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STUDIES ON FACTORS AFFECTING THE COLOUR STABILITY OF SOME COMMERCIAL PALM FATTY ACIDS

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Keywords: colour stability, palm fatty acids.

The colour stability of some commercial palm fatty acids at 90°C, 110°C and 130°C was investigated. The degree of whiteness of palm fatty acid started to decrease at 110 °C and rate in percentage of whiteness decreasing was faster at higher temperatures. The general order of colour stability of palm fatty acids to heat at 130°C and 110°C are respectively as below:

98% palmitic acid > double pressed > triple pressed > single pressed >70% stearic > 70% oleic acid.

98% palmitic acid > 70% stearic acid > triple pressed > double pressed > single pressed > 70% oleic acid.

The likely factors, viz. minor constituents and trace unsaturated acids, affecting the colour development were studied. Minor constituents were isolated from the various types of palm fatty acids and were found to consist mainly of straight chain hydrocarbons. The major hydrocarbons present in 70% oleic acid were tentatively identified as hydrocarbons $C_{26}H_{50}$ and $C_{26}H_{52}$. The exact structures are yet to be identified. The minor components which affect the colour stability of palm fatty acid could be removed by silicic acid or citric acid treatments. Dimers of oleic acid-oleic acid and oleic acid-linoleic acid were among the components identified in the yellow components fraction isolated from heated palm fatty acids which could be causing the yellow colour. The results indicate that the problem of colour stability of the palm fatty acids is rather complex and is most likely

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due to the presence of traces of unsaturated fatty acids and some unknown minor components in the fatty acids.

INTRODUCTION

The raw materials used in the manufacture of oleochemicals were mainly tallow, coconut oil or palm and palm kernel oils. Malaysia, being the world's largest producer of palm oil and palm kernel oil, is undeniably in a particularly favourable position to become a major supplier of raw materials for both the local and overseas oleochemical industries. Currently, the oleochemicals produced from palm oil and its products are widely used in lubricants, plastics, resins, soaps, surfactants, emulsifiers, cosmetics, toiletries and textile chemicals. Therefore, it is necessary to study properties of the palm-based oleochemicals to further improve their qualities and to ensure that the quality of these products are as good if not better than those derived from tallow and coconut oil.

One area of study which is of great interest is the colour stability of palm oil derived products. For palm oil, Fraser and Frank1 (1981) reported that high molecular weight coloured compounds contribute to the final colour of the oil. However, Wong (1976) attributed it to the oxidation of palm oil and its linoleate content. He observed that co-oxidation of carotenes and the unsaturated fatty acid chains gave rise to colour formation during the thermal bleaching of the carotenes. Tan *et al.* (1985) ascribed colour darkening of heated refined palm oil to the presence of phenolic compounds.

Colour stability is also one of the criteria in evaluating the quality of fatty acids. It is sometimes complained that palm derived soaps tend to be slightly off-colour during storage (Ahmad and Kifli, 1987). Saturated palm fatty acids are also widely used in candle making. However, some local factories are facing the problems of colour development of white candles made from some of these fatty acids (Ooi and Ong, 1987). Palm-based a-SME has also been known to develop yellow colour (Ahmad *et al.*, 1997). The factors causing these phenomena are still unknown and there is very little information available in these areas. Thus, it is important to study the reasons for the discoloration and find a solution to overcome them.

In this paper, some studies on the factors affecting the colour stability of some commercially available saturated and unsaturated palm fatty acids are described. These factors included effect of temperature, and presence of unsaturated compounds and minor components.

EXPERIMENTAL

Materials

Various types of fractionally distilled palm-based fatty acids were obtained from a local fatty acid producer.

The types of commercial fatty acids studied were:

a. Single pressed acid;
b. Double pressed acid;
c. Triple pressed acid;
d. 70% stearic acid;
e. 98% palmitic acid, and
f. 70% oleic acid.

Effect of Temperature on the Colour Stability of Fatty Acids

This was measured by heating 25 g of the fatty acids at a fixed temperature in the oven. At intervals, the degree of colour deterioration was measured according to the degree of whiteness of fatty acids using a colour and colour difference meter as described in Colour Measurement.

Colour Measurement

The degree of colour deterioration was reflected by the change in the colour reading and was measured using a colour and colour difference meter, model ND-1001 DP from Nippon Denshoku Kogyo Co.Ltd, Japan.

