Formation of Dihydroxystearic Acid from Hydrolysis of Palm Kernel Oil Based Epoxidized Oleic Acid

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A B S T R A C T

Dihydroxy stearic acid (DHSA) is regarded as a high value hydroxyl fatty acid commonly used in cosmetics, personal care sector, an ingredient in coloured formulations and as coating agent for pigments owing to its unique structure, hydrophilicity and polarity. This study investigates the formation of DHSA through a two-step reaction involving the epoxidation and hydrolysis steps, conducted in a semicontinuous stirred tank reactor at 55°C and agitation speed of 350rpm. The epoxidation and hydrolysis reaction were carried out by reacting commercial grade palm kernel oil based crude oleic acid with formic acid and hydrogen peroxide (30 w/w%) to first form the epoxidized oleic acid. Thereafter, the epoxidized oleic acid was hydrolysed to produce DHSA. The formation of the epoxidized oleic acid and DHSA compound was analysed and confirmed by using percent of relative conversion to oxirane (RCO %), iodine value (IV) and fourier transform infrared spectroscopy (FTIR). The epoxidation results showed that the highest yield of 76.2% for epoxidized oleic acid was achieved. The DHSA formation was confirmed when the RCO (%) value measured approached zero after 18.8 hrs. In addition, the IV calculated showed a marked decreased from 98.99 for crude oleic acid to 33.44 for epoxidized oleic acid and finally 10.4 for the DHSA. The IV showed progressive degradation of the ethylene unsaturation sites of the fatty acids. The FTIR results indicated that the absorption band of epoxy ring group (O=C-O) formed during the epoxidation step was observed at 1217.01 cm⁻¹ in replacement of the C=C double bond of oleic acid which was detected in the range of 1620-1680 cm⁻¹. After the hydrolysis step, the peak corresponding to the epoxy ring group was disappeared, indicating that the epoxy ring was cleaved by water to form hydroxyl compound that characterized the DHSA. The hydroxyl group was observed at the absorption band region of 3200-3600cm⁻¹. This study shows that the oleic acid was successfully transformed into DHSA and that oleic acid derived from palm kernel oil is a potential raw material for the production of sustainable and environmental friendly DHSA.

INTRODUCTION

Oleochemicals are generally known as chemical products derived from vegetables or animals sources. Palm oil and palm kernel oil are well known sources for oleochemical production in Malaysia. Malaysias the second largest producer of palm oil in the world after Indonesia. Efforts have been made on turning palm oil into oleochemical raw material since it can be processed for various applications. Unlike palm oil, palm kernel oil has not been exploited sufficiently for material synthesis. Huge efforts have been made by researchers to increase the applications of palm kernel oil. One of the efforts was the production of dihydroxystearic acid (DHSA) based on the palm kernel oil. DHSA also known as glycolic stearic acid (GSA) with molecular formula C₃₆H₇₀O₄ and IUPAC name dihydroxyoctadecanoic acid (Koayet al., 2011). It contains two alcohol groups and a carboxylic group in a long hydrocarbon chain. The unique structure of DHSA translated into interesting properties such as good polarity, behaves like a long-chain fatty acids and can easily bind to a polar compound. DHSA is regarded as a high value hydroxy fatty acid and is extensively utilized in cosmetic industry as a thickener, gelling agent, binding agent, mechanical properties booster and pigment dispersion enhancer in the formulation of decorative industry (Koey et al., 2009). Apart from that, it is also used in a wide range of industrial applications including lubricants, paints, coating and food.

DHSA is the product of hydrolysis epoxidized oleic acid. Epoxidation of palm kernel based oleic acid was carried out by reacting the oleic acid with formic acid to form performic acid in situ reaction with the presence of
of hydrogen peroxide (30 w/w %). In this study, oleic acid from palm kernel is the main raw material for preparing DHSA. The palm kernel oil is rich in lauric acid, C12 (48.3%) and other major fatty acids such as myristic, C14 (15.6%) and oleic acid, C18:1 (15.1%) (Norulaini et al., 2004). Epoxidation of fatty acids is a reaction of carbon-carbon double bond (C=C) with active oxygen, which results in the addition of an oxygen atom, converting the original double bond into a three-membered epoxide (oxirane) ring (Padmasiri et al., 2009). Currently, DHSA has been successfully produced from palm-based oleic acid, via epoxidation with performic acid or peracetic acid followed by hydrolysis of the epoxide (Koey et al., 2009). Improved process for the production of palm-based hydroxyl fatty acid (DHSA) was patented by Ahmad et al. (2005). According to the patent, oleic acid oxidized by performic acid in situ, in the presence of hydrogen peroxide and a catalytic amount of concentrated sulfuric acid yielded more than 98% of dihydroxy or polyhydroxy fatty acids via its hydrolysis, based on the unsaturation of the starting oleic acid. Abdullah and Salimon (2010) reported that it was possible to obtain up to 78% relative conversion to oxirane (RCO) with minimum oxirane ring cleavage by in situ technique. The reaction scheme for the production of crude DHSA was presented by Rahman and Sadi (1998), as depicted in the Figure 1:

