Characterization of Sago Palm (*Metroxylon sagu*) Lignin by Analytical Pyrolysis

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Dioxane lignin prepared from sago palm (*Metroxylon sagu*) was characterized by analytical pyrolysis coupled to gas chromatography−mass spectrometry. Large abundances of the *p*-hydroxybenzoates ester-linked to the lignin were proven by analytical pyrolysis as well as by mild alkaline treatment that produced *p*-hydroxybenzoic acid in 16.3% yield. Pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) before and after alkaline treatment also showed the presence of ester- and ether-linked *p*-hydroxybenzoates. Quantitative results of pyrolysis showed that the sago palm lignin is of syringyl type. The relative abundances of TMAH/pyrolysis products derived from the syringyl β-aryl ether substructures were 4.9 times those of the guaiacyl equivalents. Proton nuclear magnetic resonance analysis also showed the presence of the *p*-hydroxybenzoates and the predominance of the syringyl moiety over the guaiacyl ones in the sago palm lignin.

INTRODUCTION

Sago palm (*Metroxylon sagu*) is exploited as a staple and cash crop in Southeast Asia because the trunk contains a large amount of starch (150−250 kg/trunk). Its high starch content, ease of cultivation in swampy areas, and high productivity have increased the production of sago starch. Interest has also grown in utilizing sago palm as a new energy resource and for industrial raw materials, although no high-added-value applications have been found for the palm so far. With increasing production of sago starch, however, huge amounts of fibrous residues are left over in the starch mills. The residues and the trunk bark pollute the environment as well as the waste water. Effective utilization of the residues is therefore required. To utilize this biomass effectively, we need a better understanding of the composition of the fibrous residues. A previous paper characterized the fibrous residues, especially hemicelluloses (*1*). However, available literature references contain few studies of the lignin in sago palm (*1*, *2*), although many papers are available on oil palm (*3−11*). In particular, the references lack the compositional study of the sago palm lignin.

The goal of this paper was to characterize the lignin in the fibrous residues. For this purpose, analytical pyrolysis coupled to gas chromatography−mass spectrometry was used in the absence and in the presence of tetramethylammonium hydroxide (TMAH). Analytical pyrolysis has gained wide acceptance as a powerful tool for characterizing lignocellulosic materials (*12*) because of its speed, convenience, and ability to provide complementary information to wet chemical degradation methods. Pyrolyses in the absence of and in the presence of TMAH provide information on the lignin composition, the latter technique providing information about the composition of β-aryl ether substructures, the most abundant substructures in lignin [48% in spruce and 60% in birch lignins (*13*)]. The results will give insight into the use of the fibrous residues. This paper forms a part of wider study on the exploration of the utilization of sago palm.

MATERIALS AND METHODS

Sago Palm Dioxane Lignin Sample. The pith of sago palm (*Methoxylon sagu*) was collected from Narathiwat, Thailand. The acetone powder prepared from the pith was treated with a 20 mM phosphate buffer solution (pH 6.5) for 1 h to remove water-soluble polysaccharides. The residue was freeze-dried and defatted four times with benzene/ethanol (1:1 v/v) for 24 h by a Soxhlet extractor. The defatted sample was exhaustively treated with hot dimethyl sulfoxide to remove starch, washed with water, and then air-dried. To solubilize pectic polysaccharides, the fibrous residue (5.0 g) was treated 2 times with a 50 mM acetate buffer solution (pH 4.0, 300 mL) containing 50 mM EDTA at 100 °C for 1 h with occasional stirring. The insoluble residue (fibrous residue) was collected by filtration, washed with water, and air-dried (4.2 g). Dioxane lignin was isolated from the pectin-free fibrous residue (5.0 g) according to Pepper's method (*14*, *15*): yield = 170 mg (3.4%).

Alkaline Treatment of Sago Palm Dioxane Lignin. A mixture of dioxane lignin (30 mg) and 2 N NaOH (2 mL) was stirred at room temperature under an N_2 atmosphere for 10 h. The mixture was acidified with dilute hydrochloric acid. A precipitate (hydrolyzed dioxane lignin) of 20 mg was obtained. The precipitate was centrifuged and thoroughly washed with water. The supernatant liquid and washings were extracted with ethyl acetate. The ethyl acetate solution was dried over Na_2SO_4 and concentrated in vacuo to give 4.9 mg of crystals (yield = 16.3%). The crystals were subjected to FT-IR analysis (FT-IR 4300, Shimadzu, Kyoto, Japan) and HPLC analysis

