Coconut Husk Lignin. II. Characterization by Infrared and Nuclear Magnetic Resonance Spectroscopy

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SYNOPSIS

Results of the characterization of coconut husk lignin by infrared (IR) and proton nuclear magnetic resonance (H-NMR) spectroscopy are presented. Lignin was extracted with both alkaline and organosolv liquors. The IR spectra of dioxane lignin were very similar to those reported for hardwood lignins. Furthermore, these results combined with those obtained from the H-NMR studies suggest that coconut husk lignin can be classified into the Lm-type lignins. These lignins are characteristic of the monocotyledon class, of which the coconut palm is a member. The H-NMR studies showed that anthraquinone significantly inhibited the occurrence of lignin condensation during the alkaline extraction with sodium hydroxide solutions. This inhibition was more intense in the lignin extracted at 150°C than in that extracted at 100°C.

INTRODUCTION

The characterization of lignin, one of the most abundant plant constituents, has recently been the subject of much interest. It is obtained during the process to prepare cellulosic or modified pulp[1] and is used as a component in many applications.[2] For many years the characterization of lignin has presented a great challenge for chemists due to its complex and varied structure and diverse molecular weight. Nevertheless, by means of a great deal of laboratory work and the use of powerful and sophisticated analytical methods, the characterization of lignin, to varying degrees of depth, has been achieved.[3-6] The coconut husk (the fibrous covering of the fruit of the coconut palm, an angiosperm that belongs to the monocotyledon class), a by-product of the copra extraction process, is used to a small degree in a variety of areas.[7] One such area is the manufacture of particle board in which the lignin present acts as an adhesive.[8] An attempt has been made to include an extract of the coconut husk in the formulation of reinforced plastics,[9] but the lignin has not been sufficiently characterized.

This article presents the results obtained of the characterization by IR spectroscopy of coconut husk lignin extracted with alkaline solutions and organosolv systems (aqueous organic solvents). Lignins extracted with aqueous sodium hydroxide and with dioxane–water were selected for further characterization by H-NMR. Selection was based on the high yields obtained by using these alkaline systems[10] and the fact that the dioxane–water lignin is considered to be the most representative of the lignin naturally present in lignocellulosic matter.[11]

EXPERIMENTAL

Lignin Extraction

Lignin was extracted from coconut husk using the procedure reported previously;[10] the experimental conditions are summarized in Table I. The acetylation and reduction of the lignins were carried out using the methods given in the same reference.[10]

IR and NMR Spectroscopy

IR spectra were obtained on an IR spectrophotometer (Perkin-Elmer 683), using a KBr disc contain-

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Table I Composition of Liquors Used for Coconut Husk Lignin Extraction[a]

Nomenclature	System	Concentration by Wt or Ratio	Temperature (°C)	Time (h)	Other Additives
L-1	Aq. NaOH	2%	100	5	None
L-2	Aq. NaOH	2%	100	5	0.1% Aq
L-3	Aq. NaOH	2%	160	5	None
L-4	Aq. NaOH	2%	150	5	0.1% AQ
L-5	Dioxane–water	9 : 1 (v/v)	100	8	0.025N HCl
L-6	Aq. NH_4OH	5%	100	3	None
L-7	Aq. NH_4OH	5%	150	3	None
L-8	Butanol–water	1 : 1 (v/v)	170	5	1% HCl
L-9	Aq. Na_2SO_3 and $NaHSO_3$	12.5 and 3%, respect.	180	5	None
L-10	Ethylene glycol–water	4 : 1 (v/v)	120	7	1% HCl
L-11	Ethanol–water	1 : 1 (v/v)	80	7	1% HCl

[a] Aq. = aqueous; AQ = anthraquinone.

