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Chemical Characteristics of Oil Palm Trunk

By

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Summary : The chemical characteristics of oil palm trunk (*Elaeis guineensis* Jacq.) were investigated. The sample of oil palm trunk was divided into two fractions by crashing and screening processes. These fractions consisted of vascular bundles and parenchyma. The starch content of the parenchyma fraction was found to be remarkably higher than that of the vascular bundles. The sugar components of both fractions were mainly xylose and glucose. The milled wood lignin from both fractions contained *p*-hydroxybenzoic acid as an ester group, but did not contain *p*-coumaric acid ester group which is commonly found in the lignin from Gramineae. This milled wood lignin also contained a small percentage of polysaccharides which was difficult to remove by fractional precipitation and Meicellase treatment but was removed easily by alkaline treatment. This indicated a possibility of an ester linkage between the polysaccharide and the lignin moiety.

1. Introduction

Oil palm is widely planted in tropical areas to obtain palm oil from its fruit and recently its plantation area has been expanding rapidly. After approximately 25 years its economical life span, oil palm trunks are cut down so as to allow replanting, the trunks simply being left on the plantation and not used productively. During replanting a very large amount of waste trunks are exhausted and cut into pieces and burned simply to prevent the breeding of harmful insects and local environmental pollution. However, reckless deforestation has been proceeding rapidly in those same tropical areas. Therefore, to discover an end use for this massive quantity of waste oil palm trunks would lead to a reduction in the cutting of tropical woods and the preservation of precious rain forest. Since oil palm is planted regularly on large scale flatland plantation, it would be easy to collect the wasted trunks and transport them to industrial sites. The main reason for the lack of utilization of oil palm trunks lies in their extremely tough outer bark which damages cutting machine blades and its special structure which is rich in easily decayable parenchyma. However, taking a different approach to the problem, the fact that the trunk is decayable means that it contains a large quantity of polysaccharides. In this paper the chemical characteristics of oil palm trunks were examined to find out an effective end use.

2. Experimental

2.1 Plant Material

Wood samples from 25-year-old oil palm trunks (*Elaeis guineensis* Jacq.) were obtained from Socfin Palm Oil State in Batang Berjuntai, Selangor, Malaysia.

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Samples were debarked and cut into small chips which were then crashed in order to separate vascular bundles from parenchyma.

2.2 Determination of starch content

Under 200 mesh size of wood meal was prepared for the determination. Starch content was determined as described by HUMPHREYS (1961).

2.3 Preparation of milled wood lignin (MWL)

The extractive free wood meal was milled for 100 hours by using a vibratory ball mill. The MWL was extracted and purified according to the standard method of BJÖRKMAN (1956).

2.4 Alkaline nitrobenzene oxidation

Nitrobenzene (0.24 ml) and 2 N potassium hydroxide (4 ml) were added to the lignin sample (10 mg) in a stainless micro tube and the mixture was heated for 2 hours at 160°C with continuous vigorous shaking. After cooling the solution was then extracted with ethyl ether to remove the residual nitrobenzene. The solution was then acidified with hydrochloric acid and extracted again with ethyl ether. The extract was dried over anhydrous sodium sulfate and evaporated to dryness. The resultant phenols were converted to trimethylsilyl (TMS) derivatives and analysed by gas chromatograph (GC) using acetovanillon as an internal standard. GC was performed using Shimazu GC-14 A with a capillary column HiCAP-CBP1.

2.5 Alkaline hydrolysis

Lignin preparation (30 mg) was dissolved in 1 N sodium hydroxide solution (50 ml) with stirring under N_2 and left for 24 hours at room temperature. Then the solution was acidified with hydrochloric acid and the resultant precipitate was recovered by filtration and washed with hot water. The filtrate and washings were combined and extracted with ethyl ether. The ether fraction was then dried over anhydrous sodium sulfate and evaporated to dryness. The resultant phenolic acids were analysed by gas chromatography-mass spectrometry (GC-MS) as TMS derivatives. GC-MS was performed with Hewlett Packard 5890 A-JEOL JMS-DX 303 HF using the same capillary column as described above.

