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HYDROXYSTEARIC COMPOUNDS FROM UNSATURATED PALM FATTY ACID

Keywords: Hydroxylation, dihydroxystearic acid and rust inhibitor

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Initial studies on hydroxylation of unsaturated palm fatty acids were carried out with very promising results. Hydroxylation of unsaturated palm fatty acids with hydrogen peroxide-acetic acid for two hours gave products with melting points of 79°C-128°C, acid values of 135-165, saponifiable values of 119-128 and hydroxyl values of 384-440. Yield of the product was about 80%-90%. The product characteristics were very different from those obtained from other oils. For example, hydroxy fatty acid from sunflower oil has a saponifiable value of 212, acid value of 140 and hydroxyl value of 222 (Dahlke et al.*, 1995).*

The product obtained in this study was not only 9, 10-dihydroxystearic acid but also some fatty acids and 10-oxo-stearic acid. By adding hydroxystearic acid at a concentration of 0.2%, the life of steel was extended by up to 10 times, showing that hydroxystearic acid was very effective as a rust inhibitor. Therefore, hydroxylation of unsaturated palm fatty acid is a promissing process for obtaining hydroxystearic compounds.

INTRODUCTION

The vegetable oil industry has undergone a particularly rapid expansion in the last few years with phenomenal growth in crude palm oil (CPO) production in Malaysia and Indonesia. For Malaysia, production was about 6.4 million tonnes in 1992 and is expected to rise to 9.9 million tonnes in 2005 (Nielsen, 1993). For Indonesia, production was about 3.3 million tonnes in 1992 and is expected to rise to 9.9 milion tonnes in 2005 (Sadi, 1993). Total world production is estimated to be 24.2 million

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tonnes in 2005 (Nielsen, 1995). Therefore, product diversification through added value products is necessary, increasing economic returns to this industry from renewable raw materials. Some of the most valuable products that can be made from palm fatty acid are hydroxystearic compounds.

Hydroxy fatty acids have different characteristics from ordinary fatty acids (Dahlke *et al.,* 1995) such as melting point, surface tension, iodine value and saponifiable value, making them useful for surfactants, plasticizers, additives in lubricant, cosmetics and other commercial products (Weber *et al.,* 1995 and Knothe *et al.,* 1995b).

Research on epoxidation of vegetable oils have been done by several researchers (Gan *et al.,* 1992; Greenspan and Gall, 1956a and b; Gunstone, 1992; Kirk Othmer, 1947; Watanabe, 1988; Silbert and Port, 1957). Recently, a number of hydroxy fatty acid (HOFA) compounds were synthesized from monounsaturated fatty acid using catalysts like selenium oxide/ tert-butylhydroperoxide (Knothe *et al.,* 1994a, 1995b-d), ruthernium tertraoxide (Shing *et al.,* 1994), microbial enzymes (Klaas and Warwel 1995), hydrogen peroxide-formic acid (Oludipe *et al.,* 1995) and samarium iodide (Otsubo *et al.,* 1987). Epoxidized fatty acids as intermediate products for making dihydoxy fatty acids have attracted considerable interest and assumed commercial importance in recent years. Epoxidation can be carried out with perfomic acid or peracetic acid. Results using peracetic acid showed that the conversion to products based on iodine value calculation of unsaturated fatty acids was more than 90% (Sadi and Rakmi, 1996).

Hydroxylation of unsaturated palm fatty acids (UPFA) with peracetic acid has an advantage - no dangerously high peracetic acid concentration occurs in the process because it is immediately consumed after its formation. The use of hydrogen peroxide-acetic acid as an oxidant is well recognized and the chemicals are easy to obtain, non-toxic and inexpensive.

Results from studies on preparing dihydroxystearate from UPFA by hydroxylation with hydrogen peroxide-acetic acid mixture and its physicochemical properties are reported here.

MATERIALS AND METHOD

Materials

Palm fatty acid sample was obtained from PT. Pamina Adolina, PTP. VI, Perbaungan, Sumut, Indonesia. Oleic acid (purity 70%) and glacial acetic acid were from BDH Chemical, England, cation exchange resin (Amberlite IR-120) from Fluka Chemie and hydrogen peroxide 30% from Ajax Chem., Australia. After crystallizing palm fatty acid, the fatty acid compositions were determined by GC. The level were 1.57% myristic, 17.12% palmitic, 2.2% stearic, 63.48% oleic and 15.61% linoleic. The fatty acid composition of unsaturated palm fatty acid methyl esters (UPFAME) from esterification of UPFA was 1.44% myristic, 16.59% palmitic, 1.77% stearic, 64.18% oleic and 16.02% linoleic acid. The fatty acid composition of crude palm olein (CPOo)was 0.91% myristic, 41.87% palmitic, 3.22% stearic, 41.55% oleic and 12.45% linoleic acid. The physicochemical characteristics of the raw materials used in this study are shown in *Table 1.*

Epoxidation-Hydroxylation

Oleic acid of UPFA used in the hydroxylation was prepared by crystallization of palm fatty acid with methanol. For epoxidation of UPFA, a well-stirred solution of 500g UPFA, 20g cation resin, 165ml glacial acetic acid, 250ml benzene and 7.5g of concentrated sulphuric acid was heated to 60°C-70°C for two hours (Sadi *et al.,* 1995). After stirring, the acetic acid solution was decanted and benzene removed by rotaevaporation. The other epoxy compounds from UPFAME, commercial oleic acid and CPOo, were prepared in similar manner. For hydroxylation of UPFA, the reaction mixture was poured into 1000ml of hot water at 95°C-100°C and stirred well for 15 minutes. The mixture was then cooled to room temperature and filtered, and the precipitate washed with cold water. The product, which consists of a mixture of dihydroxystearic acid (DHSA) and hydroxyacetoxystearic acid, was heated at 100°C for five minutes in excess 2M NaOH and then poured into excess 2M HCI while stirring to produce DHSA from hydroxyacetoxystearic acid.

TABLE 1. PHYSICOCHEMICAL CHARACTERISTICS OF RAW MATERIALS USED

Parameter	Commercial oleic acid	UPFA	Unsaturated Palm Fatty Acid Methyl Ester
Iodine value	86.13	91.82	86.88
Acid value	150.61	155.00	5.19
Saponifiable value	202.00	196.01	182.84
Viscosity (cP), 30°C	26.37	26.35	7.39
Density	0.9289	0.8902	0.8742
Peroxide value	3.46	4.72	3.60

Hydroxy fatty acid from CPOo was prepared through hydrolysis of epoxidized crude palm olein (ECPOo) with 30% water at 117°C for eight hours using 1% ZnO as catalyst. The granular precipitate was filtered and washed until free of acid and vacuum dried in a dessicator.