![Figure 1](image)

**Fig. 1:** Formation process scheme for 9,10-dihydroxystearic acid or GSA (Rahman and Sadi, 1998).

In this study the formation of DHSA was not through the in situ method instead it was conducted by hydrolysis of the pre-prepared epoxidized crude oleic acid. Hydrolysis occurs in a biphasic liquid-liquid reaction system.

**MATERIALS AND METHODS**

1.1 Materials:

Crude oleic acid (75% purity) was obtained from Chung Chemicals Sdn Bhd, Malaysia. Formic acid, hydrogen peroxide (30 w/w% solution), sulfuric acid (99%) and aluminum oxide were obtained from Merck Sdn Bhd. All materials were used as received without further purification. Distilled water was used throughout.

1.2 Epoxidation of oleic acid:

Oleic acid was epoxidized at low temperature (25-55°C) with performic acid generated in situ. The molar ratio of hydrogen peroxide/formic acid/oleic acid was 1/1/1. The oleic acid together with formic acid were loaded into a 2L capacity semi-continuous tank reactor. The reactor was equipped with mechanical agitator. The system was connected to a control panel to control the temperature at 55°C and agitation speed at 350rpm as shown in Figure 2. Dilute hydrogen peroxide (30 w/w %) was added dropwise after the reactor temperature had reached 55°C to complete the epoxidation reaction. The whole procedure required addition of small amount of sulfuric acid as catalyst. The indicator used to measure the extent of the reaction was the percentage relative conversion to oxirane (RCO). The sample was retrieved every 5 minutes to first determine the oxirane oxygen content (OOC) value which in turn will be used for the calculation of the RCO. The end product from epoxidation step were withdrawn from the reactor and allowed to settle at ambient condition to separate the oil phase from the aqueous phase. Finally, the oil phase layer containing mostly epoxidized oleic acid was thoroughly washed with cold water at 5-10°C to reduce the acidity of the organic phase.
1.3 Ring opening/hydrolysis study:

Epoxidized oleic acid prepared earlier was used to study the opening of the oxirane ring by hydrolysis reaction. 300ml of the epoxidized oleic acid were loaded into a 2L capacity semi-continuous tank reactor. The reactor was equipped with a temperature probe and a mechanical agitator and connected to a controller. The temperature was set at 55°C and the mechanical agitator used was at 350rpm. The distilled water was added and the system was then heated to desired temperature. The hydrolysis procedure requires addition of a small amount of alumina as a catalyst. Continuous stirring is applied to the reaction mixture until the RCO (%) approached zero. Sampling for analysis was done by withdrawal of approximately 5ml of reaction mixture for every 30 minutes. The samples were cooled before being analysed using oxirane oxygen content (OOC). The OOC_exp value was determined by direct method using hydrobromic acid (AOCS Cd 9-57). The percentage of conversion can be calculated based on the theoretical OOC. The end product containing mainly DHSA were thoroughly washed to reduced the acidity and dried in a rotary evaporator.

2. Analysis and data processing:

The iodine value (IV) was determined according to the American Oil Chemists’ Society (AOCS) standard method Cd 1d-92 given by Eq.1 below.

\[
IV(\text{mg I}/100\text{g sample}) = \frac{(B - S) \times N_{Na_2S_2O_3} \times 12.69}{\text{mass of crude oleic acid}}
\]  

Where B is the volume of titrant for blank run (mL), S is the volume of titrant for sample (mL) and \( N_{Na_2S_2O_3} \) represents normality of sodium thiosulfate solution.

