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MONO- AND DIBASIC ACIDS FROM LIQUID PHASE OXIDATION OF PALM OIL PRODUCTS

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The main objective Of this research was to convert palm oil products into basic intermediates for use in the chemical industry. In this paper, oxidative cleavage of palm oil products into dibasic acids and low molecular weight monobasic acids by liquid phase oxidation of palm oil products is discussed. Identification of reaction products was done with gas chromatography and gas chromatography/mass spectroscopic techniques and it was found that the major dibasic acids formed in the reaction were suberic and azelaic acids. The dibasic acids produced were concentrated by water washing followed by crystallization. The maximum purity of azelaic acid achieved was 78%. The dibasic acids are useful materials for the syntheses of lubricants. plasticizers, polyamides and polyesters.

INTRODUCTION

The syntheses of dicarboxylic acids and their derivatives have interested scientists for a long time. This is not unexpected considering the importance of many compounds such as adipic acid, azelaic acid, maleic anhydride, terephthalic acid and oxalic acid, to the chemical industry. Dicarboxylic acids with long carbon chains are used mainly as raw materials, such as for the preparation of plasticizers, polyamides, polyurethane, lubricants and perfumes (Emery Industries, 1981; Kadesch, 1979; Carlson *et al., 1977).*

The two major fatty acids present in palm oil are palmitic (42%-47%) and oleic (37%-41%). The other fatty acids are stearic (4%-5%) and linoleic (9%-11%) (PORAM, 1984). Oleic acid is a good source of dicarboxylic acids such as azelaic acid (nonanedioc acid) and the feedstocks for the production of azelaic acid are usually tallow and vegetable oils rich in oleic acid. The syntheses of azelaic and suberic acids from other sources such as *Vernonia galamensis* oil were recently studied (Ayorinde et al., 1989). Alkali pyrolysis of castor oil to sebacic acid was studied by Vasishtha et al. (1990). However. the current commercial process for azelaic acid production is based on ozonolysis of oleic acid, primarily because of its high selectivity and reactivity (Swern, 1961). Due to the high cost of ozone, other chemical oxidations for both saturated and unsaturated fatty acids were also studied involving the use of chromic acid, nitric acid, sulphuric acid and a vanadium salt, ruthenium and osmium tetroxide, air and aqueous alkaline potassium permanganate (Johnson, 1984; Foglia et *al.*, 1977; Fitzpatrick and Myers, 1948; Cason and Rapoport, 1962; Kucestki, 1962).

This paper reports our process for the production of monobasic and dibasic acids, in particular, pelargonic and azelaic acids by liquid phase oxidation of palm oil products.

MATERIALS AND METHODS

Materials

Refined, bleached and deodorized (RBD) palm stearin and fractionated palm oleic acid (about 70% oleic acid) were obtained from Lam Soon (M) Sdn. Bhd. and Southern Acids Sdn. Bhd., Malaysia, respectively.

All the metal salts and solvents used were of analytical grade and were used as received.

Oxidation Reactions

Oxidations using different substrates were performed in a 500ml stainless steel autoclave, equipped with a magnetic stirrer, thermocouple and pressure controller. ***Figure I*** shows schematically the set-up of the reactor system.

A mixture of substrates, a solvent and a catalyst were placed in the reaction vessel. The air above the reaction mixture was then displaced by oxygen before heating the autoclave. More oxygen was then allowed into the autoclave through a pressure controller. The oxygen pressure ranged from 10kg cm^{-2} to 50kg cm^{-2}.

The reaction temperature was controlled by lowering heating mantle and cooling with ice water.

Analysis

GC analysis. The fatty acid composition of the oil or the reaction products were methylated using BF$_3$-methanolic solution before being subjected to gas chromatograph analysis. A Shimadzu GC-9APTF gas chromatograph fitted with flame ionization detector and a 50m x 0.25mm FFAP fused silica capillary column was used. The conditions were:

Injector/detector temperature : 250°C.

Column temperature : 60°C for 5 min, then increase at 5°C min^{-1} to ***230°C.***

GC-MS analysis of reaction products. The methylated reaction products were also identified by combined GC-MS analysis with the following conditions.

Instrument: JEOL double focussing mass spectrometer (model JMS-DX303) linked to JEOL Data System, model DA-5000.

