

Synthesis of Monoglycerides from Dihydroxystearic Acid : Effect of Reaction Parameters

R. Awang^{a*}, S. Ahmad^a, M.F. W. Ibrahim^b and W.M.Z. Wan Yunus^b

^aMalaysian Palm Oil Board, No. 6. Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor
Telephone: 03-89282556; Fax: 03-89262971, E-mail: roila@mpob.gov.my

^bDepartment of Chemistry, Universiti Putra Malaysia, 43400 Serdang, Selangor

Abstract : Monoglycerides from palm-based dihydroxystearic acid were synthesized. Various factors that may affect the esterification reaction were studied, such as reaction temperature, reaction time, catalyst concentration and types of catalysts. The results indicated that increasing reaction temperature and time increased the reduction of acid value. The reaction proceeded much faster with sulphuric acid than *p*-toluene sulphonic acid and sodium hydrogen sulphate at the same weight %. The effect of those parameters on colour of the product was also studied.

Keywords: synthesis, monoglyceryl stearate, monoglyceryl hydroxystearate, esterification

Abstrak : Monogliserida dari asid dihidroksistearik berasaskan sawit telah disintesis. Kesan dari beberapa parameter tindakbalas seperti suhu, masa, kepekatan mangkin dan jenis mangkin telah dikaji. Keputusan menunjukkan kadar penurunan nilai asid bertambah dengan meningkatkan suhu dan masa tindakbalas. Tindakbalas yang menggunakan asid sulfurik sebagai mangkin menunjukkan kadar tindakbalas yang lebih tinggi. Kesan parameter tindakbalas terhadap warna hasil tindakbalas juga dikaji.

Katakunci: sintesis, monogliserilstearat, monogliseril hidroksistearat, esterifikasi

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Introduction

The interest in monoglycerides resides in their structure comprising an aliphatic lipophilic chain and two hydroxyl groups in the hydrophilic part. This structure causes surfactant action, which stabilizes emulsions (1). Their abilities to form stable emulsions make the monoglycerides suitable as internal and external lubricants in fibre and textile technologies. In metal processing, the monoglycerides of long-chain fatty acids are used as emulsifying agents or lubricants. The plastics industry also utilizes long-chain fatty acid monoglycerides as internal lubricants. Nonionic surfactants provide a wide range of applications as emulsifiers in food, cosmetic and pharmaceutical industries (1-2).

Synthesized for the first time in 1853, monoglycerides have been produced since 1960 in an industrial scale by glycerolysis of triglycerides. More recently, monoglycerides have been produced by reacting a variety of substrates with glycerol. Depending on the starting substrate, monoglycerides may be prepared by direct esterification of fatty acids by glycerol, transesterification of triglycerides with glycerol, transesterification of methyl esters of fatty acids with glycerol, hydrolysis of triglycerides or fats, condensation of fatty acids with glycidol or its derivatives(3-4).

In its continuing efforts to expand uses of palm oil, the Malaysian Palm Oil Board (MPOB) has produced dihydroxystearic acid (DHSA) from oleic acid. DHSA is expected to have commercial potential as its hydroxyl group and ester linkage provide reaction sites for the preparation of many useful industrial products. In the present study, monoglycerides from palm-based DHSA was synthesized. The effect of reaction parameters on the acid value and colour of the products were studied.

Materials and Methods

Materials

DHSA was prepared in the laboratory (5). Glycerol (99%) was purchased from an oleochemical company in Malaysia and *p*-toluene sulphonic acid (*p*-TSA) was obtained from Fluka (Switzerland). Sodium hydrogen sulphate (NaHSO₄) and sulphuric acid (H₂SO₄) were purchased from Merck (Darmstadt, Germany). All other reagents were of analytical grade and were used as received.

Experimental Procedure

The experiments were carried out in a 250 mL three-necked round bottom flask equipped with a magnetic stirrer, a thermometer, an inert gas inlet tube and a condenser. Glycerol, DHSA and catalyst were placed in the flask and heated to the desired

temperature. An oil bath was used to maintain a constant temperature. The reaction mixture was stirred continuously under dry nitrogen atmosphere, for a predetermined reaction period. After this time, the hot mixture was quantitatively transferred into a separatory funnel and the mixture was allowed to separate into two layers. The bottom layer is separated from the top layer. The separation had to be carried out when the mixture was still hot in order to prevent the top layer from solidifying. The progress of reaction was monitored by analyzing the amount of unreacted DHSA in the reaction mixture by a titrimetric method.