The IV value is used to calculate the theoretical oxirane oxygen content (OOC_theo) to the oleic acid sample used, by using the following expression (Petrovic et al., 2002):

\[
\text{OOC_theo} = \frac{IV_{OA,o(2A)}}{250 + (IV_{OA,o(2A)})A_o} \times A_o \times 100
\]  

Where \( IV_{OA,o} \) refers to the initial iodine value of oleic acid sample, \( A_o \) is the molar mass of the oxygen and \( A_I \) is the molar mass of iodine. The basis for equation (2) was 100g of oleic acid sample. While the expression for OOC_exp is given by equation (3) below:

\[
OOC_{exp} = \frac{T \times N_{HBr} \times 1.6}{W}
\]  

where T is the volume (mL) of hydrogen bromide (HBr) required to titrate the sample, \( N_{HBr} \) is the normality of HBr and W is the weight (W) of an epoxy sample. From the oxirane oxygen content values, the relative percentage conversion to oxirane (RCO %) was calculated by equation (4) below. A graph of RCO as a function
of reaction time was plotted and the graph was used to investigate the effect of each reaction condition on the rate of the overall reaction.

\[
\text{RCO(\%)} = \frac{\text{OOC}_{\text{exp}}}{\text{OOC}_{\text{theo}}} \times 100
\]

The epoxidized palm-kernel oleic acid and crude DHSA were analyzed with a Perkin Elmer FT-IR spectrometer. The spectra were accumulated with a spectral resolution of 4cm\(^{-1}\) and 4 scans in the wave number range of 4000 to 515 cm\(^{-1}\). Typical infrared spectrum of functional groups corresponding to their absorption range is given in Table 1 below:

**RESULTS AND DISCUSSION**

This study examines the formation of epoxidized oleic acid and DHSA from palm kernel oil under two separate steps as opposed to common in-situ method. The products formed at the end of each step were analyzed by using Iodine Value (IV), oxirane oxygen content (OOC), relative conversion to oxirane (RCO %) and FTIR. The FTIR is a standard alternative method approved by American Oil Chemists’ Society (AOCS) and Association of Official Agriculture Chemists (AOAC) for qualitative analysis of the chemical structure of organic compounds as well as trans fatty acid (TFA) in oils and fats.

**3.1 Iodine value analysis:**

Iodine Value (IV) is the measure of the degree of unsaturation and is expressed as grams of iodine absorbed per 100 grams of material. IV is often used to determine the amount of unsaturation (ethylenic) in fatty acids. This unsaturation is in the form of double bond (C=C). The higher the iodine value, the more the presence of C=C bonds in the oil or fat. Being an ethylenic compound, oleic acid has a high IV. The IV for oleic acid, epoxidized oleic acid (EoA) and DHSA is presented in Table 2. It can be seen that the IV was almost totally decreased as the unsaturated nature of oleic acid was first transformed to EoA and finally to DHSA. The unsaturated C=C bond site was firstly converted to oxirane ring during the epoxidation step etc. indicating satisfactory accomplishment of epoxidation and hydrolysis step. The finding of this IV study is in agreement with the work of Koay et al. (2011) when they reported that the IV properties of palm based oleic acid was at 93.8±1.4, crude 9,10 DHSA was 10.2±1.6 and purified 9,10 DHSA was 1.1±0.1.

**Table 2: Iodine value for oleic acid, EoA, DHSA.**

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Iodine value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid</td>
<td>98.99</td>
</tr>
<tr>
<td>Epoxidized oleic acid</td>
<td>33.48</td>
</tr>
<tr>
<td>DHSA</td>
<td>10.4</td>
</tr>
</tbody>
</table>

