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Compositional and structural characteristics of residual biomass from tropical plantations

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Abstract Many products and abundant wastes from tropical plantations, such as latex, palm oil, and coconut production due to replantation, are waiting effective utilization. Nonutilized tropical biomass – oil palm (*Elaeis guineensis* Jacq.), coconut (*Cocos nucifera* L.) coir dust and coir fiber, and rubber (*Hevea brasiliensis*) wood – were analyzed for chemical and structural characteristics of wall polysaccharides and lignin. Coconut coir dust is mostly composed of middle lamella and is separated from coir fiber, which is composed of secondary walls. These were supported by lignin content, and structural characteristics of wall polysaccharides and lignin. The chemical and spectroscopic characteristics of walls of rubber xylem were similar to those of typical temperate angiosperm woods. Oil palm frond was significantly rich in arabinoxylan, and numerous acetyl groups were substituted to the arabinoxylan. Lignin of oil palm frond and wall polysaccharides of coconut coir dust are substituted with hydroxybenzoic acids with ester and ether linkages. Some *p*-hydroxybenzoic acid substituted to the wall polymers of coconut coir dust would contribute to the formation of associations between polysaccharides and lignin. Based on the above results it is suggested that coconut coir fiber and rubber wood are suitable resources for chemical pulp production for paper-making, but oil palm frond is not.

Key words Oil palm frond · Coconut coir · Rubber wood · Biomass utilization · Lignin and polysaccharides

Introduction

Abundant quantities of natural rubber (6.0×10^6 tons in the world and 5.6×10^6 tons in Asia in 1995 according to the FAO¹), palm oil (15.6×10^6 tons in the world, 12.7×10^6 tons in Asia), and coconut oil (45.1×10^6 tons in the world, 38.2×10^6 tons in Asia) are produced from rubber (*Hevea brasiliensis*), oil palm (*Elaeis guineensis* Jacq.), and coconut (*Cocos nucifera* L.) trees in tropical plantations, supporting the regional economy in Southeast Asian countries. Huge amounts of “wastes,” such as fronds and coir from oil palm and coir and shell from coconut, are left over in the production of commercially important palm oil and coconut oil, respectively. In addition, these plants must be cut down after 25–30 years because of replantation. These wastes are an important biomass because of the serious lack of woody biomass in these countries. Timber and boards are produced and commercialized from some parts of the waste rubber trees, and commercial activated carbon is produced from the coconut shell. A small quantity of coconut timber is also supplied for regional use. Some trials to develop effective utilization of these biomass materials have been reported (e.g., kraft pulp^{2,4} and thermomechanical pulp from oil palm^{5,6}). We have developed an effective use for oil palm frond, as binderless boards.⁷

It is important for effective utilization of this biomass to know the exact chemical composition and structural characteristics of the major components, such as wall polysaccharides and lignin; unfortunately, only basic information is available. In this study the chemical composition and structural characteristics of wall polysaccharides and lignin of the little-utilized tropical biomass, oil palm frond, coconut coir dust and coir fiber, and rubber wood were analyzed using chemical and spectroscopic procedures to discuss their effective utilization.

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Materials and methods

Coconut (*Cocos nucifera* L.) coir and coir dust, which had been separated mechanically from the coconut husk, were supplied from a coconut coir factory (Soriano Industry, San Pablo, Southern Luzon Island, Philippines). Sawdust (does not contain bark) of rubber trees (*Hevea brasiliensis*) older than 30 years was collected from a complex for production of timbers and boards at Songkula Province in southern Thailand. Fronds from the oil palm tree (*Elaeis guineensis* Jacq.) approximately 10–15 years old were harvested at Krabi Province in southern Thailand. The fronds were cut and chopped using a hammer mill after removing the leaflets.

The materials were ground by a Wiley mill to pass through a 420- μm sieve, extracted successively with boiling diethylether (1h, three times), boiling 80% (v/v) ethanol (1h, three times), then water overnight at 37°C with shaking. The residues were washed with ethanol and dried in a vacuum oven at 50°C.