ing either 1% finely ground coconut husk or 0.4% extracted lignin. Samples were previously vacuum dried at 120°C. The H-NMR spectra of the chloroform-soluble acetylated fractions of lignin were obtained at ambient temperature using deuterated chloroform as the solvent, TMS as internal reference, and an NMR spectrometer (Varian EM-390) with frequency 60 MHz, sweep width 10 ppm, sweep time 5 min, spectrum amplitude 2.5 × 1000, filter 0.05 s, and RF power 0.04 mG.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The analysis of the chemical structure of lignin has been the subject of extensive research in the past.[1] Various spectroscopic methods (UV, IR, H-NMR, ^{13}C-NMR, etc.) combined with chemical derivatization, depolymerization techniques, and chromatographic separation have been applied for this purpose.[1,12–14] Characterization of lignin model compounds has been a very important route to establish criteria for interpreting the complex spectra obtained with the above spectroscopic methods.[15–20] So, to assign the different bands in the IR spectra of the extracted lignins (Figs. 1–5) and to discuss these results, the criterion summarized by Hergert[17] was followed. This criterion is based on a great deal of IR studies on lignins and lignin model compounds, which have been reported by many researches. The most important IR bands of the lignins studied in this work are included in Table II.

The band at 1500 cm^{-1}, assigned to aromatic skeletal vibrations, is used as a reference to determine whether the lignin is guaiacyl or syringyl in nature.[18] The band at 1600 cm^{-1} on the coconut husk lignin spectrum is much more intense than that at 1500 cm^{-1} (Fig. 1). Also, the intensity of the bands at 1130, 1235, 1430, 1470, and 1600 cm^{-1}, assigned to the vibrations in the syringyl rings, is higher than that occurring at 1500 cm^{-1}, while that at 1275 cm^{-1}, corresponding to a guaiacyl ring vibration,[17] is relatively weaker. These results are characteristic of L-type lignins having a higher syringyl content.[18] L-type lignins are those encountered in hardwoods (angiosperms) and monocotyledon plants.[18,21–25] In fact, the IR spectrum of coconut husk (Fig. 1) re-

Table II Assignment of Infrared Absorption Bands of Lignins[a]

Group Vibrations	ν OH	ν C—H	ν C=O	ν ϕ	δ C—H	ν ϕ-G	ν C—O	ν C—O—C	δ C—O
Band position (cm^{-1})	3630–2980	2900	1690	1600 1500 1440	1370	1260	1210	1110	1020

[a] ν = stretching vibrations; δ = wagging vibrations; ϕ = aromatic ring; G = guaiacyl unit.

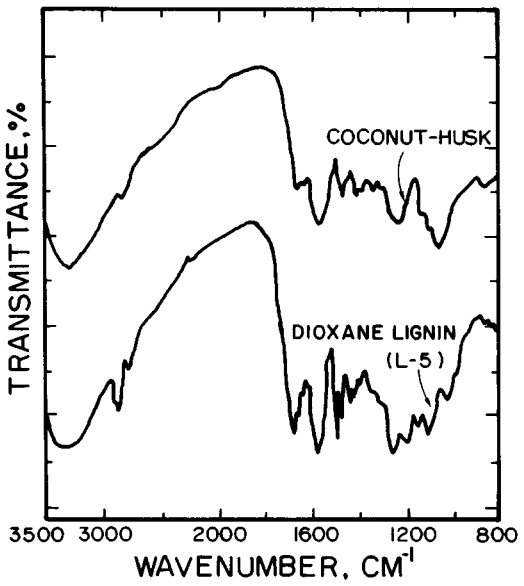

Figure 1 IR spectra of coconut husk and dioxane lignin.

sembles very well in its general features those reported for hardwood lignins,[26] which is an expected result taking into account that coconut palms are monocotyledon plants. In contrast, guaiacyl-type lignins, which are present in softwoods (gimnosperms), show the opposite behavior, the band at 1500 cm^{-1} being weaker than that at 1275 cm^{-1}. In the following paragraphs, some differences observed in the IR spectra of coconut husk lignins are discussed in more detail.

Lignins containing both guaiacyl and syringyl nuclei show a complex mixture of bands in the 1400–1000 cm^{-1} region but it is usually possible to distinguish them from softwood lignins on the basis of their relative band intensities. In softwood lignins the 1270 cm^{-1} band is more intense than that at 1230 cm^{-1}, and the 1035 cm^{-1} band is equal to or greater than the 1140 cm^{-1} band, while the reverse is true for hardwood lignins.[17] In the IR spectrum of L-5 (dioxane lignin) the 1025 cm^{-1} band is weaker than that at 1130 cm^{-1}, but the 1270 cm^{-1} band is more intense than that at 1220 cm^{-1}. Therefore, coconut husk lignin cannot be rigorously classified as guaiacyl–syringyl type (L-type lignins). However, the intensity of these bands could be affected by the low methoxyl content in these lignins (Tables III–V). This could indicate a higher content of *p*-hydroxyphenyl structures than normally present in typical hardwoods thus impeding the application of the above criteria for lignin classification.

