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CHEMICAL COMPOSITION OF OIL PALM EXTRACTIVES

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Abstract

The extractives from oil palm trunk (OPT) were isolated by successive extractions with solvents of increasing polarity. The amounts of extracted materials (based on oven dry) with petroleum ether, ethyl ether, acetone/water (9:1), ethanol/water (8:2) and hot water were 0.15%, 0.3%, 3.3%, 3.9% and 1.1% respectively. The ash content (determined on a separate specimen) was 1.9%. The petroleum ether extract was fractionated into free acids (0.0315%) and neutral parts (0.1185%). The latter was saponified and subsequently fractionated into acids (0.0533%) and unsaponified compounds (0.0498%). The total amount of acids in OPT extractives was also very low (0.1346%). After derivatization with diazomethene, the methylesters were analyzed by gas chromatograhpy. The composition of the acids in OPT resembles that of palm oil from the pericarp. The unsaponified compounds were fractionated with the modified silica gel (Aminopropyl-Bond Elut) with hexane and chloroform into hydrocarbons and hydroxyl containing substances. The gas chromatographic analysis of the hydrocarbons revealed the occurrence of various n-alkanes, starting from $C_{16}H_{34}$ to $C_{33}H_{68}$.

The composition resembles that of cuticle wax from some palms. The hydroxyl containing fraction was mainly made up of sterols and minor amounts of fatty alcohols. Using authentic materials as references, ß-sitosterol, stigmasterol and cholesterol were identified and quantified by gas chromatography. The amounts of these sterols were very small. Remarkable is the occurrence of cholesterol which is usually not classified as phytosetrol. Some of the compounds already detected in the petroleum ether extract occurred also in the ethyl ether extract. Only 27% of the ether extract, comprising 1.05% (based on o.d. wood) could be identified. Probably the unidentified compounds are made up of oxidized fatty acids or fat accompanying compounds.

The polar extractive materials from the extraction with acetone/water and ethanol/water were fractionated into water soluble and insoluble compounds. Using a modified gel (Bond Elut C^{18}) the water soluble substances were separated into soluble phenolics, and soluble carbohydrates, by successive elution with water and methanol. The acetone/water extract contained 0.5% (OD) soluble phenolics, 1.9% (OD) soluble sugars, and 0.9% (OD) insoluble substances. The respective amounts of the ethanol/water extract were 0.6%, 2.3% and 0.7%. The soluble phenolics could not be separated satisfactorily by TLC. Condensed tannins were not detected. The soluble sugars in the acetone/water extract were mainly made up of low molecular weight sugars (90%) and minor amounts of erythrite and two cyclithes. The sugars were analysed by gas chromatography in the form of their tetramethyl silylether. The main sugars were saccharose, fructose and glucose. The acetone/water extract contained only 60% low molecular weight sugars. The water insoluble parts from both the acetone/water and ethanol/water extracts were probably low molecular weight lignin fractions. In the hot water extract no low molecular weight sugars were detected. Hemicelluloses, which on hydrolysis give monomer sugars, were detected in this fraction.

According to the examinations more than 50% of the total extractives, or 3.8% (based on OD OPT) were sugars besides small amount of cyclithes.

Introduction

Edible oil from oil palm and products derived from it are a major commodity in Malaysia. Research and development are being undertaken to industrially utilize other by-products or wastes from the oil palm industry and oil palm plantations. The trunk of the oil palm, cut after 25 years to be replaced by younger trees, is one of these by-products. The lignocellulosics derived from these trunks are suitable to make various kinds of panels, and also pulp (Khozirah *et al.* 1991). Some data on the chemical composition of such lignocellulosics with regard to cellulose, lignin and hemicellulose have been reported (Halimahton & Abdul Rashih 1991, Tomimura 1992). Since only limited data on the chemical composition of the extractives of oil palm trunk are available, the following examination was accomplished and the results reported.

Materials and methods

Oil palm trunk material was obtained from the Forest Research Institute Malaysia, Kepong, Kuala Lumpur. According to FRIM the material was obtained from the United Plantations Sdn. Bhd. in Teluk Intan. The fresh trunk was chipped, dried in an oven and shipped by air in air dry condition to Hamburg. The material consisted of chips from the bottom, middle and top of the trunk. Due to lack of material all fractions were mixed together and milled to pass a sieve with 0.5 mm grating.