2.6 Sugar analysis

The sugar composition of the oil palm trunks was determined by HPLC using the spent liquor from klason lignin preparation. The sugar composition of MWL was determined by HPLC with the hydrolysate by 2 M trifluoroacetic acid at 120°C for 1 hour. HPLC was performed using Shimazu LC-3 A with column ISA 07/S 2504.

Acidic sugars in the hemicellulose were determined by GLC as alditol acetates, according to the method of MAEKAWA (1988).

2.7 Gel permeation chromatograph (GPC) analysis of MWL

About 1 mg acetylated MWL was dissolved in 10 ml tetrahydrofuran and 2 ml of the solution was applied to TOSOH HLC-8020. Untreated MWL was also applied to Sephadex LH-20 using dioxane-water (8 : 2) as an eluent.

2.8 ^{13}C NMR spectroscopy

About 100 mg of samples were dissolved in 0.5 ml DMSO-d_6 and spectra were obtained with JEOL JNM GXS-400.

3. Results and discussion

Fig. 1 shows a model structure of the cross section of oil palm trunks. Vessels, phloems and fibers constitute long shape vascular bundles and they are scattered in the parenchyma. This type of structure is quite common in many monocotyledons. Vascular bundles and parenchyma can be easily separated by crashing the chips of oil palm trunks. Vascular bundles and parenchyma consisted 71-76% and 24-29% of the whole chips respectively.

Table 1 shows the results of analysis of both fractions. The ash mainly consisted of silica. Both fractions contained silica but under microscopic observation particles of crystalline silica were observed along the outer surface of the vascular bundles (IMAMURA, 1990). The high content of ash in the parenchyma may be due to contamination from vascular bundles by pulverlization during the sample preparations. The starch content showed a remarkable contrast between the two fractions. Parenchyma contained a lot of starch which amounted to more than half of its dry weight. This was in accordance with the microscopic observation that the parenchyma cell contained many starch particles (IMAMURA, 1990). It was found that klason lignin content was under 20% in both fractions but was slightly higher in parenchyma. The klason lignin was also

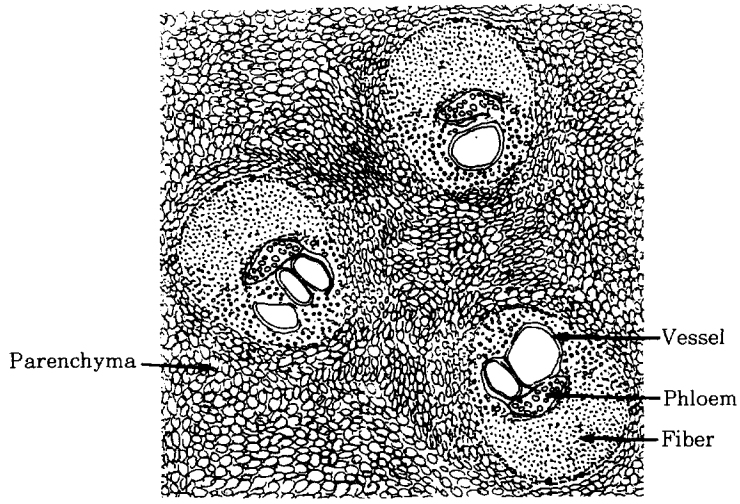

Fig. 1. Model of tissue structure of an oil palm trunk.

Table 1. Analysis of vascular bundle and parenchyma. (%)

	Ash	Starch	Lignin(Acid soluble)	Sugar composition				
				Man	Ara	Gal	Xyl	Glu
Vascular bundle	2.2	2.4	15.7 (3.9)	2.0	+	+	34.8	63.2
Parenchyma	2.9	55.5	20.0 (4.5)	1.3	6.5	1.9	34.8	55.5

contaminated with crystalline silica. Sugar analysis of both fractions indicated that xylose and glucose were the main components, as is the case with Gramineae.