The spectrum of powdered coconut husk possesses the same features as that of the extracted lignin, except for a carbonyl band at 1750 cm^{-1}, attributable to ester groups, and strong bands in the 1200–1000 cm^{-1} region, which can be ascribed to the carbohydrates present in the husk.

It can be seen in Figure 2 that the intensities of the 1270 and 1210 cm^{-1} bands in the spectra of the organosolv and sulfite lignins are different to those of the alkaline lignins. Since the 1270 cm^{-1} band has been assigned to coupling of the guaiacyl ring stretching band with that of the carbonyl group,[17] it may be assumed that the difference in relative intensity of the bands results from the higher proportion of guaiacyl nuclei in the organosolv lignins. Further research is presently being carried out to confirm this statement.

In the spectrum of the lignin obtained with butanol–water at boiling point, the characteristic band of aromatic rings is not clearly observed. In view of this, the sample cannot be considered as being representative of coconut husk lignin. This result may be due to the sample extract containing a low proportion of lignin relative to the carbohydrates present.

The broad band between 3600 and 3000 cm^{-1}, corresponding to vibrations of the hydroxyl groups,

Table III Relative Amounts of Several Types of Protons in H-NMR Spectra of Acetylated Lignins

Proton Types	δ (ppm)	Lignin[a]				
		L-1	L-2	L-3	L-4	L-5
Aromatic	6.3–7.5	—	—	4	19	24
Methoxyl	3.3–4.2	12	6	10	27	26
Aromatic acetoxyl	2.2–2.4	8	6	11	14	14
Aliphatic acetoxyl	1.7–2.2	10	3	11	20	18
Higly shielded aliphatic	0.7–1.7	74	22	48	22	18

[a] Nomenclature of lignin type as in Table I.

Table IV Relative Amounts of Some Functional Groups as Estimated from Table III

	Acetoxyls			
Lignin[a]	Total	Aromatic	Aliphatic	Methoxyls
L-1	5.9	2.6	3.3	4.0
L-2	3.0	2.0	1.0	2.0
L-3	7.3	3.6	3.7	3.3
L-4	11.4	4.7	6.7	9.0
L-5	10.7	4.7	6.0	8.7

[a] Nomenclature of lignin type as in Table I.

appears to be slightly stronger for the lignins extracted with NaOH, NaOH–anthraquinone (NaOH–AQ), and NH_4OH, particularly so in the last case. This may be due to the ability of these systems to generate more hydroxyl groups than the organosolv systems;[27] therefore this band cannot be used for hydroxyl group quantification.

Methine, methylene, and methyl group vibrations appear in the 2900 cm^{-1} region and are always present as shoulders in all lignin spectra. However, in the NaOH lignin spectrum only a small peak can be detected while for the lignin extracted with *n*-butanol–water–HCl (170°C, 5 h) the peak is very strong. This may result from a butanol–lignin reaction similar to that reported in the ethanol–water–HCl system in which a significant portion of α-hydroxyls of lignin reacts with ethanol thus forming ether linkages.[28]

The carbonyl group band for ketones or aldehydes, observed between 1700 and 1670 cm^{-1}, is strong in the lignins extracted with NaOH but very weak in the NH_4OH-extracted samples and in those isolated with ethylene glycol and ethanol. For the samples in which *n*-butanol was used as the extracting medium, a very strong carbonyl band is observed at 1710 cm^{-1}. This is coupled with an increase in the methylene and methyl signals as previously mentioned. The broad band between 330 and 360 nm observed in the UV spectra of these lignins[10] must correspond to the conjugated carbonyl groups on the backbone.[29]

The reaction of the alkaline-extracted and the dioxane–water-extracted lignins with sodium borohydride caused a significant decrease in the intensity of the 1690 and 1600 cm^{-1} bands, as can be seen in Figure 3. This result indicates that some of the carbonyl groups, probably those that were nonconjugated, have been reduced, whereas the conjugated groups have not. In the IR spectra of the lignin extracted with the NaOH–AQ system the relative intensity of the 1700 and the 1500 cm^{-1} bands was retained. This is consistent with the reducing character of anthrahydroquinone.[30] Hence the sodium borohydride treatment does not further affect the number of carbonyl groups of this lignin.

