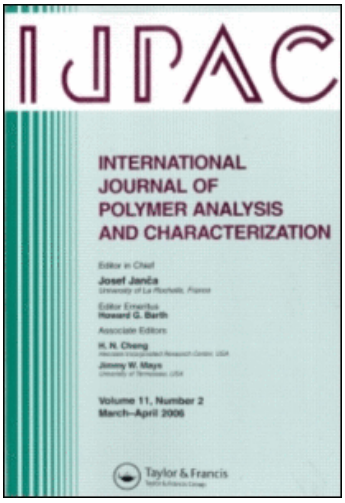

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Comparative and Structural Characterization of Organosolv and Alkali Lignins from Abaca Fiber

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In this study, one organosolv lignin preparation and two alkali lignin preparations were extracted with 95% ethanol, 1% NaOH from abaca fiber, and 17.5% NaOH from the fiber *holocellulose*, respectively. The three lignin preparations were compared using spectroscopic and degradative techniques. The very small chemical differences between the one organosolv lignin and two alkali lignin preparations were mainly that the organosolv lignin contained 3.70% neutral sugars and 1.88% uronic acids. The two alkali lignin preparations, however, were relatively free of neutral sugars and had lower uronic acid content. The weight-average molecular weights (M_w) of the lignins ranged between 2,160 and 3,340. All three lignin preparations showed a large proportion of syringyl units and fewer guaiacyl and *p*-hydroxyphenyl units. The lignin preparation B, extracted with 1% NaOH at 25°C for 0.5 h, is mainly composed of β-*O*-4 and β-β ether bonds, together with some β-β and β-5 carbon–carbon linkages between the lignin structural units. Furthermore, it was found that *p*-coumaric acids and uronic acids were esterified to lignin, while ferulic acids are etherified to lignin molecules.

Keywords: Abaca fiber; Organosolv lignin; Alkali lignin; Phenolic acids and aldehydes; FT-IR; ^{13}C-NMR; Molecular weight; Alkaline nitrobenzene oxidation

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INTRODUCTION

Based on environmental considerations, an increasing interest has been shown in applying natural fibers in preference to synthetic or chemically produced cellulose.[1] Abaca fibers, like flax fibers, have a number of unique properties, and especially their high fiber strength makes them particularly well-suited for industrial purposes. They contain approximately 60% cellulose and 21% hemicelluloses, but a low content of lignin, 12–16%. These qualities can be useful in the manufacturing of specialty papers, such as bag papers, cigarette papers, carbon papers, safety and banknote papers, filter papers, and tea bags.[2] To maximize the exploitation of this crop, a more complete understanding of its fiber composition and structure is required. This is particularly important for the associated lignins since the knowledge of lignin structure is important for controlling the pulping process and thus paper quality.

Lignin has a large molecular size and is closely associated with other cell-wall polymers, which makes isolation of representative lignin preparations difficult and handicaps analytical research on its structure.[3] There are a series of standard preparations that have traditionally been used in studies of lignin, but none of these methods facilitates the production of lignin preparations from straw and grass relatively free of associated polysaccharides. The lignins, obtained by a traditional ether precipitation method, contain much higher amounts of nonlignin materials such as polysaccharides, and cause losses of ether-soluble lignin. With extensive studies of the lignins from wheat straw,[4] oil palm,[5] and sugar beet pulp,[6] we have proposed an alternative two-step precipitation method to traditional ether precipitation procedure for the isolation and purification of alkali, ball milled, enzyme, and organosolv lignins, which are relatively free of associated polysaccharides. Moreover, several applications for the lignin obtained from fractionation and pulping processes have been considered. One of its main use so far has been as a phenol substitute in the formation of phenol–formaldehyde resins for board manufacture.[7–12] The chemical modification of lignin for use in the preparation of polyurethanes, acrylates, epoxies, polymer blends, and composites has also received considerable attention.[13] It is apparent that a thorough study and structural characterization of lignins from abaca fiber are necessary. This paper

describes the physicochemical properties and structural features of organosolv lignin and alkali lignins obtained from abaca fiber.

MATERIAL AND METHODS

Material

Abaca fiber was obtained from the Radcliffe Mill, England. The fibers were cut into 1–2 cm lengths, and then ground to pass a 0.7-mm screen.