Table 2 illustrates the results of analysis of acidic sugars from oil palm hemicellulose. The ratio of 4-O-methyl glucitol and glucitol to xylitol in aldobiouronic acid was 0.94 : 0.06 : 1.00. This is far closer to that from beech (0.90 : 0.07 : 1.00) than that from bamboo (0.68 : 0.29 : 1.00) (MAEKAWA, 1988). Thus the acidic sugars from oil palm hemicellulose were of the hardwood type rather than the Gramineae type.

The results of nitrobenzene oxidation of MWL are shown in Table 3. Both MWLs produced vanillin, *p*-hydroxybenzoic acid, syringaldehyde and a small amount of phenolic acids such as vanillic acid and syringic acid though *p*-hydroxybenzaldehyde was not found in the degradation products. This proves that both MWLs do not contain *p*-coumaric acid ester structure which is a typical characteristic of the lignin from monocotyledon. Fig. 2 shows the total ion chromatogram and mass spectra of alkaline hydrolysis products of parenchyma MWL by GC-MS analysis. The largest peak was attributed to *p*-hydroxybenzoic acid from retention time and mass pattern. There were also small peaks attributed to vanillic acid and syringic acid. Thus the phenolic acid ester structure consisted of the C_6-C_1 type. However, phenolic acids of the C_6-C_3 type such as *p*-coumaric acid, ferulic acid and sinapic acid were not found in alkaline hydrolysis products. Analysis of vascular bundles also showed the same result meaning that the oil palm lignin is different from the Gramineae lignin. The phenolic acid ester and especially the *p*-hydroxybenzoic acid ester structure is characteristic of poplar lignin (OKABE, 1965). It is of interest that the oil palm lignin contains the same structure as poplar lignin. The content of *p*-hydroxybenzoic acid was higher in parenchyma than in vascular bundles (Table 3) thus showing the same tendency of sugarcane parenchyma which contains far more *p*-coumaric acid ester structure than fiber fraction (HE, 1990). The ratios of syringyl/guaiacyl unit were also slightly different between the two fractions. The vascular bundles (S/V, 2.68) were slightly richer in syringyl unit than parenchyma (S/V, 2.22).

Table 2. Composition of aldobiouronic acid prepared from hemicellulose of oil palm (molar ratio).

Xylitol	4-O-Me glucitol	Glucitol
1.00	0.94	0.06

Table 3. Yield of nitrobenzene oxidation products. (%)

	Vanillin	p-Hydroxybenzoic acid	Syringaldehyde
MWL from vascular bundle	4.1	9.8	11.0
MWL from parencyma	3.6	14.9	8.0