GC conditions.

Column: 50m x 0.25mm FFAP fused silica capillary column.

Column temperature: 80°C to 220°C at 8°C min^{-1}.

Helium carrier gas flow: 1ml min^{-1}

Injector temperature: 250°C.

Separator temperature: 250°C

MS conditions.

Ion chamber temperature : 250°C.

Ionizing energy : 70eV.

Acclerating voltage : 3.0kV.

'Inlet : 250°C.

Mode of ionization : EI.

RESULTS AND DISCUSSION

The fatty acid compositions of the materials used in this study are given in ***Table 1. Two*** types of palm oil products were chosen for the study – RBD palm stearin and a fractionated palm oleic acid which contains about 70% oleic acid.

Earlier studies on oxidative cleavage of palm stearin catalyzed by metal (II) ion exchanged zeolites gave low yields of dibasic acids (Shiina *et* al., 1986). However, one of later studies (Niwa ***et al.,*** 1986) found that Co $(OAc)_2.4H_2O$ as catalyst gave the highest total yield of pelargonic and azelaic acids from pressurized oxidation of oleic acid. With this catalyst, oxidation of linoleic acid gave mainly n-caproic and azelaic acids. In both oxidations, there were little oxidation products of over C10. This suggested that the oxidative cleavage selectively occurred around the C-C double bonds. Thus, this could be the method which dispenses with ozone in the oxidation of oleic acid to azelaic and pelargonic acids industrially. Besides unsaturated fatty acids, oxidative cleavage of saturated acids such as palmitic acid to mono- and dibasic acids of C4-C14 was also shown to occur smoothly but at higher temperatures. The reaction was not very selective as can be seen from ***Figure 2. Table 2*** summarizes a comparison of the products formed from oxidation of the various saturated and unsaturated fatty acids in palm oil. It should be noted that there was very little reaction when oxidation of a saturated acid was carried out at 90°C. Only at higher temperatures were there substantial reaction occurred.

Once it was learnt that unsaturated and saturated acids can be converted to mono- and dibasic acids, this work was extended to the use