The degree of whiteness of the fatty acids was calculated using Hunter's Whiteness equation.

$$W = 100 - [(100-L)^2 + (a^2 + b^2)]^{1/2}$$

In this equation, the reflection coefficient of a perfect white solid at 457 µm is assumed to be 100%. For a sample, the deviation from the 100% reflection coefficient can be due to differences in lightness (L) or colour hue (a and b) or both. These differences can be measured using the colour and colour difference meter.

Isolation of Minor Components from the Fatty Acids (unsaponifiable matter)

About 5 g well mixed sample was weighed accurately into a round bottom flask. A 30 ml of ethanol and 5 ml of aqueous potassium hydroxide solution were then added. The mixture was refluxed for 1 hr. Then 40 ml of hot distilled water and 40 ml of cold distilled water were added. The mixture was allowed to cool to room temperature.

The mixture was then transferred into a separating funnel. A 50 ml of ethanol was used to wash the flask. A 50 ml of petroleum ether was added and shakened vigorously for 1 min: It was then allowed to settle until both layers were clear. The ether layer was collected and the extraction was repeated for another five times.

The combined extract was then washed with 25 ml of distilled water (containing 10% ethanol). This was repeated until the wash was neutral to phenolphthalein.

The ether extract was then transferred into a round bottom flask and dried with anhydrous sodium sulphate. Then, it was transferred into a weighed round bottom flask and the ether was removed using a rotoevaporator. The unsaponifiable matter was then dried under nitrogen until a constant weight was obtained. It was redissolved in n-hexane for GC analysis.

Gas Chromatography Analysis of the Unsaponifiable Matter

The samples to be analysed were dissolved in n-hexane and the conditions used were as follows:

Instrument: Shimadzu GC-9APTF fitted with flame ionization detector.

Column: a fused silica BP-l capillary column, 50 m x 0.25 mm internal diameter.

Column temperature: 90°C (5 min) → 3°C min^{-1} → 365°C.

Injection/detector temperature: 380°C.

N_2 gas flow rate: 1 ml min^{-1}.

Make up gas rate: 60 ml min^{-1}.

GC/MS Analysis of the Unsaponifiable Matter from Fatty Acids

The analysis conditions were:
Instruments used: JEOL model JMS-DX 303 double focusing mass spectrometer linked to a JEOL data system, model DA-5000.

Ionization chamber temperature: 250°C.

Mode of ionization: EI.

Ionization voltage: 70 eV.

Accelerating voltage: 3 kV.

Column used: a fused silica capillary column, methyl silicone, 50 m x 0.25 mm.

Column temperature: 90°C → 8°C min^{-1} → 290°C.

Injector temperature: 290°C.

Helium flow rate: about 1 ml min^{-1}.

Treatment to Improve Colour Stability and Reduction of Unsaponifiable Matter

An amount of 5.0 g silicic acid or citric acid was weighed into a 25 ml conical flask. A 25.0 g of fatty acid sample was added. The mixture was then heated at 60°C-70°C in a water bath and stirred well by using magnetic stirrer for 2 hr. The fatty acid sample was then decanted. A 5 g was used for minor components isolation and about 20 g used for colour measurement.

RESULTS AND DISCUSSION

Table 1 shows the fatty acid composition of the various types of palm fatty acids while ***Tables***

2 and 3 show the effect of temperature on the percentage of whiteness of the various types of palm fatty acids produced locally. The heating temperatures studied were at 90°C, 110°C and 130°C, and for a range of time of at least greater than 30 hr. It was observed that little change on the percentage whiteness of palm fatty acids occurred for all types of palm fatty acid studied at 90°C. The percentage of whiteness of palm fatty acids started to decrease at 110°C and the rate of decrease was faster at the higher temperatures (Tables 2 and 3). The results also showed that the most stable saturated palm fatty acid under heating conditions was 98% palmitic acid. Addition of some of the antioxidants did not improve the percentage of whiteness significantly and some even became worse. From the results, it can be seen that the general order of the stability of whiteness of various types of palm fatty acids upon heating at 130°C and 110°C were respectively in the order:

> 98% palmitic > double pressed > triple pressed > single pressed > 70% stearic acid > 70% oleic acid.