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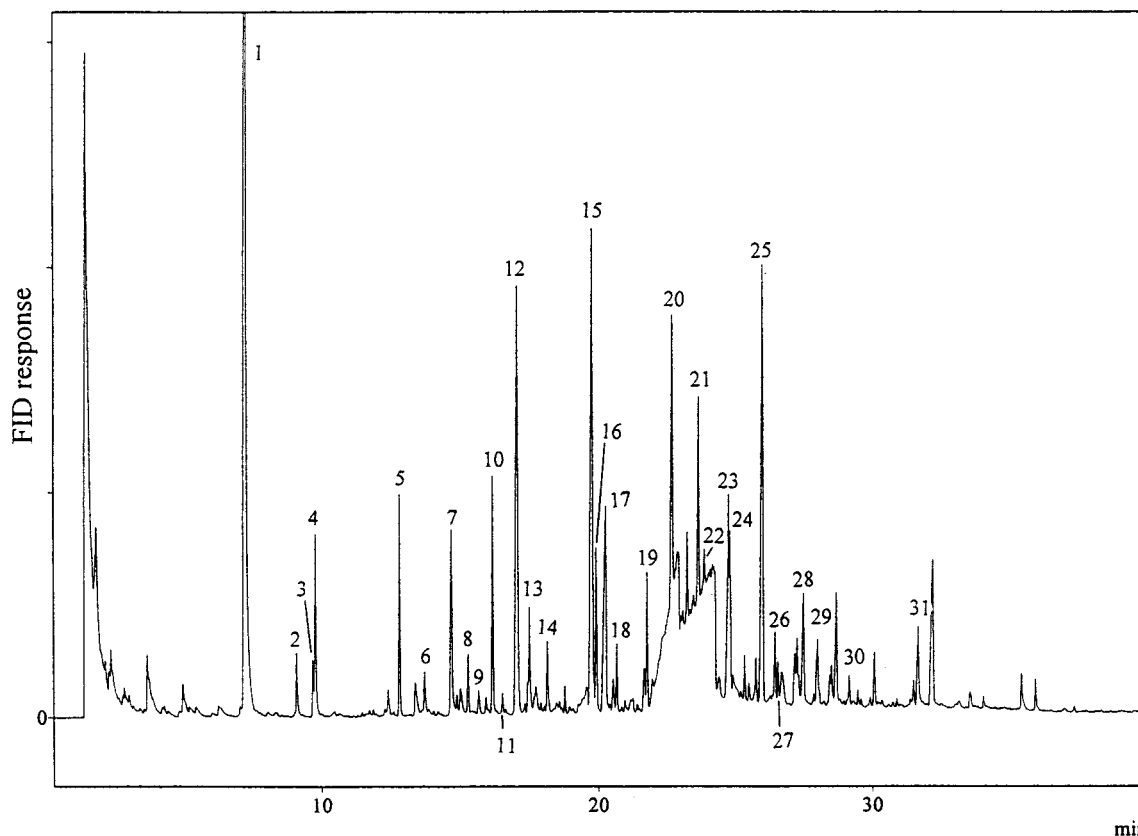
Figure 1. Py-GC/FID trace of sago palm dioxane lignin. Pyrolysis was done at 500 °C for 4 s. Peak numbers and names refer to those in Table 1.

using a model 576 pump (GL Sciences, Tokyo, Japan), a TSKgel ODS-80Ts column (5 μm, 4.6 × 150 mm) and a solvent system (flow rate = 0.6 mL/min) of 25% acetonitrile and 0.01% trifluoroacetic acid. The eluate was monitored at ultraviolet light of wavelength 280 nm (502T model, GL Sciences). The hydrolyzed dioxane lignin was subjected to analytical pyrolysis.

Pyrolysis—Gas Chromatography (Py-GC/FID). The Py-GC/FID system was a combination of a Curie-point pyrolyzer (JHP-3 model, Japan Analytical Industry, Tokyo, Japan) and a Shimadzu GC-17 gas chromatograph (Shimadzu, Kyoto, Japan) with a flame ionization detector (FID). The Py-GC/FID analyses of the dioxane lignins were carried out under the same conditions as those of coniferous lignocellulosics (*16*). The dioxane lignins (~0.1−0.2 mg) were tightly wrapped in a 50 μm ferromagnetic pyrofoil; in the pyrolysis in the presence of TMAH (TMAH/Py), 5 μL of a 25% TMAH methanolic solution (Aldrich) was added to the samples with a syringe. The sample-loaded pyrofoil was inserted into a sample tube. The sample holder with the sample tube was centered in the pyrolyzer heated at 270 °C. After the pyrolysis system had been flushed with helium gas for 15 s, pyrolysis was performed at 500 °C for 4 s; our Curie-point system heats the pyrofoil to 500 °C in 300×10^{-3} s. The products were transferred into the GC via a transfer line heated at 270 °C. Separation of volatile products was achieved on a 25 m Quadrex MS fused-silica capillary column (inner diameter = 0.25 mm; film thickness = 0.25 μm) coated with poly(methyl silicone). The column temperature was kept at 50 °C for 1 min and programmed to 250 °C at increments of 5 °C min^{-1}, after which isothermal conditions were maintained for 15 min. The GC conditions were as follows: injector with a 100:1 split ratio at 170 °C, FID at 270 °C, helium as the carrier gas (flow rate = 1.3 mL min^{-1}).

Pyrolysis—Gas Chromatography—Mass Spectrometry (Py-GC-MS). The Py-GC-MS system was a combination of a JHP-3 model Curie-point pyrolyzer (Japan Analytical Industry) and an HP 5890 series II gas chromatograph (Hewlett-Packard, Palo Alto, CA) with an HP 5972A quadru-

pole mass selective detector (Hewlett-Packard). The Py-GC-MS conditions were similar to those of the Py-GC/FID runs. The volatile products were sent to the GC-MS with a fused-silica capillary column (Quadrex MS, 25 m × 0.25 mm, film thickness = 0.25 μm). The injection and detector ports were kept at 280 °C. Spectra were acquired by an HP ChemStation software package. Ions were generated at a 70 eV electron impact voltage in a 200 °C ion source. The mass range used was m/z 70−600, and the scan speed was 10 scans/s. Peak assignments were carried out on the basis of mass fragmentation patterns and by comparing the MS data with published data (*17, 18*) and the retention times with those of standard compounds.

^{1}H Nuclear Magnetic Resonance (NMR) Spectrometry. The ^{1}H NMR spectrum was obtained on a JEOL JNM-α400 spectrometer and reported by chemical shifts (relative to TMS), splitting patterns, integration areas, and proton assignments. Solvent used was DMSO-d_6.

RESULTS AND DISCUSSION

Yields of Sago Palm Dioxane and Hydrolyzed Dioxane Lignins. The fibrous residue, consisting of 64.4% cellulose, 25.1% hemicellulose, and 10.5% lignin (determined by acidic sodium chlorite) (*1*), provided dioxane lignin in 35.2% yield based on the total lignin. Alkaline treatment of the dioxane lignin at room temperature produced hydrolyzed dioxane lignin in 66.7% yield.