Preparation of Björkman lignin

The extract-free sample was further milled with a vibratory ball mill with cooling (<25°C) by water flow without solvent⁸ for 96h. Björkman lignin was extracted with 96% (v/v) dioxane and purified by the procedure of Björkman.⁹ The yields of purified Björkman lignins from coconut coir dust, rubber wood, and oil palm frond were 17%, 52%, and 85% of total lignin (sum of Klason and acid-soluble lignin), respectively.

Determination of chemical composition

The dried sample was analyzed for lignin content by the Klason procedure together with the acid-soluble lignin¹⁰ and acetyl bromide procedure.¹¹ Neutral sugar composition was determined by the alditol acetate procedure modified from the method reported by Blakeney et al.¹² for the sulfuric acid concentration (4%, w/w) during digestion at 121°C. The monosaccharide acetates were quantified by gas chromatography using a DB17 capillary column attached to a GC-17 Shimadzu Gas Chromatograph. Uronic acid content in the sulfuric acid hydrolysate for neutral sugar analysis was determined spectrophotometrically using 3,5-dimethylphenol.¹³ The content of acetyl groups probably substituted in arabinoxylan was determined by nuclear magnetic resonance (¹H-NMR) using Bruker AC300NMR Spectroscopy after acid hydrolysis of walls with 25% (v/v) D₂SO₄ in D₂O for 90min at 90°C.¹⁴

Esterified phenolic compounds and the sum of those esterified and etherified to wall polymers were determined by gas chromatography (column: NB1) as trimethylsilyl derivatives after their release by alkaline hydrolyses with 0.5M NaOH overnight at 37°C¹⁵ and 4M NaOH for 2h at 170°C,¹⁶ respectively. Ether-linked phenolics were calculated as the differences between yields of phenolics from

both hydrolyses. The aromatic composition of lignin was examined by an alkaline nitrobenzene oxidation.¹⁷ The products (trimethylsilyl derivatives) were recorded using a Shimadzu GC-14B Gas Chromatograph with capillary column NB1 and were quantified using ethylvanillin as an internal standard. The yields of products were corrected for the products from the esterified and/or etherified phenolics.¹⁷ Their chemical composition was compared with that of the Björkman lignins isolated from spruce (*Picea abies*) and beech (*Fagus crenata*).

Spectrophotometric characteristics of Björkman lignins

Björkman lignins were dissolved in ethyleneglycol monomethyl ether, and their ultraviolet (UV) spectra were recorded by a Shimadzu UV-200 Spectrometer. The unconjugated phenolic hydroxy groups were quantified by the $\Delta\epsilon_i$ procedure.¹⁸ Fourier-transfer infrared (FTIR) spectra were measured by a Shimadzu FTIR-8100 Spectrometer as KBr tablets. The Björkman lignins were analyzed by ¹H- and ¹³C-NMR spectroscopy in deuterium chloroform after acetylation by acetic anhydride-pyridine and in deuterium dimethylsulfoxide (DMSO), respectively, using a Bruker AC300 NMR Spectrometer.

Analytical pyrolysis–gas chromatography/mass spectrometry

Björkman lignins (ca. 100 μg) were pyrolyzed by a Curie Point Pyrolyzer (JHP-3; Japan Analytical Industry, Tokyo, Japan) at 500°C. Products were identified and quantified using gas chromatography/mass spectrometry (GC/MS) (Shimadzu GC17/QP5000 system) with an NB1 capillary column. The conditions for the GC were 50°C for 1min, then programmed linearly at 5°C/min to 270°C.^{19,20}

