Chemical Identification of Palm Leaf

(Corypha umbraculifera)

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Palm leaf from various kinds of palm trees in the family Palmae was used as writing material in Asian countries before the advent of paper.[1] *The palm leaf was cut to size and a pointed metal was used to incise letter and drawing on the palm leaf. Black charcoal powder was then applied and rubbed on the writing in order to make it visible.*

The Bangkok National Museum has a large number of palm leaf manuscripts dated from the Ayutthaya to Rattanakosin periods about 16th-19th centuries AD. A typical palm leaf manuscript is illustrated in Figure 1. However some of the palm leaf manuscripts, after being kept for a long period of time, became brittle and damaged as shown in Figure 2. In order to find a suitable method of preserving and conserving these palm leaf manuscripts, it is necessary to understand the chemical and physical nature of the palm leaf.

There are three main species of palm trees found in Thailand. These are Corypha lecomtei, Corypha umbraculifera and Corypha elata but Corypha umbraculifera is mainly used for making palm leaf manuscript.[2]

Venugopal et al.[3] reported that the major constituents of palm leaf from Corypha umbraculifera were α-cellulose (41-49%) and lignin (28-43%). However the other components were not yet determined. The objective of this work was to carry out further studies on the chemical characterization of compounds found in this palm leaf.

EXPERIMENTAL SPECTROSCOPIC ANALYSIS

Infrared (IR) spectra were recorded on a Hitachi I-300I spectrometer. Nuclear Magnetic Resonance (NMR) spectra were recorded in deuterium chloroform at 60 MHZ on a Varian EM 360L instrument or at 300 MHZ on a Bruker AM-300 instrument. Chemical shifts were determined from internal tetramethylsilane for 60 MHZ or trichloromethane for 300 MHZ.

GAS LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) ANALYSIS

GC-MS analysis was carried out using a Hewlett-Packard 5986 Computer data system.

PALM-LEAF EXTRACTION

Dried palm leaves from Corypha umbraculifera (8.92 gram) were extracted with diethyl ether using a continuous extraction apparatus for 35.5 hours. The ether extract was dried with magnesium sulphate and filtrated through a short silica gel column eluted with diethyl ether. The solvent was evaporated and a colourless waxy material (0.70 gram) was obtained.

HYDROLYSIS

The crude palm leaf extract (62 milligram) was dissolved in methanol (5 millilitre) and sodium hydroxide (1 gram) in water (5 millilitre) was added. The mixture was refluxed for 3 hours. The reaction mixture was cooled to room temperature and was extracted with diethyl ether. The ether layer was separated and dried with magnesium sulphate. The solvent was evaporated under reducing pressure to give a neutral fraction as light yellow viscous oil (18.2 milligram)

The basic fraction was acidified with 1 molar hydrochloric acid and extracted with ethyl acetate and washed with water and dried with magnesium sulphate. Evaporation of the solvent gave the acid fraction as a viscous brown oil (46.8 milligram).

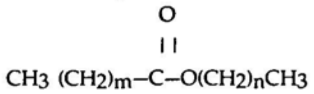
NETHYLATION

The acid fraction (46.8 milligram) was dissolved in methanol (20 millilitre) and concentrated sulphuric acid (1 millilitre) was added. The mixture was refluxed for 5.5 hours and was diluted with water. The mixture was extracted with ethyl acetate and washed with water, saturated sodium bicarbonate, water and then dried with magnesium sulphate. Evaporation of the solvent gave a mixture of methyl esters as viscous brown oil (53.6 milligram).

RESULTS AND DISCUSSION

Continuous extraction of palm leaves (Corypha umbraculifera) with diethyl ether gave palm fibres and lignin as insoluble materials (8.2 gram) in an extraction thimber as shown in Figure 3. Evaporation of the ether extract gave a waxy material and soon solidified as colourless solid (0.7 gram) as shown in Figure 3. Venugopal and his co-workers already characterized the palm fibres therefore our interest focused on the identification of the compounds obtained from the ether extract.

Infrared spectrum of the mixture from the ether extract showed two strong absorption bands at 1740 and 1168 cm^{-1} suggesting a carbonyl ester group. Two very strong absorption bands at 2920 and 2856 cm^{-1} together with the absorption bands at 1476 and 1466 cm^{-1} hence a long chain methylene group. The high field NMR spectrum provided a confirmation of the ester structure by two triplets at ∫ 4.19 and 2.28 due to two methylene groups adjacent to the carbonyl ester group. A large broad band at ∫ 1.22 and a triplet at ∫ 0.88 also established a long chain alkyl group. From the above evidences, it might be proposed that the major components of the ether extract was a mixture of esters (l) of long chain fatty acids and long chain alcohols.



$CH_3(CH_2)_m-\overset{\overset{O}{||}}{C}-O(CH_2)_nCH_3$ (1)

$CH_3(CH_2)_mCOOH$ (2)

$CH_3(CH_2)_nOH$ (3)

Where m and n are any number

Two triplets at ∫2.35 and 3.65 in a high field NMR spectrum and a broad band at 3132-3636 cm^{-1} and a carbonyl band at 1712 cm^{-1} in the infrared spectrum indicated that small amounts of carboxylic acids (2) and alcohols (3) may also be present in the mixture.