TABLE 1. FATTY ACID COMPOSITION OF VARIOUS TYPES OF FATTY ACIDS

	Percentage (wt %)						
Types	**C12**	**C14**	**C16**	**C18**	**C18:1**	**C18:2**	**Others**
Single pressed acid (SP)	t	1.4	62.3	30.9	5.0	-	0.4
Double pressed acid (DP)	0.2	1.2	59.9	34.2	4.8	-	0.3
Triple pressed acid (TP)	0.2	1.3	54.0	44.2	0.1	-	0.2
70% Stearic acid	0.3	0.6	26.8	70.5	0.5	-	0.4
98% Palmitic acid	0.1	0.3	97.0	2.2	-		0.4
70% Oleic acid	-		6.6	10.0	68.4	13.3	1.7

Note: t - trace.

TABLE 2. EFFECT OF TEMPERATURE ON THE DEGREE OF WHITENESS OF VARIOUS TYPES OF PALM FATTY ACIDS

A: heating condition = 110°C (oven)

	Palm fatty acids					
Heating duration (hr)	**SP**	**DP**	**TP**	**70% Stearic**	**98% Palmitic#**	**70% Oleic***
0	76.6	83.1	77.9	82.9	82.4	92.5
4	76.0	83.3	74.0	81.1	83.6	90.2
8	75.8	82.1	73.4	81.1	81.0	89.4
12	74.2	81.7	73.3	81.3	81.0	87.8
16	76.3	82.4	74.2	83.8	81.0	85.1
20	75.2	81.3	71.3	81.5	83.5	85.5
24	75.7	73.1	74.2	82.2	82.4	82.4
28	74.5	75.8	73.5	80.6	85.8	82.3
32	72.5	75.4	73.0	81.2	84.0	82.0
36	72.8	74.5	72.4	80.9	85.1	82.8
40	72.6	75.8	72.4	80.1	85.0	80.5

Notes: * semi-solid. Heat to liquid before measurement was taken.
Reasons for the increase after 28 hr is not known.

TABLE 3. EFFECT OF TEMPERATURE ON THE DEGREE OF WHITENESS OF VARIOUS TYPES OF PALM FATTY ACIDS
B: heating condition = 130°C

Heating duration (hr)	Palm fatty acids					
	SP	DP	TP	70% Stearic	98% Palmitic	70% Oleic*
0	76.6	83.1	77.9	82.9	82.4	92.5
6	76.3	82.3	74.1	82.3	82.4	88.4
12	77.1	82.6	75.1	74.9	83.5	73.7
18	74.8	83.2	71.1	68.1	82.6	61.2
24	76.4	80.2	74.1	69.3	82.2	53.5
30	74.7	82.0	72.7	67.9	82.4	45.1
36	77.6	80.2	75.7	67.7	81.2	40.6

Notes: * semi-solid. Heat to liquid before measurement was taken.

98% palmitic acid > 70% stearic acid > triple pressed > double pressed > single pressed > 70% oleic acid.

N.B. The stability of 70% stearic acid was better than that of single pressed, double pressed and triple pressed acid at below 110°C.

The two most likely factors that caused the colour development were suspected to be (i) the minor constituents present in the fatty acids, and (ii) the presence of traces of unsaturated acids. In view of this, these two factors were investigated.

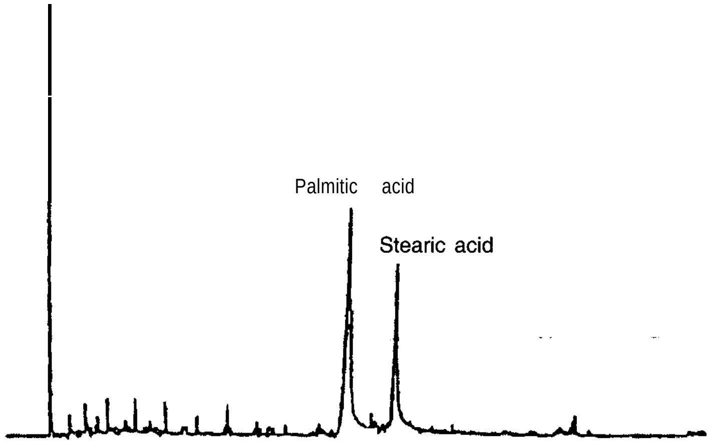
The percentages of unsaponifiable matter in some commercial palm fatty acids are shown in *Table* 4. As can be seen, the highest percentage of unsaponifiable matters was found present in 70% palm stearic acid and 70% palm oleic acid. Since the unsaponifiable matter is suspected as one of the possible causes which cause the colour development, it will be beneficial if we can reduce the unsaponifiable matters present. For this purpose, the various types of palm fatty acids were treated with silicic acid and citric acid. The percentage of unsaponifiable matter that remained after treatment are shown in *Table* 4. The results clearly indicate that unsaponifiable matter of the palm fatty acids could be reduced by both treatments. The isolated unsaponifiable matter of the various types of palm fatty acids before treatment and after treatment with silicic acid and citric acid were also analysed by using gas chromatography. A typical gas chromatogram is shown in *Figure 1*. By comparing the GC chromatograms of the unsaponifiable matters present in the various types of palm fatty acids for the non-treated, silicic acid treated and citric acid treated, it was shown that some of the unsaponifiable matter