Isolation of Organosolv and Alkali Lignins

Crude lipids were extracted using ethanol–toluene (1 : 2, v/v) in aoxhlet extractor for 6 h. The organosolv lignin was isolated from the dewaxed sample (50 g) using 95% ethanol (1,500 mL) in asoxhlet extractor for 4 h. After filtration and evaporation of ethanol, the solubilized organosolv lignin was obtained by direct precipitation of the aqueous solution at pH 1.5 with 20% HCl, and purified by ether precipitation. The residues were then delignified with sodium chlorite in acidic solution at 70°C for 2 h. The residual lignin was then extracted with 17.5% NaOH (4.2 g residue/100 mL extractant) at 20°C for 2 h from the *holocellulose*. After filtration, the filtrate was acidified to pH 5.5 with 20% HCl, concentrated with a rotary evaporator under reduced pressure at 40°C and then mixed with four volumes of ethanol. The precipitated hemicelluloses were filtered, washed with 70% ethanol, and air-dried. The residual alkali lignin was then obtained by precipitation of the supernatant solution at pH 1.5, and washed with acidified water (pH 2.0).

To obtain alkali-soluble lignin from undelignified sample, the ground abaca fiber was extracted with 1% NaOH at 25°C for 0.5 h (10 g fiber/600 mL extractant). The dissolved polysaccharides were recovered by precipitation of the neutralized hydrolysate in four volumes of ethanol. The solubilized alkali lignin was then precipitated at pH 1.5 with 20% HCl from the supernatant solution, and washed with acidified water (pH 2.0). The air-dried organosolv lignin, 1% NaOH soluble lignin, and 17.5% NaOH extracted residual lignin were labeled as fractions A, B, C, and kept in a refrigerator at 5°C until analysis.

Lignin Analysis

Neutral sugar composition in isolated lignin fractions was determined as alditol acetates.[14] Alkaline nitrobenzene oxidation of the lignins was performed at 170°C for 3 h. Methods of uronic acid analysis and determination of phenolic acids and aldehydes via HPLC of nitrobenzene oxidation mixtures have been described in previous papers.[4,15,16]

UV spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. A lignin sample (5 mg) was dissolved in 95% (v/v) dioxane–water (10 mL). A 1-mL aliquot was diluted to 10 mL with 50% (v/v) dioxane–water, and the spectrum between 240 and 400 nm was measured. FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet, 750) using a KBr disc containing 1% finely ground samples.

The molecular-weight averages of the lignin fractions were determined by gel permeation chromatography on a PLgel 5 μm Mixed-D column (Polymer Laboratories, Shropshire, UK). The samples were dissolved in tetrahydrofuran at a concentration of 0.2%, and 200 μL sample in solution was injected. The columns were operated at 40°C and eluted with tetrahydrofuran at a flow rate of 1 mL min^{-1}. The column was calibrated using polystyrene standards.

The solution-state ^{13}C-NMR spectrum was obtained on a Brucker 250 AC spectrometer operating in the FT mode at 62.4 MHz under total proton decoupled conditions. It was recorded at 25°C from a 250 mg sample dissolved in 1.0 mL DMSO-d_6 after 30,000 scans. A 40° pulse flipping angle, a 3.0 μs pulse width and 0.85 s acquisition time were used.

RESULTS AND DISCUSSION

Delignification of wood and the annual plant in organic solvents ('organosolv pulping') has been the subject of considerable research activity since the idea was introduced early in the century and has generated increasing interest.[17] The advantages of the organosolv process over the Kraft process include higher pulp yield, ease of bleachability, low capital and production costs, and diminished environmental stress.[18] Previous studies have reported that hydrogen

ion concentration plays a very important role in delignification since lignin dissolution is expected to be preceded by the acid-catalyzed cleavage of α-aryl and β-aryl ether linkages in the lignin macromolecule.[19] In Table I, the yield of dissolved lignins resulting from the three different procedures was expressed as a percentage of the total lignin determined by acidic sodium chlorite oxidation ($\sim$12%). As can be seen, the yield of organosolv lignin, extracted with 95% ethanol in asoxhlet apparatus for 4 h from dewaxed abaca fiber, was low (4.8%), as compared to the yield (27.9%) of organosolv lignin obtained from wheat straw by using ethanol–water (60/40, v/v) and 0.1 N H_2SO_4 as a catalyst at 75°C for 2 h.[20] The reason for this low yield of lignin is probably due to the lack of acid catalyzation. In addition, lignin condensation is probably encouraged at the high alcohol concentration of over 90%, resulting in a low rate of delignification. This trend has been reported previously for organosolv pulping from wood samples.[19] The authors stated that delignification increased with decreasing ethanol concentration over the range studied (50–70%, v/v). Optimum selectivity in terms of delignification and pulp viscosity was obtained at 60% ethanol concentration.