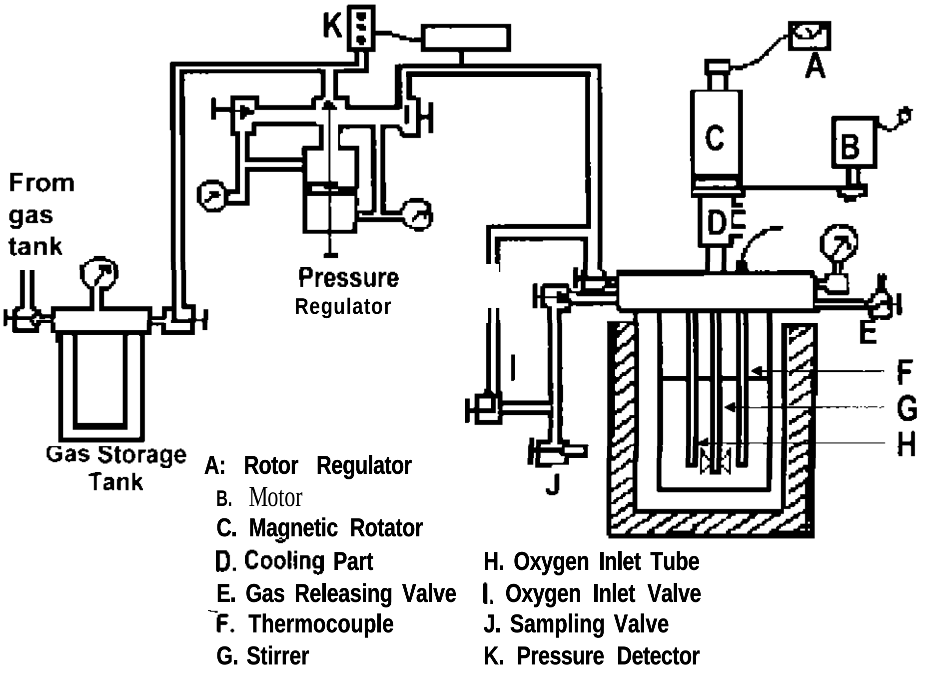

Figure 1. Schematical set-up of autoclave for oxidation under pressure

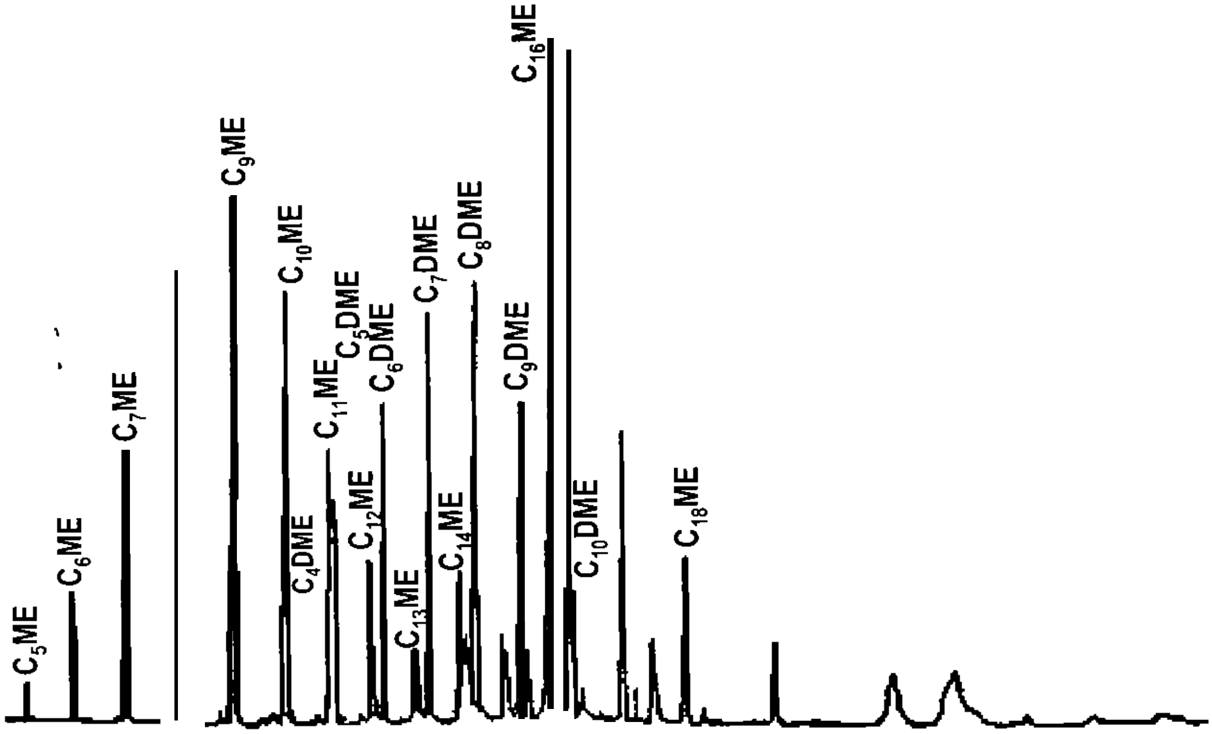

Figure 2. A typical gas chromatogram of oxidation products of palmitic acid (after methylation).

of palm products as the feedstocks for oxidation. It was not certain whether oxidation was possible in palm products because they usually contain a lot of impurities and antioxidants such as tocopherols which may inhibit the process, Thus, oxidation was done on using refined, bleached, deodorized (RBD) palm stearin (the solid fraction of palm oil). This fraction is under-utilized and contains about 600ppm of tocopherols and tocotrienols. The fatty acid composition of the RBD palm stearin used in the experiments is shown in *Table* 1 and the oxidation products formed at various temperatures are summarized in *Table 3.* When the reaction was carried out at 90°C, the conversion of palm stearin was only 30%. This percentage is almost consistent with the total content of unsaturated acids in RBD palm stearin. Furthermore, the contents of palmitic (C16) and stearic (C18) acids in the reaction mixture are in good agreement with those in RBD palm stearin respectively. Among the monobasic and dibasic acids produced, pelargonic and azelaic acids showed the highest yields. These observations indicated that at 90°C, mostly the unsaturated acids were oxidized and the saturated acids largely unreacted. However, as the reaction temperature increased, the conversion of RBD palm stearin increased and the contents of palmitic and stearic acids decreased simultaneously. That is, at temperatures above 110°C, oxidation of saturated acids proceeded smoothly. Figure 3 gives gas chromatograms showing the products from oxidative cleavage of RBD palm stearin before and after reaction.