TABLE 4. PERCENTAGE OF UNSAPONIFIABLE MATTERS FROM PALM FATTY ACIDS

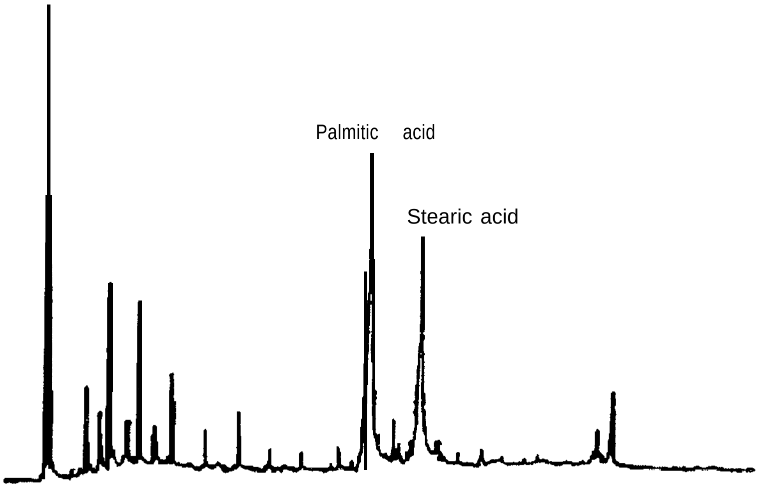
Sample	Percentage of unsaponifiable matters		
	Without treatment	Treated with silicic acid	Treated with citric acid
SP	0.82	0.44	0.56
DP	0.70	0.46	0.43
70% Stearic acid	1.23	0.76	0.93
98% Palmitic acid	0.96	0.41	0.42
70% Oleic acid	1.66	0.89	0.71

Notes:
SP = single pressed acid.
DP = double pressed acid.

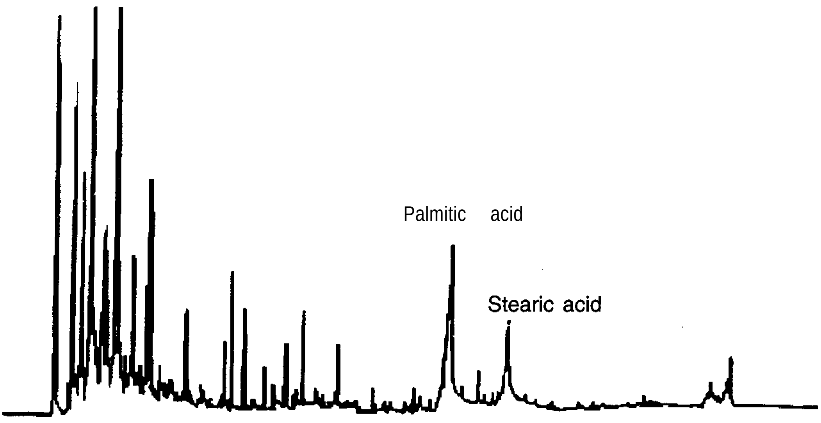
Sample: single pressed acid



Silicic acid treated



Citric acid treated



Non-treated

Figure 1. Chromatograms of unsaponifiable matters.

present in various types of palm fatty acids was removed by the treatment process. The effect of silicic acids or citric acid treatment on the degree of whiteness of palm fatty acids was also studied. The treated palm fatty acids were heated to 130°C for a period of at least 30 hr. It was found that both the silicic acid and citric acid treatments enhanced the colour stability of most of the palm fatty acids upon heating as can be seen from ***Table*** 5. The results indicated that citric acid treated palm fatty acids generally had a better colour stability than silicic acid treated palm fatty acids. All these could be attributed to the fact that certain components in the unsaponifiable matter responsible for the development of yellow colour had been removed by silicic acid or citric acid. The mechanism of removal is not known.