During the alkaline extraction process, some alkali-labile linkages between lignin molecules, or between lignin and polysaccharides, might be broken by alkali. Acidic moieties such as carboxylic or phenolic groups, ionized in alkaline solution, might also promote the solubilization of the lignin, either by increasing the solubility of individual fragments or by inducing swelling of the cell wall.[21] As expected, 1% NaOH treatment at 25°C for 0.5 h produced a dissolution of 6.9% total lignin. Further studies showed that extension of

TABLE I Yield of dissolved lignin (% acidic chlorite lignin) and the contents of neutral sugars and uronic acids (% lignin, w/w)

Lignin fractions	*Yield* (%)	*Neutral sugars* (%)					*Uronic acids* (%)
		Ara	*Xyl*	*Man*	*Glc*	*Gal*	
A[a]	4.8	0.18	1.70	0.20	1.14	0.48	1.88
B[b]	6.9	ND[d]	0.20	trace	trace	ND	1.22
C[c]	1.0	trace	0.10	trace	trace	ND	0.88

[a] Extracted with 95% ethanol in aoxhlet apparatus for 4 h from dewaxed abaca fiber.
[b] Extracted with 1% NaOH at 25°C for 0.5 h from abaca fiber.
[c] Extracted with 17.5% NaOH at 20°C for 2 h from abaca fiber holocellulose.
[d] Not detected.

alkaline-treatment time, or increases of either treatment temperature or alkali concentration resulted in a significant increase of dissolution of lignin (data not shown). The current yield of dissolved lignin was much higher than the alkali lignin obtained from wheat straw in our previous studies.[4] We reported that the yield of lignin, released during the 1.5% NaOH treatment of wheat straw at 20°C for 0.5 h, was only 2.6%. The reason for this higher solubility of alkali lignin obtained from abaca fiber was probably due to the higher amounts of ester-linked hydroxycinnamic acids, such as *p*-coumaric acid and ferulic acid in abaca fiber cell walls, which may play an important role in the high extraction of the lignins.[3] After delignification with sodium chlorite in acidic solution at 70°C for 2 h, the residual lignin, solubilized during the extraction of hemicelluloses with 17.5% NaOH at 20°C for 2 h, was rather low (1.0%), suggesting that nearly all of the lignin was degraded or oxidized under the delignification condition given.

The contents of neutral sugars and uronic acids in the isolated three lignin fractions are also given in Table II. As can be seen, the fraction A contained relatively low neutral sugars (3.70%), suggesting that the bonds anchoring lignin to polysaccharides in abaca fiber cell walls are readily hydrolyzed under the organosolv condition. This is in agreement with the hypothesis that these bonds consist of ether linkages between the polysaccharides and the α-carbon atoms of lignin side chains since ether bonds are known to be more readily hydrolyzed

TABLE II The yield (% lignin, w/w) of phenolic acids and aldehydes from the alkaline nitrobenzene oxidation of lignin fractions isolated from abaca fiber

Phenolic acids and aldehydes	*Lignin fractions*		
	A[a]	*B*[b]	*C*[c]
p-hydroxybenzoic acid	0.94	0.072	trace
p-hydroxybenzaldehyde	3.99	3.93	0.95
vanillic acid	0.26	0.30	0.13
syringic acid	0.80	1.03	0.34
vanillin	2.52	2.38	0.87
syringaldehyde	10.35	13.47	2.93
p-coumaric acid	0.0041	0.0083	ND
ferulic acid	ND[d]	trace	ND
Total	18.90	21.19	5.22

[a]Extracted with 95% ethanol in aoxhlet apparatus for 4 h from dewaxed abaca fiber.
[b]Extracted with 1% NaOH at 25°C for 0.5 h from abaca fiber.
[c]Extracted with 17.5% NaOH at 20°C for 2 h from abaca fiber holocellulose.
[d]Not detectable.

than the β-*O*-4 bonds during the organosolv process.[17] Xylose and glucose were found as the major sugar components, together with galactose, arabinose and mannose as the secondary monosaccharides. As compared to the organosolv lignin (fraction A), it is observed that the two alkali lignins (fractions B and C) are relatively free of neutral sugars, indicating that the alkali treatment can peel off the lignins from most of their neighboring polysaccharide moieties. The relatively high content of uronic acids in all the isolated three lignin fractions implied the appearance of ester bonds between glucuronic or galacturonic acid and lignin units, which was confirmed by a signal at 174.7 ppm in the ^{13}C-NMR spectrum (Figure 4).