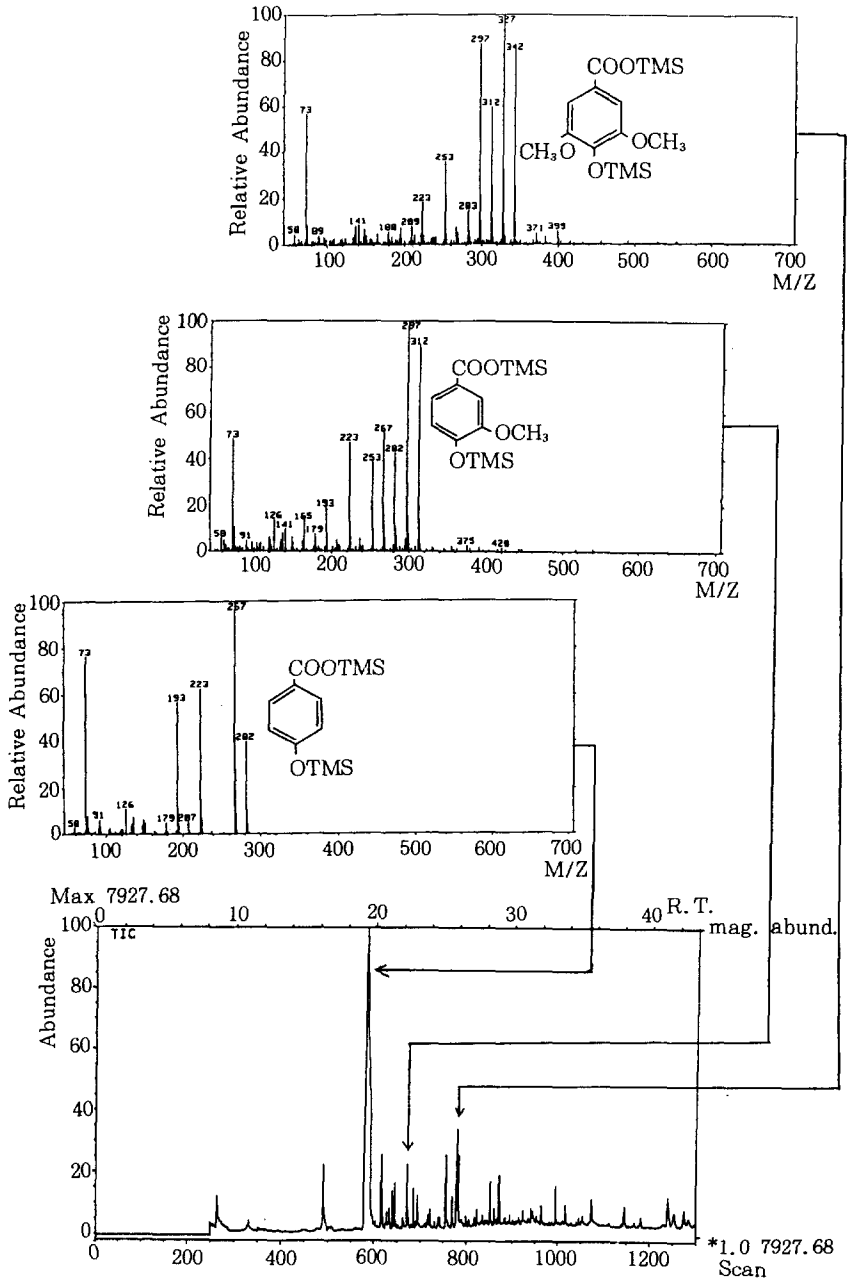

Fig. 2. GC-MS analysis of phenolic acids produced by alkaline hydrolysis.

Fig. 3 shows the ^{13}C NMR spectra of oil palm MWL from vascular bundles. Before alkaline treatment peaks at 166 and 162 ppm attributed to *p*-hydroxybenzoic acid ester appeared clearly. But after alkaline hydrolysis these peaks disappeared. This change in spectra was accompanied by the disappearance of a peak at 63 ppm which was

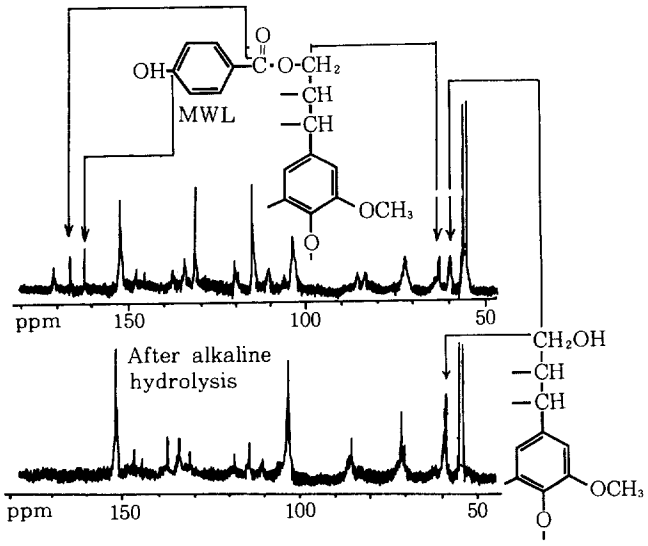

Fig. 3. ^{13}C-NMR spectra of MWL before and after alkaline hydrolysis.