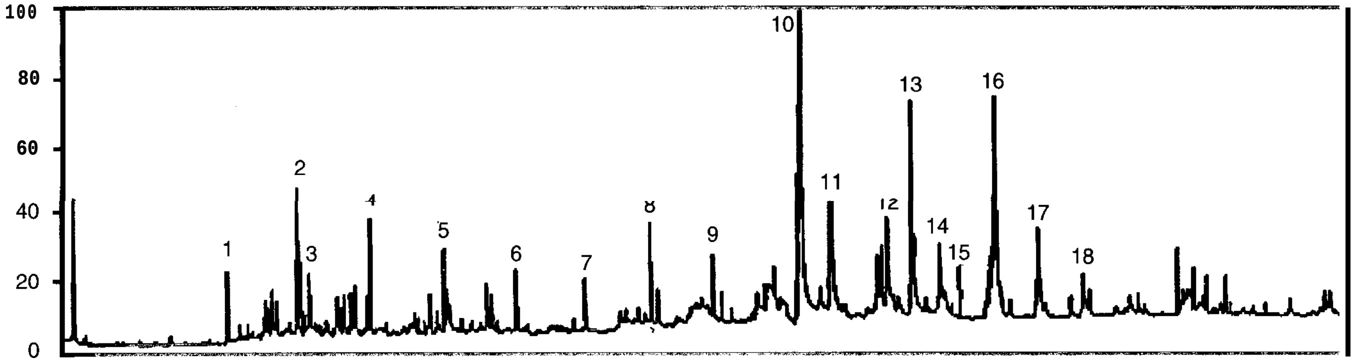
Since it was also interesting to know what were the compounds present in the unsaponifiables which caused the colour development of the palm fatty acids, attempts to identify the components present in the unsaponifiables were carried out. The unsaponifiables of two palm fatty acid samples, i.e. single pressed acid and 70% oleic acid without treatment, were ana-

TABLE 5. EFFECT OF SILICIC ACID OR CITRIC ACID TREATMENT ON THE DEGREE OF WHITENESS OF PALM FATTY ACIDS

Type of treatment	Heating duration (hr)	Heating condition = 130°C (oven)					
		Palm fatty acids					
		SP	DP	TP	70% Stearic	98% Palmitic	70% Oleic
No treatment (control)	0	76.6	83.1	77.9	82.9	82.4	92.5
Silicic acid							
Citric acid		75.4	80.8	72.8	81.7	81.1	90.7
No treatment (control)	6	76.3	82.3	74.1	82.3	82.4	88.4
Silicic acid		74.5	84.5			84.1	80.2
Citric acid		80.0	82.2	75.6	81.1	81.1	76.5
No treatment (control)	18	74.8	83.2	71.5	68.1	82.6	61.2
Silicic acid		75.8	81.8			84.5	61.9
Citric acid		75.9	81.2	75.5	82.0	83.3	62.3
No treatment (control)	24	76.4	80.2	74.1	69.3	82.2	53.5
Silicic acid		77.0	78.9			82.4	50.0
Citric acid		75.8	82.4	74.0	79.6	84.3	50.1
No treatment (control)	30	74.7	82.0	72.7	67.99	82.4	45.1
Silicic acid		75.5	79.7			84.3	45.6
Citric acid		81.0	81.1	77.6	77.7	82.4	47.9