***p*-Hydroxybenzoates in Sago Palm Lignin.** The Py-GC/FID trace of the dioxane lignin in the absence of TMAH is shown in Figure 1. Identified products are listed in Table 1 with their relative abundances (mole percent), which were calculated on the basis of the effective carbon numbers (ECNs) of the products (*19,*

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Table 1. Identified Mass Peaks in Pyrolysis of Dioxane Lignin

peak	M_w	product	relative abundance[a] (mol %)	origin[b]
1	94	phenol	28.22	B[c]
2	108	2-methylphenol	0.78	H
3	108	4-methylphenol	0.57	H
4	124	guaiacol	2.48	G
5	138	4-methylguaiacol[d]	2.19	G
6	120	4-vinylphenol	0.57	H[e]
7	140	3-methoxycatechol	3.80	S[f]
8	152	4-ethylguaiacol	0.66	G
9	123	4-methylcatechol	0.31	T
10	150	4-vinylguaiacol	2.28	G[e]
11	154	5-ethylpyrogallol	0.31	T
12	154	2,6-dimethoxyphenol	8.83	S
13	122	p-hydroxybenzaldehyde	1.54	H
14	152	vanillin	1.08	G
15	168	2,6-dimethoxy-4-methylphenol	8.26	S
16	164	(E)-isoeugenol	1.45	G
17	152	p-hydroxybenzoic acid methyl ester	4.77	B
18	166	acetoguaiacone	0.74	G
19	182	4-ethyl-2,6-dimethoxyphenol	1.29	S
20	180	2,6-dimethoxy-4-vinylphenol	9.08	S[e]
21	194	4-allyl-2,6-dimethoxyphenol	4.13	S
22	138	p-hydroxybenzoic acid	ND	B
23	194	(Z)-2,6-dimethoxy-4-propenylphenol	2.87	S
24	182	syringaldehyde	1.81	S
25	194	(E)-2,6-dimethoxy-4-propenylphenol	5.99	S
26	196	acetosyringone	1.07	S
27	178	coniferaldehyde	0.57	G
28	210	syringylacetone	1.79	S
29	210	propiosyringone	1.19	S
30	208	syringyl vinyl ketone	0.19	S
31	208	(E)-sinapaldehyde	1.21	S
		total	100.00	

[a] ND, not determined. [b] B, p-hydroxybenzoate; H, p-hydroxyphenyl lignin moiety; G, guaiacyl lignin moiety; T, tannin; S, syringyl lignin moiety. [c] Some phenol may come also from the p-hydroxyphenyl lignin moiety. [d] Containing a small abundance of catechol. [e] Some vinyl compound comes from the corresponding p-hydroxycinnamic acids. [f] Tentative.

20). The relative molar yield (Y_j) of each pyrolysis product was determined by

$$Y_j \, (mol\,\%) = \frac{\dfrac{A_j}{ECN_j}}{\displaystyle\sum_{j=1}^{m}\dfrac{A_j}{ECN_j}} \times 100 \qquad (1)$$

where A_j and ECN_j are the peak area observed on the Py-GC/FID trace and the ECN for the jth peak, respectively.

No carbohydrate-derived products such as 2-furaldehyde and levoglucosan were observed. The sum of the phenolic pyrolysis products roughly correlates with the lignin content (*21*). Faix et al. (*21*) showed that the yield of carbohydrate-derived products does not exceed 5% when Björkman lignins from woods are pyrolyzed. Therefore, Figure 1 suggests that the carbohydrate content in the dioxane lignin is rather small. Therefore, our lignin sample is comparable with wood Björkman lignins with regard to the lignin content.

Sago palm is a monocotyledon so that the core lignin comprises p-hydroxyphenyl, guaiacyl, and syringyl lig-

nin moieties. Pyrolysis of the dioxane lignin therefore produces a high level of phenols derived from the p-hydroxyphenyl lignin moiety. A series of p-hydroxyphenyl-type products was observed as expected (see Figure 1): phenol (peak 1), 2- and 4-methylphenol (peaks 2 and 3), 4-vinylphenol (peak 6), p-hydroxybenzaldehyde (peak 13), and p-hydroxybenzoic acid methyl ester (peak 17). Of these, a large abundance of phenol (peak 1, 28.2%) is noted. Compared to the contribution of phenol, however, those of the other phenols are very small. Therefore, we suspected that the pyrolytic origin of the phenol is the p-hydroxyphenyl lignin moiety in the sago palm. We considered the other candidates for the pyrolytic origins of the phenol. Under the pyrolysis conditions employed, authentic p-hydroxybenzoic acid was decarboxylated to produce a significant amount of phenol, along with a broad peak that corresponds to a mountain-like peak appearing between 20 and 25 min in Figure 1. Ohtani et al. (*22*) also showed the formation of phenol in the pyrolysis of liquid crystalline aromatic polyesters made from p-hydroxybenzoic acid. These findings suggest that most of the phenol obtained in pyrolysis of the dioxane lignin came from the p-hydroxybenzoates bound to the lignin molecule by either ester and/or ether linkages. Mild alkaline treatment of the dioxane lignin yielded crystalline p-hydroxybenzoic acid in 16.3% yield; identification was carried out by comparing the FT-IR spectrum and HPLC chromatogram of the crystals with those of authentic p-hydroxybenzoic acid. This strongly supports the pyrolysis results.