In the IR spectra of acetylated lignins, two bands of approximately the same intensity appear at 1750 and 1720 cm^{-1}. These bands can be respectively assigned to the phenolic and alkyl esters generated by the acetylation reaction (Fig. 4). It must also be pointed out that the chloroform-soluble acetylated lignin fractions show stronger carbonyl bands than their insoluble counterparts (Fig. 5). This result indicates that the chloroform-soluble fractions have a higher degree of acetylation than the insoluble fractions, which may be a consequence of both a difference in the hydroxyl content and a difference

Table V Relative Amounts of Some Functional Groups in Lignins as Estimated from Tables III and IV, and the Total Hydroxyl Content from Ref. 10

	Hydroxyl Content						
	Phenolic		Aliphatic		Methoxyl Content		
Lignin[a]	Wt %	(OH/C-9)[b]	Wt %	(OH/C-9)	Wt %	(MeO/C-9)	Aromatic Protons (H_{Ar}/C-9)
L-1	4.8	0.50	6.0	0.65	7.3	0.76	—
L-2	4.9	0.52	2.4	0.26	4.9	0.52	—
L-3	4.3	0.44	4.3	0.46	3.9	0.40	0.82
L-4	2.7	0.29	3.9	0.41	5.2	0.54	1.95
L-5	2.1	0.22	2.8	0.30	4.0	0.42	1.95

[a] Nomenclature of lignin type as in Table I.
[b] C-9 = number of functional group per phenylpropane unit.

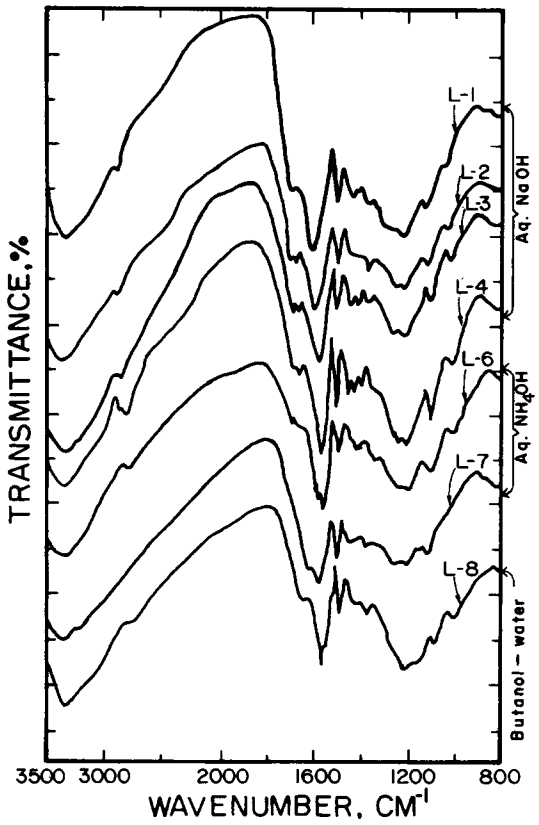

Figure 2(a) IR spectra of alkaline and sulfite lignins (spectra are shifted on vertical axis for clarity. Extraction media are also indicated on the right vertical axis).