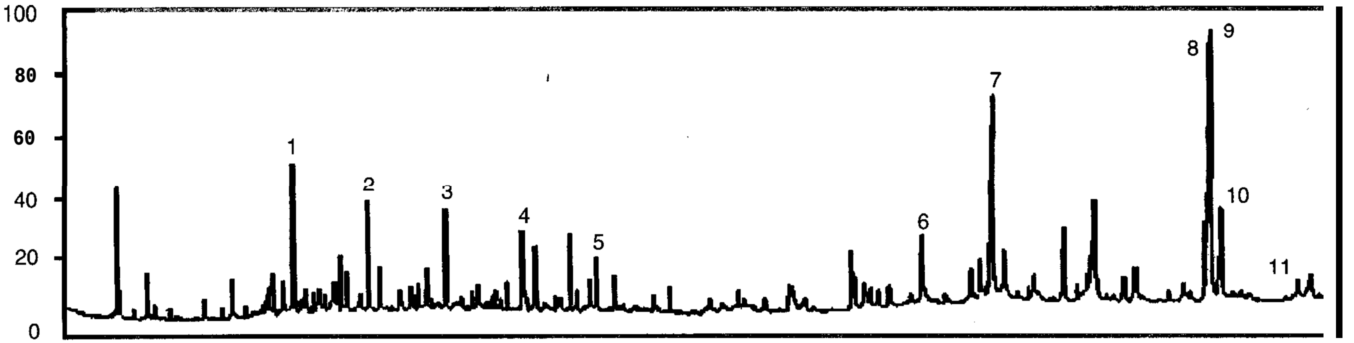
lysed by GC and GC/MS. From the analysis, it was found that the major compounds present in the unsaponifiable matter of these palm fatty acids were mainly saturated or unsaturated straight chain hydrocarbons. Thus, the compounds which caused the colour development were present only in much smaller quantities. A more detailed study should be carried out for better understanding of the causative minor components. In the case of 70% oleic acid, the major components present in the unsaponifiable matter were identified to be $C_{26}H_{50}$ and C_{26} H,,. The others were also mainly straight chain hydrocarbons. The total ion chromatograms are shown in *Figures* 2 and 3.

It may also be useful if the identity of the coloured component/components could be known by heating the fatty acids as a whole. Thus, single pressed acid was chosen for the study and was heated to 150°C in an oven for 48 hr. At the end of the heating, the fatty acid turned yellowish. Initial attempts to separate the co-



1. $C_{11}H_{24}$
2. $C_{12}H_{26}$
3. $C_{13}H_{28}$
4. $C_{13}H_{28}$
5. $C_{14}H_{30}$
6. $C_{15}H_{32}$
7. $C_{16}H_{34}$
8. $C_{17}H_{36}$
9. $C_{18}H_{36}$
10. Methyl palmitate
11. $C_{18}H_{36}$
12. $C_{19}H_{38}$
13. Methyl stearate
14. $C_{22}H_{46}$
15. $C_{23}H_{48}$
16. Methyl oleate
17. $C_{24}H_{50}$
18. $C_{25}H_{52}$

Figure 2. Total ion chromatogram of unsaponifiable matters of single pressed fatty acid.



1. $C_{11}H_{24}$
2. $C_{12}H_{26}$
3. $C_{13}H_{26}$
4. $C_{14}H_{30}$
5. $C_{15}H_{32}$
6. $C_{18}H_{36}$
7. Methyl oleate
8. $C_{26}H_{50}$
9. $C_{26}H_{50}$
10. $C_{26}H_{52}$
11. $C_{26}H_{52}$

Figure 3. Total ion chromatogram of unsaponifiable matters of 70% oleic acid.