Analytical Method

Acid value, iodine value, saponifiable value and hydroxyl value were determined according to The American Oil Chemists' Society (AOCS) methods (Mehlenbacker *et al.*, 1989). The composition of fatty acid methyl esters (0.25μg-0.30μg) was determined by gas chromatography (model GC 14B, Shimadzu, Kyoto, Japan) equipped with a flame-ionization detector. A packed column (GP3%-2310/2%SP-2300 on 100/120 mesh chromosorb W AW) was used with nitrogen as carrier gas at a flow rate of 60 ml/min and hydrogen at 70 ml/min. The column was programmed at 180°C, and injector and detector temperature at 230°C. For gas chromatography/mass spectroscopy (GC/MS) analysis, samples were injected into a Varian 3400 GC equipped with a 0.25 mm I.D. x 25 mm BPX5 fused-silica capillary column. The carrier gas was helium at a flow rate of 150 ml/min. The column temperature was initially 180°C for 30 min, then increased to 300°C at the rate of 7°C/min. Electron impact (EI) mass spectra mode 70eV of methyl esters derivatives were obtained on a mass spectrometer (model MS Finnigan Mat SSQ710 made in USA) with a filament current of 200μA and electron multiplier of 1200μA. Data storage and processing were done in a DEC station 2100 with digital UNIX system and NST IUPAC library.

Surface tension measurements conducted with a Fisher Scientific Surface Tensiomat 21. All data points were the means from five measurements. The infrared spectra of products were recorded by Fourier transform infrared (FTIR) model FTS 165, Bio-Rad spectrometer on KBr pellets.

Rust inhibition properties of the products were evaluated using stainless steel rod in bis (2-ethylhexyl) sebacate and tris (2-ethylhexyl) phosphate. Rust characteristic of stainless steel rod with steam turbine oil test in synthetic sea water (ASTM Method, 1975) at 60°C was made using lubricants (bis (2-ethlyhexyl) sebacate and tris (2-ethylhexyl) phosphate) to which had been added the product at 0%-0.2%. The product was dissolved in the lubricant using ether, an intermediate volatile solvent that was later boiled off. The rust spot was visually assessed daily. A test specimen was passed if it contained no more than three dots of rust, not one larger than 1 mm in diameter. On the other hand, it failed if it contained one or more dots of rust larger than 1 mm in diameter or four or more dots of any size. The rust surface was studied by scanning electron microscopy (SEM).

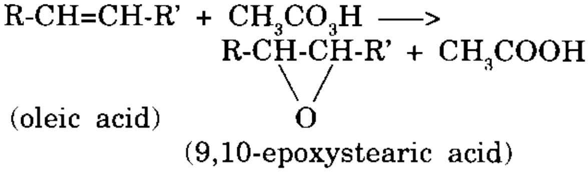
RESULTS AND DISCUSSION

Epoxidation of UPFA

Epoxidized UPFA can be used as an intermediate product to produce dihydroxystearic acid. The influence of reaction time on the iodine value of the product from epoxidation of UPFA is shown in *Figure 1.* The reaction for epoxidation of UPFA by peracetic acid is:

(i) $H_2O_2 + CH_3COOH \Longleftrightarrow CH_3CO_3H + H_2O$

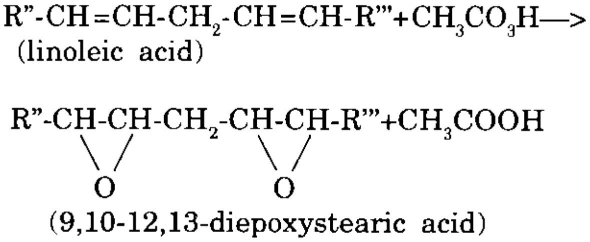
(ii)



$$R\text{-}CH{=}CH\text{-}R' + CH_3CO_3H \longrightarrow R\text{-}\underset{\diagdown\ O\ \diagup}{CH\text{-}CH}\text{-}R' + CH_3COOH$$

(oleic acid) (9,10-epoxystearic acid)

(iii)



$$R''\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}R''' + CH_3CO_3H \longrightarrow R''\text{-}\underset{\diagdown\ O\ \diagup}{CH\text{-}CH}\text{-}CH_2\text{-}\underset{\diagdown\ O\ \diagup}{CH\text{-}CH}\text{-}R''' + CH_3COOH$$

(linoleic acid) (9,10-12,13-diepoxystearic acid)

where $R = CH_3(CH_2)_7$, $R' = (CH_2)_7COOH$, $R'' = CH_3(CH_2)_4$ and $R''' = (CH_2)_7COOH$.

The optimum yield of the epoxidation product is reached within two hours (*Figure 1*). The results showed a decreasing iodine value of UPFA from 91.82 to 0.43 in two hours. It meant that saturation of the carbon double bond of epoxidized UPFA was 99.5% complete within the time. The epoxidized UPFA product, an intermediate product, had an oxirane oxygen of 4.15% and iodine value of 0.43. Oxirane oxygen is the oxygen (% of mass) contained in the epoxy-group in fatty acids/oils. Based on the fatty acid composition, UPFA oxirane oxygen has a theoretical maximum of 5.2%. Thus the yield of epoxystearic acid was 79.80% of the theoretical value.

$$\text{Yield (\%)} = \frac{\text{epoxy (oxirane) oxygen found}}{\text{epoxy (oxirane) oxygen calculated}} \times 100$$

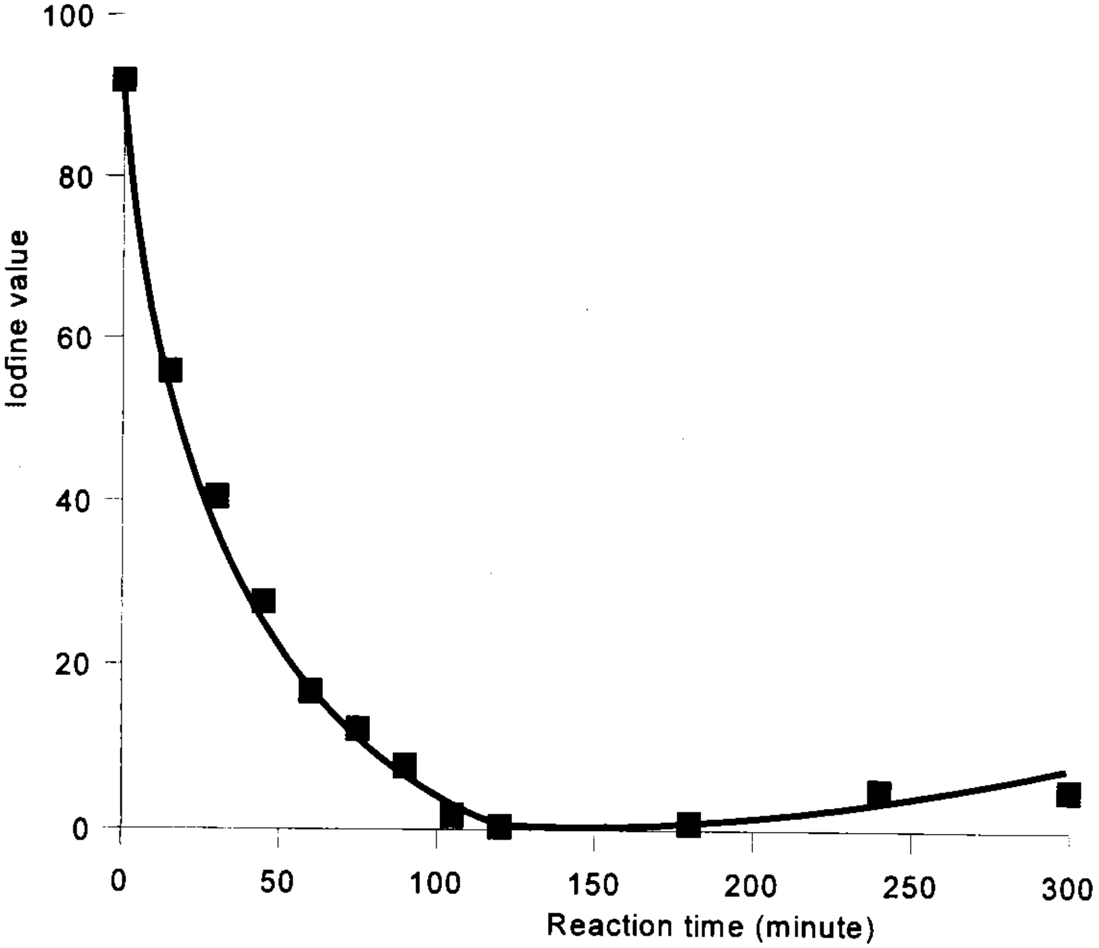
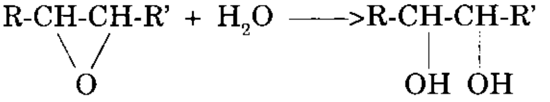