attributed to γ-carbon of the lignin side chain attached to the ester group (KATO, 1985). The intensification of the peak at 60 ppm was attributed to hydroxymethyl γ-carbon. Therefore the site of ester bonding in lignin moeity may be at the γ-carbon of the side chain. The region of α-carbon range 72–75 ppm was also changed by alkaline treatment but it is not so clear in this spectra. The same tendency was observed in MWL from the parenchyma.

In the NMR spectra there were some peaks attributed to carbohydrates. Peaks at 20 ppm and 172 ppm assigned to an acetyl group in hemicellulose were observed in untreated MWL and these disappeared after the alkaline treatment.

Sugar analysis indicated that untreated MWL contained 4–5% of carbohydrate. This carbohydrate was very difficult to remove by purification and remained even after treatment by crude Meicellase which has activity against hemicellulose. The sugar in MWL consisted mainly of xylose with a small amount of glucose and arabinose which was different from that of oil palm trunks (Fig. 4). After alkaline treatment sugar analysis indicated that MWL from both fractions contained only a trace amount of glucose and xylose (Fig. 5). This implied that the carbohydrate in MWL might be bonded to lignin moiety by ester linkage through the carboxyl group containing sugar such as uronic acid.

Fig. 6 shows the results of gel permeation chromatography of MWL. The peak of molecular weight distribution of oil palm MWL was not significantly changed after alkaline treatment. In this experiment acetylated MWL was used to obtain better solubility in THF but even then there was a small amount of insoluble fraction. Therfore that another gel filtration experiment was carried out using Sephadex LH-20 with

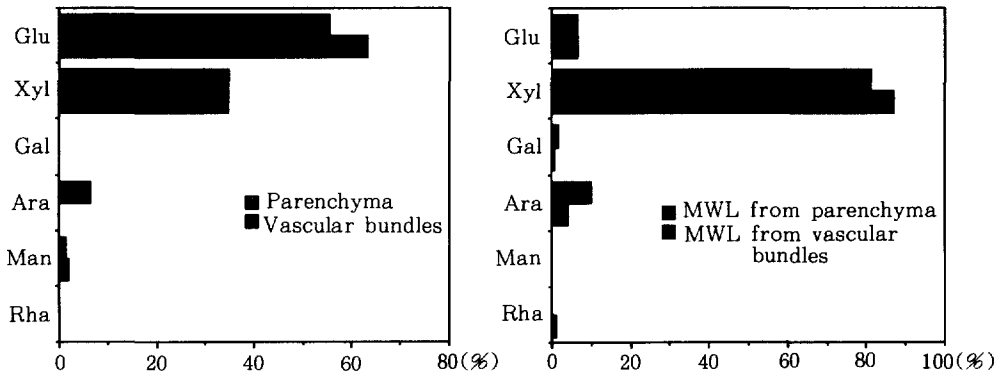

Fig. 4. Sugar composition of trunk and MWL.

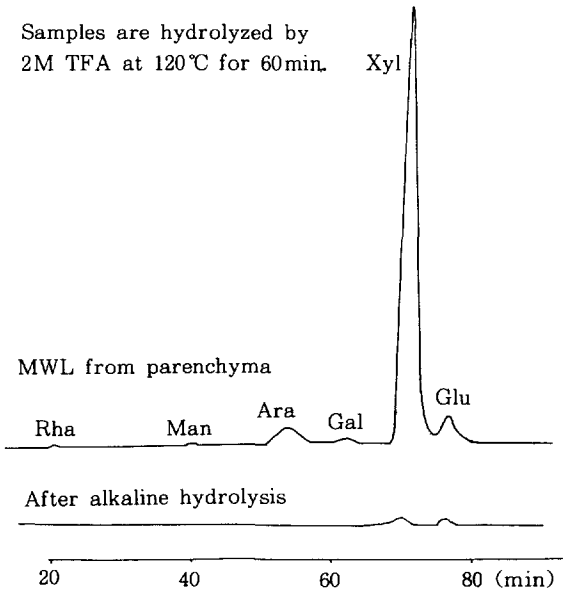

Fig. 5. HPLC chromatogram of sugar analyses of MWL.