Results and discussion

Characteristics of chemical composition

The lignin concentration in coconut coir dust was high according to the Klason procedure (Table 1). It could not be determined by an acetyl bromide procedure due to incomplete dissolution of wall materials in solvent, suggesting that the lignin of coir dust is characterized by a high level of carbon–carbon intermonomer linkages and fewer β -ether linkages.²¹ This fact was supported by the high concentration of unconjugated phenolic hydroxy groups in the Björkman lignin of coconut coir dust (0.51 mol/C6-C3; 0.43, 0.31, 0.32, and 0.24 for Björkman lignins of oil palm frond, rubber, beech, and spruce woods, respectively) and the low total yields of alkaline nitrobenzene oxidation products as described later (see Table 3). In addition, the molar ratio of arabinosyl to xylosyl residues of coconut coir dust was significantly high (Table 1). These results suggest that coconut

coir dust could be composed mostly of middle lamella and primary wall fragments separated mechanically from coconut coir fiber which could be composed of secondary walls.²² The development of an effective use for these materials

should be based on these characteristics. Coconut coir fiber may be a good resource of pulp for papermaking.

The chemical composition of oil palm fronds suggests an effective use. High levels of arabinoxylan and pectic substances give low yields of pulp and high alkaline consumption in the presence of high concentrations of esterified phenolics and acetyl groups during alkaline pulping.^{2,3}

Epidermis cells of the rubber tree contain significant amounts of diethylether extracts, isoprene, and proteins. The content of ether extractives of the xylem portion was low (Table 1). The chemical characteristics of rubber wood xylem were similar to those of most of the temperate angiosperm woods (Table 1), suggesting that rubber woods may be a good resource of pulp production for papermaking in addition to their use as timber and board production.

We showed previously that significant amounts of hydroxybenzoic and hydroxycinnamic acids are esterified to lignin in the walls of the oil palm frond.⁷ Their low concentrations in extract-free meal of the oil palm frond (Table 2) suggest that most of them are substituted to lignin, not to polysaccharides. These moieties should not be involved in lignin because of the definition of lignin derived from the biosynthetic pathway, as discussed in previous papers.^{23,24} Lignin has to be composed of β -O-4 intermonomer linkages²⁵ as the major intermonomer linkages, resulting in the radical coupling of hydroxycinnamyl alcohols.

Wall polymers of coconut coir dust and coir fiber also contained substitutions of hydroxybenzoic acids, hydroxycinnamic acids, and hydroxybenzaldehydes (Table 2), but significant portions of these acids are esterified to polysaccharides, not lignin. Some of them may form bridges between lignin and polysaccharides, as shown for some temperate grasses,²⁶⁻³⁰ because of the presence of a significant amount of insoluble fractions in dichloroethane-ethanol (2:1, v/v) during isolation of the Björkman lignin, behavior similar to that of grass lignin.²⁶ No substitutions by hydroxybenzoic acids, hydroxycinnamic acids, or

Table 1. Chemical composition of samples

Sample	Oil palm frond	Coconut coir dust	Coconut coir fiber	Rubber wood
Extracts				
Ether extract	0.4	0.3	0.4	0.8
80% EtOH	8.8	1.8	4.1	2.4
Total	9.2	2.1	4.5	3.2
Lignin				
Klason	13.0	42.0	19.2	15.3
ASL ¹⁰	2.2	0.3	0.6	3.1
Total	15.2	42.3	19.8	17.8
AcBr ¹¹	15.8	—	20.5	17.8
Neutral sugar				
Rha	0.5	0.7	0.2	0.4
Ara	1.7	3.2	0.9	0.7
Xyl	23.7	7.9	18.2	21.8
Man	1.7	1.3	0.3	3.2
Gal	1.0	2.8	0.4	1.2
Glc	28.8	16.8	27.8	37.3
Total	57.4	32.7	47.8	64.5
(Ara/Xyl)	0.076	0.413	0.049	0.031
(Xyl/Glc)	1.010	0.569	0.804	0.716
Uronic acid				
GalA	2.6	2.1	1.8	2.3
GlcA	1.3	1.4	0.9	4.3
Total	3.9	3.5	2.7	3.4
Acetyl group				
(Ac/Xyl)	0.52	0.42	0.46	0.43
Ash	1.5	1.9	0.8	0.5

Results are given as the percent of oven-dried material.