Identification of the products was based on the retention times of the GC analysis which were compared with those of known samples determined under the same GC analysis conditions. The major monobasic acids formed were C8 to Cl0 whereas dicarboxylic acids were C6 to C9. The presence of all these acids were further confirmed from the mass spectra of GC-MS analysis and mass chromatogram analysis. Figures 4 and 5 show the typical mass spectra of the methyl esters of the C9 mono and dibasic acids obtained in the reaction products respectively.

The methyl esters of saturated dicarboxylic acids were recognized mass spectrometrically by their fragments M-31 and M-59, corresponding to the losses of OCH, and $COOCH_3$, respec-

TABLE 1. FATTY ACID COMPOSITIONS OF RBD PALM STEARIN AND FRACTIONATED PALM OLEIC ACID

Fatty acid		Wt (%)	
		RBD palm stearin	Fractionated palm oleic acid
Lauric	C12:0	0.2	-
Myristic	C14:0	1.3	-
Palmitic	C16:0	59.9	2.9
Stearic	C18:0	4.2	9.0
Oleic	C18:1	27.2	73.5
Linoleic	c m 2	5.7	13.1
Linolenic	C18:3	0.1	0.4
Arachidic	C20:0		0.8
Others		1.4	0.3

TABLE 2. PRODUCTS FORMED FROM THE OXIDATION OF PALM OIL COMPONENT FATTY ACIDS (catalyzed by cobalt acetates in acetic acid at 90°C)

Fatty acid	Conversion (%)	Ester yield (Wt %)*											Oxygen absorption (dm^3)
		Methyl ester of monocarboxylic acid carbon number					Methyl ester of dicarboxylic acid carbon number						
		5	6	7	8	9	4	5	6	7	8	9	
Palmitic	6				-	-							1.3
Stearic	4												0.8
Oleic	99.9	-	3	7	15	28	t	t	4	4	9	21	9.3
Linoleic	99.9	7	30	1	5	-	1	1	1.5	2	8	31	13.9

Reaction condition: Component acid (initial), 50g; Acetic acid, 100g; Time, 12hr, Catalyst, Co $(OAC)_2.4H_2O$ 1.6mmol (about 0.4g); Oxygen pressure, 30kg cm^{-2}.

* : based on component acid used.

t : trace.

tively (McLafferty, 1963). For instance, the mass spectrum of methyl azelate (*Figure 5*) does not give a molecular ion (M), although, there are many prominent diagnostic ions m/z 185 ($M-OCH_3$), m/z 152 ($M-2CH_3OH$) m/z 143 ($M-CH_2CO_2CH_3$), m/z 124 ($M-2CH_3OH-CO$). Similar corresponding ions were observed for all the other dibasic acids.

Therefore, the results indicated that antioxidants such as tocopherols, in the palm products do not inhibit significantly the oxidation.

As the reaction gave rise to a mixture of mono- and dicarboxylic acids, it was important to separate and purify the products in order to make the process more viable. Figure 6 shows a flow diagram of the separation by hot water and *Table* 4 the fatty acid composition in the various portions. The substrate oxidized was fractionated palm oleic which contained about 70% oleic acid; its fatty acid composition is shown in *Table 1.* It is interesting to note that the dicarboxylic acids were concentrated in Portion A3 and the mono carboxylic acids in Portion A2. So far, the maximum possible purity of the azelaic acid was about 76% and *Table 5* shows some of the characteristics of the prepared azelaic acid sample.

