbohydrates, and its behavior during pulping [1-3]. However, in order to maximize the exploitation of this interesting fiber for paper pulp production, a more complete understanding of its composition is required.

In the present study, we report the lipid and lignin composition of jute fibers. The composition of the lipophilic compounds was studied by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) using short- and medium-length high temperature capillary columns, respectively, with thin films, which enables the elution and analysis of intact high molecular weight lipids such as waxes or sterol glycosides [4]. The lignin composition was characterized “in situ” by Py-GC/MS, a rapid and highly sensitive technique for characterizing the chemical structure of lignin [5,6]. In addition, for a more complete structural characterization, the milled wood lignin (MWL) was isolated and analyzed by 2D-NMR, which is a powerful tool for lignin structural

characterization revealing both the aromatic units and the different interunit linkages present in the lignin [7-11].

## EXPERIMENTAL

### Samples

Jute fibers were supplied by CELESA pulp mill (Tortosa, Spain). The dried samples were milled and successive extracted with acetone in a Soxhlet apparatus for 8 h and hot water (3h at 100°C). Klason lignin content was estimated as the residue after sulphuric acid hydrolysis of the pre-extracted material according to Tappi rule T222 om-88 [12]. The acid-soluble lignin was determined, after the insoluble lignin was filtered off, by spectroscopic determination at 205 nm wavelength. Ash content was estimated as the residue after 6h at 575°C. The immediate analysis of jute fibers (as percent of whole fiber) is as follows: ash, 1.0%; acetone extractives, 0.4%; water soluble extractives, 1.0%; Klason lignin, 13.3%; acid-soluble lignin, 2.8%.

### Isolation of Milled Wood Lignin

Milled-wood lignin (MWL) was extracted from finely ball-milled (*ca.* 100 h) plant material, free of extractives and hot water soluble material, using dioxane-water (9:1, v/v), followed by evaporation of the solvent, and purified as described [13].

### GC and GC-MS analyses

An HP 5890 gas chromatograph 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. The capillary column used was a DB5-HT (5 m x 0.25 mm I.D., 0.1  $\mu$ m film thickness). The oven was temperature-programmed from 100°C (1 min) to 350°C (3 min) at 15°C min<sup>-1</sup>. Peaks were quantified by area, and a mixture of standards (octadecane, palmitic acid, sitosterol, cholesteryl oleate, and sitosteryl 3 $\beta$ -D-glucopyranoside) was used to elaborate calibration curves. The GC-MS analysis were performed on a Varian Saturn 2000 system equipped with a similar column (DB-5HT, 15 m x 0.25 mm i.d., 0.1  $\mu$ m film thickness). The oven was heated from 120°C (1 min) to 380°C (5 min) at 10°C/min. The temperature of the injector during the injection was 120°C, and 0.1 min after injection was programmed to 380°C at a rate of 200°C/min and held for 10 min. The temperature of the transfer line was set at 300°C.

### Pyrolysis-gas chromatography/mass spectrometry

The pyrolysis was performed at 610 °C in a Curie-point pyrolyser coupled to a Varian Saturn 2000 GC-MS, using a 30 m x 0.25 mm i.d., 0.25  $\mu$ m DB-5 column. The GC 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, equipped with a liquid carbon dioxide cryogenic unit was programmed from -30 °C (1 min) to 300 °C at 200 °C/min, while the GC/MS interface was kept at 300 °C. 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 [5,6].