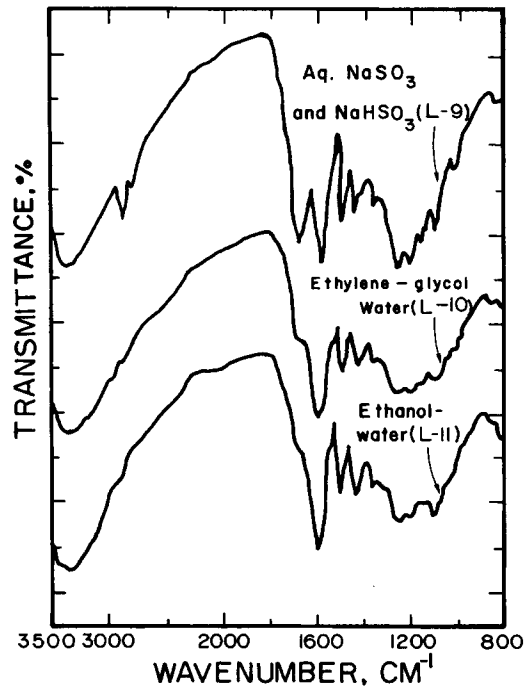

Figure 2(b) IR spectra of organosolv lignin (spectra are shifted on vertical axis for clarity. Extraction media are also on the right axis).

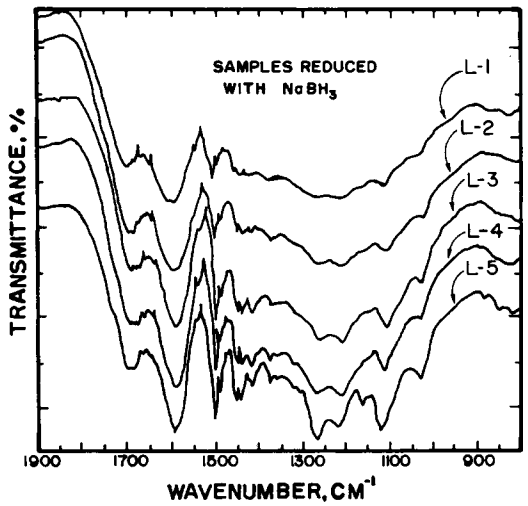

Figure 3 IR spectra of lignins reduced with sodium borohydride.

in their degree of condensation, as has been reported,[10] the latter factor being associated with a difference in the accessibility for the acetylating mixture.[31,32]

In all IR spectra of the extracted lignins, as well as in those of acetylated lignins, a doublet is present at 1500 cm^{-1}. This doublet is very strong in dioxane lignin (L-5) but very weak in NaOH–AQ lignin (L-4). As expected, the intensity in NaOH–AQ lignin remains unaltered even after reduction and acetylation of the substrate. This doublet is characteristic of the stretching vibration of the aromatic (guaiacyl and syringyl) units in lignin.[17]

A strong band at 1200 cm^{-1} in the acetylated lignin spectra corresponds to the stretching vibrations

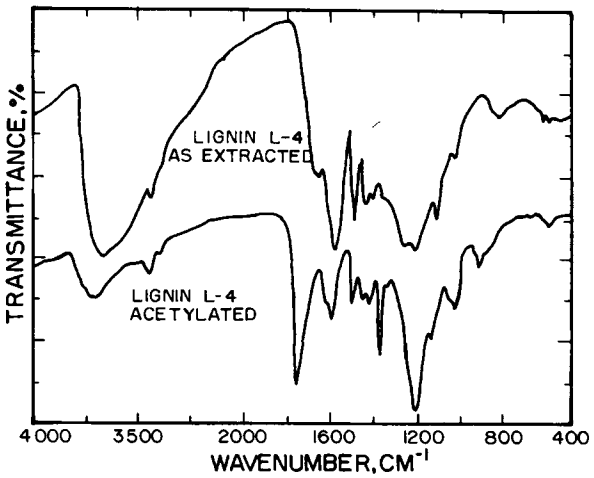

Figure 4 IR spectra of NaOH–AQ (150°C) lignin (L-4) and its acetate.