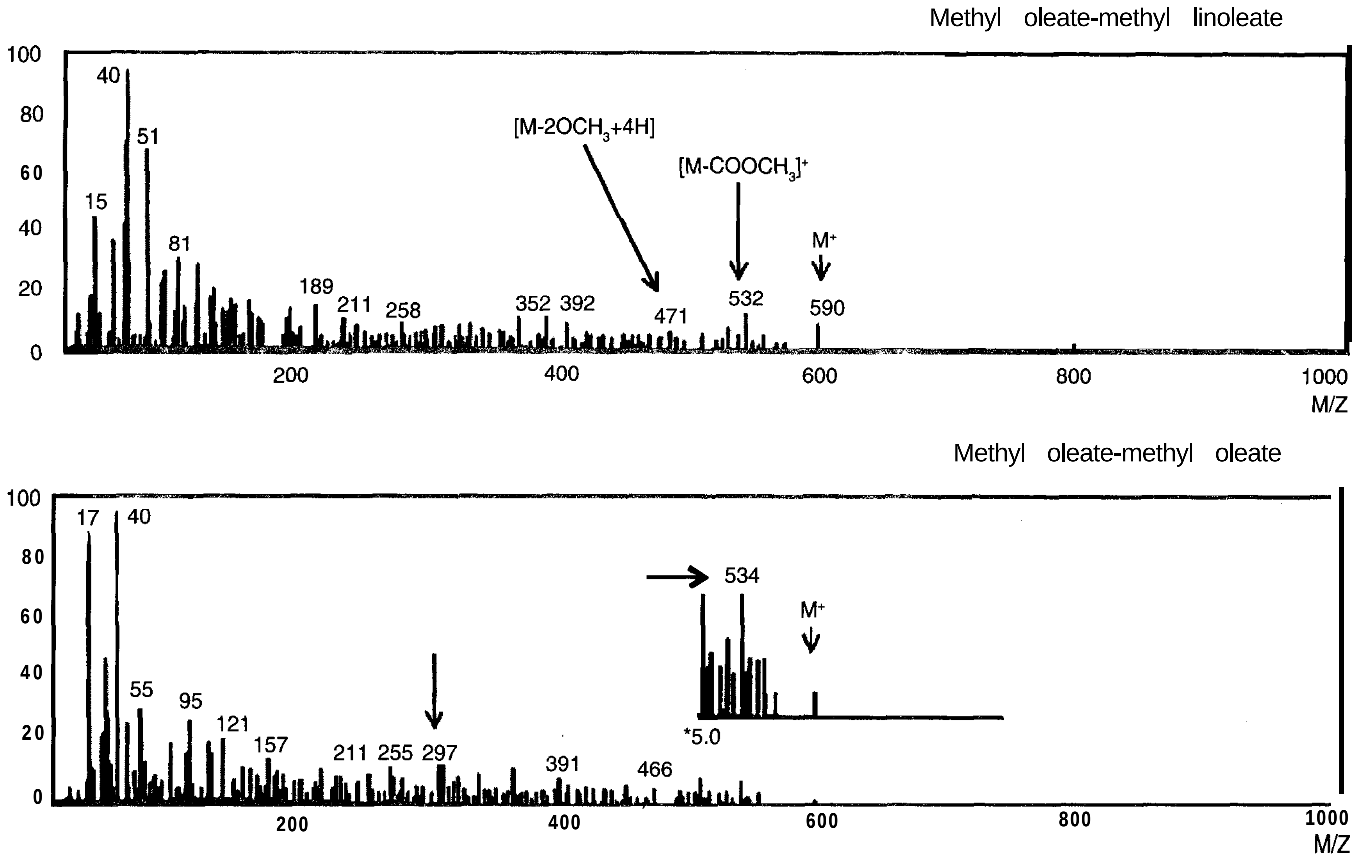


Figure 4. Mass spectra of the coloured fraction (methylated).