Analytical methods.

The products obtained were tested for different physical and chemical properties. Acid value, hydroxyl value and saponification value were determined by standard procedures (AOCS official methods): acid value, Te 1a-64; hydroxyl value, Cd 13-60; saponification value, TI 1a-64 (6). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-IR550 (Nicolet, Madison, WI) spectrophotometer. Colour of the product was measured using Lovibond PFX990 tintometer (Salisbury, United Kingdom)

GC analysis was carried out using a Hewlett-Packard HP-6860A plus gas chromatograph (Palo Alto, CA). The samples undergo silylation process before being injected into GC (7). The trimethylsilyl (TMS) derivatives of the samples were separated on a nonpolar column HT-5 (Hewlett-Packard, 30 m X 0.25 mm X 0.25 μ m) with helium as the carrier gas. The oven was programmed to hold at 120°C for 1

min, followed by ramping from 120°C to 300°C at a rate of 6°C/min. The final temperature was held at 300°C for 6 min. The injector and flame ionization detector were set at 340°C.

Results and Discussion

To prove that esterification had occurred, FTIR spectra of starting materials and final products were compared. In the FTIR spectrum, the absorption band at 1709 cm^{-1} assigned to C=O stretching of DHSA has shifted to 1741 cm^{-1} for the product suggesting that esterification has taken place (Figure 1). FTIR spectrum of the product showed the presence of C-O stretching band for ester at 1180 cm^{-1} while the transmittance peak for OH group can still be observed at 3300-3400 cm^{-1} . However, the intensity of the transmittance peak has changed. OH bending bands were observed at 1655 cm^{-1} and 1044 cm^{-1} . Formation of monoglyceride of DHSA (MGDHSA) was confirmed by gas chromatography (GC) analysis (Figure 2). The tentative identification of the product mixture was based on the comparison of retention times (RT) of the peaks with glyceryl monostearate (GMS) and impure glyceryl monohydroxystearate (MGHSA). Because of the presence of extra two hydroxyl groups in MGDHSA therefore, the RT for MGDHSA peak is slightly shifted to 16.83 min compared to RT for GMS peak at 14.49 min and MGHSA at 16.08 min. The chromatogram also indicated that the reaction product is not only monoglycerides but also isomeric and diastereoisomeric diglycerides of DHSA, which appeared at 30.21 min and 30.62 min.

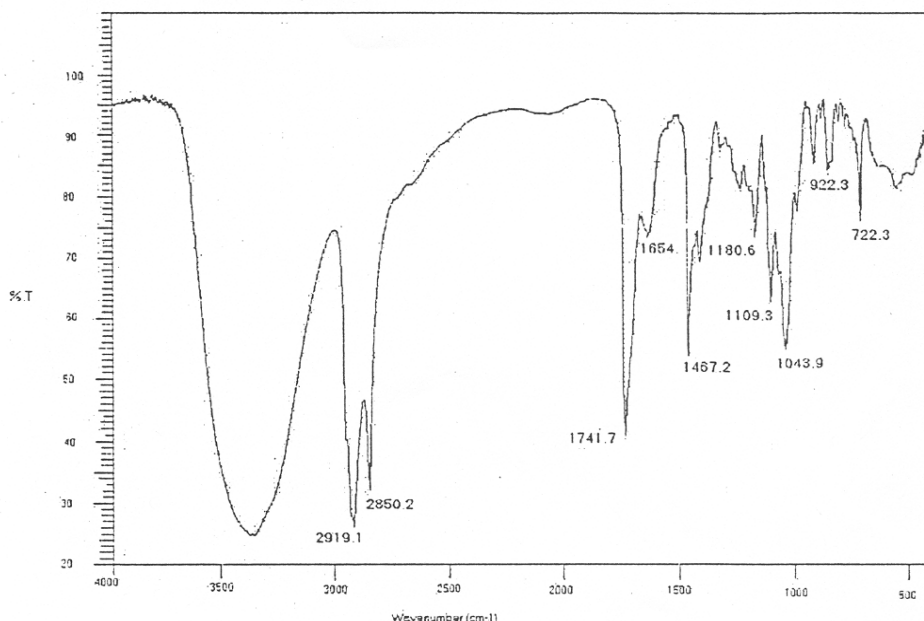


Figure 1: FTIR spectrum of the product obtained from the p-TSA-catalyzed esterification of DHSA and glycerol at 150°C for 4h.