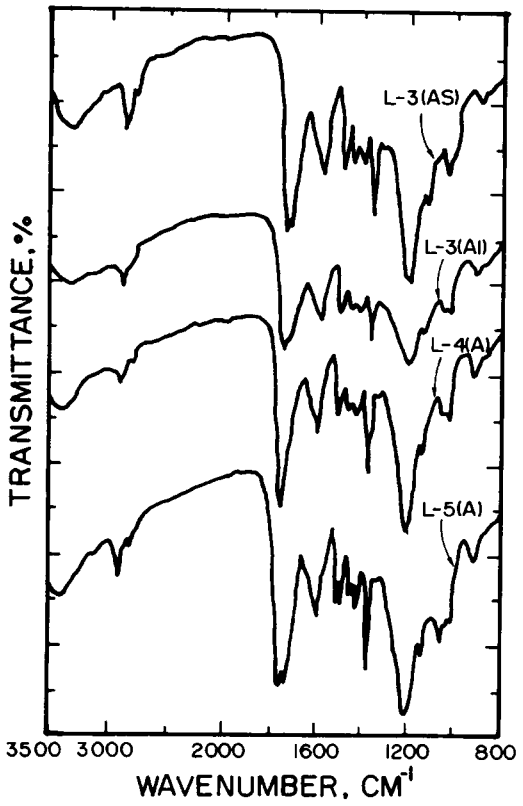

Figure 5 IR spectra of acetylated lignins. A = acetylated, S = chloroform-soluble fraction, I = chloroform-insoluble fraction.

of the ester C–O bond. It was noted that the band at 1025 cm^{-1}, which might be assigned to primary hydroxyl vibration, did not disappear in the acetylated substrates. Therefore, with basis on the IR analysis of lignin model compounds,[17] this band was assigned as a vibration of an ether unit (Fig. 5 and Table II).

NMR Spectroscopy

The NMR spectra of the acetylated lignins extracted with NaOH (with and without anthraquinone) and dioxane–water are shown in Figure 6. The relative amounts of the different types of protons are given in Table III; assignments were carried out according to the table by Ludwig[19] adapted for acetylated lignins dissolved in deuterochloroform.

The H-NMR spectra (Fig. 6) and the data of Table III indicate that lignin extracted with NaOH at 100°C possesses a relatively large amount of highly shielded aliphatic protons (between 0.7 and 1.7 ppm). Taking into account that H-NMR spectra of coumarin-type lignin model compounds[19] show a similar feature in this region, one can assume that

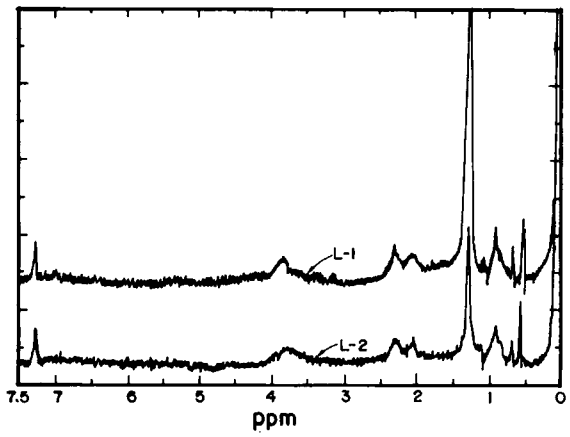

Figure 6(a) H-NMR spectra of chloroform-soluble fractions of acetylated lignins L-1 and L-2.

coumarin-like structures were generated by condensation of the lignin fragments, during the extraction of this lignin. In contrast, the lignins extracted with NaOH–AQ at 150°C or with dioxane–water show lower quantities of such protons, present in comparable amounts to those reported in other acetylated lignins.[19]

The aromatic and aliphatic acetoxyl–methyl group signals (2.2–2.4 and 1.7–2.2 ppm, respectively) are clearly defined in all the spectra with the exception of that of lignin extracted with NaOH at 160°C (L-3 in Fig. 6). Indeed, this spectrum contains four

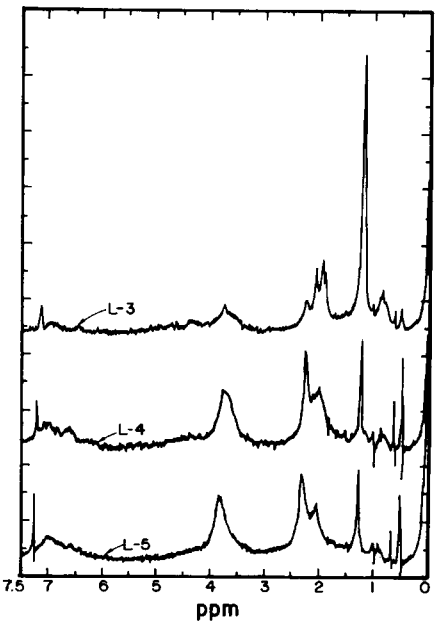

Figure 6(b) H-NMR spectra of chloroform-soluble fractions of acetylated lignins L-3 to L-5.