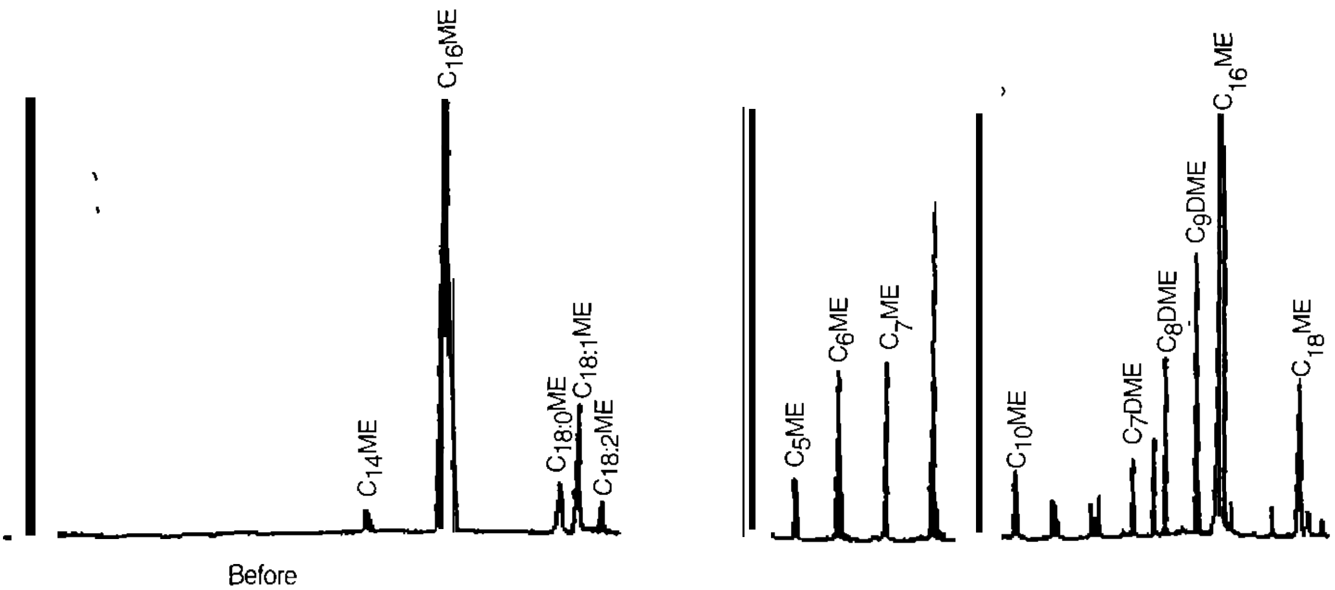

Figure 3. Gas chromatogram of RBD palm stearin before and after oxidation (after methylation)

TABLE 3. EFFECT OF REACTION TEMPERATURE ON PRODUCTS FORMED FROM THE OXIDATION OF RBD PALM STEARIN IN ACETIC ACID

		Ester yield (Wt %)*															
Reaction temp. (°C)	**RBD** palm** **stearin conversion (%)**	**Methyl esters of mono carboxylic acids carbon number**							**Methyl esters of dicarboxylic acids carbon number**								**oxygen absorption (dm³)**
		5	6	7	8	9	16	18	4	5	6	7	8	9	10	11	
90	30	1	1	2	4	6	59	4	-		t	1	1	3	t	-	4.9
110	35	3	5	4	6	9	48	1	1	1	2	3	4	6	1	1	5.6
130	40	2	4	3	6	9	36	1	1	1	2	3	4	7	1	1	6.8
150	55	3	5	4	6	9	26	2	1	2	2	3	4	7	1	1	8.8

Reaction conditions: RBD palm stearin (initial), 50g; Acetic acid, 100g; Reaction time, 24hr.; Catalyst, Co $(OAc)_2 \cdot 4H_2O$ 1.6mmol (about 0.4g); Oxygen pressure, 30kg cm^{-2}.

* : based on palm stearin fed.

** : composition of acids in RBD palm stearin is shown in *Table 1.*

t : trace.