200 g of air dry wood meal was extracted for 10 h using a Twisselmann extractor. The successive extraction method using petroleum ether (b.p. 40 to 60 °C), ether, acetone/water (9:1), ethanol/water (8:2), and hot water has been successfully used for the analysis of various wood extractives (Kubel *et al.* 1988; Weissmann *et al.* 1992; Lange 1992a,b). After each extraction the wood meal was air dried before they were extracted with the next more polar solvent. To obtain the hot water extract the wood meal - after the successive extraction with the organic solvents - was treated three times with water at 60 °C. The various extractives were then worked up according to the scheme shown in Figure 1. The ash content of the wood meal was determined using a separate sample.

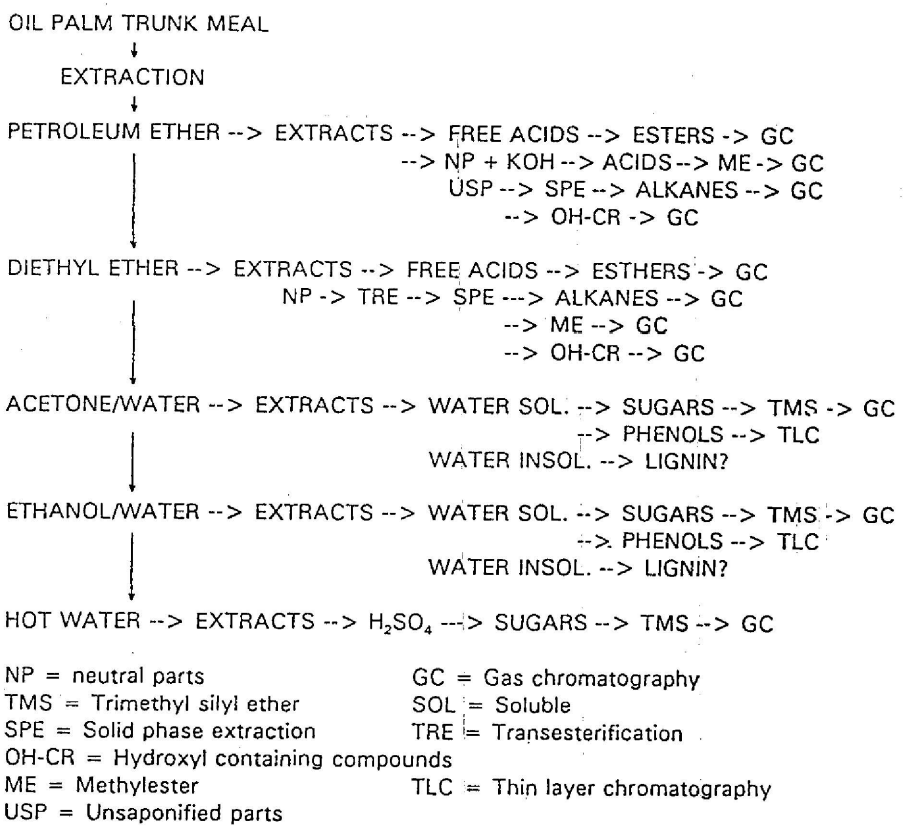

Figure 1. Schematic of fractionation and analysis of OPT extracts

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The results of the gas chromatographic analyses of the methyl esters of the fatty acids are listed in Table 3. To simplify the table only the amounts of C in the fatty acids, rather than the trivial names, are given together with the unsaturated bonds. A comparison of the composition of the fatty acids of the oil palm trunk (OPT) with those of the pericarp and endosperm of the same plant is shown in Table 4. It clearly shows that the composition of the fatty acids of the OPT resembles those of the pericarp (Hegnauer 1963).

Table 3. Composition of free and bound fatty acids in oil palm trunk

Fatty acid methyl ester	Free acids %	Bound acids %
C-12:0	1.9	4.7
C-14:0	1.0	3.7
C-15:0	1.2	1.3
C-16:0	33.7	23.4
C-17:0	3.5	1.8
C-18:2	7.3	14.2
C-18:1	30.9	29.5
C-18:0	4.7	3.2
C-19:0	0.5	?
C-20:0	1.0	0.4
C-22:0	1.0	0.7
C-24:0	2.5	1.8

Unsaponified parts

The recovery during the separation using the SPE cartridges was only 80%. The fractions eluted with hexane - the paraffin hydrocarbons -, and those with chloroform - the hydroxyl-containing compounds -, amounted to 35% and 65%, respectively.