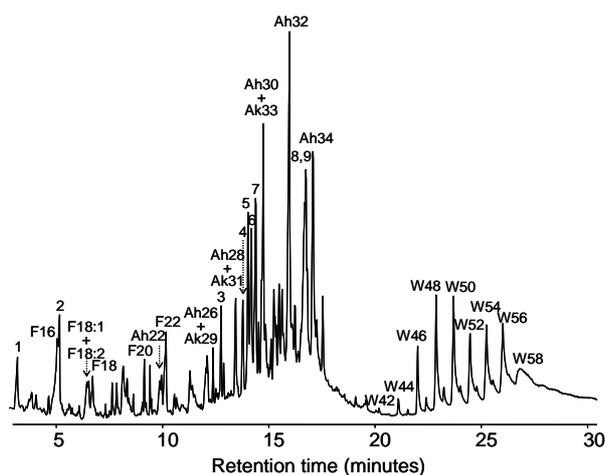
## NMR spectroscopy

NMR spectrum of jute MWL was recorded at 25 °C on a Bruker AVANCE 500 MHz equipped with a z-gradient triple resonance probe. Around 40 mg of jute MWL were dissolved in 0.75 mL of deuterated dimethylsulfoxide (DMSO- $d_6$ ) and 2D-NMR spectra were recorded in HSQC (heteronuclear single quantum correlation) experiments. The  $^1J_{CH}$  used was 140 Hz. The  $J$ -coupling evolution delay was set to 3.2 ms. The central solvent peak was used as an internal reference ( $\delta_C$  39.5;  $\delta_H$  2.50 ppm). HSQC cross-signals were assigned by comparing with the literature [7-11]. A semiquantitative analysis of the intensities of the HSQC cross-signal intensities was performed. The integration on the cross-signals was performed separately for the different regions of the HSQC spectrum, which contain signals that correspond to chemically analogous carbon-proton pairs. In the aliphatic oxygenated region, the relative abundance of side-chains involved in inter-unit linkages were estimated from the  $C_\alpha$ - $H_\alpha$  correlations to avoid possible interference from homonuclear  $^1H$ - $^1H$  couplings. In the aromatic region, C-H correlations from S and G units were used to estimate the lignin S/G ratio.

## RESULTS AND DISCUSSION

### Lipid composition

The acetone extractives of jute fibers accounts for 0.4% of dry material. The lipophilic extracts were analyzed by GC and GC-MS using short- and medium-length high temperature capillary columns, respectively, according to the method previously described [4]. The GC-MS chromatogram of the underivatized lipid extracts from jute fibers is shown in **Figure 1**. The identities and abundances of the main lipophilic compounds identified are detailed in **Table 1**.



**Figure 1: GC-MS of the lipophilic extracts from jute fibers. F(n): *n*-fatty acids; Ak(n): *n*-alkanes; Ah(n): *n*-fatty alcohols; W(n): high molecular weight ester waxes; *n*: carbon atom number. Other compounds are: 1, *trans*-coniferyl alcohol; 2, *trans*-sinapyl alcohol; 3, stigmasta-3,5,7-triene; 4, campesterol; 5, stigmasterol; 6, isomultiflorenone; 7, sitosterol; 8 and 9, compounds with epoxydammarane-type structure.**

**TABLE 1: COMPOSITION OF LIPIDS FROM JUTE (*C. CAPSULARIS*) FIBERS**

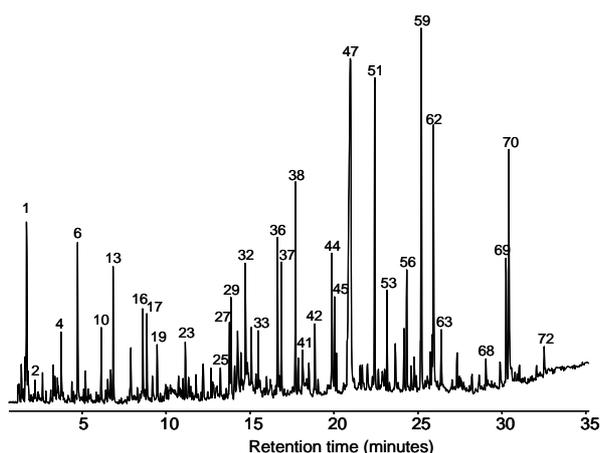
Series of Compounds	Abundance (mg/Kg)
<i>n</i> -Alkanes	48.5
<i>n</i> -Fatty acids	130.2
$\alpha$ -Hydroxyfatty acids	102.8
$\omega$ -Hydroxyfatty acids	34.5
<i>n</i> -Fatty alcohols	127.0
Steroid hydrocarbons	16.1
Sterols	43.4
Epoxydammarane-type triterpenoids	64.8
Tocopherols	3.1
Steroid/triterpenoid ketones	25.1
Steryl glycosides	8.4
Waxes	181.2
Monoglycerides	7.5
Diglycerides	13.5

The most predominant lipophilic compounds present in jute fibers were series of high molecular weight ester waxes, followed by series of free fatty acids, free fatty alcohols and  $\alpha$ -hydroxyfatty acids. Additionally, lower amounts of other aliphatic series such as *n*-alkanes and  $\omega$ -hydroxyfatty acids, were also found. Steroid and triterpenoid compounds were also present among jute lipophilic extracts, together with minor amounts of tocopherols as well as mono- and diglycerides.

### Lignin composition

Jute fibers presented a Klason lignin content of 13.3%, that amounted up to 16.1 % by taking into account the acid-soluble lignin, in agreement with previous studies [2,3]. This lignin content is higher than that in other nonwood bast fibers such as hemp or flax, with a lignin content less than 5% [14] although comparable to that reported for kenaf bast fiber [15]. The composition of the lignin in jute fibers was analyzed *in situ* by Py-GC/MS. The program is shown in **Figure 2**.