Figure 1. Effect of reaction time on iodine value of product during epoxidation

Hydroxylation

Epoxidation of long chain unsaturated fatty acid gave virtually complete conversion to oxirane within two hours. At this stage, the reaction can be stopped to remove the solvent and proceed to hydroxylation. The oxirane oxygen content of UPFA product was zero after hydroxylation. This was because of nucleophilic attack at the epoxy carbon by H_2O during hydroxylation followed by nucleophilic attack to open the adjacent epoxide. According to the proposed biosynthetic pathway of epoxides hydroxylation in brown alga (Barrow and Capon, 1990) and plant oils (Weber *et al.*, 1995), the product was not only dihydroxystearic acid but also dihydroxy tetrahydrofuran moiety. The reactions involved were:

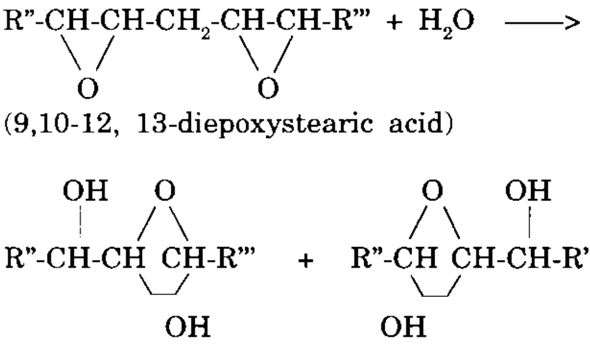
(i)



$$\text{R-CH-CH-R'} + H_2O \longrightarrow \text{R-CH(OH)-CH(OH)-R'}$$

(9,10-epoxystearic acid) (9,10-dihydroxystearic acid)

(ii)



(9,10-12, 13-diepoxystearic acid)

(10,13-dihydroxy-9,12-epoxystearic acid) (9,12-dihydroxy-10,13-epoxystearic acid)

GC/MS analysis of purified dihydroxystearic acid (DHSA) showed the presence of methyl esters and methyl 9, 10-dihydroxystearate. Ion peaks at *m/z* 242, 270 and 298 were seen for tetradecanoate, hexadecanoate and octadecanoate methyl esters, respectively (with the base peaks trough at *m/z* 74). Further support for this was given by GC analysis of the starting materials for their fatty acids. The other product, presumably a dihydroxystearic acid, was not obtained in pure from. A ketonic product, 10-oxo-octadecanoic acid (10-OOA), was present in the purified product. Unsaturated fatty acid can be degraded by β-oxidation (Meuβdoerffler, 1989). In hydroxylation, a possible by-product, *viz.* 10-OOA, was produced to the level of 5.6%.

The structure of 10-oxo-octadecanoate was confirmed by GC MS. In the mass spectrum of 10-OOA, loss of the alkyl group, $CH_2{=}C{=}O{=}CH_2^+$, gave a peak at *m/e* = 55 (Pavia *et al.*, 1996) because the larger of the two alkyl groups attached to the carbonyl group was mostly lost. The mass spectrum of methyl 10-oxo-octadecanoate showed a fragment ion peak at *m/z* 312 $[M]^+$, indicating a C_{18} chain with keto (oxo) group and saturation. The two significant fragment ions obtained as a result of α-cleavages on either side of the keto group were present at *m/z* 199 and 141. Another set of fragment ions resulting from β-cleavage on both sides of the keto group due to γ-hydrogen abstraction (McLafferty rearrangement) (Pavia *et al.*, 1996) appeared at *m/z* 214 and 516. These fragment ion peaks indicated an oxo group at the position C_{10}.

The mass spectrum of purified 9, 10-dihydroxystearate methyl esters exhibits an intense peak due to a cleavage between the 9 and 10 hydroyxyl functions. Peaks at *m/z* 155, 187 and 355 were formed. A peak at *m/z* 155 was observed due to rearrangement by cyclyzation of hydroxystearate acid (Asselineau and Asselineau, 1984). The mass impact for 9, 10-dihydroxystearate methyl ester was indicated by two peaks of 155 and 187.

Niehaus and Schroepfer (1967) proposed that methyl 9, 10-dihydroxystearate, upon electron impact, did not give a significant quantity of molecular ions for determination of its isotopic composition but a significant peak at *m/z* 187 corresponding to a fragment containing carbon atoms 1 to 9. This peak can be used to quantify the labeled oxygen on carbon atoms 9 and 10 while the peak of hydroxy tetrahydrofuran in this product can not be detected.

The crystalization of HOFA was an important and complex problem for this study. The physical properties of palm oil derivatives are closely related to the size and shape of their crystals. The particle size of this crystalline product, after saponification, neutralization and crystallization, was about 20μm-60μm. Crystal size was uniform, possibly because the crystal aggregates were stable and not broken up. However, the crystals did not aggregate before saponification. The appearance of this product was slightly yellow, and similar to wax or stearin. However, the hydroxylation yields of both UPFA and oleic acid were similar - based on gravimetric analysis of the products, the overall yield of 9, 10-dihdroxystearic acid from YPFA and oleic acid were 48.74% and 48.48%, respectively. The yield of crude dihydroxystearic acid from both the starting materials was about 81%. The difference in crystal size between unsaponified and purified 9, 10-dihydroxystearic acid is shown in *Figure 2.*