ASL, acid-soluble lignin; AcBr, lignin determined by acetyl bromide procedure; Rha, Ara, Xyl, Man, Gal, Glc, GalA, GlcA, dehydrated rhamnosyl, arabinosyl, xylosyl, mannosyl, galactosyl, glucosyl, galacturonyl, and glucuronyl residues, respectively; Ara/Xyl, Xyl/Glc, molar ratios of dehydrated arabinosyl residue to dehydrated xylosyl residue and dehydrated xylosyl residue to dehydrated glucosyl residue, respectively; Ac/Xyl, molar ratio of acetyl group to dehydrated xylosyl residue.

Table 2. Phenolics esterified and etherified to wall polymers

Phenolic	Oil palm frond		Coconut coir dust		Coconut coir fiber	Rubber wood	
	Extract-free meal	Björkman lignin	Extract-free meal	Björkman lignin	Extract-free meal	Extract-free meal	Björkman lignin
Esterified							
HA	0.87	4.29	2.07	0.17	1.36	>0.001	n.d.
VA	0.04	0.14	0.47	0.19	0.02	>0.001	n.d.
SA	0.00	0.08	0.39	0.21	0.02	>0.001	n.d.
PCA	0.03	0.12	0.02	0.13	0.01	>0.001	n.d.
FA	0.12	0.15	0.15	0.03	0.25	n.d.	n.d.
Total	1.06	4.78	3.10	0.73	1.66	0.00	0.00
Etherified							
V	0.23	1.05	0.20	0.46	0.18	n.d.	n.d.
S	0.36	1.98	0.12	0.30	0.15	n.d.	n.d.
HA	0.14	0.64	0.71	1.85	0.23	n.d.	n.d.
VA	0.18	0.92	0.22	0.50	0.20	n.d.	n.d.
SA	0.10	0.66	0.15	0.35	0.14	n.d.	n.d.
PCA	0.00	0.00	0.03	0.10	0.01	n.d.	n.d.
FA	0.09	0.44	0.08	0.20	0.12	n.d.	n.d.
Total	1.10	5.69	1.51	3.76	1.03	0.00	0.00