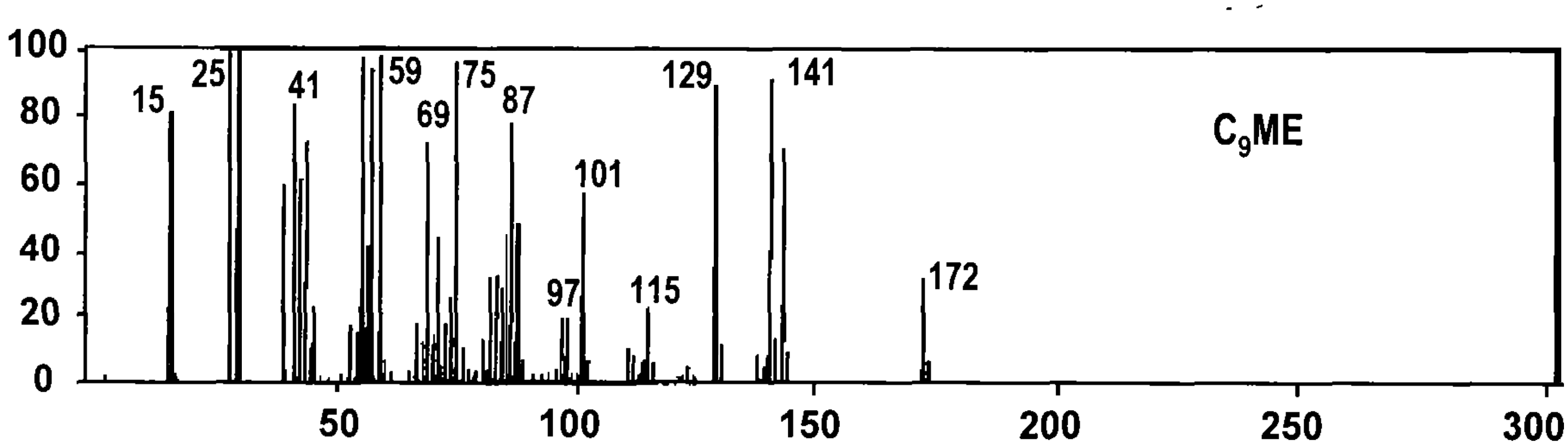

Figure 4. Typical mass spectrum of methyl ester of pelargonic acid.

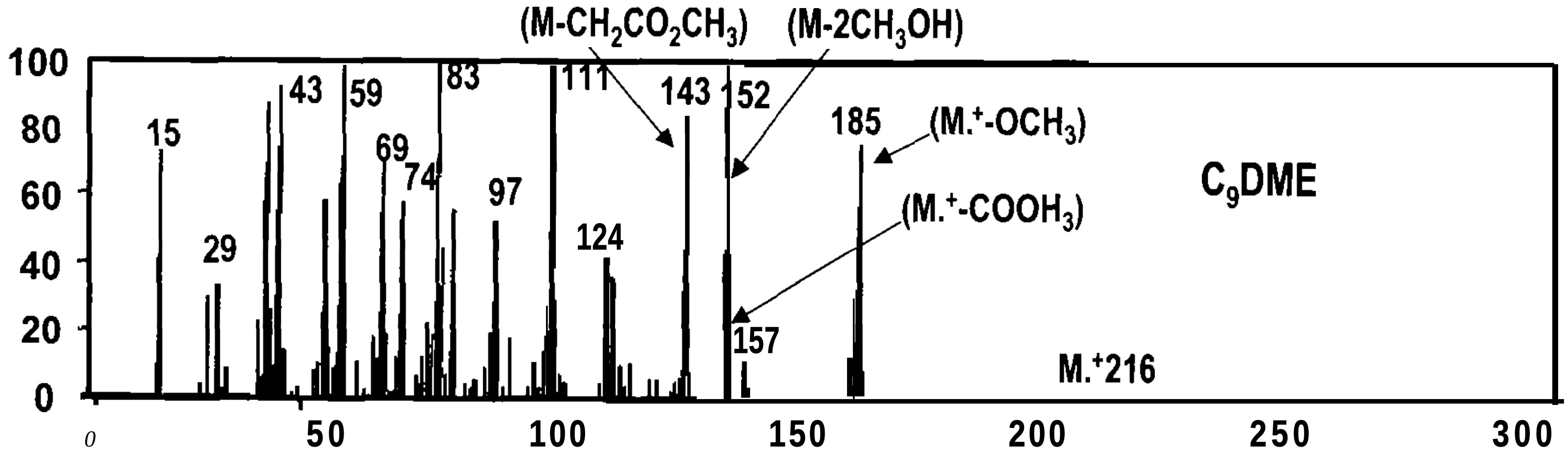

Figure 5. Typical mass spectrum of methyl ester of azelaic acid.