Table 4. Comparison of composition of fatty acids of pericarp, endosperm and trunk of oil palm

Fatty acid	Pericarp %	Endosperm %	Oil palm trunk %
C-8		4.3	
C-10		4.8	
C-12		51.3	1.9/4.7
C-14	0.5-5.9	16.5	1.0/3.7
C-16	32.2-47.0	7.5	23.4/33.7
C-18:0	1.0-6.1	1.7	3.2/4.7
C-18:1	39.5-52.5	11.3	29.5/30.9
C-18:2	5.0-11.3	1.3	7.3-14.2

The gas chromatography of these paraffin hydrocarbons revealed the occurence of n-alkanes with the composition $C_{16}H_{34}$ to $C_{33}H_{68}$. These compounds amounted to around 50% of the total paraffin hydrocarbon fractions. Their distribution was the following: $C_{24}H_{50}$ 6.0%; $C_{25}H_{52}$ 8.3%; $C_{26}H_{54}$ 12.1%; $C_{27}H_{56}$ 16.4%; $C_{28}H_{58}$ 9.0%; $C_{29}H_{60}$ 9.5%; $C_{30}H_{62}$ 7.6%; and $C_{31}H_{64}$ 7.1%. The rest of 50% of these fractions occurred in the gas chromatogram as unidentified by very small peaks. The distribution of the n-alkanes show some similarities with those of cuticle wax of some palmae (Hegnauer 1963). It has to be mentioned that the amount of n-alkanes in OPT was very small, namely around 0.015%.

The fractions which contain the hydroxyl-containing compounds were also analyzed by gas chromatography. The most important compounds were sterols. Beside that, small amounts of fatty alcohols were detected. The results of the GC analysis are listed in Table 5. Remarkable is the occurrence of cholesterol which is usually not classified as a phytosterol.

The separation of the unsaponified parts into paraffin hydrocarbons and hydroxyl-containing compounds was accomplished with solid phase extraction (SPE) using disposable cartridge (Aminopropyl-Bond elut, Analytichem International). The paraffin hydrocarbons were eluted with hexane and the hydroxyl-containing compounds were successively eluted with chloroform (Kaluzny *et al.* 1985). To separate sugars from phenolics in the water soluble parts of acetone/water and ethanol/water extracts a cartridge filled with a C_{18}-modified silica gel (Bond Elut C_{18}, Analytichem International) was used. Sugars and phenolics were eluted with water and methanol respectively.

The free acids were esterified with diazomethane in ether. Transesterification was accomplished with sodium methoxide in benzene (Supelco Inc. 1979). The reaction products were separated according to Kaluzny *et al.* (1985) using SPE. Gas chromatographic analysis (GC) were performed with a Perkin Elmer Type Sigma 2B apparatus, equipped with a flame ionization detector. The peaks were integrated with a Shimadzu Recording Data Processor (Type Chromatopac, C R1B). A non-polar capillary column (DBV-5), made of quartz 30 m long, was applied. The carrier gas was hydrogen with a flow rate of 2 ml/min and a split of 1:40. The temperature varied from 150 to 260°C. The separated compounds were identified by comparison with authentic samples. The sugars were analyzed as their trimethylsilyl derivatives by gas chromatography.

Results and discussion

Successive extractions

The yields and kinds of compound detected in the various fractions are listed in Table 1.

Petroleum ether extracts

Fatty acids

The extract was firstly separated into free fatty acids and neutral parts by treating with a 2N sodium carbonate solution and ether. The neutral parts were then hydrolysed with an ethanolic potassium hydroxide (0.5N) solution. The free fatty acids were isolated with ether after acidification with diluted sulfuric acid. Based on a glycerol