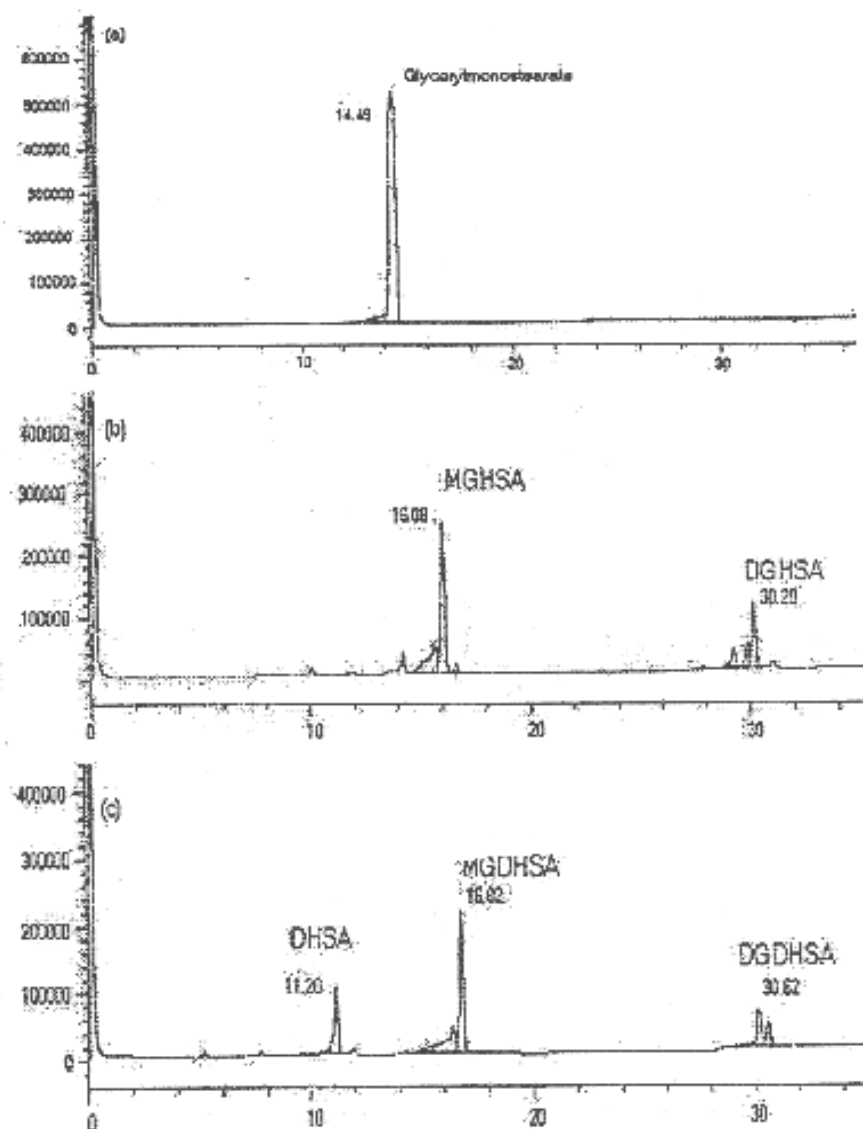


Figure 2: GC chromatogram (a) silated glyceryl monostearate, GMS (b) silated MGHSA containing some DGHSA (c) prepared sample of MGDHSA and some DGDHSA

Parameter	Glycerol	DHSA	Crude Product
Acid Value, <i>mgKOH/g</i>	ND	178.7	53.5
Hydroxyl Value, <i>mgKOH/g</i>	1612.4	317.2	322.7
Sap. Value, <i>mgKOH/g</i>	0.0	183.9	141.2
Melting Point, °C	LRT	90.6-91.3 ^a	67.5-69.1

*The reaction was carried out at 150°C for 4h using 0.5%p-TSA as catalyst.