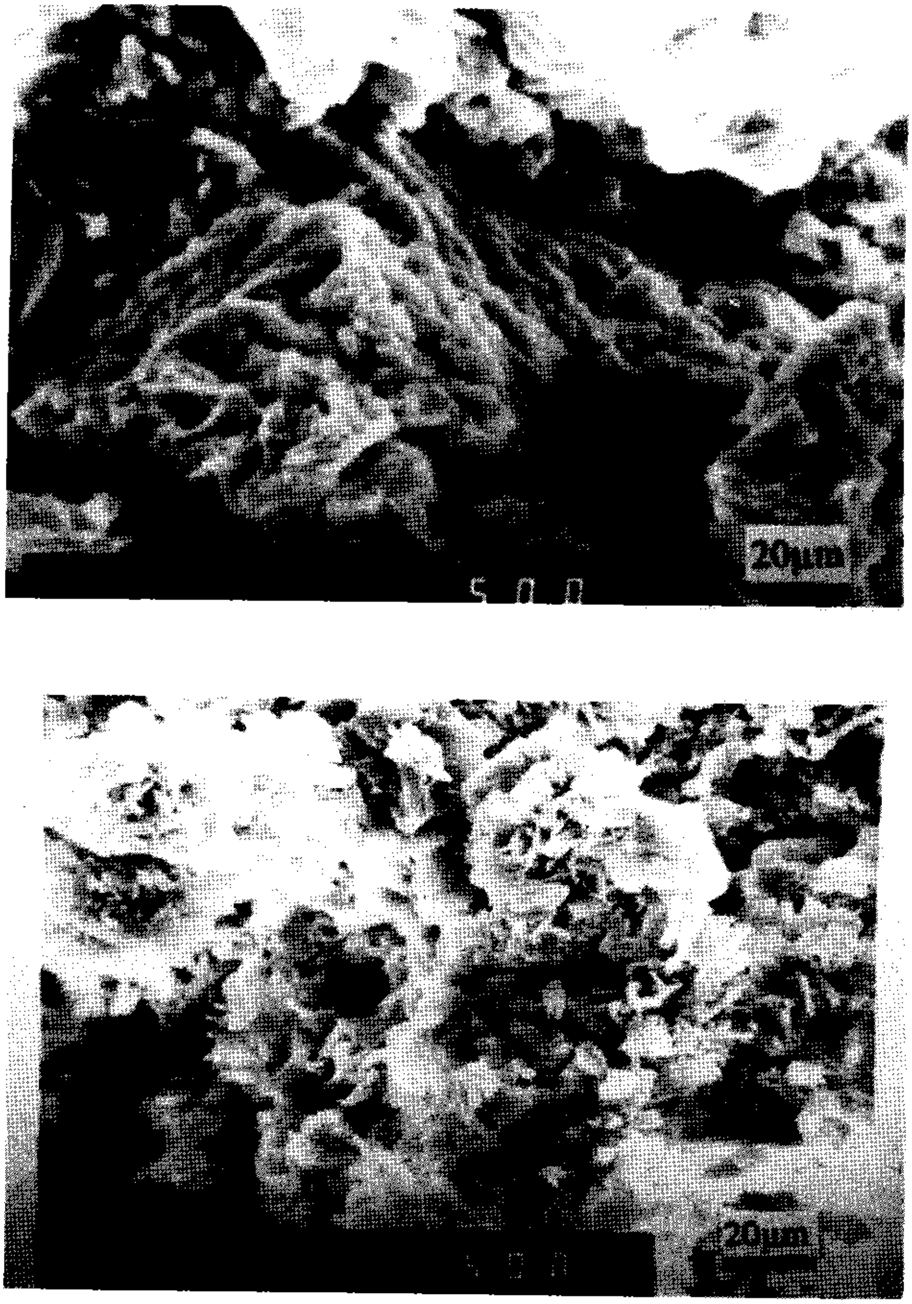


Figure 2. Crystalline structure of dihydroxy fatty acid from unsaturated palm fatty acids by scanning electron microscopy (Magnification 500x). Upper: before purified; lower: after purified

Both compounds, 9, 10-dihydroxystearic acid of UPFA and oleic acid, before saponification and acidification had similar low melting points (m.p.79°C-80°C). However, after saponification acidification and crystallization, their melting points increased (m.p. 120°C-130°C).

In hydroxylation 218.55g of unsaturated palm fatty acid methyl ester, a semi-solid, slightly yellow upper layer was obtained and, after drying, 202.34g of product (a yield of 92.58%) with a melting point of 61°C. Crystallization from ethanol (10ml/g) at 0°C-5°C yielded 89.24g of purified 9, 10-dihydroxystearic acid with a mixture of other acids (a yield of 40.83%) with a melting point of 120°C-128°C and hydroxyl value of 349.64 (%OH = 10.63).

The result showed that the yield of purified 9, 10-dihydroxystearic acid after saponification, acidification and crystallization was lower than the yield when peracetic acid (hydrogen-peroxide mixture) was used to hydroxylate UPFA methyl ester, UPFA or oleic acid. The lower yields of these products are believed to be due to the higher solubility of the products in the methanol or ethanol used as solvents in the crystallization. However, the advantage of these products is their insolubility in water because of differences in polarities.

Product Properties

Physicochemical properties of dihydroxystearic acid from UPFA and oleic acid after purification by crystallization with ethanol, such as acid value, iodine value, colour, specific gravity, peroxide value, saponifiable value and hydroxyl value are shown in *Table 2*.

In comparing with dihydroxystearic acid from epoxidized crude palm olein (ECPOo), the product from hydrolysis of ECPOo was given lower characteristic than UPFA because of lower UPFA content of crude palm olein. Crude palm olein contains about 42% of palmitic acid. The product is semi solid because hydrolysis of ECPOo into hydroxy fatty acid and glycerol was not complete. This was indicated by the low acid value of the product (16.55 after eight hours). In this work, hydrolysis of ECPOo was done at low pressure (1.8 bars). Therefore, the hydroxylation encountered several problems such as the occurence of by-products, incomplete hydrolysis of triglyceride and incomplete hydrolysis of epoxy ring. To obtain a higher yield of hydroxy fatty acid, crude palm olein (CPOo) can first be fractionated by secondary filtration and hydrolysis then carried out at a higher temperature and pressure to yield com-

TABLE 2. PHYSICOCHEMICAL PROPERTIES OF DIHYDROXYSTEARIC ACID FROM ECPOo, OLEIC ACID, UPFA AND UPFA METHYL ESTER

Parameter	9, 10-dihydroxysteric acid from			
	ECPOo[a)]	**Oleic acid**	**UPFA**	**unsaturated palm methyl ester**
Iodine value	2.70	0	0	0.87
Acid value	16.55	135.11	164.03	159.27
Saponifiable value	182.59	128.42	119.03	152.73
Melting pont (°C)	37-38	125-128	79-80[b)]	120-128
Colour/form	White/ Semi solid	White/ Crystalline	White/ Crystalline	White/ Crystalline
Hydroxyl value	91.00	438.61	384.21	439.64
Oxirane oxygen (%)	0.01	0.78	0.26	0.20

a) Hydrolysis of epoxidized crude olein (ECPOo) at 117°C for eight hours using 1% ZnO as catalyst
b) Before saponification and acidification

pletely glycerine and a mixture of fatty acids. Fractional crystallization of CPOo with secondary filtration would have less palmitic acid in the liquid phase.