**3.2 Epoxidation of oleic acid:**

The epoxidation experiment was carried out at moderate temperature of 55°C, low agitation speed at (350 rpm) and assisted by addition of small amount of concentrated sulfuric acid as catalyst. Figure 3 shows that the maximum yield of epoxidized oleic acid obtained was 76.2% as indicated by the highest percentage of RCO point at 25 min reaction time. Our previous work (Mohd et al., 2014) also suggested that the optimum reaction temperature for epoxidation of palm-kernel oil occurred at 55°C. It seems that moderate epoxidation condition encourages the formation of oxirane ring from palm kernel oil oleic acid. Abdullah and Salimon, (2010) noted that epoxidation reaction conducted at higher temperature and acid concentration resulted in undesirable increase in the extent of oxirane ring cleavage to glycol and hence reduced the yield. Other epoxidation studies reported at moderate temperature; Campanella and Baltanas (2005) used a temperature of 40°C in the epoxidation of vegetables oils while Meshram et al. (2011) found the optimum reaction temperature of 60°C for the epoxidation of safflower oil. As for the agitation speed it was suggested that a stirring speed of 350 rpm was sufficient to overcome mass transfer resistance under the investigated temperature (Derawi and Salimon, 2010).
Figure 3 also illustrates the corresponding IV for both the crude oleic acid and epoxidized oleic acid, indicating the reduction in the degree of ethylenic unsaturation (formation of epoxy group) as the reaction progressed. The epoxidized oleic acid sample was further subjected to FTIR analysis to qualitatively confirm the functional groups present. The FTIR spectrum of the epoxidized oleic acid is presented in Figure 4. The spectrum showed several absorption band signals that characterized the epoxidized oleic acid sample at 2922.84 cm$^{-1}$, 1709.31 cm$^{-1}$, and 1217.01 cm$^{-1}$. The appearance of absorption band signal at 1217.01 cm$^{-1}$ confirmed the formation of the oxirane groups (C=O bond). Interestingly, the C=C double bond peak normally observed in the region of 1550-1650 cm$^{-1}$ wave number was not detected indicating significant transformation of the ethylenic unsaturation sites. These observations are similar to those of Rahman and Sadi (1998).

### 3.3 Hydrolysis of epoxidized oleic acid:

The hydrolysis experiment was conducted at moderate reaction condition similar to the epoxidation condition with the epoxide volume fraction set at 0.75. Heterogenous catalysis by aluminum oxide was applied considering that alumina is an effective catalyst for oxirane ring opening by oxygen-and nitrogen-containing nucleophiles (Piazza et al., 2003). The progress of the hydrolysis reaction was followed by measuring the RCO (%) and considered as complete when the RCO (%) approaches zero value as shown in Figure 5. It also shows the corresponding IV value for both the epoxidized oleic acid and the hydrolysed product. The final DHSA product obtained is visually appeared as a white and waxy materials as shown in Figure 6 below.
Fig. 5: DHSA as a function of RCO (%) and IV.

Fig. 6: DHSA physically appeared as a white and waxy material.

Figure 7 depicts the FTIR spectrum of the DHSA produced from palm kernel oil oleic acid. After hydrolysis, the absorption band region of 1210-1320 cm\(^{-1}\) corresponding to the C-O-C stretching (the epoxy group) had disappeared. This indicates that the epoxy ring of epoxidized oleic acid compound was cleaved by water to produce secondary hydroxyl compound O-H to form DHSA. The Spectrum bores two distinctive functional groups; the carbonyl and hydroxyl groups. The carboxyl functional group was identified through the typically assigned absorption band signal of 1708.82 cm\(^{-1}\), while the hydroxyl group which confirmed the formation of DHSA was observed at the region of 3200-3600 cm\(^{-1}\). The observed hydroxyl band region was similar to those reported by Awang et al. (2001) at 3250-3345 cm\(^{-1}\), Rahman and Sadi (1998) at 3448.44 cm\(^{-1}\), Koay et al. (2006) at 3300-3400 cm\(^{-1}\) and Awang et al. (2006) at 3467 cm\(^{-1}\).

Fig. 7: FTIR for hydrolyzed product (DHSA).
4. Conclusions:

DHSA was successfully formed through hydrolysis of epoxidized oleic acid derived from palm kernel oil. Firstly, it was observed that considerably high yield of epoxidized oleic acid (76%) was obtained from the commercial grade of oleic acid at moderate reaction conditions. The completion of epoxidation reaction step was marked by the highest point at which the (RCO%) was recorded. The FTIR analysis was found to be useful in confirming the formation of C-O-C epoxy functional groups at 1210-1320 cm\(^{-1}\) absorption band region. The completion of hydrolysis reaction or the ring opening is indicated by the RCO(%) approaching zero value indicating the cleavage of all epoxy rings. The formation of hydroxyl compound which characterized the DHSA was further confirmed by using the FTIR. Our result showed that the absorption band of hydroxyl group was detached at the region 3200-3600cm\(^{-1}\). Besides the findings from RCO(%) and FTIR, the Iodine value test conducted on the DHSA was found to be at 10.4 which is within the range commonly reported for DHSA. This work demonstrate that oleic acid, a by product derived from palm kernel oil was a potential sustainable and environmental friendly raw material for DHSA production.

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