LRT: Liquid at room temperature

ND: not determined

^a Theoretical value :94-95°C

Table 1: Properties of starting materials and crude product*

Properties of the starting materials and the crude products, such as acid values, hydroxyl values, saponification values and melting points are shown in Table 1. The results showed that the acid value decreased in the conversion of the reactant to the product. This indicates the formation of ester compounds. The saponification value also decreased, this may be due to the increasing of molecular weight of the product. While the hydroxyl value of the product is lower than that of glycerol but slightly higher than DHSA.

The reaction progress can be described by means of the changes of the substrate concentrations e.g.

fatty acid (DHSA) and glycerol. In this study, the change of fatty acid concentration was monitored. In order to optimize the reaction, the effect of the following variables on the reduction of acid value were investigated: (i) temperature, (ii) reaction time, (iii) catalyst concentration, (iv) type of catalyst, and (v) substrate.

Effect of temperature and reaction time. Table 2 showed that the acid value decreased when the temperature increased as expected. Effect of reaction time on acid value is shown in Figure 3. The reaction was carried out at 150°C using *p*-TSA as catalyst. During the reaction samples were

Temperature, °C	Acid Value	Iodine Value	%	
			MGDHSA	DGDHSA
100	137.37	1.56	11.84	1.04
120	109.40	1.84	18.19	1.64
150	67.97	2.31	43.55	8.90
180	9.71	2.78	72.91	12.39

Reactions were carried out at 150°C for 4 h in the presence of 0.5% (w/w) *p*-TSA as catalyst. The ratio of DHSA to glycerol is 1:6

Table 2: Effect of reaction temperature on composition of the product and iodine value

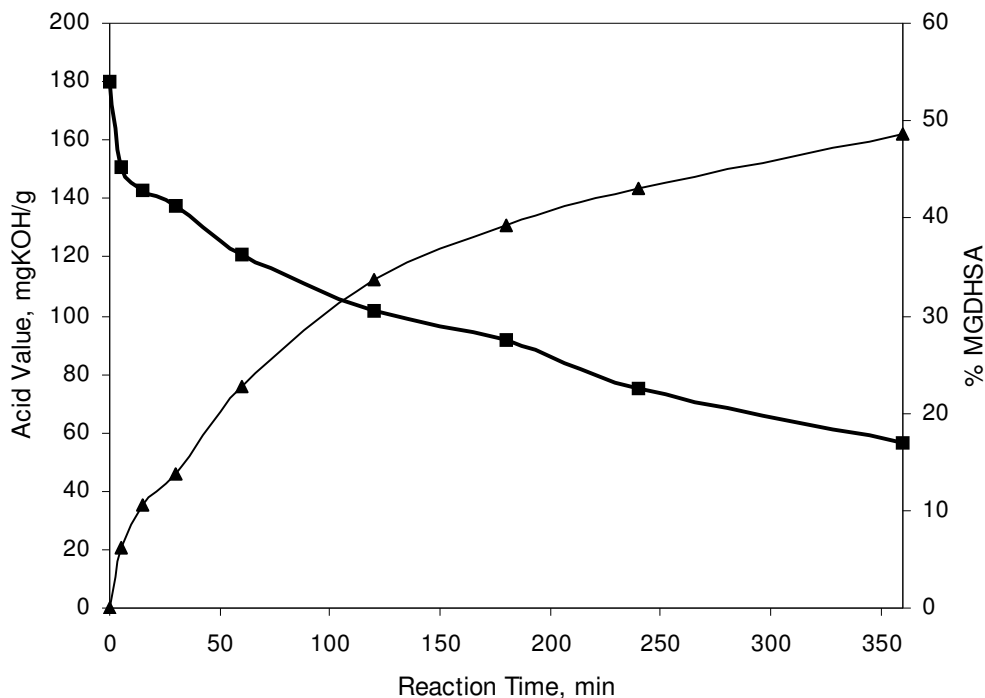


Figure 3: Effect of reaction time on acid value and composition of MGDHSA for the esterification of DHSA and glycerol. Reaction temperature: 150°C; catalyst: *p*-TSA (0.5%, w/w); mole ratio of DHSA to glycerol: 1:6

drawn at different intervals. Acid value of each sample was analyzed. The results indicated that during the reaction, the acid value decreased continuously while the saponification value increased. Time course studies indicated the performance of catalyst as well as the progress of reaction, and helped to determine the shortest time necessary to obtain good yields and thereby make the process cost-effective.