Results are given as the percent of oven-dry sample or lignin

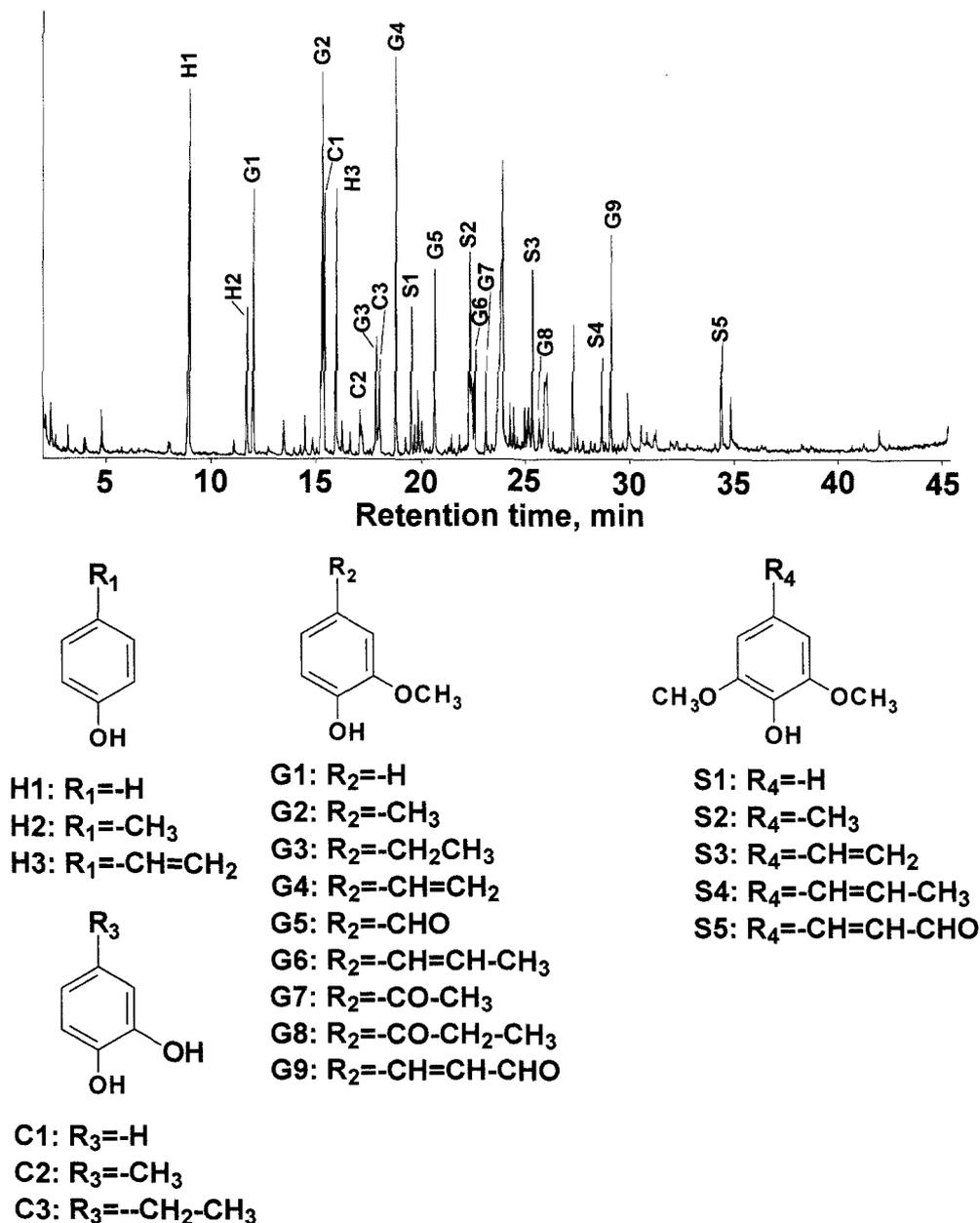
HA, *p*-hydroxybenzoic acid; VA, vanillic acid; SA, syringic acid; PCA, *p*-coumaric acid; FA, ferulic acid; V, vanillin; S, syringaldehyde; n.d., not detected.

Table 3. Alkaline nitrobenzene oxidation products of original samples and their Björkman lignin

	Oil palm frond		Coconut coir dust		Coconut coir fiber (extract-free meal)	Rubber wood	
	Extract-free meal	Björkman lignin	Extract-free meal	Björkman lignin		Extract-free meal	Björkman lignin
Total yield (% of total lignin)	38.9	27.1	10.5	9.8	33.0	44.4	39.2
H/V	0.03	0.05	0.06	0.04	0.02	0.00	0.00
S/V	1.68	1.40	0.45	0.41	0.56	1.84	1.73

H/V, molar ratio of *p*-hydroxyphenyl nuclei to guaiacyl nuclei; S/V, molar ratio of syringyl nuclei to guaiacyl nuclei.

The yields of *p*-hydroxybenzaldehyde and vanillin were corrected for the products from wall-bound *p*-coumaric and ferulic acids, respectively.¹⁷

Fig. 1. Pyrogram of oil palm frond and pyrolysis products

hydroxybenzaldehydes were detected in the walls of wood from rubber trees (Table 2).

The total yields and molar syringyl/guaiacyl nuclei (S/V) ratio of the alkaline nitrobenzene oxidation products of

extract-free samples of both rubber tree wood and oil palm frond were, on average, like those of lignins in the walls of temperate angiosperm plants; but the S/V ratios of lignin in both coconut coir dust and coir fiber were significantly

lower than others (Table 3) and even than that for lignins in grasses.³¹ It has been noted that lignins of some species of tropical angiosperm dicotyledonous woody plants, such as malas [*Homalium foetidum* (Roxb.) Benth.], calophyllum (*Calophyllum inophyllum* Linn.), and kuila [*Intsia bijugai* (Colebr.) O. Kuutze], have *S/V* ratios of less than 1.0.⁷ After correction for products from the phenolics substituted to wall polymers, the *p*-hydroxyphenyl/guaiacyl nuclei (*H/V*) molar ratio of all samples tested during the present study were similar to the average of lignins of most plants.³¹