dioxane as an eluent. The results showed the same tendency and there was no significant change before and after alkaline treatment (Fig. 7). This is a quite different tendency from that of sugarcane MWL reported by HE (1990). In that report sugarcane MWL was treated with alkaline solution at room temperature and it was found that the molecular weight of the resultant lignin was very greatly reduced. From this result they presumed the presence of crosslinkage in lignin molecule through phenolic acids. However according to the present results for oil palm MWL there in fact might be little crosslinkage via *p*-hydroxybenzoic acid.

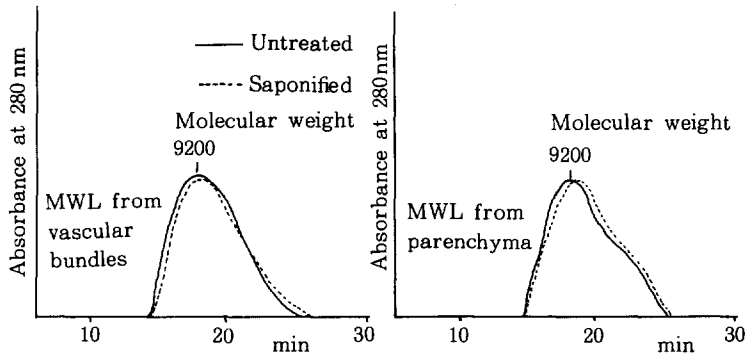

Fig. 6. GPC analyses of MWLs.
* Samples were acetylated.

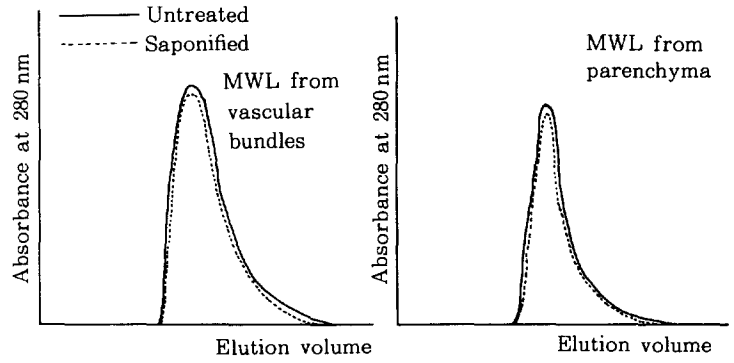

Fig. 7. Gel filtration curves of MWLs by Sephadex LH-20.

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オイルパーム材の化学的特性

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摘　要

25年生マレーシア産オイルパーム材の樹幹部を，繊維束部分と柔組織部分に分けて化学成分の特性を調べた。粉砕によりこの両者は容易に分けることができ，その割合は繊維部分が71～76%，柔組織部分が24～29%であった。柔組織部分は多量の澱粉を含み，その割合は55.5%に達していた。糖組成は両部分ともキシロースとグルコースが主体であった。オイルパームのリグニンはp-オキシ安息香酸エステル構造を含み，その量は柔組織のMWL（磨砕リグニン）では15%に達した。しかし，禾本科植物や草本類によくみられるC_6-C_3のフェノール酸のエステル構造は含まれていなかった。MWL中には4～5%の糖が含まれていたが，これはアルカリ処理で消失することから，この糖もまたリグニンにエステル結合をしていると推定された。

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