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ABSTRACT

Air dry meal of oil palm trunk was successively extracted (yields in brackets are based on oven dry oil palm trunk material) with petroleum ether (0.15%); ethyl ether (0.3%); acetone/water ratio 9:1 (3.3%); ethanol/water ratio 9:1 (3.9); and hot water (1.1%). . The petroleum ether extracts were fractionated into free acids (0.0315%) and neutral parts (0.1185%). The neutral fraction was hydrolysed and yielded 0.0533% of acids and 0.0498% unsaponified parts. The total fatty acids are only 0.1346%. The gas chromatography (GC) of the fatty acid methylesters shows similarities with those of the oil of the pericarp of oil palm. The unsaponified fractions was separated by solid phase extraction (SPE), and the fractions examined by GC. Very small amounts of paraffin hydrocarbons are detected. In the hydroxyl-group containing substances ß-sitosterol, stigmasterol and cholesterol, and minor amounts of fatty alcohols were detected. Remarkable is the occurrence of cholesterol which is usually not classified as phytosterol. The ethyl ether extracts contain some of the compounds found in the petroleum ether extracts. Only 27% of the total ether extracts could be identified. The rest are probably oxidized fats and fat accompanying compounds.
The polar extractives were separated into hot water soluble and insoluble fractions. Further fractionation were accomplished by SPE. The acetone/water extracts contain 0.5% soluble phenolics, 1.9% soluble sugars, and 0.9% water insoluble substances. The respective fractions in the ethanol/water extracts are: 0.6%; 2.3%; and 0.7%. Condensed tannin was not detected in the soluble phenolic fractions. The soluble sugars in the acetone/water extracts are mainly low molecular sugars (90%), and minor amounts of erythritol and cyclitol. The sugars are sucrose, glucose and fructose. The ethanol/water extracts contain only 60% low molecular sugars with nearly the same composition as those of the acetone/water extracts. The rest of 40% were not identified. The water insoluble in the acetone- as well as in the ethanol-water extracts are probably low molecular ligninlike compounds.
The hot water extracts do not contain low molecular weight sugars. The main sugars after acid hydrolysis of the polysaccharides are glucose and xylose. Minor sugars are galactose, mannose, arabinose,

and rhamnose. More than 50% of the total extractives of OPT consist of carbohydrates.

INTRODUCTION

Edible oil from oil palm and products derived from it are a mayor commodity in Malaysia. Research and developments are being accomplished to industrially utilize other byproducts or wastes from the oil palm industry and oil palm plantations. The trunk of oil palm, cut after about 25 years to be replaced by younger trees, is one of these byproducts. The lignocellulosic derived from these trunks are suitable to make various kinds of panels, but also pulp (Khozirah Shaari et al. 1991). Some data on the chemical composition of such lignocellulosic with regard to cellulose, lignin and hemicellulose have been reported (Halimahton Mansor and Abdul Rashih Ahmad 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 the FRIM the material was obtained from the United Plantation 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 consist 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 extractions 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.

The separation of the unsaponified parts into paraffine 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 the 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. Transestesterification 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 analysises (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 RIB). 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 DISCUSSIONS

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 2 N sodium carbonate solution and ether. The neutral parts were then hydrolysed with an ethanolic potassium hydroxide (0.5 N) solution. The freed fatty acids were isolated with ether after acidification with diluted sulfuric acid. Based on a glycerol 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 the various fractions is shown in Table 2. The total yield of fatty acids is very low (0.0848%).

The results of the gas chromatographic analysises of the methyl esters of the fatty acids were listed in Table 3. To simplify the table only the amount 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 OPT resembles those of the pericarp (Hegnauer 1963).

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.

The gas chromatography of these paraffin hydrocarbons revealed the occurrence 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 is 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 this fraction occurr in the gas chromatogram as unidentified 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 is 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.

Diethyl ether extracts

The results indicate that the diethyl ether extracts partly consist 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 an Aminopropyl-Bond elut cartridge. The various groups of compound were eluted with solvents of increasing polarity. The eluate consist of the following classes of compounds: 56% methylesters and paraffine hydrocarbons; and 44% hydroxyl-containing substances.

The methylesters and paraffine hydrocarbons were analyzed by GC. Only 13% of the total amount of this fraction are fatty acid methylesters. Their composition resembles those of the compounds in the petroleum ether extracts. The paraffin hydrocarbons amount to 16% of the total fraction. They consist of n-alkanes with C-numbers of C_{20} to C_{34}. The rest (71% of the fraction) give in the gas

chromatogram many small peaks. It was not attempted to identify these peaks. Probably they consist of oxidized fatty acids.

The hydroxyl-containing compounds were also analyzed by GC. Only 27% of these (based on the gas chromatogram) could be identified. Sterols, e.g. cholesterol, stigmasterol and ß-sitosterol, are the mayor compounds in this fraction. Beside that smaller amounts of fatty alcohols with a C-number of C_{14} to C_{24} accompany the sterols. The unidentified compounds are 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 are 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 C_{18} modified silica gel (Bond Elut C_{18}, 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.

The carbohydrates were transformed into trimethyl silylether derivatives and analyzed by gas chromatography. The results are presented in Table 7. Sucrose is the main sugar, followed by glucose and fructose. Only minor amounts of cyclic sugar alcohols are detected. According to Table 6 58% or 4.2% (based on oven dry OPT material), of the total extractives in both the acetone- and ethanol-water extracts polar extractives are soluble carbohydrates. The carbohydrates in the acetone/water extracts are mainly sucrose, glucose, fructose, and small amounts of sugar alcohols. The compounds in the ethanol/water extracts show a rather different pattern. The above mentioned carbohydrates and inositol comprise of only 60% of the total soluble carbohydrates. The rest are of unknown structure. These substances are, however, neither sugars or cyclitol. Some of it are probably amino acids.