Phenol (H_1) and 4-vinylphenol (H_2) were identified in pyrograms of the Björkman lignin in coconut coir dust, which would be produced from *p*-hydroxybenzoic acid and *p*-coumaric acid etherified to the lignin (Fig. 1), but none of these products was detected in the Björkman lignin of rubber tree wood. Significantly lower syringyl products were seen in the pyrograms of Björkman lignin from coconut coir dust than in those for rubber tree wood. These results reflect the low *S/V* ratio of alkaline nitrobenzene oxidation products of lignin in coconut coir dust. In addition, catechol derivatives, such as catechol (C_1), 4-methylcatechol (C_2), and 4-vinylcatechol (C_3) were detected as pyrolysis products (Fig. 1), suggesting the presence of catechol nuclei in lignin from coconut coir dust, maize (*Zea mays* L.), and some tropical angiosperm woody plants.⁷ It also reflects the significantly lower *S/V* ratio.

Spectroscopic characteristics of Björkman lignin

It is well known that for IR spectra of lignins the absorption at 1270cm^{-1} , which is assigned as a signal of guaiacyl ring breathing with CO stretching,³² is stronger than that at 1225cm^{-1} . It is due to guaiacyl and syringyl nuclei breathing with CO stretching³¹ in lignin of gymnosperms ($A_{1270\text{cm}^{-1}} \geq A_{1225\text{cm}^{-1}}$), in contrast to the $A_{1270\text{cm}^{-1}} \leq A_{1225\text{cm}^{-1}}$ for lignin of angiosperms.³¹ Björkman lignins of oil palm frond and rubber wood showed IR spectra typical for the lignins of angiosperms (Fig. 2), but the FTIR spectrum of Björkman lignin in coconut coir dust was typical of that seen for gymnosperm lignins, although it is classified as a monocotyledon of angiosperm. Björkman lignin from coconut coir dust had a peak at 275 nm in the UV spectrum, which is typical of angiosperm lignin composed of guaiacyl and syringyl nuclei (data not shown).

Clear signals of 61, 64, 73–75, and 83–87 ppm are assigned in the side chain γ -carbon of β -etherified guaiacyl nuclei, the γ -carbon of β -etherified syringyl nuclei, the β -carbon of β -etherified guaiacyl and syringyl nuclei, and the α -carbon of β -etherified guaiacyl and syringyl nuclei, respectively, in the ^{13}C -NMR spectrum of Björkman lignin from coconut coir dust (Fig. 3). This finding confirms that the polyphenolic component is real lignin.²⁴ The presence of β -ether linkages was also supported by signals around 6 ppm (H_{α} of β -ether