The results showed that 9, 10- dihydroxystearic acid from whichever - UPFA, UPFA methyl ester and oleic acid - were not different in their characteristics such as form, hydroxyl value and melting point.

Infrared Spectroscopic Analysis

Infrared spectroscopy can be used to qualitatively analyse the chemical structure of organic compounds. To check that epoxidation had occurred, the spectra of epoxidized unsaturated palm fatty acids (EUPFA) can be measured. The infrared spectrum of EUPFA has an absorption band at 1743cm^{-1} corresponding to stretching the >C=O vibration of the ester carbonyl - COO group, and the band at 2900 cm^{-1} for C-H and 1172cm^{-1} for C-O epoxy group. A peak with a wave number around 1080cm^{-1}-1300cm^{-1} meant that the epoxidized compound had been formed *(Figure 3)*. The double bond carbon of long chain fatty acids was no longer present in the 1640cm^{-1}-1680 cm^{-1} region because the epoxidized compound had been formed - the bond was broken and the carbon linked to an epoxy group. After hydroxylation, C-O of the epoxy group was not seen in the 1172cm^{-1} area because the ring of the epoxidized compound had been opened by water to produce 9, 10-dihydroxystearic acid *(Figure 4)*.

Surface Tension

Surface tension studies on novel allylic mono and dihydroxy fatty compounds were done by Knothe *et al.* (1996) to distinguish critical micelle concentrations (CMC) between mono and dihydroxy fatty acids. They found critical micelle concentrations of novel dihydroxy fatty acids in the range 10^{-4}-10^{-3} mol/l with surface tensions at CMC (γ_{CMC}) in 1M NaOH in the range 38-41 mN/m. Similar results were also obtained in surface tension (γ) measurements of the product. In this study, surface tension for 1M NaOH (blank sample) on a tensiometer was 75.92 mN/m and blank value for distilled water 71.80mN/m. These values served as references for the initial surface tensions before adding the product. Critical micelle concentration (CMC) of the product was determined graphically by plotting surface tension (γ) against log concentration (mol/L) of the product in 1M sodium hydroxide solution. The result showed that the CMC of the product was about 10^{-4} mol/l with a surface tension (γ_{CMC}) of about 39mN/m. *Figure 5* shows the surface tension of the product in 1MNaOH at 25°C. Dihydroxystearic acid exhibited a satisfactory surface activity with no difference in surface properties between the product and dihydroxy fatty acids obtained by Knoth *et al.* (1996). Therefore, this compound can be used as a surfactant.

Evaluation of the Product as a Rust Inhibitor

The rust inhibiting property of the product was evaluated using bis(2-ethylhexyl) sebacate and tris (2-ethylhexyl) phosphate. Rust characteristic of stainless steel rod (ASTM Method, 1975) in the presence of 30% synthetic sea water at 60°C was made using lubricants (bis (2-ethylhexyl) sebacate and tris (2-ethylhexyl) phosphate) to which had been added the product at 0%-0.2%. The product was dissolved in bis) 2-ethylhexyl) sebacate and tris (2-ethylhexyl) phosphate by means of ether, an intermediate volatile solvent that was later boiled off. The effectiveness of 9, 10-dihydroxystearic acid in inhibiting rusting is shown in *Table 3*.

Adding hydroxystearic acid at a concentration of 0.2% in bis (2-ethylhexyl) sebacate and tris (2-ethylhexyl) phosphate, the life of steel (type ASTM AZ 69, Brasmet) was extended by up to 10 times. Thus, hydroxystearic acid is a very effective rust inhibitor.

Infrared Spectroscopy of Rust Protective Film

The infrared spectrum of a rust protective film (product added at 0.1%) after 16 days protection at 60°C is shown in *Figure 6*. There were localized group modes in the CH stretching region (2800cm^{-1}-3000cm^{-1}) and spaced bands