Table 1. Yield of successive extraction and ash content of oil palm trunk

Solvent	Extractives %	Class of compounds
Petroleum ether	0.15	Free fatty acids, glycerides, wax esters, fatty alcohols, sterols, paraffin hydrocarbons
Ether	0.3	Partly oxidized fats and fat accompanying compounds, glycerides, wax alcohols, sterols, paraffin hydrocarbons, free fatty acids
Acetone/water (9:1)	3.3	Sugars, cyclitols, phenolics, soluble lignin
Ethanol/water (8:2)	3.9	Sugars, amino acids cyclitols, phenolics, soluble lignin
Total extractives	7.65	
Hot water	1.1	Water soluble polysaccharides
Ash content	1.9	Inorganic compounds

determination, it was calculated that before hydrolysis about 30% of the fatty acids were esterified with glycerol (as triglycerides). The rest or 70% may be wax- or sterol-esters. The yield of various fractions is shown in Table 2. The total yield of fatty acids was very low (0.0848%).

Table 2. Amounts of free and bound fatty acids in petroleum ether extracts of oil palm trunk

Compound	Amount % (Based on od OPT)
Free fatty acids	0.0315
Neutral parts	0.1185
Fatty acids after saponification Unsaponified parts	0.0533 0.0498
Total fatty acids	0.0848

material), of the total extractives in both the acetone- and ethanol-water extracts polar extractives were soluble carbohydrates. The carbohydrates in the acetone/water extracts were mainly sucrose, glucose, fructose, and small amounts of sugar alcohols. The compounds in the ethanol/water extracts showed a rather different pattern. The above mentioned carbohydrates and inositol comprised only 60% of the total soluble carbohydrates. The rest were of unknown structure. These substances were, however, neither sugars or cyclitol. Some of it were probably amino acids.

Table 7. Composition of soluble carbohydrate fration of acetone/water and ethanol/water extracts

Compound	Acetone/water extract % total sugars	Ethanol/water extract % total sugars
Erythritol	0.2	2.8
Fructose	20.7	12.5
Glucose	33.6	9.8
Scyllo-inositol	1.3	7.8
Myo-inositol	1.6	3.3
Sucrose	42.5	63.6

The amount of total soluble phenolics was only 1.1% (o.d. OPT). It was not possible to achieve a satisfactory thin layer chromatographic separation. The partial hydrolysis of these phenolics with hydrochloric acid did not result into a deep red coloured products, as shown by anthocyanidine hydrochloride. The negative result of this test showed the absence of proanthocyanidines condensed tannin. Due to the small amounts of the phenolics no further examinations were accomplished.

Hot water extracts

In this fraction no low molecular weight carbohydrates were detected. The composition of the monomers after acid hydrolysis, based on the gas chromatographic analysis of the silyl ether derivatives, is listed in Table 8. The major sugars were glucose followed by xylose. Small amounts of galactose and mannose were also detected. The results of the carbohydrate analysis indicated the occurrence of hot water soluble polysaccharides. Also starch might occur in this hot water extracts.

Table 8. Composition of hydrolysate of hot water soluble parts

Monomer sugar	Amount %
Arabinose	6.9
Rhamnose	1.3
Xylose	11.5
Mannose	6.9
Galactose	7.1
Glucose	53.6

Conclusion

The extractives of OPT consisted of 0.45% apolar and 7.2% (based on o.d. OPT) polar compounds. In the hydrophobic parts of the extracts on 0.0848% of fatty acids, either free or bonded, were detected. The rest consisted of paraffin hydrocarbons, sterols, wax esters, fatty alcohols, and partly oxidized fats and fat accompanying compounds. The fatty acids showed similarities with those of the pericarp of oil palm.

The polar extractives had the following groups of compounds (all based on oven dry OPT) : low molecular carbohydrates 4.2%; phenolics 1.1%; and 1.6% lignin-resembling substances. Small amounts of cyclitol were also detected. Condensed tannins were not detected in the phenolic fractions.

The amount of hot water extracts was 1.1%. They consisted of polysaccharides which on hydrolysis yielded glucose and xylose as the main sugars. Smaller amounts of galactose, mannose arabinose, and rhamnose were also detected.