Sun et al. (*6*) and Suzuki et al. (*9, 10*) observed p-hydroxybenzoic acid in the alkaline nitrobenzene oxidation products of oil palm samples. However, the yield of the acid reported by Sun et al. was only 0.13−0.48% based on the lignins. Suzuki et al. reported a larger amount of p-hydroxybenzoic acid. However, their reported yield (∼5% based on the Björkman lignin) was at least 3 times lower than our result (>16.3%). A phenolic acid such as p-hydroxybenzoic acid is used as a raw material for manufacturing engineering plastics. Tomimura (*7*) pointed out that oil palm trunk is a potential raw material for the manufacture of engineering plastics because of its high content of p-hydroxybenzoic acid, which is readily releasable by alkaline treatment at room temperature. This suggests that sago palm trunk would be preferred over oil palm trunk as the raw material for the manufacture of engineering plastics because sago palm contains much larger abundances of the p-hydroxybenzoates than oil palm.

The presence of the p-hydroxybenzoates in the sago palm lignin was identified also by TMAH/Py. TMAH/Py induces high-temperature saponification and subsequent methylation of the formed free hydroxyl groups. Therefore, TMAH/Py of the dioxane lignin releases p-hydroxybenzoic acid from the p-hydroxybenzoates (if present) ester- and/or ether-linked to the core lignin, yielding methyl 4-methoxybenzoate by methylating the carboxylic acid and phenolic hydroxyl group of the p-hydroxybenzoic acid. Figure 2 clearly shows that the TMAH pyrolysate of the dioxane lignin contains large abundances of methyl 4-methoxybenzoate 3m. Additional proof of the presence of the p-hydroxybenzoates in the dioxane lignin was shown by ^{1}H NMR spectrometry in which a signal (due to the carboxylic acid proton)
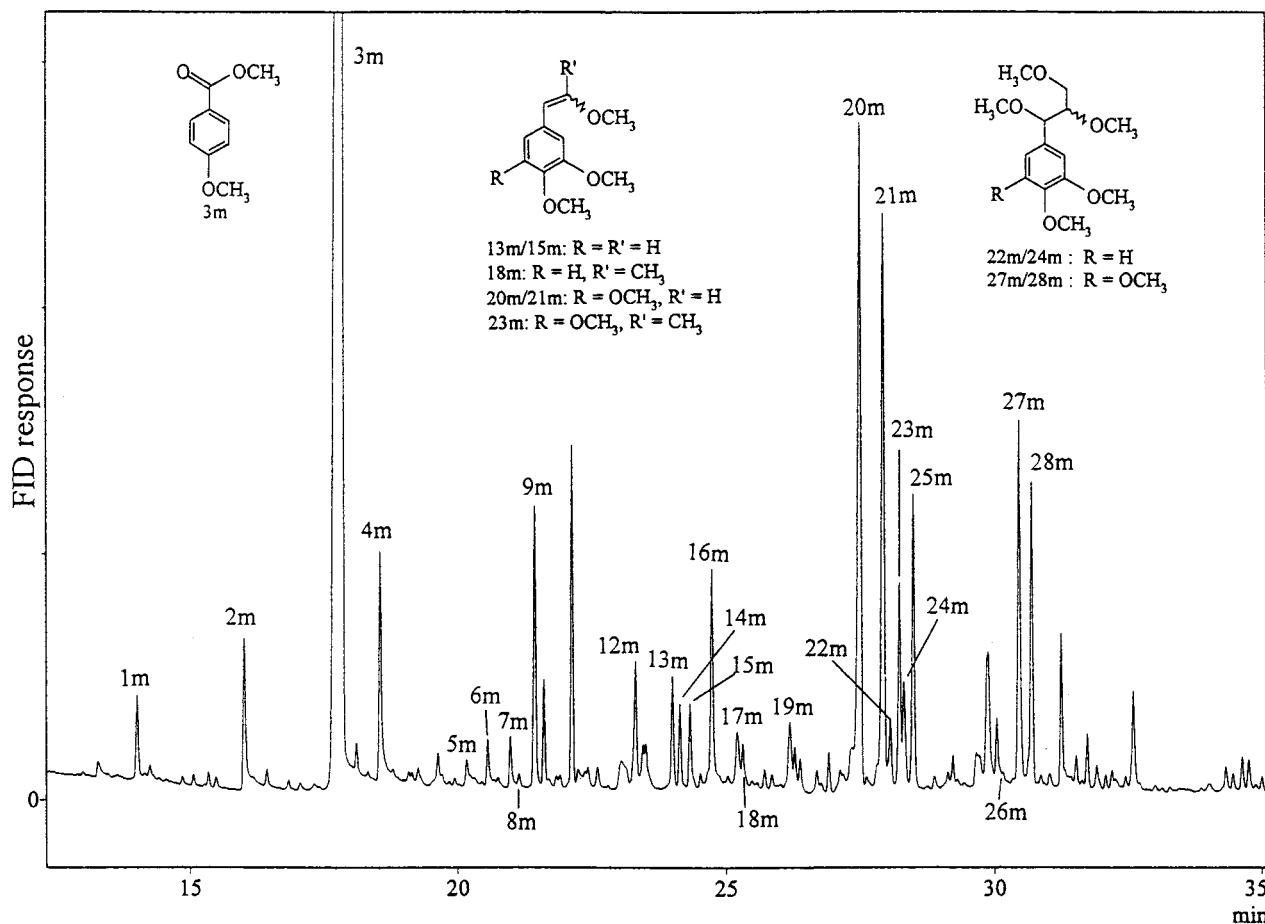
Figure 2. TMAH/Py-GC/FID trace of sago palm dioxane lignin. Pyrolysis was done at 500 °C for 4 s. Peak numbers and names refer to those in Table 2.

at 10.2 ppm and signals (due to the p-hydroxyphenyl nuclei protons) at 7.3−7.8 ppm are contained (Figure 3).