The UV absorption spectra of three lignins are shown in Figure 1. The spectra showed well-known lignin characteristics such as the two maxima at 280 and 314 nm. The first absorption maximum originates from nonconjugated phenolic groups (aromatic ring) in lignin, and the second maximum at 312 nm attributes to the conjugated phenolic groups in hydroxycinnamic acids, such as ferulic and *p*-coumaric acids.[21,22] The relatively lower absorption, particularly at 312 nm in lignin fraction B, resulted from the cleavage of more ester or ether bonds between hydroxycinnamic acids and lignin during the alkali extraction process since this peak disappeared completely in the lignin fraction C, isolated with a much higher concentration of alkali (17.5% NaOH) at 20°C for 2 h from abaca fiber *holocellulose*.

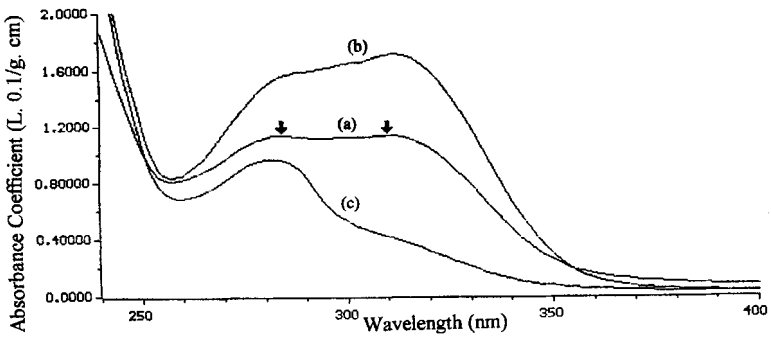

FIGURE 1 UV spectra of lignin fractions: (a) extracted with 95% ethanol for 4 h from dewaxed abaca fiber; (b) extracted with 1% NaOH at 25°C for 0.5 h from abaca fiber; (c) extracted with 17.5% NaOH at 20°C for 2 h from holocellulose.

To gain insight into the lignin and for comparison purposes, the isolated three lignin fractions were also investigated by nitrobenzene oxidation, and the results are given in Table II. As can be observed, the molar ratios of phenolic acids and aldehydes in three lignin fractions were not significantly different, indicating the same original lignin. The predominant degradation product, syringaldehyde, results from the degradation of noncondensed syringyl (S) units. The presence of small quantities of vanillins is due to the degradation of noncondensed guaiacyl (G) units. The occurrence of a low amount of *p*-hydroxybenzaldehyde is considered most probably to be indicative of noncondensed *p*-hydroxyphenyl (H) units with the lignin 'core'. The occurrence of a large proportion of noncondensed S units and fewer G and H units in the isolated lignin preparations implied that these three lignins can be justified as SGH-lignin, such as straw or grass type lignin. The presence of rather low contents of syringic acid, vanillic acid, and *p*-hydroxybenzoic acid results from the further oxidation of the corresponding benzaldehydes, syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde. As compared to the corresponding yields of wood lignins, the lower yields of alkaline nitrobenzene oxidation of the three lignin fractions indicated a higher degree of condensation of these lignin preparations. The lignin fraction C, isolated with 17.5% NaOH at 20°C for 2 h from the abaca fiber *holocellulose*, produced the lowest yield (5.22%) of phenolic monomers, implying a high degree of condensation of the residual lignin fraction.

The recovery yields of ferulic and *p*-coumaric acids, detected in the products of the alkaline nitrobenzene oxidation, decreased with increase in temperature and reaction time for both wheat straw internodes and leaves. Ferulic acid was not detected among the oxidation products after 4 h at 170°C or 2 h at 180°C, and the molar content in ferulic acid corresponded to an equivalent molar increase in vanillin.[23] These results suggested that nearby all of the ferulic acids were quantitatively oxidized to vanillin by nitrobenzene under the reaction conditions given in our studies (170°C, 3 h), as shown by the disappearance of ferulic acid in the three nitrobenzene oxidation mixtures. Similarly, most of the *p*-coumaric acids appeared to be quantitatively oxidized to *p*-hydroxybenzaldehyde under the conditions of the alkaline nitrobenzene oxidation as shown by the trace of *p*-coumaric acid in the nitrobenzene oxidation products (Table II).