The amount of total soluble phenolics is only 1.1% (od 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 colored products, as shown by anthocyanidine hydrochloride. The negative result of this test show 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 are glucose followed by xylose. Small amounts of galactose and mannose are also detected. The results of the carbohydrate analysis indicate the occurrence of hot water soluble polysaccharides. Also starch may occurs in this hot water extracts.

CONCLUSION

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

The polar extractives have 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. The main sugars are sucrose, followed by glucose and fructose. Small amounts of cyclitol are also detected. Condensed tannin are not detected in the phenolic fractions.

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

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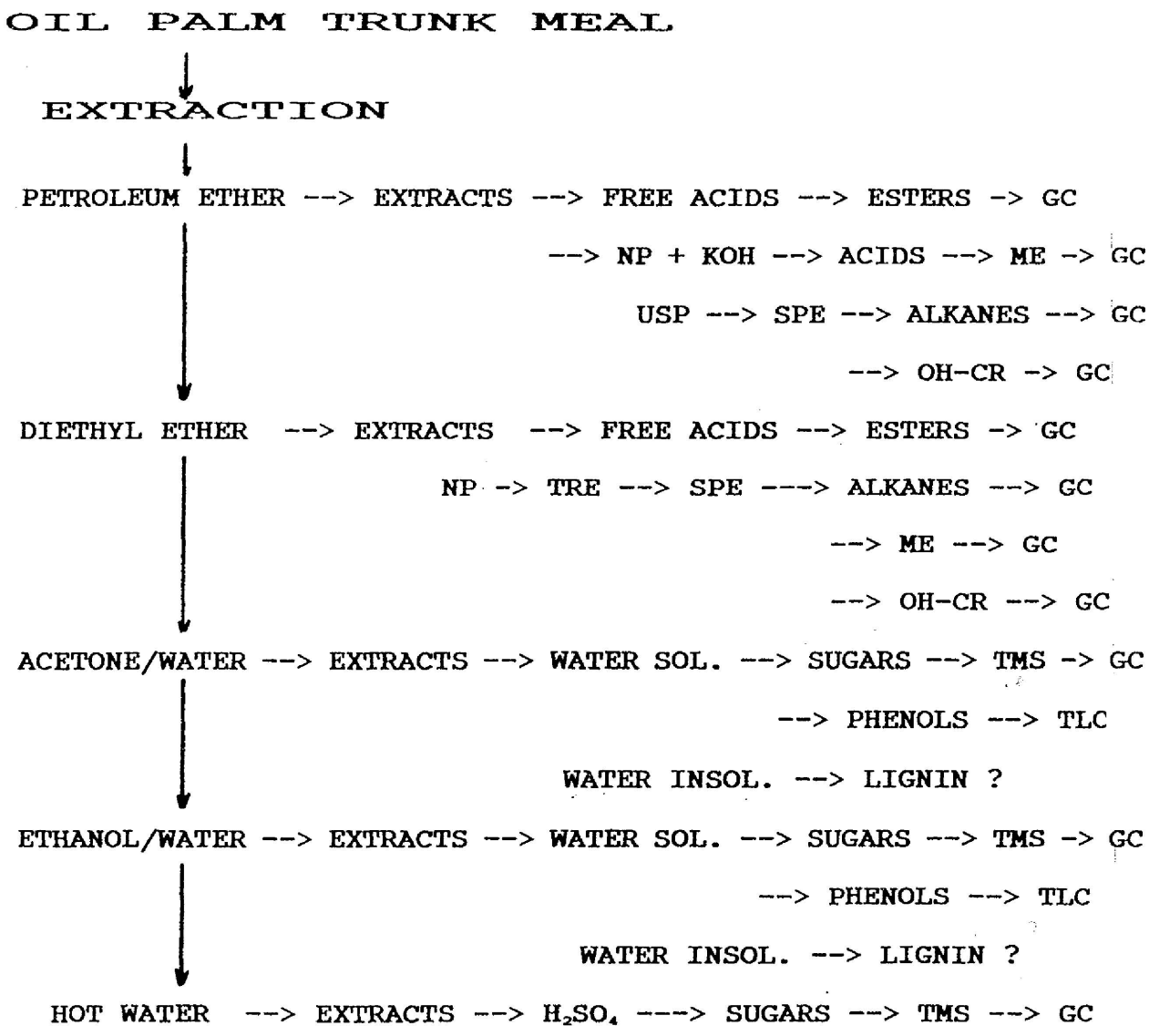
FIGURE 1. Schematic of fractionation and analysis of OPT extracts



NP = Neutral Parts GC = Gas chromatography

TMS = Trimethyl silyl ether SOL = Soluble

SPE = Solid phase extaction TRE = Transesterification

OH-CR = Hydroxyl containing compounds

ME = Methylester TLC = Thin layer chromatography

USP = Unsaponified parts

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

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

TABLE 3. COMPOSITION OF FREE AND BOUND FATTY ACIDS OF 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

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	7.6	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

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
β-SITOSTEROL	45.1
DIHYDROSITOSTEROL	2.5

TABLE 6. FRACTIONATION OF POLAR PARTS OF ACETONE/WATER AND ETHANOL/WATER EXTRACTS

FRACTION	ACETONE/WATER EXTRACTS (OD OPT) %	ETHANOL/WATER EXTRACTS (OD 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

TABLE 7. COMPOSITION OF SOLUBLE CARBOHYDRATE FRACTION 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

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