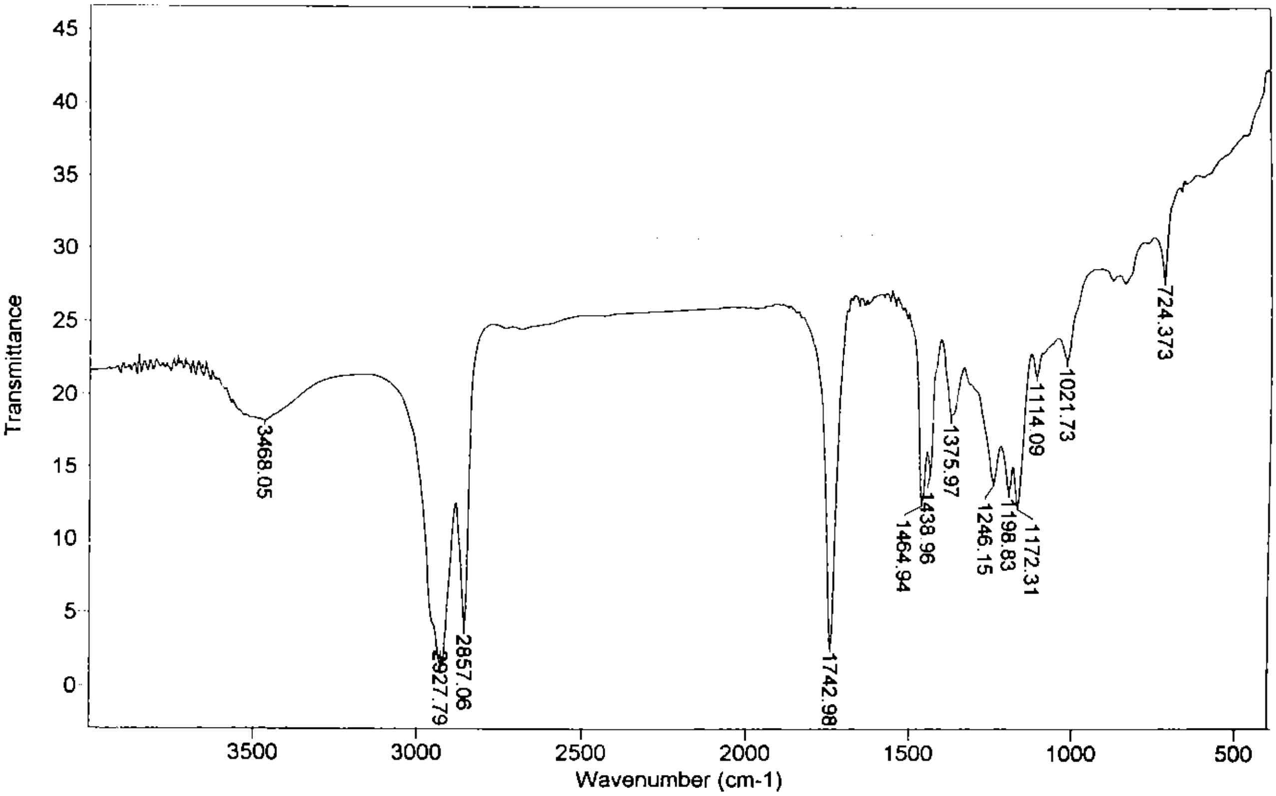


Figure 3. Infrared spectrum of epoxidized unsaturated palm fatty acids

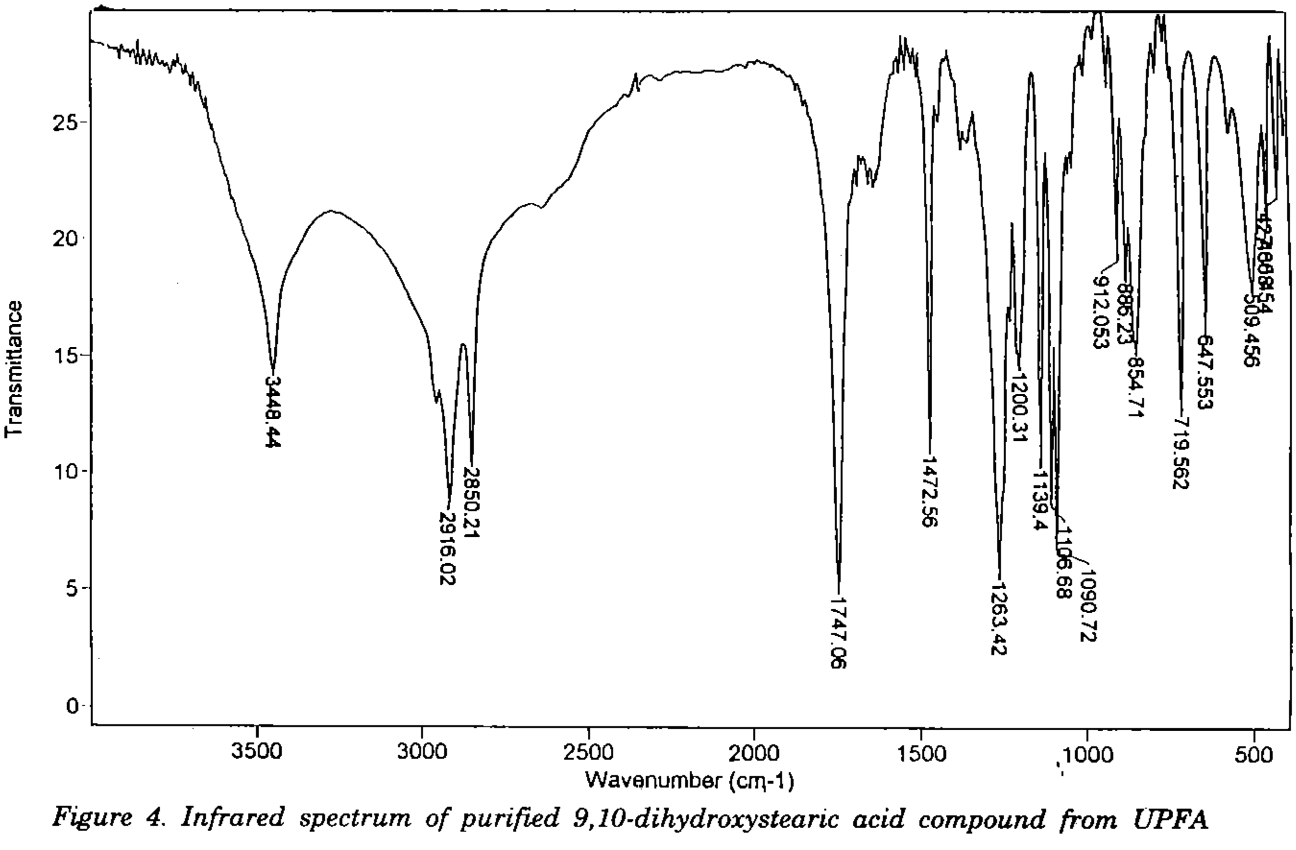


Figure 4. Infrared spectrum of purified 9,10-dihydroxystearic acid compound from UPFA

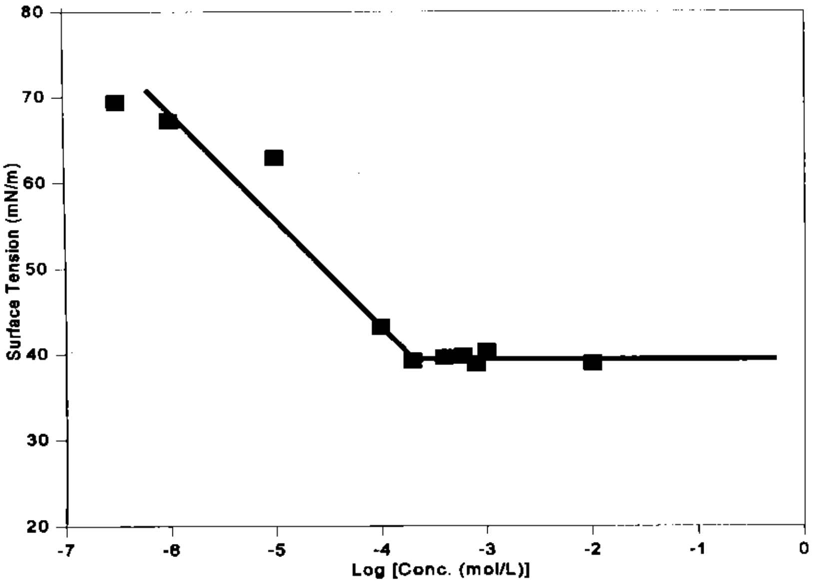


Figure 5. Log concentration (mol/L) of product in 1M NaOH vs. surface tension

TABLE 3. EFFECT OF DIHYDROXYSTEARIC MIXED WITH BIS(2-ETHYLHEXYL) SEBACATE AND TRIS(2-ETHYLHEXYL) PHOSPHATE ON RUSTING TEST OF STEEL

Synthetic Lubricant	9, 10-dihydroxy stearic acid (%)	Change in viscosity (cP)	Acid formed (acid value)	Hours to failure
Bis(2-ethylhexyl) sebacate	none	+0.76	+1.85	24
Bis(2-ethylhexyl) sebacate	0.1	+0.41	+0.34	144
Bis(2-ethylhexyl) sebacate	0.2	+0.32	+0.22	192
Tris(2-ethylhexyl) phosphate	0.2	-1.20	+0.06	240

between 1500cm^{-1} and 1100cm^{-1}. According to vibration of CH_2 groups (Fetty, 1996), they were associated with CH_2 wagging, twisting and rocking. Also seen was a strong absorption band at 1742cm^{-1} due to stretching of the C=O bond.

The results showed that absence of an absorption peak in the 3400cm^{-1} region was due to water molecule. Because the steel was covered by a dihydroxy fatty acid film, water could not attack the metal. Fetty (1996) proposed that interesting infrared vibrations in long-chain fatty acids are due to CH_2 scissoring vibrations around 1470cm^{-1}. In this study, the peak was a singlet at 1473cm^{-1}. It meant that there was a splitting band caused by a change in the crystal structure of the purified dihydroxystearic acid.