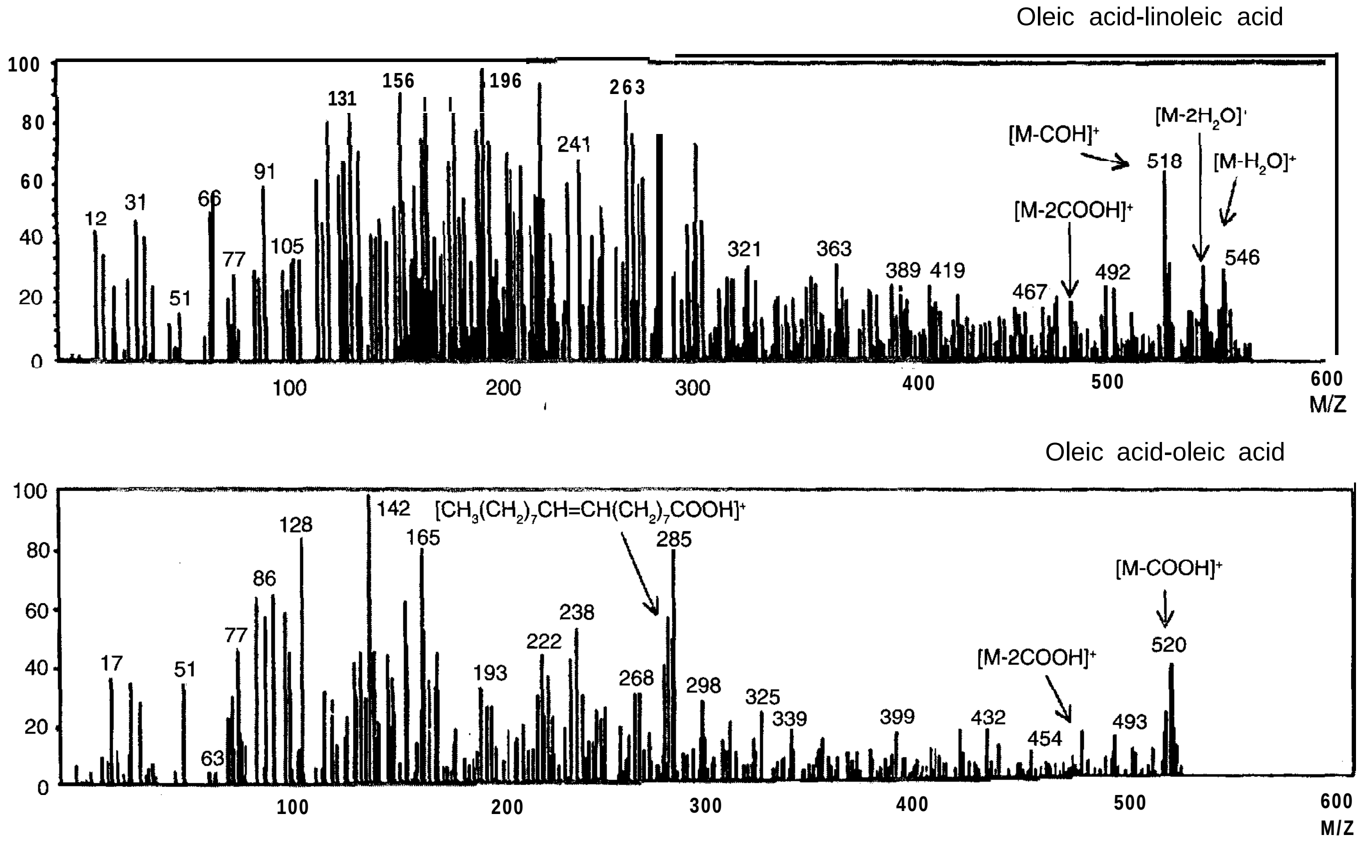


Figure 5. Mass spectra of the coloured fraction.

loured components from the fatty acid resulted in the adsorption of the coloured components onto the silica gel at the top of the column showing that the components were quite polar. The yellow band changed to a brownish band after some time. In view of these difficulties, the heated fatty acid was methylated prior to isolation by column chromatography. By this method, the coloured yellowish band was successfully collected and concentrated. From the interpretation of the mass spectra, two of the compounds were identified as methyl esters of the dimers of oleic acid-oleic acid and oleic acid-linoleic acid. These were the compounds identified in the yellow-component fraction. This was further confirmed by vacuum distilling the heated single pressed acid so as to obtain a concentrated yellow fraction prior to analysis. The MS analysis of the unmethylated sample again showed that the compounds present in the yellow component fraction were the dimers of the unsaturated acids. From these studies, it is believed that the colour development of the palm fatty acids was also most likely due to the presence of the unsaturated acids. This is further supported by the FAC analysis of the various types of fatty acids. As can be seen from *Table* 1, the one with more unsaturated acid will generally develop the yellow colour faster. For instance, 70% oleic acid has about 13.3% of C18:2 while the others not.

CONCLUSION

From the experimental results, the following conclusions can be made:

a. The possible factors which cause colour development of palm fatty acids are:
   i. the traces of unsaturated fatty acids present and
   ii. unsaponifiable matter compounds (yet to be identified, believed to be present in very small amounts compared with the hydrocarbons).
b. The major unsaponifiable compounds in the single pressed fatty acid and 70% oleic acid are mainly the saturated and unsaturated straight chain hydrocarbons. The major hydrocarbons present in the 70% oleic acid are $C_{26}H_{50}$ and $C_{26}H_{52}$.
c. Compounds present in the unsaponifiable matter of palm fatty acids which enhance colour development could be removed by silicic acid and citric acid treatment. Citric acid treatment generally gives better results in terms of removing the unsaponifiable matter.

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