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Table 5. Composition of hydroxyl fraction of neutral parts of petroleum ether extracts

Hydroxyl compound	Amount %
Dodecanol-1	0.3
Tetradecanol-1	0.3
Hexadecanol-1	1.3
Octadecanol-1	1.9
Eicosanol-1	0.2
Cholesterol	15.8
Campesterol	3.3
Stigmasterol	18.5
ß-sitosterol	45.1
Dihydrositosterol	2.5

Diethyl ether extracts

The results indicate that the diethyl ether extracts partly consisted of real fats and fat accompanying compounds. After distilling off the solvents, the residue was very difficult and not wholly soluble in ether again. If the ether soluble parts were treated with a sodium carbonate solution to separate free acids, the resulting alkaline liquid was very dark. After acidification with diluted sulfuric acid only a small part of these freed acids could be redissolved in ether. These insoluble fractions were not further examined, because the amount was very small.

The neutral parts of the diethyl extracts were transesterified with sodium metoxide. The reaction products were then separated by SPE using the Aminopropyl-Bond elut cartridge. The various groups of compound were eluted with solvents of increasing polarity. The elute consisted of the following classes of compounds; 56% methylesters and paraffin hydrocarbons; and 44% hydroxyl-containing substances.

The methylesters and paraffin hydrocarbons were analyzed by GC. Only 13% of the total amount of this fraction were fatty acid methylesters. Their composition resembles those of the compounds in the petroleum ether extracts. The paraffin hydrocarbons amounted to

16% of the total fraction. They consisted of n-alkanes with C-numbers of C_{20} to C_{34}. The rest (71% of the fraction) gave in the gas chromatogram many small peaks. There were no attempts to identify these peaks. Probably they consisted of oxidized fatty acids.

The hydroxyl-containing compounds were also anlayzed by GC. Only 27% of these (based on the gas chromatogram) could be identified. Sterols, e.g. cholesterol, stigmasterol and ß-sitosterol, were the major compounds in this fraction. Beside that smaller amounts of fatty alcohols with a C-number of C_{14} to C_{24} accompanied the sterols. The unidentified compounds were probably oxidized fatty accompanying substances.

Acetone- and ethanol-water extracts

The first step in the analysis of these polar fractions was shaking of each 100 mg of extracts with 20 ml of warm water (45°C) for 1.5 h. Insoluble parts were filtered off with a porous glass filter. The water insoluble parts were probably lignin-like substances which are also detected in the same fractions of the extracts of beech and spruce (Kubel *et al.* 1988). The filtrate was further separated into carbohydrates and soluble phenolics, utilizing SPE. A disposable cartridge filled with a C18 modified silica gel (Bond Elut C18, Analytichem International) was applied. Carbohydrates were eluted with water and the phenolics stripped off with methanol. The yield of both classes of compounds are listed in Table 6.

Table 6. Fractionation of polar parts of acetone/water and ethanol/water extracts

Fraction	Acetone/water extracts (o.d. OPT)	Ethanol/water ectracts (o.d. OPT)
Total extractives	3.3	3.9
Soluble phenolics	0.5	0.6
Soluble carbohydrates	1.9	2.3
Water insolubles	0.9	0.7

The carbohydrates were transformed into trimethyl silylether derivatives and analyzed by gas chromatography. The results are presented in Table 7. Sucrose was the main sugar, followed by glucose and fructose. Only minor amounts of cyclic sugar alcohols were detected. According to Table 6, 58% or 4.2% (based on oven dry OPT

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FLUORESCENT WHITENING AGENTS FOR PAPER

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Abstract

The growing sophistication of the consumer is constantly increasing the pressure on manufacturers of white paper and board to improve the quality of their products. The results of many studies show that the considered application of FWAs can play a key part in optimising product quality.

Introduction

As a result of the number of supplies of flourescent whitening agents (FWA), and the quantities used in the paper industry, particularly in printing, writing and coated papers, the tendency is to categorise these chemicals as commodities. This is not without justification, particularly in markets where brightness or whiteness levels are quite low, as performance differences between products are often outweighted by price differentials. Nevertheless, a lack of awareness of the technical considerations, can lead to overuse, which could prove costly over a prolonged period of time, if an unsuitable FWA is used something which has happened in many paper mills around the world.

The situation is changing constantly as development take place to improve product quality and the result is that demands on the performance of FWAs are also changing.

Performance of different types of FWA

FWAs commonly used in the paper industry are based on di-amino stilbene sulphonic acid. It is the central part of the stilbenic molecule which shows fluorescence. The triazinyl groups forming the remainder of the molecule can be modified to alter the solubility, and affinity for cellulose. By so doing, the performance in application can be influenced to favour specific conditions.