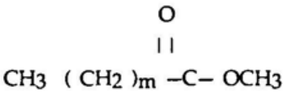
A further attempt was then made to identify the length of the aliphatic side chain. A simple procedure was employed. This involved hydrolysis of the crude ether extract and then methylation of the carboxylic acids so that the resultant methyl esters and alcohols may be identified by GC- MS.

Hydrolysis of the ether extract gave a neutral fraction and an acid fraction. The NMR spectrum of the neutral fraction showed a triplet at ∫ 0.89, a broad band at ∫ 1.15-1.40 and a triplet at ∫ 3.78 as expected for a long chain primary alcohol. GC-MS analysis of the neutral fraction gave a major component at retention time 7.55 minutes and a minor component at retention time 8.54 minutes as shown in Figure 4. The mass spectral data was summarized in Table 1. The m/e of each parent peak gave the length of each alcohol. Therefore it might be suggested that two alcohols were heptadecanol (4) and nonadecanol (5)

$CH_3(CH_2)_nOH$
4 : n = 16
5 : n = 18

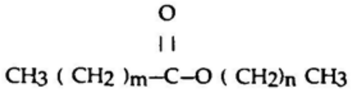
The NMR spectrum of the acid fraction illustrated two triplets at ∫ 0.89 and Z.35, a large broad peak at ∫ 1.28 and a small broad band at ∫ 5.45 confirmed the structure of a long chain fatty acid. Methylation of the carboxylic acids gave a mixture of methyl esters. An ethyl ester was confirmed by a singlet at ∫ 3.74 in the NMR spectrum due to a methoxy group.

The results of GC-S analysis of the methyl esters are shown in Figure 5 and Table 2. Four methyl esters were obtained. Each compound showed the parent ion peak and a parent ion minus 31 peak together with the typical fragmentation of methyl ester at m/e 87, 74, 59 and 43. The major methyl ester was assigned as methyl palmitate (6). Three minor methyl esters were methyl stearate (7) methyl behenate (8) and methyl tetracosanoate (9).



$CH_3(CH_2)_m-\overset{\overset{O}{||}}{C}-OCH_3$
6 : m = 14
7 : m = 16
8 : m = 20
9 : m = 22

With the above information, it might be assigned that the major ester in the ether extract was heptadecanyl palmitate (10) and the minor esters might be esters (11-17). Small proportions of four carboxylic acids (palmitic acid, stearic acid, behenic acid and tetracosanoic acid) and two alcohols (heptadecanol and nonadecanol) might also present in the mixture.



$CH_3(CH_2)_m-\overset{\overset{O}{||}}{C}-O(CH_2)_nCH_3$
10 : m = 14 , n = 16
11 : m = 16 , n = 16
12 : m = 20 , n = 16
13 : m = 22 , n = 16
14 : m = 14 , n = 18
15 : m = 16 , n = 18
16 : m = 20 , n = 18
17 : m = 22 , n = 18

ACKNOWLEDGEMENTS

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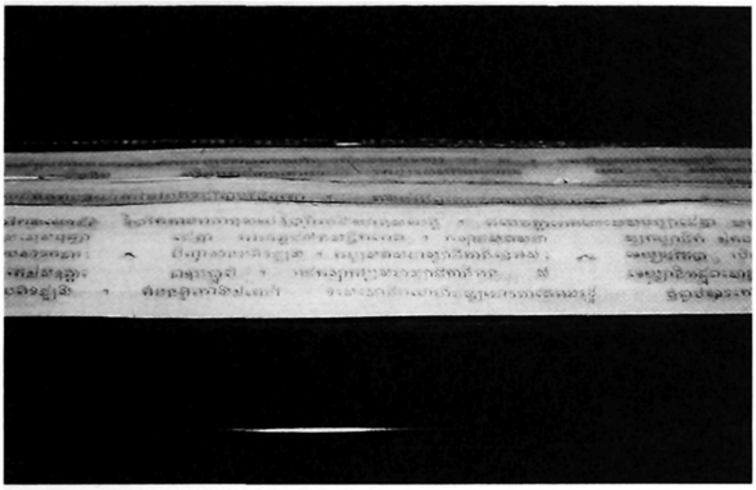