The compounds released arise from the carbohydrate and lignin moieties. Among the lignin derived phenols, the pyrogram showed compounds derived from guaiacyl (G) and syringyl (S) lignin units. Compounds derived from *p*-hydroxyphenyl (H) lignin units were found in minor amounts (2 %). The lignin-derived S-type phenols were present in higher abundances than the respective G-type phenols, with a H:G:S composition of 2:32:66 and a S/G ratio of 2.1, in agreement with previous studies [2,3]. The high lignin S/G ratio is comparable to those observed in hardwood lignins [11,16]. Other bast fibers commonly used for pulp and papermaking, such as flax or hemp, have very low lignin S/G ratios (0.8 and 0.3, respectively) [14,17], although a high S/G ratio has been found in kenaf [15,17]. The high S-lignin content observed in jute fibers is advantageous for delignification due to the higher reactivity of the S-lignin in alkaline systems [18,19]. Higher S/G ratios imply higher delignification rates, less alkali consumption and therefore higher pulp yield [20,21].

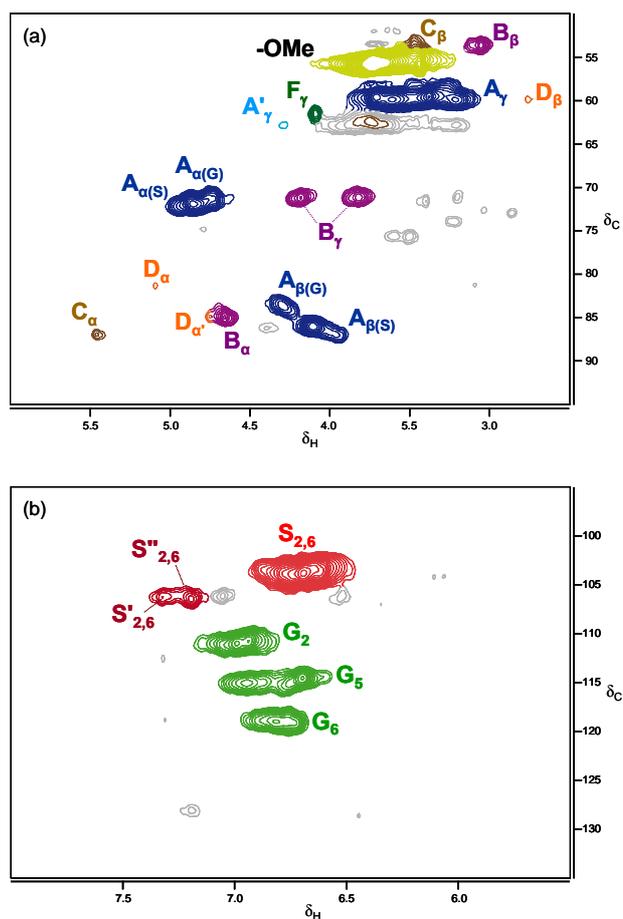


**Figure 2: Py-GC/MS of jute fibers. Carbohydrates (peaks 1-14, 16-20, 22, 25-27, 29, 30, 32, 36, 47, 50), H-lignin compounds (peaks 15, 21, 24); G-lignin compounds (peaks 23, 28, 31, 34, 37, 39, 42, 43, 45, 46, 49, 57, 61, 62, 64, 67); S-lignin compounds (peaks 38, 44, 48, 51, 52-56, 58-60, 63, 65, 66, 68-72).**

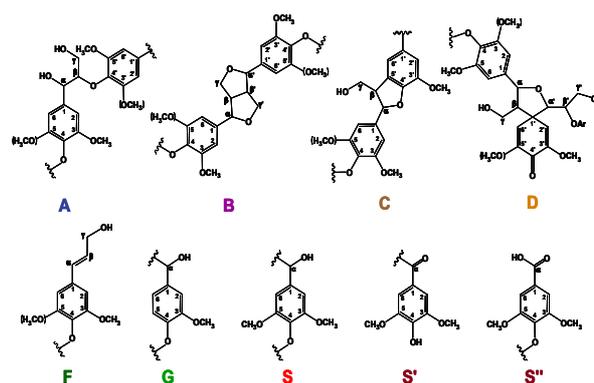
For a more in-depth structural characterization of jute lignin, the MWL was isolated and subjected to 2D-NMR analysis. The side-chain ( $\delta_C/\delta_H$  50-95/2.5-6.0 ppm) and the aromatic ( $\delta_C/\delta_H$  95-135/5.5-8.0 ppm) regions of the HSQC spectrum of jute MWL are shown in **Figure 3** and the main substructures found are depicted in **Figure 4**.