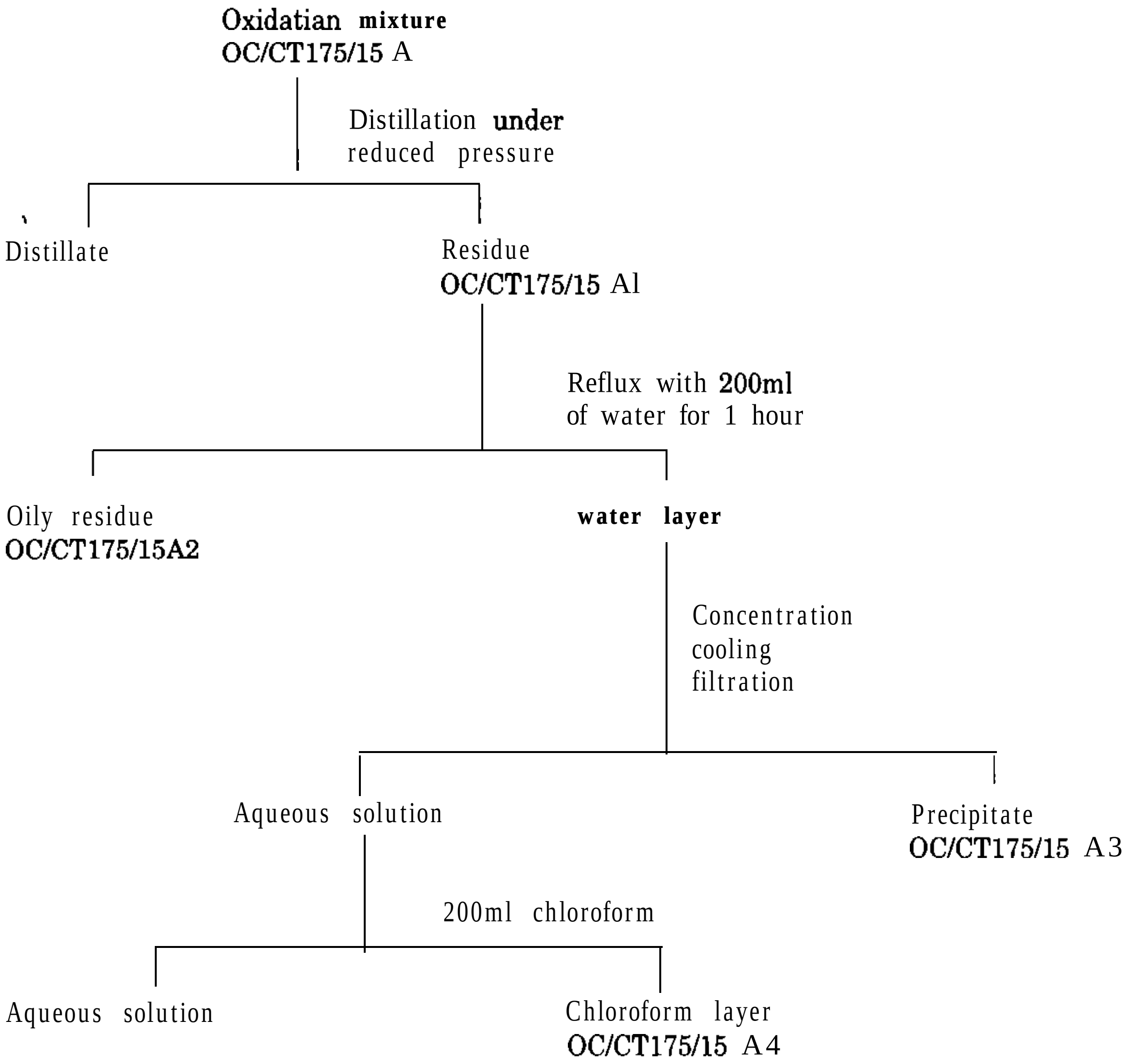

Figure 6. Separation of oxidation products of fractionated palm oleic acid mixture (about 70%).

CONCLUSION

The study showed that oxidative cleavage of palm products into mono and dibasic acids particularly pelargonic and azelaic acids is possible and that the tocopherols in palm products do not significantly inhibit the oxidation. The reaction products obtained could be separated into mono and dibasic acids and purified by washing with hot water. The maximum possible purity of the azelaic acid obtained was 78%.