peaks in the acetoxyl–methyl group region similar to those present in the NMR spectrum of dilignols,[19] which have been used as lignin model compounds. It has been assumed that this effect is due to the presence of bulky aromatic acetoxyl groups in the ortho-position with respect to the 5–5 bonds between two aromatic rings of the dilignols, forcing the rings to remain in different planes and increasing the shielding on the aromatic acetoxyl groups. The acetoxyl–methyl groups are thus displaced toward the high field of the aliphatic acetoxyls.[19] Taking into account this study on these lignin model compounds, one can assume that dilignol-like structures taked place in the lignin extracted with NaOH at 160°C. In contrast, this effect was not observed in the NMR spectra of lignin obtained using the same system but at 150°C. These results are congruent with others already mentioned and indicate that anthraquinone prevents the formation of bonds between the 5–5 carbons of the aromatic rings of lignin (condensed structures) at relatively high delignification temperatures.

The content of methoxyl group protons and that of aromatic rings found in the chloroform-soluble acetylated fractions are higher for the NaOH–AQ (150°C) and dioxane–water extracted lignins (Fig. 6 and Table III). This confirms these fractions as lignin representative.

It is possible to semiquantitatively estimate the functional groups of lignin by using the number of protons calculated by integration of the NMR spectra.[20,33] This is particularly true when using the protons of the acetoxyl–methyl group since these are not subject to interference by other protons.[19,20] Thus, in order to estimate the percentage of methoxyl groups, at least in the lignins that yielded large chloroform-soluble fractions (NaOH–AQ at 150°C and dioxane–water extracted), the following method was used:

1. The number of acetoxyl groups was calculated by dividing the integrated acetoxyl–methyl protons by 3. The resulting value is approximately equal to the relative number of hydroxyls present in the corresponding lignin before acetylation.
2. The relative number of methoxyl groups was obtained by dividing the integrated number of methoxyl protons by 3.
3. Finally, the percentage of methoxyl groups (%MeO) of the lignin was calculated using the following equation:

$$(\%\mathrm{MeO}/\%\mathrm{OH}_{tot}) = (\mathrm{MeO}/\mathrm{Ac}) = R \quad (1)$$

where % OH_{tot} is the total percentage of hydroxyl groups determined by acetylation and potentiometric titration,[10] MeO and Ac are the relative numbers of methoxyl and acetoxyl groups, respectively, calculated in (1) and (2). Therefore, from Eq. (1), the percentage of methoxyl is calculated as follows:

$$\%\mathrm{MeO} = R(\%\mathrm{OH}_{tot}) \quad (2)$$

The number of phenolic and aliphatic hydroxyl groups of each C-9 unit was estimated by using the respective ratio of phenolic and aliphatic acetoxyl groups to the total acetoxyl groups from the NMR spectrum and using the value of OH_{tot} per C-9 unit from Ref. 10. Results of the calculations carried out are given in Tables IV and V.

It is possible to speculate on the type of units (i.e., syringyl, guaiacyl, and *p*-hydroxyphenyl units) that make up coconut husk lignin based on the mean value of methoxyl groups per C-9 unit reported in Table V, following the assumptions that the number of methyl groups are the same of the methoxyl groups.[12,33] Thus, if it is assumed that lignin does not contain *p*-hydroxyphenyl groups, the mean value of methoxyls per C-9 unit would be between 1 and 2, depending on the ratio of syringyl to guaiacyl groups. With this in mind, the mean number of 0.42 methoxyl groups per C-9 unit (Table V) for lignin extracted with dioxane–water indicates that dioxane–lignin (L-5) contains the three types of groups, that is, including the *p*-hydroxyphenyl groups. This result is consistent with the fact that both the previously discussed IR spectra and the NMR spectra of the extracted lignins are very similar to those of hardwood (angiosperms) lignins. With the basis on these results, coconut husk lignin can be classified as a Lm-type lignin having an appreciable proportion of *p*-hydroxyphenyl groups. This is characteristic of the lignins of the monocotyledon class,[1] of which the coconut palm is a member.[34,35] The values of 4.0 and 5.2% of the methoxyl groups estimated in the dioxane–water and NaOH–AQ (150°C) lignins, respectively, are lower than the 12.8% determined for lignin extracted from the nut shells of coconut using thioglycolic acid.[36] However, as it is well known, such variations may depend on the part of the plant selected for extraction of the lignin.