We anticipated that the dioxane lignin would produce a scarcity of 3m after mild alkaline treatment. However, a considerable abundance of 3m was still observed in the TMAH/pyrogram (Figure 4), although the abundance of 3m of the hydrolyzed dioxane lignin dramatically decreased compared to that of the dioxane lignin. This shows that the p-hydroxybenzoates ether-linked to the core lignin polymer remain in the hydrolyzed dioxane lignin because the ester linkages are easily cleaved under the alkaline treatment conditions employed (23), whereas phenolic benzyl aryl ethers are cleaved only at high temperatures such as 170 °C. Sun et al. (6) have pointed out that 58% of p-hydroxybenzoic acid were esterified to lignin in oil palm trunk cell walls. Kim et al. (24) have reported a significant abundance of ester- and ether-linked p-hydroxybenzoic acid in the Björkman lignin of poplar by using the difference between the acid yields in alkaline hydrolysates at room temperature and at 170 °C. The ^{1}H NMR signal at 10.2 ppm may be due to the ether-linked p-hydroxybenzoates with the free carboxylic acid. However, our dioxane lignin may be not fully saponified. Therefore, 3m derived from the ester-linked p-hydroxybenzoates may be still displayed in the TMAH/pyrogram of the hydrolyzed dioxane lignin. Repeated alkaline treatments are probably required to prepare the hydrolyzed dioxane lignin possessing only ether-linked p-hydroxybenzoates. Despite these facts, however, we conclude that most of the

p-hydroxybenzoates are present as the ester form in the sago palm lignin. Ralph et al. (25) have clarified that p-coumarate esters in maize extensively attach at the γ-position of the lignin side chain. Probably, the p-hydroxybenzoates in sago palm also attach at the γ-position of the core lignin side chain.

A minor amount of cinnamic acid derivatives such as 4-coumaric acid and ferulic acid, characteristic phenolic acids of grass plants such as wheat (23) and paddy rice (26), was proven by the pyrolysis methods both with and without TMAH: on the contrary, the conventional and TMAH pyrolysates of rice (27) and kenaf (28) have lacked products derived from the p-hydroxybenzoates. p-Hydroxycinnamic acids are decarboxylated upon pyrolysis to the corresponding 4-vinylphenols (26, 29). Figure 1 also displays such products: 4-vinylphenol (peak 6, 0.6%), 4-vinylguaiacol (peak 10, 2.3%), and 2,6-dimethoxy-4-vinylphenol (peak 20, 9.1%). Their contributions, however, are rather small compared to that of peak 1. Therefore, the abundances of the cinnamic acids are rather small compared to those of the p-hydroxybenzoates in the sago palm lignin. The TMAH/pyrograms (Figures 2 and 4) also show a minor abundance of methyl esters of cinnamic acid derivatives, methyl 4-methoxycinnamate 8m (0.13%) and methyl 3,4-dimethoxycinnamate 26m (0.09%); methyl 3,4,5-trimethoxycinnamate was absent in the TMAH/pyrograms. The large differences in contributions between the 4-vinylphenols and the methyl esters of cinnamic acid derivatives suggest that these 4-vinylphenols are the fragments of the corresponding lignin moieties

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Table 2. Identified Peaks in TMAH/Pyrolysis of Dioxane Lignin

peak	M_w	product[a]	relative abundance[b] (mol %)	origin[c]
		1,2-dimethoxybenzene[d]	2.47	G
1m	152	3,4-dimethoxytoluene	0.94	G
2m	168	1,2,3-trimethoxybenzene	2.28	S
3m	166	methyl 4-methoxybenzoate	54.58	B
4m	182	3,4,5-trimethoxytoluene	3.36	S
5m	166	3,4-dimethoxybenzaldehyde	0.46	G
6m	196	1-(3,4-dimethoxyphenyl)-1-methoxyethane	0.44	G
7m	178	(*E*)-4-(prop-1-enyl)-1,2-dimethoxybenzene	0.41	G
8m	192	methyl 4-methoxycinnamate	0.13	CA
9m	194	1,2,3-trimethoxy-5-vinylbenzene	2.34	S
10m	196	methyl 3,4-dimethoxybenzoate	ND	G
11m	196	3,4,5-trimethoxybenzaldehyde	ND	S
12m	212	1,2,3-trimethoxy-5-(methoxymethyl)benzene	1.42	S
13m	194	(*Z*)-2-(3,4-dimethoxyphenyl)-1-methoxyethene	1.09	G
14m	210	1,2-dimethoxy-4-(3-methoxypropyl)benzene	0.67	G
15m	194	(*E*)-isomer of 13m	0.87	G
16m	208	5-((*E*)prop-1-enyl)-1,2,3-trimethoxybenzene	2.44	S
17m	210	1-(3,4,5-trimethoxyphenyl)-ethan-1-one	0.92	S
18m	208	2-(3,4-dimethoxyphenyl)-1-methoxy-1-methylethene	0.48	G
19m	226	methyl 3,4,5-trimethoxybenzoate	0.48	S
20m	224	(*Z*)-1-methoxy-2-(3,4,5-trimethoxyphenyl)ethene	7.26	S
21m	224	(*E*)-isomer of 20m	5.81	S
22m	270	*erythro*-1,2-dimethoxy-4-(1,2,3-trimethoxypropyl)benzene	0.69	G
23m	238	2-(3,4,5-trimethoxyphenyl)-1-methoxy-1-methylethene	1.63	S
24m	270	*threo*-isomer of 22m	0.91	G
25m	238	(*E*)-3-(3,4,5-trimethoxyphenyl)-1-methoxyprop-2-ene	2.61	S
26m	222	methyl 3,4-dimethoxycinnamate	0.09	CA
27m	300	*erythro*-1,2,3-trimethoxy-5-(1,2,3-trimethoxy-propyl)benzene	2.87	S
28m	300	*threo*-isomer of 27m	2.32	S
29m	268	1-(3,4,5-trimethoxyphenyl)di-methoxypropene isomer	ND	S
30m	268	1-(3,4,5-trimethoxyphenyl)di-methoxypropene isomer	ND	S
31m	268	1-(3,4,5-trimethoxyphenyl)di-methoxypropene isomer	ND	S
		total	100	