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TABLE 4. FATTY ACID COMPOSITIONS OF THE ORIGINAL MIXTURE AND THE VARIOUS FRACTIONS*

	Monocarboxylic acids (%)					Dicarboxylic acids (%)		Others
	C8	C9	C16	C18:0	C18:1	C8	C9	
Oleic acid **(about 70%)**			**2.7**	**13.3**	71.6			**12.4**
OC/CT175/15 A	**4.5**	11.8	**7.0**	**17.2**	19.1	**4.7**	**10.2**	**25.5**
OC/CT175/15 A1	**3.2**	**9.4**	**7.1**	**20.2**	**22.7**	**4.7**	10.6	22.1
OC/CT175/15 A2	**4.1**	**10.0**	**8.7**	**25.2**	**26.2**	**1.6**	**4.1**	**20.1**
OC/CT175/15 A3	0.0	1.2	2.1	**3.4**	**4.6**	**5.1**	**72.1**	**10.9**
OC/CT175/15 A4			1.0	**0.8**	**3.4**	**25.1**	**50.7**	**19.0**

* See *Figure* 6

TABLE 5. SOME PROPERTIES OF PREPARED AZEWC ACID

Melting point (°C)	**87-96**
Composition (%)	
C9 dibasic	**78**
Less than C9 dibasic	**8.1**
Greater than C9 dibasic	**2.4**
Monobasic	**5.0**
Others	**6.5**
Acid value, (mg KOH/g)	545-571
Colour	87/88

REFERENCES

AYORINDE, F 0; OSMAN, G; SHEPHARD, R D and POWERS, F T (1989). Synthesis of azelaic acid and suberic acid from *Vernonia galamensis* oil. ***J. Amer. Oil Chem. Soc. Vol.* 65**. *No.11:* 1774-1777.

CARLSON, K D; SOHNS, V E; PERKINS JR. R B and HUFFMAN, E L (1977). Brasylic acid: chemical intermediate from high erucic oils. ***Ind. Eng. Chem. Prod. Res. Dev. 16:*** 95-101.

CASON. J and RAPOPORT, H **(1962).** ***Laboratory Text in Organic Chemistry,*** 2nd ed. Prentice-Hall, Englewood Cliffs, N.J.

FITZPATRICK, J D and MYERS, L D (1948). U. S. Pat. 2 450 858 to Emery Industries.

FOGLIA, T A; BARR, P A; MALLOY, A J and COSTANZO, M J (1977). Oxidation of unsaturated fatty acids with ruthesium and osmium tetroxide. ***J. Amer. Oil. Chem. Soc.:*** 870A-872A.

JOHNSON, R W (1984). The chemistry of dibasic and polybasic fatty acids. ***J. Amer. Oil Chem. Soc. Vol. 61, No. 2:*** **241-246.**

KADESCH, R G (1979). Fat-based dibasic acids. ***J. Amer. Oil Chem. Soc., Vol. 56:*** 845A-849A.

KUCESTKI, V P (1962). U.S. Pat. 3 021 348 to C.P. Hall.

MC LAFFERTY, F W (1963). ***Mass Spectrometry of Organic*** Ions, Academic Press, New York and London.

NIWA, S; MIZUKAMI, F; TOBA, M and OOI, T L (1986). Pressurized oxidation of oleic acid, 53th Japan Chemical Society Symposium, Nagoya, Japan.

PALM OIL REFINERIES ASSOCIATION OF MALAYSIA (PORAM) (1984). ***PORAM Technical Brochure 198411985.***

SHIINA, H; KUBOTA, Y; MAMURO, H; NAKASATO, S; 001, T L and ONG, S H (1986). Oxidative cleavage of palm stearin catalyzed by metal (II) ion-exchanged zeolites. ***J. Japan Oil Chem. Soc. Vol. 35, No.5: 349-353.***

SWERN, D (1961). ***Fatty Acids Part 2,*** 2nd ed. by Markley, K S, Interscience, New York. p. 1307.

TECHNICAL BULLETIN (1981). Emerox Azelaic Acid and Polymer Intermediates. Emery Industries, Cincinnati, Ohio.

VASISHTHA, A K; TRIVEDI, R K and DAS, G (1990). Sebacic acid and 2-octanol from castor oil, ***J. Amer. Oil Chem. Soc. Vol. 67, No.5: 333-*** **337.**