FIGURE 1 PALM LEAF MANUSCRIPT

FIGURE 2 TWO PIECES OF BRITTLE AND DAMAGED PALM LEAF MANUSCRIPT

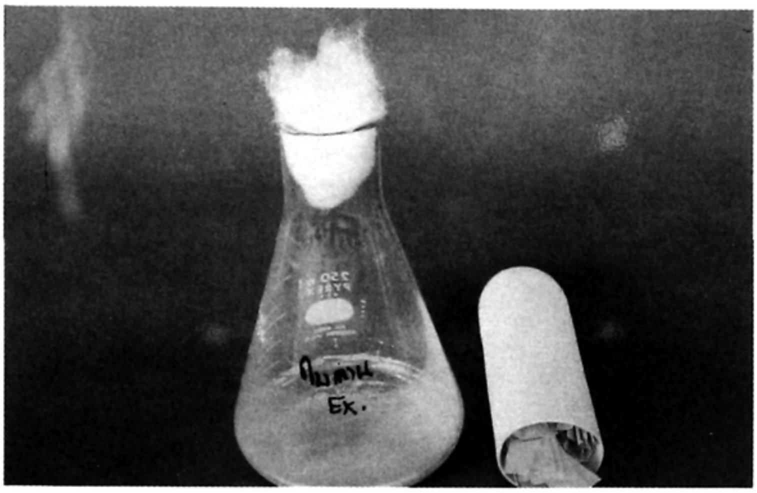

FIGURE 3 COLOURLESS SOLID (IN AN ERLENMEYER FLASK) FROM ETHER EXTRACT AND PALM FIBRES IN AN EXTRACTION THIMBER

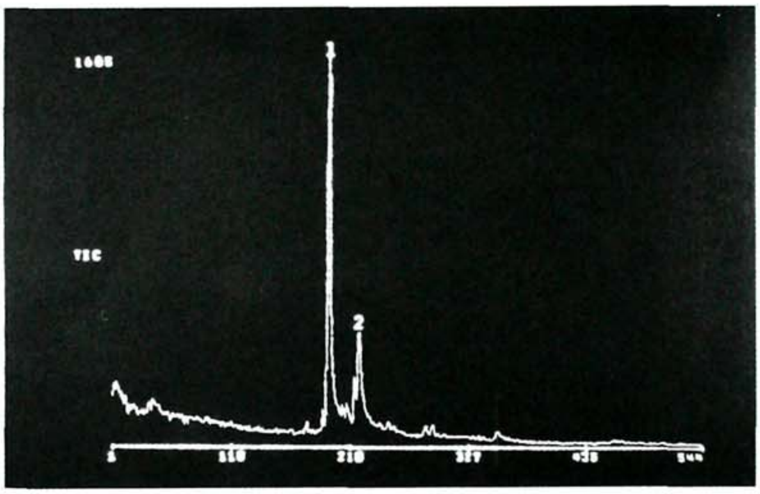

FIGURE 4 GAS CHROMATOGRAM OF THE NEUTRAL FRACTION

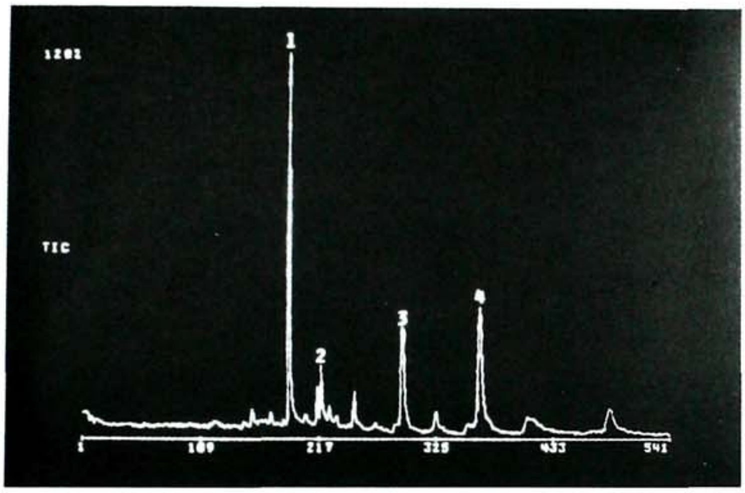

FIGURE 5 GAS CHROMATOGRAM OF THE

METHYL ESTERS

COMPOUND	PEAK IN FIGURE 4	RETENTION TIME (MINUTE)	MASS SPECTRUM (m/e)
4	1	7.55	256(M, 6%), 129(27), 97(17), 73(100), 60(90), 57(70), 43(86).
5	2	8.54	284(M, 5%), 185(9), 129(26), 97(39), 83(51), 73(100), 60(71), 57(87), 43(80)

TABLE 1 GC-MS ANALYSIS OF THE NEUTRAL FRACTION

COMPOUND	PEAK IN FIGURE 5	RETENTION TIME (MINUTE)	MASS SPECTRUM (m/e)
6	1	7.39	270(M, 15), 239(1), 143(8), 87(53), 74(100), 59(4), 57(10), 43(20).
7	2	8.41	298(M, 8%), 267(2), 143(17), 87(78), 74(100), 59(8), 57(19), 43(27).
8	3	11.18	354(M, 4%), 323(1), 143(15), 87(87), 74(100), 59(5), 57(31), 43(33).
9	4	13.52	382(M, 7%), 351(0.5), 143(15), 87(62), 74(100), 59(3), 57(26), 43(21).

TABLE 2 GC-MS ANALYSIS OF THE
METHYL ESTERS