The side-chain region of the spectrum (**Figure 3a**) gave information about the inter-unit linkages present in the lignin. The spectrum showed prominent signals corresponding to  $\beta$ -O-4' ether linkages (substructure A). In addition, other linkages were also observed. Signals for resinol ( $\beta$ - $\beta'$ / $\alpha$ -O- $\gamma'$ / $\gamma$ -O- $\alpha'$ ) (B), phenylcoumaran ( $\beta$ -5'/ $\alpha$ -O-4) (C) and spirodienone ( $\beta$ -1'/ $\alpha$ -O- $\alpha'$ ) substructures (D), could also be observed. Other small signals in the side-chain region of the spectrum corresponded to  $C_\gamma$ - $H_\gamma$  correlations of *p*-hydroxycinnamyl (F) end-groups. The main signals in the aromatic region of the spectrum (**Figure 3b**) corresponded to the benzenic rings of the different lignin units. Signals from syringyl (S) and guaiacyl (G) units were observed, however, signals of H-lignin units were not detected, in agreement with the low abundance of these units observed by Py-GC/MS (2%). The NMR estimation of the S/G ratio accounts for 2.0, similar to that observed by Py-GC/MS.

The relative abundances of the main inter-unit linkages and the molar S/G ratios calculated from the HSQC spectrum are shown in **Table 2**. The data indicated that the structure of jute lignin is very similar to a hardwood lignin, with a high S/G ratio, a predominance of  $\beta$ -O-4' aryl ether linkages (72% of total side-chains), followed by  $\beta$ - $\beta'$  resinol linkages (16% of total side-chains) and lower amounts of  $\beta$ -5' phenylcoumaran and  $\beta$ -1' spirodienone-type linkages and cinnamyl end-groups.



**Figure 3: HSQC NMR spectrum of jute MWL. (a) expanded side-chain region  $\delta_C/\delta_H$  50-95/2.5-6.0 ppm, and (b) expanded aromatic region  $\delta_C/\delta_H$  95-135/5.5-8.0 ppm. See Figure 3 for the main lignin structures identified.**



**Figure 4: Main structures present in jute lignin: (A)  $\beta$ -O-4' linkages; (B) resinols (C) phenylcoumarane s (D) spirodienones (F) *p*-hydroxycinnamyl alcohol end-groups; (G) guaiacyl units; (S) syringyl units; (S') oxidized syringyl unit bearing a carbonyl group at  $C_\alpha$  (phenolic); (S'') oxidized syringyl unit bearing a carboxyl group at  $C_\alpha$ .**

**TABLE 2: STRUCTURAL CHARACTERISTICS OF THE MWL FROM JUTE FIBERS FROM SIGNALS IN THE HSQC SPECTRA**

<u>Linkage relative abundance (% of side-chains)</u>	
$\beta$ -O-4' aryl ether units (A)	72
Resinols (B)	16
Phenylcoumarans (C)	4
Spirodienones (D)	4
<i>p</i> -Hydroxycinnamyl alcohols (F)	4
<u>Erythro/threo ratio</u>	3.5
<u>S/G ratio</u>	2.0

The high predominance of the S-lignin units, together with the high predominance of  $\beta$ -O-4' aryl ether linkages, which are easily cleaved during alkaline cooking, are advantageous for pulping.