The phenolic hydroxyl content calculated from the data of the NMR spectra and total hydroxyl content of the lignins (Table V) are greater than those determined using the UV method.[10] This discrepancy may be due to interference of the carbonyls present in the lignin, this being a recognized dis-

advantage of the UV method.[37] The number of aromatic protons per C-9 unit (H_{Ar}/C-9) was calculated in a similar way as for the number of methoxyl groups per C-9 unit on the basis of the (OH_{tot}/C-9) values reported previously:[10]

$$(H_{Ar}/C\text{-}9) = (OH_{tot}/C\text{-}9)(H_{Ar}/Ac) \quad (3)$$

As can be seen in Table V, the H_{Ar}/C-9 values are lower than expected. However, integration of the NMR spectrum in the aromatic proton region also includes other types of protons and is not considered reliable. Nevertheless, it should be noted that these values show similar variations to those of the percentages of noncondensed phenolic units.[10] This indicates that the L-4 and L-5 lignins (extracted with NaOH–AQ at 150°C and dioxane–water, respectively) display a lower degree of condensation.

Qualitative comparisons can only be made of the data in Table V with the values of hydroxyl groups determined by the UV method[10] since these correspond to the chloroform-soluble fraction of acetylated lignin. These fractions were relatively low in the acetylated L-1, L-2, and L-3 lignins.

Finally, it can be seen that the quantity of phenolic hydroxyl groups is approximately equal to that of the aliphatic hydroxyl groups (Table V). This is consistent with the IR spectroscopy results for acetylated lignins, in which a doublet possessing approximately equal intensity bands appears at 1725 and 1750 cm^{-1}.

CONCLUSIONS

The fact that no reduction of carbonyl groups by sodium borohydride was observed in lignins obtained with anthraquinone concurs with the idea that anthraquinone reduces lignin during the delignification process thus avoiding significant changes in its chemical structure. Furthermore, this idea is reinforced with the findings that the IR and NMR spectra, as well as the percentages of methoxyl and hydroxyl groups, are similar for both the lignin obtained with anthraquinone and that extracted with dioxane–water. The latter being considered to be the least modified among the extracted lignins. On this basis, lignin extraction from coconut husk by using aqueous NaOH–AQ becomes a convenient method for obtaining a high yield of lignin having a low extent of structural changes. In contrast, extraction with NaOH having no anthraquinone (AQ) as an additive rendered highly modified lignins. Indeed, the lignin extracted with NaOH at 100°C showed coumarin-like structures and that extracted with NaOH at 160°C showed dilignol-like structures in their NMR spectra. These chemical structures are associated with a high extent of condensation suffered by lignins during the extraction process.

The NMR results of the acetylated lignins were used to semiquantitatively estimate that the aromatic and aliphatic hydroxyl contents are approximately equal. This agrees very well with the doublet observed at 1750 and 1720 cm^{-1} in the IR spectra of the same acetylated lignins, since these peaks are similar in their intensity.

The general features observed in both the IR and the NMR spectra of coconut husk lignin would allow us to roughly classify this lignin in the guaiacyl–syringyl type lignins (so-called L-type lignins). However, due to its low methoxyl content and, consequently, to its high proportion of *p*-hydroxyphenyl groups, coconut husk lignin can be classified more rigorously in the Lm-type lignins. This result is in accord with the finding that Lm-type lignins are characteristic of monocotyledons, of which class the coconut palm (*Cocos nucifera L.*) is a member.

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