The weight-average (M_w) and number-average (M_n) molecular weights, and polydispersity (M_w/M_n) of the three lignin preparations were computed from their chromatograms and are given in Table III. The data showed that the three lignin preparations had the weight-average molecular weights (M_w) between 2,160 and 3,340 g/mol. A lower molecular weight of lignin fraction C was probably due to the extensive cleavage of the interunit linkages in lignin molecules during a high concentration of alkali treatment processes. The three lignin fractions also gave a fairly similar elution pattern (see Figure 2 as an example) showing a wide molecular weight range from 770 to 34,700 g/mol.

TABLE III The weight-average (M_w) and number-average (M_n) molecular weights, and the polydispersity (M_w/M_n) of lignin fractions isolated from abaca fiber

Lignin fractions	M_w	M_n	M_w/M_n
A[a]	2,460	1,810	1.36
B[b]	3,340	1,750	1.91
C[c]	2,160	1,540	1.40

[a]Extracted with 95% ethanol in aoxhlet apparatus for 4 h from dewaxed abaca fiber.
[b]Extracted with 1% NaOH at 25°C for 0.5 h from abaca fiber.
[c]Extracted with 17.5% NaOH at 20°C for 2 h from abaca fiber holocellulose.

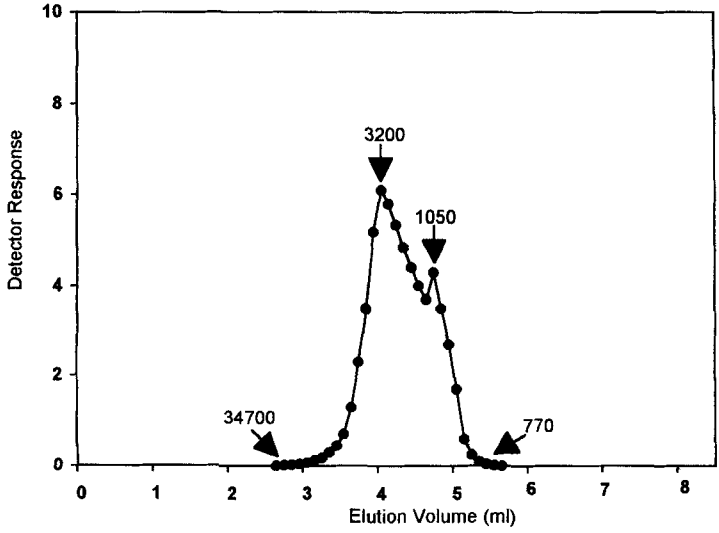

FIGURE 2 GPC molecular weight distribution of lignin fraction isolated by 95% ethanol for 4 h from dewaxed abaca fiber.

The elution maximum corresponded to polystyrene molecular weight 3,200. The small second peak corresponded to low molecular components.

The FT-IR spectra of the three lignin preparations are shown in Figure 3. There are no significantly distinct differences among the spectra. The absorbance at 1718 cm^{-1} can be assigned to the unconjugated ketone and unconjugated carbonyl groups.[5] Aromatic skeleton vibrations in the three lignin fractions are assigned at 1600, 1510, and 1424 cm^{-1} (1412 cm^{-1} in fraction B). Absorption at 1464 cm^{-1} indicates the C–H deformations and aromatic ring vibrations. The strong intensities of the bonds at 1330, 1230, and 1130 cm^{-1} are associated with syringyl structures in lignin molecules, while the relative intensities of the bands at 1230 and 1040 cm^{-1} are associated with guaiacyl units in lignin molecules. The spectra of the organosolv lignin also show two other absorbances at 1370 and 1267 cm^{-1}, which correspond to aliphatic C–H stretch in $-CH_3$ and guaiacyl ring breathing with CO stretching, respectively. However, these two absorbances are lacking in the two alkali lignin spectra. A band at 1165 cm^{-1} corresponds to C=O ester groups in conjugation with an aromatic ring.