Effect of catalyst concentration: The effect of using various percentages of catalysts ranging from 0.0 to 2.0% was also studied. The catalyst used in this study was p-TSA. As shown in Table 3, increasing the amount of catalyst from 0.0 to 0.2% had a

significant effect on the acid value of the product. Further increasing the catalyst from 0.2% to 0.8% did not have any effect on the acid value. However, increasing the catalyst to 1.0% and 2.0% drastically reduced the acid value of the product.

Type of catalyst: In this study, 3 different acid catalysts (*p*-TSA, sodium hydrogen sulphate and sulphuric acid) were used. All the experiments were carried out at 150°C for 4 h using 0.5% catalyst. It was found that the reaction using sulphuric acid as catalyst proceeded much faster compared to the other 2 catalysts for the first 60 min reaction. However, there was not much different in reduction of acid value after this time for all catalysts used (Figure 4).

Catalyst, %	Acid Value	Iodine Value	%	
			MGDHSA	DGDHSA
0.0	99.94	2.43	36.90	8.99
0.2	69.84	2.42	43.72	10.25
0.4	64.19	2.84	43.50	10.96
0.6	58.67	2.67	41.90	10.58
0.8	55.78	3.59	40.61	12.35
1.0	18.01	8.11	21.25	0.00
2.0	8.09	14.72	0.00	0.00

Reaction was carried out at 150°C for 4 h in the presence of various concentration of *p*-TSA as catalyst. The ratio of DHSA to glycerol is 1:6

Table 3: Effect of catalyst concentration on composition of the product and iodine value

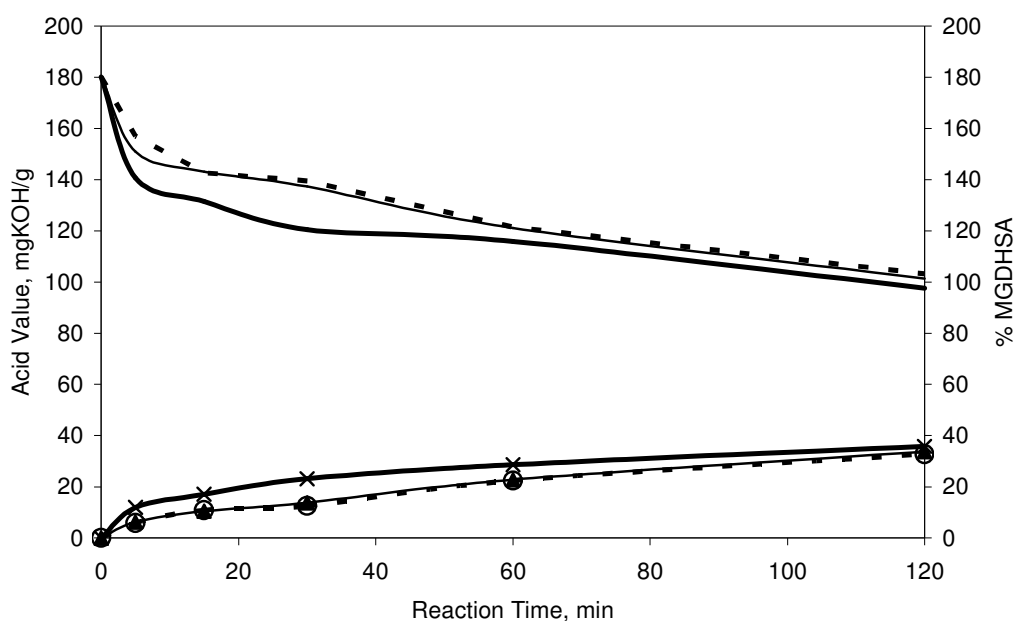


Figure 4: Reduction of acid value and increased in MGDHSA composition for the reaction catalyzed by various types of acid catalyst. Reaction temperature: 150°C; catalyst concentration: 0.5%, w/w; mole ratio of DHSA to glycerol: 1:6 (—) H₂SO₄; (---), NaHSO₄; (—), *p*-TSA