Fig. 2. Infrared spectra of Björkman lignins from various plants

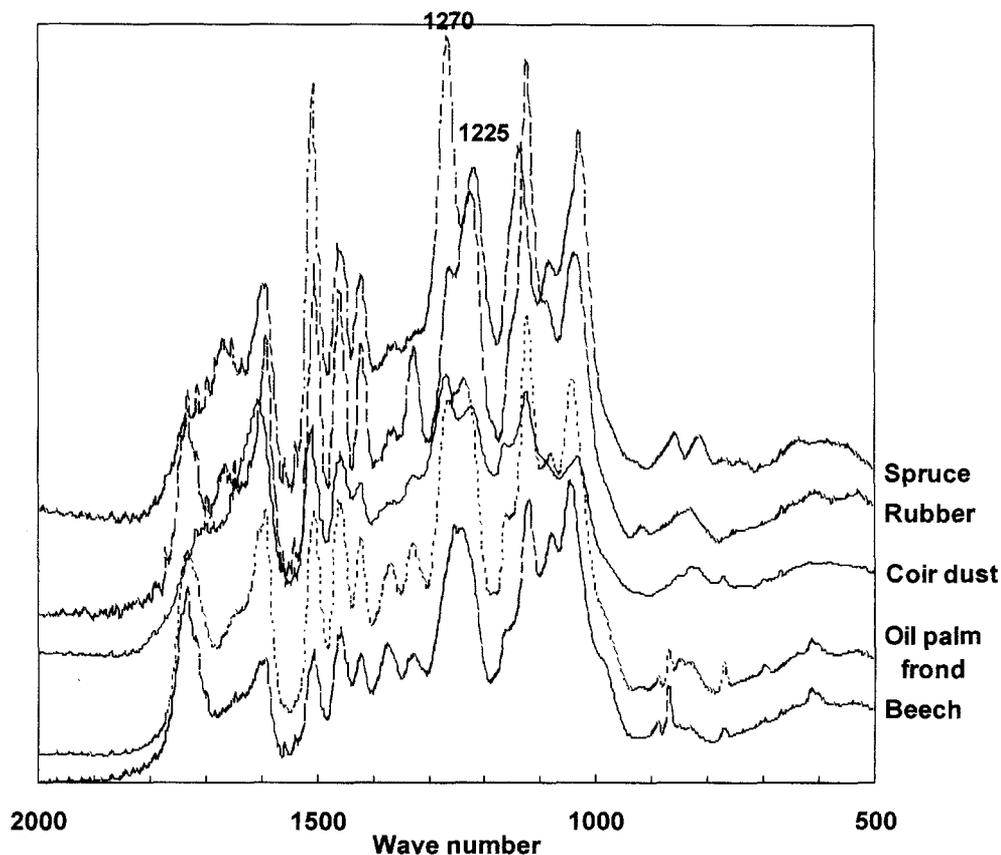
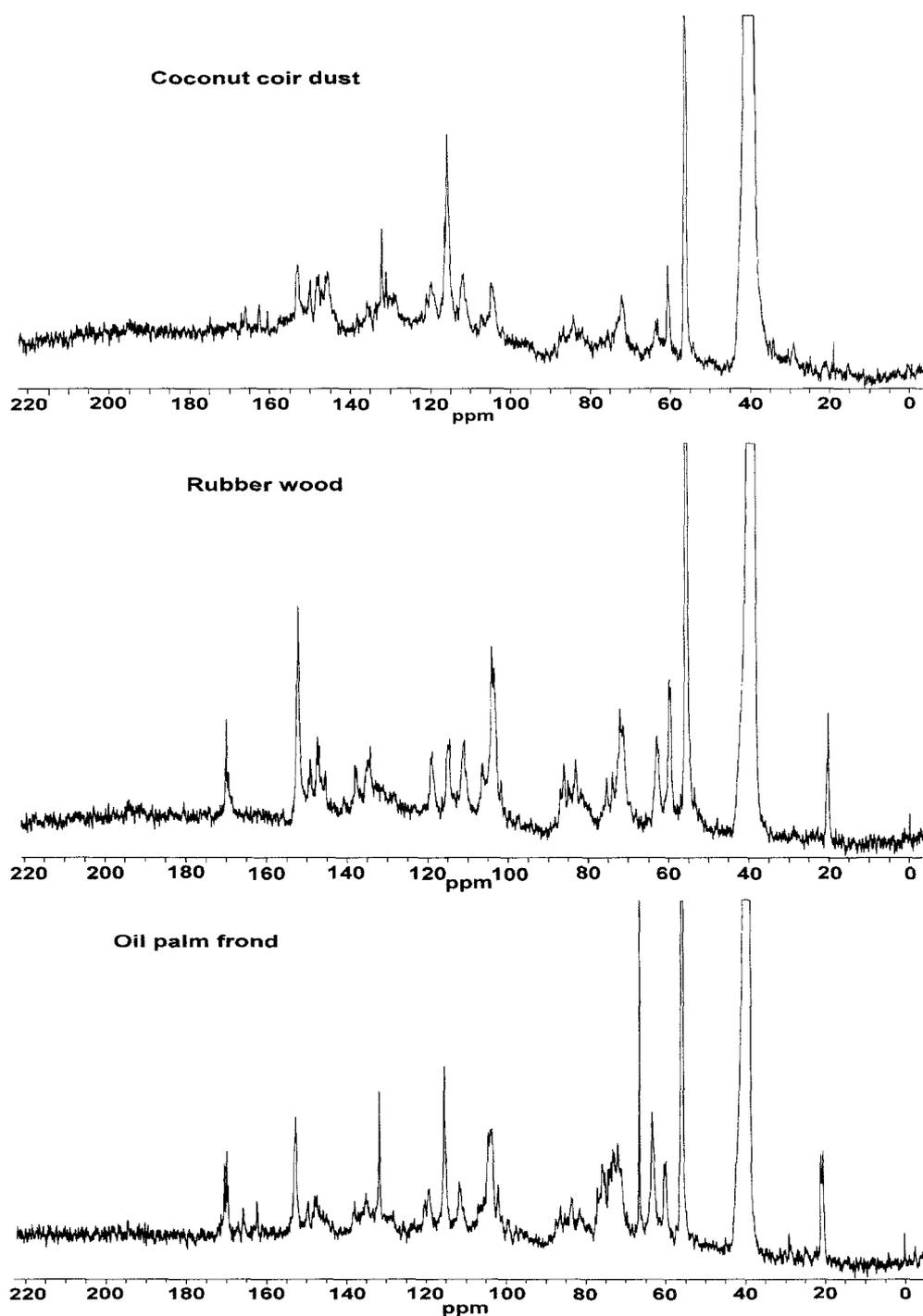