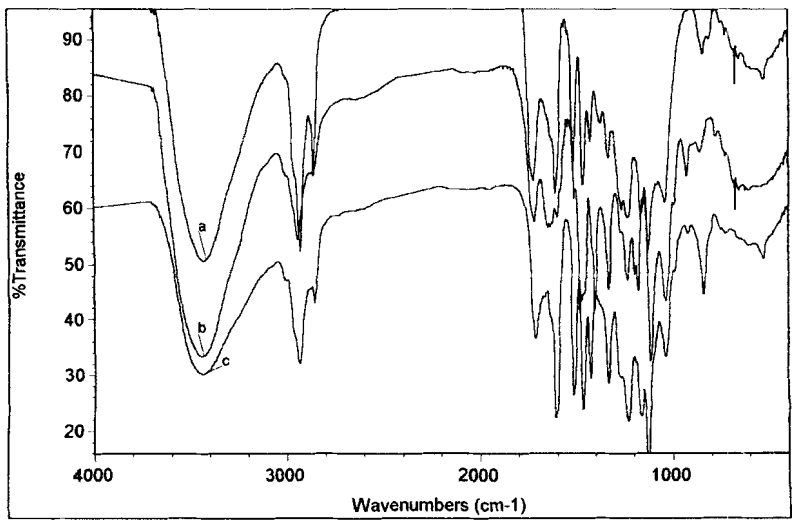

FIGURE 3 FT-IR spectra of lignin fractions: (a) extracted with 95% ethanol from dewaxed abaca fiber; (b) extracted with 1% NaOH at 25°C for 0.5 h from abaca fiber; (c) extracted with 17.5% NaOH at 20°C for 2 h from the abaca fiber holocellulose.

Aromatic C–H out of bending can be identified with a band at 838 cm^{-1}.

The alkali lignin fraction, isolated by 1% NaOH at 25°C for 0.5 h, was also studied by ^{13}C-NMR spectroscopy (Figure 4). Most of the observed signals have been previously assigned in straw and wood lignin spectra.[22,24–29] As expected, the most striking characteristic of the ^{13}C-NMR spectrum is the absence of typical neutral polysaccharide signals between 57 and 103 ppm. This is undoubtedly due to the removal of associated neutral polysaccharides in the alkali lignin fraction B, which was isolated by using a two-step precipitation method. The carbonyl resonances from uronic acids and esters may contribute to the signal at 174.7 ppm, which corresponds to C-6 in methyl uronates.[24]

The region between 104.3 and 160.0 ppm can be assigned to the aromatic part of the lignin. The syringyl (S) residues were indicated by signals at 152.2 (C-3/C-5, S), 138.2 (C-4, S etherified), 134.3 (C-1, S etherified), 132.9 (C-1, S nonetherified), 106.8 (C-2/C-6, S with α-CO), and 104.3 ppm (C-2/C-6, S). Guaiacyl (G) residues gave signals at 149.3 (C-3, G etherified), 147.6 (C-4, G), 134.3 (C-1, G etherified), 132.9 (C-1, G nonetherified), 119.5 (C-6, G), and 115.0 ppm (C-5, G). The *p*-hydroxyphenyl (H) residues appeared as a signal at 127.9 ppm (C-2/C-6, H). These signals confirmed that the alkali lignin fraction B could be justified as SGH-lignin. The signals at 166.5 and 165.7 (C-γ, PC ester), 159.8 (C-4, PC ester), 130.2 and 129.8 (C-2/C-6, PC ester), 125.3 and 125.1 (C-1, PC ester), and 115.9 and 115.4 ppm (C-3/C-5, PC ester) represented the esterified *p*-coumaric acid. Etherified ferulic acid was observed with three signals at 168.1 and 167.1 (C-γ, FE ether), and 144.3 ppm (C-α, FE ether). Therefore, it seems very likely that the *p*-coumaric acids were linked to lignin by ester bonds, while the ferulic acids are linked to lignin by ether bonds.