[a] Some of the 3,4,5-trimethoxybenzenes were tentatively assigned on the basis of the MS data. [b] ND, not detected. [c] G, guaiacyl lignin moiety; S, syringyl lignin moiety; B, *p*-hydroxybenzoates; CA, cinnamic acids. [d] Not displayed (retention time of 6.0 min).

because the 4-vinylphenols are also present in the pyrolysates of wood lignins (*16*) and enzymatic dehydrogenative polymers of cinnamyl alcohols (*30*) containing no *p*-hydroxycinnamic acid derivatives. These findings demonstrate that the cinnamic acid derivatives are present in, at most, minor abundance in the sago palm lignin. Similar findings were obtained in oil palm lignin (*3−10*).

Composition in Sago Palm Lignin. The dioxane lignin pyrolysate also contains guaiacols (2-methoxyphenols) derived from the guaiacyl lignin moiety and syringols (2,6-dimethoxyphenols) derived from the syringyl lignin moiety (see Figure 1). Large differences in
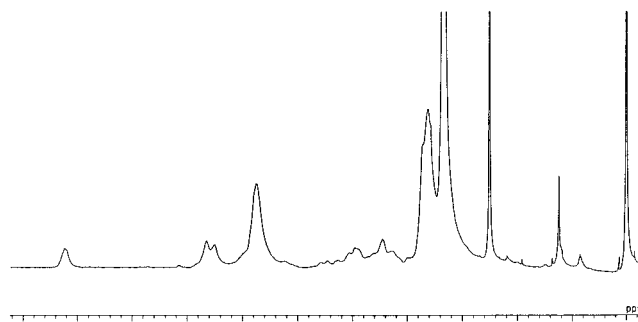
**Figure 3.** ^{1}H NMR spectrum (DMSO-d_6) of dioxane lignin.

abundances are observed between guaiacols and syringols. Of the guaiacols observed, the abundances of three major guaiacols, guaiacol (peak 4, 2.5%), 4-methylguaiacol (peak 5, 2.2%), and 4-vinylguaiacol (peak 10, 2.3%), were almost the same and followed by (*E*)-isoeugenol (peak 16, 1.5%). The contributions of vanillin (peak 14), acetoguaiacone (peak 18), and coniferaldehyde (peak 27) were small (≤1%).

Major syringols were 2,6-dimethoxy-4-vinylphenol (peak 20, 9.1%), (*Z*)- and (*E*)-2,6-dimethoxy-4-propenylphenol (peaks 23 + 25, 8.9%), 2,6-dimethoxyphenol (peak 12, 8.8%), and 2,6-dimethoxy-4-methylphenol (peak 15, 8.3%). These abundances are >3 times those of guaiacols shown by peaks 4, 5, and 10. In the dioxane lignin pyrolysate, clearly, the syringyl-type pyrolysis products are present in a greater abundance than the guaiacyl-type pyrolysis products.

Richness in syringols in the sago palm pyrolysate suggests that the sago palm dioxane lignin contains a large abundance of the syringyl lignin moiety compared to the guaiacyl lignin moiety. Comparing the contributions of pyrolysis products provides quantitative information on the lignin composition. The ratio of the syringyl-type pyrolysis products to the guaiacyl-type pyrolysis products (pyrolytic S/G) has been used for the determination of the proportion of the syringyl lignin moiety and guaiacyl lignin moiety because pyrolytic S/G ratios are well consistent with wet chemical S/G ratios determined by alkaline nitrobenzene oxidation (*21*, *30*, *31*) and thioacidolysis (*20*).

The lignin composition was determined. Other than phenol derived from the *p*-hydroxybenzoates, some *p*-hydroxyphenyl-type products (peaks 2, 3, 6, and 13) were observed (Figure 1). However, we did not evaluate the contribution of these products to the *p*-hydroxyphenyl lignin moiety in the sago palm lignin because (1) these products may come from the *p*-hydroxybenzoates and *p*-coumaric acids, not from the core lignin, and (2) the pyrolysate lacks *p*-hydroxyphenyl-type products with a three-carbon side chain such as 4-(prop-1-enyl)phenol. In addition, the TMAH pyrolysate contained no *p*-hydroxyphenyl lignin-derived products such as anisole and 4-methylanisole. Even if present, therefore, the proportion of the *p*-hydroxyphenyl lignin moiety is rather small in the sago palm lignin, as well as in oil palm lignin (*6*, *10*).

The pyrolytic S/G ratio was calculated on the basis of the sum of the molar yields of syringyl- and guaiacyl-type products listed in Table 1. High repeatability for this technique is reported (*20*). Calculating the summed contributions of the syringyl products and those of the guaiacyl products gave a 4.2 pyrolytic S/G ratio for the dioxane lignin, showing that the sago palm dioxane