Fig. 3. ^{13}C -NMR spectra of Björkman lignins of oil palm fronds, rubber wood and coconut coir dust



linkages) in the ^1H -NMR spectrum. The signals from aromatic carbons of syringyl nuclei at 153 (C_3 and C_5), 138 (C_1), 135 (C_4), and 104–105 (C_2 and C_6) ppm in Björkman lignin from coconut coir dust is significantly weaker than those from oil palm frond (Fig. 3), suggesting less syringyl unit in the lignin from coconut coir dust. These findings agree with the results from chemical analysis, as well as no signals at 170–171 ppm (assigned to benzyl carbon of *p*-hydroxybenzoyl nuclei esterified to lignin) and weaker signals at 163 and 152 ppm (assigned to the benzyl carbon of the free carboxyl group, and C_2 and C_6 carbons of etherified *p*-hydroxybenzoyl nuclei, respectively) than

those of Björkman lignin from oil palm frond. The results suggest that significant amounts of *p*-hydroxybenzoic acid are esterified to lignin in the walls of the oil palm frond but mostly to polysaccharides in the walls of the coconut coir dust.

Conclusions

The chemical composition and structural characteristics of tropical biomass – oil palm (*Elaeis guineensis* Jacq.), coconut

(*Cocos nucifera* L.) coir dust and coir fiber, and rubber tree (*Hevea brasiliensis*) wood, which are rarely utilized residues from commercially important plantations in Southeast Asia – were analyzed for their chemical composition and structural characteristics of wall polysaccharides and lignin. Coconut coir was mechanically separated in the middle lamella (coir dust) and secondary walls (coir fiber); which was suggested by the chemical composition and structural analyses of polysaccharides and lignin in the walls. The chemical and spectroscopic characteristics of walls of rubber tree wood xylem are similar to those of typical temperate angiosperm woody plants. Oil palm frond is significantly rich in noncellulosic polysaccharides, especially arabinoxylan; a large number of acetyl groups are substituted, probably to arabinoxylan. The lignin of oil palm frond and the wall polysaccharides of coconut coir dust are substituted with hydroxybenzoic acids, mainly *p*-hydroxybenzoic acid with ester and ether linkages. Some extent of the *p*-hydroxybenzoic acid substituted to wall polymers of coconut coir dust would contribute to the formation of associations between polysaccharides and lignin.

Based on the above results it is suggested that coconut coir fiber and rubber tree wood are suitable sources of the chemical pulp used for paper making. Oil palm frond is not.

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