The major ether linkages between lignin structural units are identified as β-*O*-4 ether bonds by signals at 72.3 (C-α in β-*O*-4), 86.2 (C-β in β-*O*-4), and 60.1 and 59.7 ppm (C-γ in β-*O*-4). The etherified β-5 bonds are also identified by a small signal at 52.3 ppm (C-β in β-5 ether). The less common β-β (C-β in β-β units, 55.0 ppm) and β-5 (C-4 in β-5 units, 144.3 ppm, overlapped with C-α, FE ether) carbon–carbon linkages were also present. These signals indicated that the alkali lignin is mainly composed of β-*O*-4 and β-5 ether bonds,

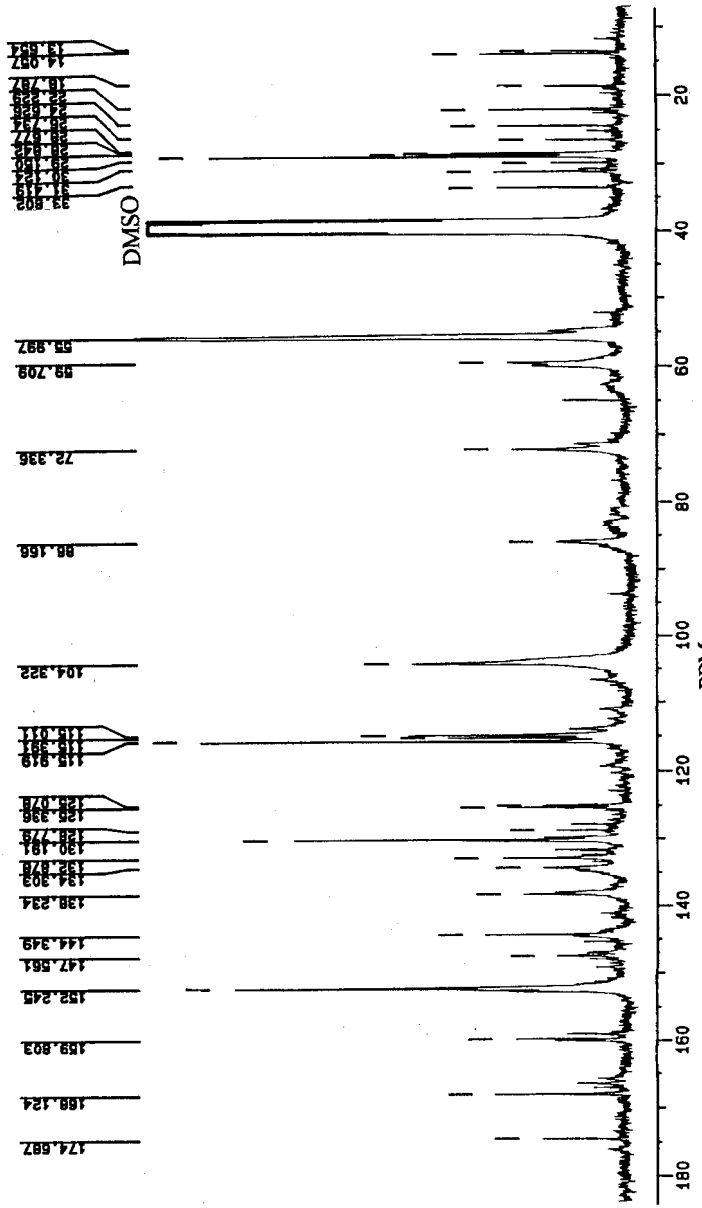

FIGURE 4 ^{13}C-NMR spectrum of lignin fraction isolated by 1% NaOH at 25°C for 0.5 h from abaca fiber.

together with small amounts of β-β and β-5 carbon–carbon linkages. The signals representing the γ-methyl, α- and β-methylene groups in n-propyl side chains appeared in the spectrum between 13.7 and 33.8 ppm. A very strong signal at 56.0 ppm corresponded to the OCH_3 in syringyl and guaiacyl units.

CONCLUSIONS

Apart from the differences in the extraction yield, the organosolv lignin, obtained by a direct one-step precipitation method, contained 3.70% neutral sugars and 1.88% uronic acids, while the two alkali lignin preparations, obtained by a two-step precipitation method, were relatively free of neutral sugars. The results obtained by alkaline nitrobenzene oxidation showed that all the three lignin preparations contained a large proportion of noncondensed syringyl units with small amounts of noncondensed guaiacyl and *p*-hydroxyphenyl units. They seem more condensed than the wood lignins. Meanwhile, the lignins in abaca fiber cell walls appeared to be closely associated with hydroxycinnamic acids and uronic acids. *p*-Coumaric acids and uronic acids were found to be esterified to lignin, whereas the ferulic acids are linked by their phenolic groups via ether bonds to lignin. The lignin preparation B is mainly composed of β-*O*-4 and β-5 ether bonds between the lignin structural units. The less common β-β and β-5 carbon–carbon linkages were also found to be present in lignin molecules.

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