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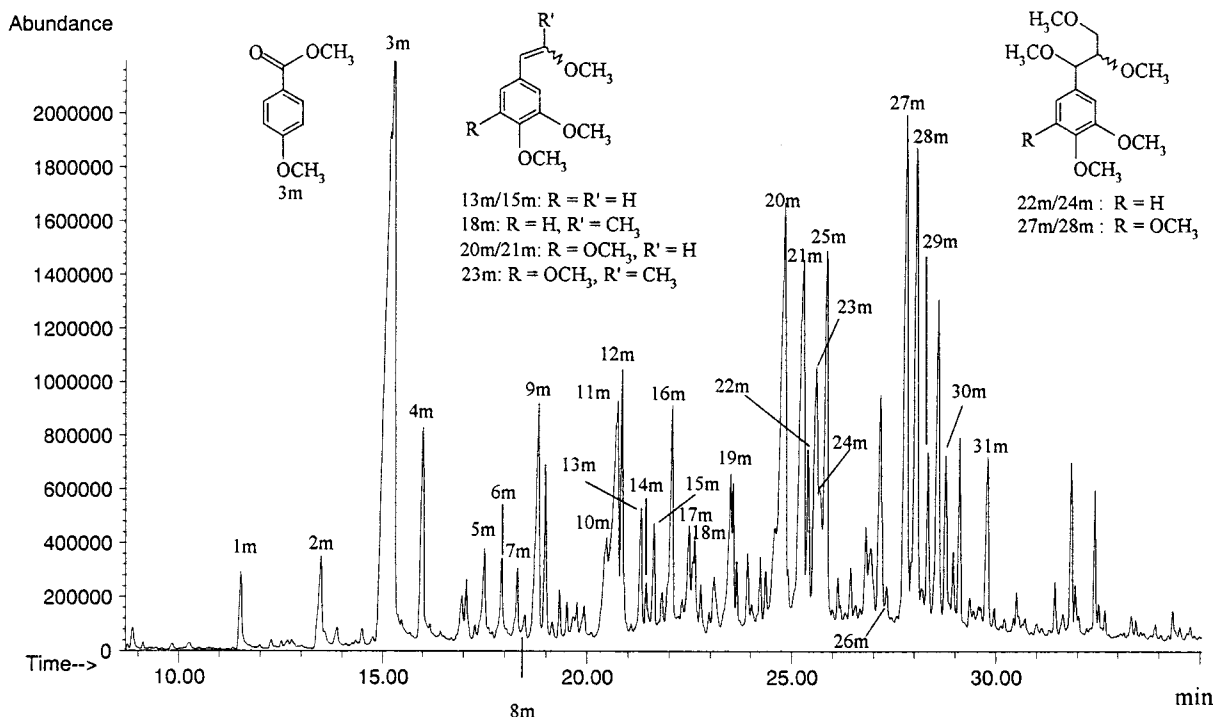
Figure 4. TMAH/Py-GC-MS trace of sago palm hydrolyzed dioxane lignin. Pyrolysis was done at 500 °C for 4 s. Peak numbers and names refer to those in Table 2.

lignin is a syringyl-rich type. This and the molar yields of the products derived from the *p*-hydroxybenzoates therefore show that the dioxane lignin comprises guaiacyl lignin, syringyl lignin, and *p*-hydroxybenzoates in an approximately 12.4:51.8:35.8 proportion.

The predominance of the syringyl lignin moiety over the guaiacyl lignin moiety was proven also by ^{1}H NMR analysis. Figure 3 shows a much larger signal area (due to the syringyl nuclei protons) at ~6.4−6.9 ppm than that (due to the guaiacyl nuclei protons) at ~6.9−7.1 ppm.

Comparison of Frequencies of β-Aryl Ether Substructures in Sago Palm Lignin. To confirm the richness in syringyl lignin of sago palm, we compared the abundances of the pyrolysis products derived from the arylglycerol moieties involved in the arylglycerol-β-aryl ether substructures, the most abundant substructures in lignin. TMAH/Py was used for this; the relative abundances of the methylated products were also calculated using eq 1.

TMAH/Py cleaves most of the β-aryl ether linkages with assistance of alkaline hydrolysis and then methylates the released fragments (*32−35*). In the TMAH/pyrograms (Figures 2 and 4), we observe methylated products retaining the structural attributes of the β-aryl ether substructures. Products from the guaiacyl β-aryl ether substructures are (*Z/E*)-4-(2-methoxyvinyl)-1,2-dimethoxybenzene (peaks 13m/15m), 2-(3,4-dimethoxyphenyl)-1-methoxy-1-methylethene (peak 18m), and *erythro/threo*-1,2-dimethoxy-4-(1,2,3-trimethoxypropyl)-benzene (peaks 22m/24m) (*32, 33*). Similarly, the syringyl equivalents are obtained from the syringyl β-aryl ether substructures: the enol ethers (peaks 20m and 21m), 23m, and the 1,2,3-trimethoxypropanes (peaks 27m and 28m). In particular, the trimethoxypropanes are important indices for evaluation of the relative abundance of the β-aryl ether substructures in lignin because they retain the intact glycerol side chain of the β-aryl ether substructures.

TMAH/Py has been applied to the characterization of lignocellulosic materials (*18, 27, 28, 32−40*). Hatcher's group (*33−37*) has extensively developed off-line TMAH/Py in which the pyrolysis is carried out in a glass ampule including a mixture of lignocellulosic materials and TMAH at lower temperature for longer time [e.g., 250 °C for 30 min (*36*) or 300 °C for 10 min (*37*)]; the resulting methylated products are extracted with a solvent such as methylene chloride, and the extracts are then subjected to the chromatographic separation. This method enables us to analyze the methylated products quantitatively by adding an internal standard in the lignin TMAH pyrolysates. Because of the absolute determination of the product yields being rather difficult in on-line TMAH/Py, this offers an attractive advantage to pyrolysis. However, off-line TMAH/Py of a Japanese cedar wood, carried out as preliminary experiments, provided products derived from the β-aryl ether substructures in a small abundance and unfavorable products (e.g., methyl 3,4-dimethoxybenzoate 10m) with less structural information on the lignin in a large abundance compared to on-line TMAH/Py, although no large qualitative differences were observed between the pyrograms provided by the two methods. Therefore, this study employed on-line TMAH/Py.