Physical Surface Features of Rust

The microstructure of steel rusted at 60°C

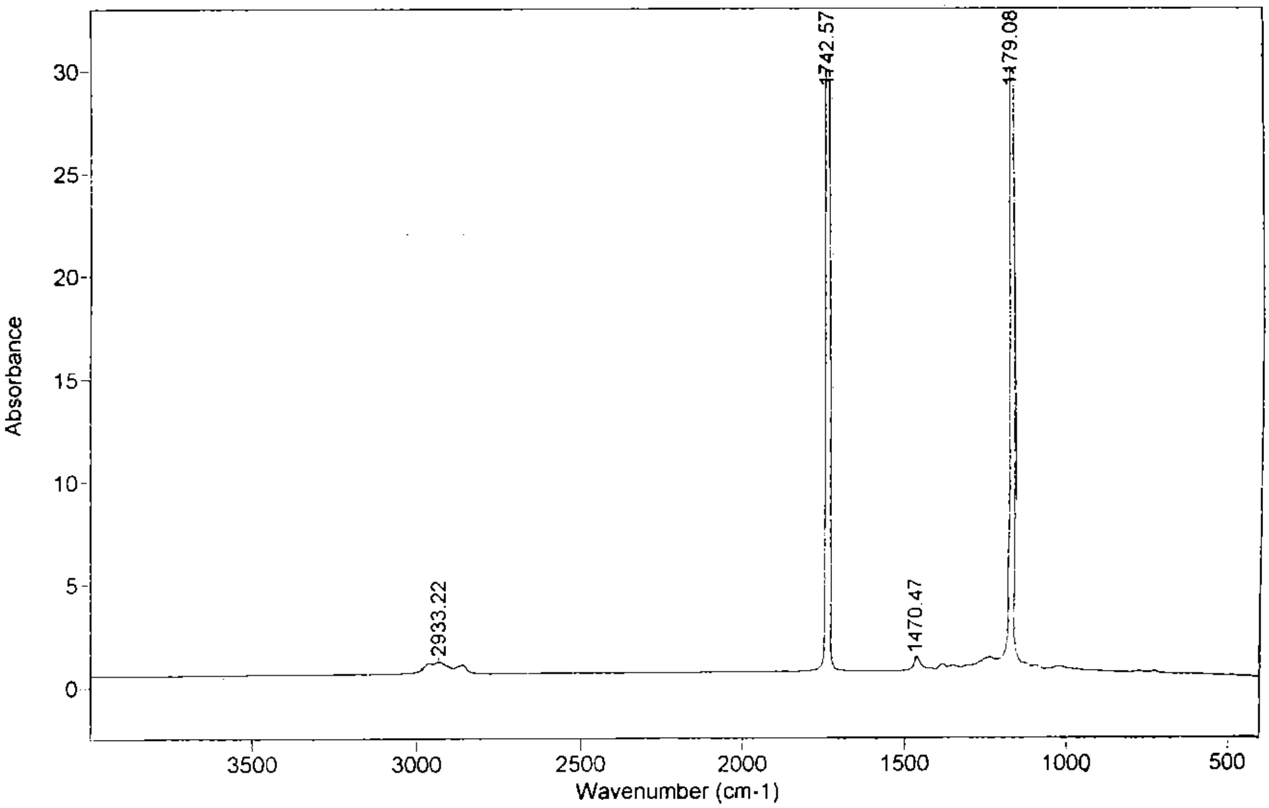


Figure 6. Infrared spectrum of dihydroxystearic acid protective film after rusting test on steel in bis(2-ethylhexyl) sebacate for 16 days at 60°C.

for one day and 16 days were assessed by scanning electron microscopy (SEM) and the results shown in *Figures 7* and *8*. *Figure 7* shows the microstructure of rust on steel without adding 9, 10-dihydroxystearic acid. The darker region is the steel surface and the lighter region the rust. In *Figure 7a*, the rust seems to be a fractured solid surface. Otherwise, it was a black spot. The steel had a rusted area of approximately 48%.

Figure 8 is a scanning electron micrograph of a film of dihydroxystearate salts on steel at a concentration of 0.1% after 16 days at 60°C. The surface did not have much rust nor microcracking. At the end of the test, it had only five rust spots and a total rust area of only approximately 0.5%.

CONCLUSION

Dihydroxysteric acid can be prepared from UPFA with hydrogen peroxide-acetic acid at 60°C-65°C. The yield of crude 9, 10-dihydroxystearic acid before crystallization was 80%-93% and, after purification 40%-50%. The product was tested for its rust inhibition properties and found to be very effective.

Abbreviations

CPO : Crude Palm Oil
CPOo : Crude Palm Olein
DHSA : Dihydroxystearic Acid
ECPOo : Epoxidized Crude Palm Olein
EUPFA : Epoxidized Unsaturated Palm Fatty Acid
HOFA : Hydroxy Fatty Acid
PAA : Peracetic Acid
PFA : Palm Fatty Acid
UPFA : Unsaturated Palm Fatty Acid
UPFAME : Unsaturated Palm Fatty Acid Methyl Ester
10-OOA : 10-oxo-octadecanoic acid

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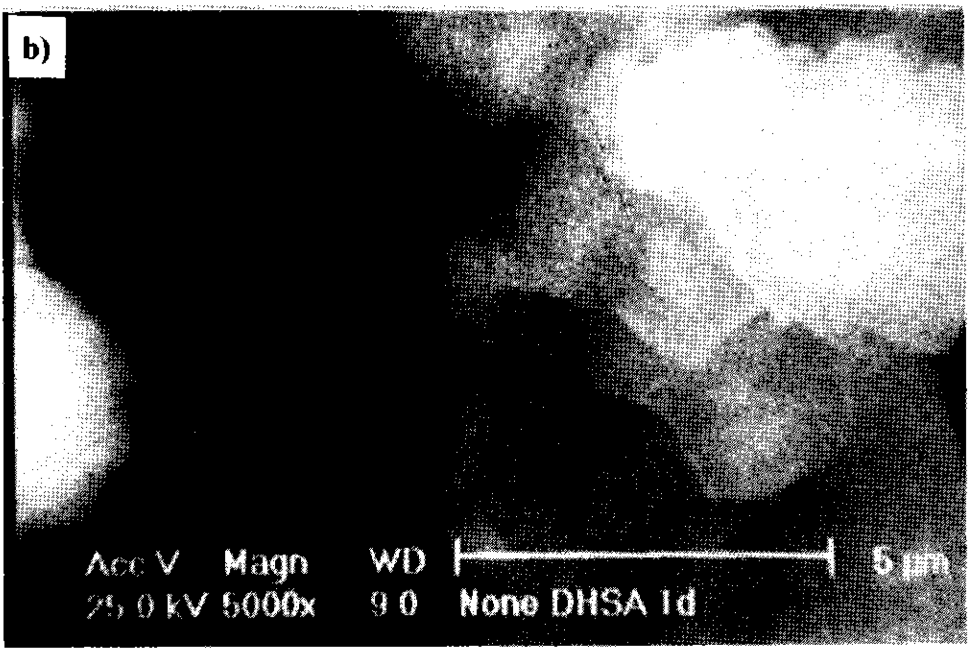
Figure 7. Scanning electron micrographs of rust surfaces on steel.