## CONCLUSIONS

We have reported a detailed study of the chemical composition of the lipophilic extractives and the structure of the lignin from jute fibers. This knowledge will help to maximize the exploitation of this interesting fiber for pulp and paper production.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Akhtaruzzaman, A.F.M., Shafi, M. (1995) "Pulping of jute" *Tappi J.* **78**:106-112
- Islam, A., Sarkanen, K.V. (1993) "The isolation and characterization of the lignins of jute (*Corchorus capsularis*)" *Holzforchung* **47**:123-132
- Jahan, M.S., Kanna, G.H., Mun, S.P., Chowdhury, D.A.N. (2008) "Variations in chemical characteristics and pulpability within jute plant (*Corchorus capsularis*)" *Ind. Crops & Prod.* **28**:199-205
- Gutiérrez, A., del Río, J.C., González-Vila, F.J., Martín, F. (1998) "Analysis of lipophilic extractives from wood and pitch deposits by solid-phase extraction and gas chromatography" *J. Chromatogr. A* **823**:449-455
- Faix, O., Meier, D., Fortmann, I. (1990) "Thermal degradation products of wood. A collection of electron-impact (EI) mass spectra of monomeric lignin derived products" *Holz Roh-Werkstoff* **48**:351-354
- Ralph, J., Hatfield, R.D. (1991) "Pyrolysis-GC/MS characterization of forage materials" *J. Agric. Food Chem.* **39**:1426-1437
- Capanema, E.A.; Balakshin, M.Y.; Kadla, J.F. (2005) "Quantitative characterization of a hardwood milled wood lignin by nuclear magnetic resonance spectroscopy" *J. Agric. Food Chem.* **53**:9639-9649
- Liitiä, T.M.; Maunu, S.L.; Hortling, B.; Toikka, M.; Kilpeläinen, I. (2003) "Analysis of technical lignins by two- and three-dimensional NMR spectroscopy" *J. Agric. Food Chem.* **51**:2136-2143
- Ralph, J., Marita, J.M., Ralph, S.A., Hatfield, R.D., Lu, F., Ede, R.M., Peng, J., Quideau, S., Helm, R.F., Grabber, J.H., Kim, H., Jimenez-Monteon, G., Zhang, Y., Jung, H.-J.G., Landucci, L.L., MacKay, J.J., Sederoff, R.R., Chapple, C., Boudet, A.M. (1999) "Solution-state NMR of lignin", in *Advances in lignocellulosics characterization* pp 55-108, Argyropoulos, D.S. (ed.), Tappi Press, Atlanta
- Ralph, S. A.; Ralph, J.; Landucci, L. *NMR database of lignin and cell wall model compounds*; US Forest Prod. Lab., One Gifford Pinchot Dr., Madison, WI 53705, (<http://ars.usda.gov/Services/docs.htm?docid=10491>) (accessed: January 2009), **2004**
- Rencoret, J., Marques, G., Gutiérrez, A., Ibarra, D., Li, J., Gellerstedt, G., Santos, J.I., Jiménez-Barbero, J., Martínez, A.T., del Río, J.C. (2008) "Structural characterization of milled wood lignin from different eucalypt species" *Holzforchung* **62**:514-526
- "Tappi Test Methods 2004-2005" (2004) Tappi Press, Norcross, GA 30092, USA
- Björkman, A. (1956) "Studies on finely divided wood. Part I. Extraction of lignin with neutral solvents" *Sven. Papperstidn.* **59**:477-485
- Gutiérrez, A., Rodríguez, I.M., del Río, J.C. (2006) "Chemical characterization of lignin and lipid fractions in industrial hemp bast fibers used for manufacturing high-quality paper pulps" *J. Agric. Food Chem.* **54**:2138-2144
- Gutiérrez, A., Rodríguez, I.M., del Río, J.C. (2004) "Chemical characterization of lignin and lipid fractions in kenaf bast fibers used for manufacturing high-quality papers" *J. Agric. Food Chem.* **52**:4764-4773
- Rencoret, J., Gutiérrez, A., del Río, J.C. (2007) "Lipid and lignin composition of woods from different eucalypt species" *Holzforchung* **61**:165-174
- del Río, J.C., Gutiérrez, A.; Martínez, A.T. (2004) "Identifying acetylated lignin units in non-wood fibers using pyrolysis-gas chromatography/mass spectrometry" *Rapid Commun. Mass Spectrom.* **18**:1181-1185
- Chang, H.-M., Sarkanen, K.V. (1973) "Species variation in lignin. Effect of species on the rate of kraft delignification" *Tappi* **56**:132-134
- Tsutsumi, Y., Kondo, R., Sakai, K., Imamura, H. (1995) "The difference of reactivity between syringyl lignin and guaiacyl lignin in alkaline systems" *Holzforchung* **49**:423-428
- González-Vila, F.J., Almendros, G., del Río, J.C., Martín, F., Gutiérrez, A., Romero, J. (1999) "Ease of delignification assessment of wood from different Eucalyptus species by pyrolysis (TMAH)-GC/MS and CP/MAS <sup>13</sup>C-NMR spectroscopy" *J. Anal. Appl. Pyrol.* **49**:295-305
- del Río, J.C., Gutiérrez, A., Hernando, M., Landín, P., Romero, J., Martínez, A.T. (2005) "Determining the influence of eucalypt lignin composition in paper pulp yield using Py-GC/MS" *J. Anal. Appl. Pyrol.* **74**:110-115