TMAH/Py of the dioxane lignin produced the isomeric pairs of the syringyl enol ethers (peaks 20m and 21m) and trimethoxypropanes (peaks 27m and 28m) as the major products other than 3m. The contribution of the former isomers was larger than that of the latter isomers; the contributions of the enol ethers (20m + 21m) and the trimethoxypropanes (27m + 28m) were 28.8 and 11.4%, respectively, to the TMAH/Py products except 3m. Contrary to this, the guaiacyl equivalents were present in rather small abundances, although the contribution of the guaiacyl enol ethers was likewise larger than that of the guaiacyl trimethoxypropanes. The contribution of 25m was similar to that of 28m. The TMAH/Py products other than the β-aryl ether sub-

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structure derived products were also mainly of syringyl type. Similarities were observed in Figure 4, although the contributions of the products differed from those in Figure 2.

The TMAH/Py cleavage of the β-aryl ether substructures produces phenolic trihydroxypropanes such as 1-(4-hydroxy-3-methoxyphenyl)propane-1,2,3-triol as precursors of trimethoxypropanes such as 22m, 27m, and their *threo*-isomers. Subsequent methylation of hydroxyl groups attached to the three-carbon side chain and the phenolic hydroxyl group, however, competes with the thermally assisted removal of the terminal methylol group from the precursors and simultaneous formation of the enol ethers [e.g., 13m, 20m, and their (*E*)-isomers], whereby the α-OH and the β-proton are removed to give a water. Therefore, larger contributions of the enol ethers suggest that the pathway of forming the enol ethers is favored over the methylation under the TMAH/Py conditions employed.

Figures 2 and 4 clearly show the predominance of products derived from the syringylglycerol moieties in the dioxane lignin because the relative abundances of peaks 27m and 28m overwhelm those of peaks 22m and 24m. As indices for the relative frequency of the arylglycerol-β-aryl ether substructures, we determined the relative abundances of the syringyl- and guaiacyl-type products derived from the arylglycerol-β-aryl ether substructures. The molar ratio of abundances of the syringyl-type enol ethers (20m, 21m) plus 23m plus 1,2,3-trimethoxypropanes (27m, 28m) to those of the guaiacyl-type equivalents (13m, 15m, 18m, 22m, and 24m) was 4.9, showing that the guaiacyl/syringyl β-aryl ether substructure proportion is approximately 17:83. This value is comparable with the pyrolytic S/G ratio (4.2) obtained by conventional Py-GC/FID.

The difference in the pyrolytic results observed between the pyrolyses with and without TMAH may be due to the difference in the pyrolytic origins of the products. Unlike TMAH/Py products that mostly come from the β-aryl ether substructures, conventional pyrolysis products come from various substructures in lignin. Evaluation for correlating TMAH/Py-GC/FID quantitative data to the wet chemical data is difficult because so far correlation of data obtained by the TMAH/Py and wet chemical methods is not accumulated sufficiently, unlike conventional Py-GC/FID data by which the pyrolytic S/G ratios obtained have good correlation with wet chemical S/G ratios obtained by wet chemical methods (*20, 21, 30, 31*). However, the quantitative data obtained here are enough to know the relative frequencies of the β-aryl ether substructures in the sample. Consequently, the TMAH/Py quantitative data demonstrate that in sago palm the syringyl β-aryl ether substructures are present in a greater frequency than the guaiacyl β-aryl ether substructures.

Others. 3-Methoxycatechol (peak 7), 4-methylcatechol (peak 9), and 5-ethylpyrogallol (peak 11) were observed. A small amount of catechol overlapped peak 5; therefore, the yield of catechol was not determined. Galletti and Reeves (*41*) showed that pyrolysis of tannin gives catechol and 4-methylcatechol. Therefore, tannin in the bark of sago palm is probably a source of low levels of peaks 9 and 11. Van Bergen et al. (*42*) also detected the catechols as tannin-derived impurities in the pyrolysate of *Nymphaea nelumbo*. 3-Methoxycatechol has been observed in the pyrolysates of forages (*17*), an archaeological oak (*Quercus* sp.) wood (*43*), and

tannin from grape seeds and skins (*41*). A 5-hydroxyguaiacyl lignin moiety has been proposed as a pyrolytic origin of this catechol (*44*). Related products with a side chain such as a propenyl group (e.g., 3-methoxy-5-prop-1-enylbenzene-1,2-diol) should be observed if pyrolysis occurs in the 5-hydroxyguaiacyl lignin moiety. However, the pyrolysate of our sago palm dioxane lignin lacked the other 5-hydroxyguaiacyl products, such as 4-vinyl-3-methoxycatechol and 3-methoxy-5-propenylcatechol, expected as major pyrolysis products. Another origin, demethylated syringyl units, has been proposed for 3-methoxycatechol (*43*).

Coniferyl and sinapyl alcohols, precursors of lignin, were not observed in the dioxane lignin pyrolysate. Kuroda et al. (*16*) showed that the abundance of coniferyl alcohol in lignin pyrolysates is greatly influenced by lignin isolation procedures. For example, treatment with dioxane/hydrochloric acid, acidolysis, provided dioxane lignins with a small abundance of pyrolytic origins of coniferyl alcohol (*16*). Therefore, the dioxane lignin isolation procedure may result in the lignin that produces no cinnamyl alcohols upon pyrolysis. However, in situ sago palm lignin also produced negligible abundances of the alcohols in pyrolysis as well as the dioxane lignin, regardless the use of the Py-GC/FID (or -MS) conditions that produce a considerable abundance of coniferyl alcohol and coniferaldehyde from softwoods (*16*). Similar observations have been made in the pyrolysis of the Björkman lignin of oil palm (*9*).

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