(a) Showing the roughness of the rust surface after 24 hours without product addition



(b) Surface magnification of the rust in (a)

Figure 8. Scanning electron micrograph of the surface showing little rust after 384 hours at 60°C with product added at 0.1%.

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REFERENCES

ASTM (1975). Standard method of test for rust-preventing characteristics of steam turbine oil in the presence of water. ASTM D 665-60, Part 23, pp. 304-311.

BARROW, R A and CAPON, R J (1990). Epoxy lipids from the Australian epiphytic from alga, *Notheia anomala. Aust. J. Chem., 43* : 895-911.

DAHLKE, B S; HELLBARDT, M and ZETH, W H (1995). Polyhydroxy fatty acid and their derivatives from plant oils. *JAOCS, 72 (3)* : 349-353.

GAN, L H; GOH, S H and OOI, K S (1992). Kinetic studies of epoxidation and oxirane cleavage of palm olein methyl ester. *JAOCS, 69(4)* : 347-351.

GREENSPAN, P F and GALL, R J (1956a). Epoxy compounds from unsaturated fatty acid ester. *Ind. Eng. Chem., 47* : 147-148.

GREENSPAN, P F and GALL, R J (1956b). Epoxy compounds from unsaturated esters plasticizer. *JAOCS, 33* : 393-394.

GUNSTONE, D F (1992). The study of epoxy oil and epoxidized vegetable oils by ^{13}C NMR spectroscopy. *JAOCS, 70 (11)* : 1139-1143.

KIRK-OTHMER (1947). Epoxidation and peroxy compounds. *Encyclopedia of Polymer Science & Technology, Vol. 3,* New York. Interscience Encyclopedia Inc.

KLAAS, M R and WARWEL, S (1995). Enzymatic preparation of peroxy-, epoxy- and peroxy-epoxy fatty acids. *Proc. of the 21st World Congress of the International Society for Fat Research (ISF),* The Hague, October 1995, Ed. Castenmiller, W.A.M. (1996), PJ Barnes & Associates, England, Vol. 3, p. 469.

KNOTHE, G; BAGBY, M O; WEISLEDER, D and PETERSON, R E (1994a). Allylic mono- and di-hydroxylation of isolated double bonds with selenuim dioxide-tert-butyl hydroperoxide. NMR characterization of long chain enols, allylic and saturated 1, 4-diols, and enones. *J. Chem. Soc. Perkin Trans. 2* : 1661-1669.

KNOTHE, B; DUNN, R O and BAGBY, M O (1995b). Surface tension studies on novel allylic mono- and di-hydroxy fatty compounds: A method to distinguish erythro/threo diastereomers. *JAOCS, 72 (1)* : 43-47.

KNOTHE, G; DAHLKE, B; HELLBARDT, S; PAETOW, M and ZECT, W H (1995c). Polyhydroxy fatty acid and their derivatives from plant oils. *JAOCS, 72 (3)* : 349-353.

KNOTHE, B; BAGBY, M O; WEISLEDER, D and PETERSON, R E (1995d). Analysis of hydroxy fatty compounds with Δ5-, Δ7-, Δ-8, and Δ-10 unsaturation. *JAOCS, 72 (6)* : 703-706.

MEHLENBECKER, V C; SALEE, E M; WALKER, R O; FIRESTONE, D; HOPPER, T H; LINK, W E and WALKER, R C (1989). Official Methods and Practices of the AOCS. Official Method, Sampling and Analysis of Commercial Fats and Oils, 4. ed., Champaign, Illinois.

MEUβDOERFFLER, F (1989). Oxidative processes during microbial production of dicarboxylic acids. *Henkel-Referate 25,* Int. ed. : 19-25.

NIEHAUS, W G and SCHROEPFER, G J (1967). Enzymatic stereospecificity in the hydratation of epoxy fatty acids. Stereo incorporation of the oxygen of water. *JACS, 89 (16):* 4227-4228.

NEILSEN, B B (1993). Production of high quality palm oil during harvesting, processing, refining and shipment. Paper presented at Shipping and Handling of Palm Oil Products Course, Kuala Lumpur, 22-23 October 1993.

NIELSEN, B B (1995). Meeting the needs for oils and fats in the 21st century. *Malaysian Oil Science and Technology, 4 (2)* : 7-18.

OLUDIPE, J O; IYUKE, S E and ADEREMI, B O (1995). Kinetics and mechanism of maleic acid hydroxylation by hydrogen peroxide. Part I: Formal kinetic studies by immobilized catalysis in a pseudo-homogeneous system. *J. Chem. Tech. Biotechnol., 63* : 147-152.

OTSUBO, K; INANAGA, J and YAMAGUCHI, M (1987). SmI_2-induced highly regioselective reduction of α,β-epoxy esters and γ,δ-pepoxy-α,β-unsaturated esters. An efficient route to optically active β-hydroxy and δ-hydroxy esters. *Tetrahedron Lett., 28 (38)* : 4437-4440.

PAVIA, D L; LAMPMAN, G M and KRIZ, G S (1996). *Introduction to Spectroscopy.* 2nd ed., p. 511. New York, Saunder College Publ.

PETTY, M C (1996). *Langmuir-Blodgett films: An Introduction.* First edition, p. 234. Cambridge University Press.

SADI, S (1993). Penggunaan minyak sawit dan inti sawit sebagai bahan baku surfaktan. *Berita PPKS, 1(1)* : 57-63.

SADI, S; PAMIN, K and DARNOKO (1995). Preparation of butyl epoxystearate from palm oil and palm fatty acid. *Proc. of the 21st World Congress of the International Society for Fat Research (ISF),* The Hague, October 1995, Ed. Castenmiller, W.A.M. (1996), PJ Barnes & Associates, England, Vol. 3, p. 465.

SADI, S; and RAKMI A RAHMAN (1996). Hydroxylation of Unsaturated Palm Fatty Acid with Hydrogen Peroxide-Acetic Acid mixture. *Proc. of the 1996 PORIM International Palm Oil (Soap & Detergent),* p. 549.

SHING, T K M; TAI, V W F and TAM, E K W (1994). Practical and rapid vicinal hydroxylation of alkenes by catalytic ruthenium tetraoxide. *Angew. Chem. Int. Ed. Engl., 33 (22)* : 2312-2313.

SILBERT, L S and PORT, W S (1957). Epoxidized ester of fatty acids as internal and external plasticizer for polyvinyl acetate. *JAOCS, 34 (1)* : 9-11.

WATANABE, S; FUJOTA, T and SAKAMOTO, M (1988). Epoxides of unsaturated fatty acids as an anti-rust additives in water-based cutting fluids. *JAOCS, 65 (8)* : 1311-1312.

WEBER, N; VOSMANN, K; FEHLING, E; MUKHERJEE, K D and BERGENTHAL, D (1995). Analysis of hydroxylated fatty acids from plant oils. *JAOCS, 72 (3)* : 361-368.