Effect of substrate. Esterification of 12-hydroxystearic acid (18:1OH), stearic acid (18:0) and oleic acid (18:1) with glycerol was also investigated. Slightly higher acid value was observed in the reaction of fatty acid having hydroxyl group in the alkyl chain. The conversion of fatty acids to their corresponding glycerides is about 96.1% conversion for stearic acid, 97.2 % conversion for oleic acid, 94.4% conversion for 12-hydroxystearic acid and 80.6 % for DHSA. This phenomenon may be due to the steric or neighbouring group effects. It was reported that as the substituent increases, so does steric hindrance to attack and the rate falls off.

Effect of temperature and catalyst concentration on the product composition. The previous results show that the acid value can be reduced by increasing the temperature. The question was, what impact this positive effect would have on the composition of the products. As shown in Table 2, composition of MGDHSA and DGDHSA were increased with increasing temperature from 100°C to 180°C. However, the iodine value of the product also increased. This phenomenon may be due to dehydration of hydroxyl groups of DHSA into diene compounds. It has been reported that dehydration of 9,10-dihydroxystearic acid at high temperature followed by distillation, gave a distillate consisting primarily a mixture of diene compound and its esters (8).

Different result was observed for the effect of catalyst concentration. Our result showed that a higher acid concentration causes a higher degree of the unwanted polymerization and a decreased formation of the desired MGDHSA compound (Table 3). The presence of excess catalyst may promote polymerization reaction of glycerol rather than esterification of glycerol and DHSA.

Effect of reaction parameters on colour of the product. It was reported that colour is used as an indicator of the quality of raw material, which may influence the colour of the finished product (9). The effect of reaction parameters such as temperature, catalyst concentration and type of catalyst were determined. Table 4a shows the effect of reaction temperature on colour of the product. The yellow and red scale increased with temperature. The product obtained from the reaction using H₂SO₄ as catalyst shows lighter colour compared to the product from the reaction using NaHSO₄ and *p*-TSA (Table 4b). As shown in Table 5, catalyst concentration also can affect colour of the product. In this study, the reaction was carried out at 150°C for 4 h using various concentration of *p*-TSA as catalyst. Based on yellow and red scale, colour of the product increased by increasing the catalyst concentration to 0.2% and decreased slightly from 0.2% to 0.8%. Drastic increase in colour was observed when the catalyst concentration reached 2.0%. However, this behaviour is not well understood.

Temperature, °C	Colour Scale	
	R	Y
100	0.0	0.3
120	0.1	0.3
150	0.7	2.5
180	3.6	5.8

Colour of the product was measured using Tintometer PFX 990 at 1% (w/w) concentration in isopropanol

Table 4a: Effect of reaction temperature on colour of the products

Catalyst	Colour Scale	
	R	Y
H ₂ SO ₄	0.2	0.9
NaHSO ₄	0.6	1.6
<i>p</i> -TSA	0.7	2.4

Colour of the product was measured using Tintometer PFX 990 at 1% (w/w) concentration in isopropanol

Table 4b: Effect of type of catalysts on colour of the products

Catalyst Concentration	Colour Scale	
	R	Y
0.0	0.8	1.8
0.2	1.3	4.3
0.4	0.6	2.4
0.6	0.2	1.1
0.8	0.1	1.1
1.0	1.7	4.2
2.0	6.2	27.0

Colour of the product was measured using Tintometer PFX 990 at 1% (w/w) concentration in isopropanol

Table 5: Effect of p-TSA catalyst concentration on colour of the product

Conclusion

Esterification of DHSA with excess glycerol by acid catalysts at 150°C for 4h gave up to 40% yields of monoglycerides.

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