Green Chemistry on Intermediate Product of Biolubricant Synthesis from Oleic Acid: A Review

Yehezkiel Steven Kurniawan[1*], Isna Munawaroh[1] and Tutik Dwi Wahyuningsih[1]

[1]Chemistry Department, Mathematics and Natural Sciences Faculty, Gadjah Mada University, Sekip Utara, Yogyakarta 55281 Indonesia
E-mail: yehezkiel.steven@yahoo.co.id

Abstract

Synthesized of 9.10-dihydroxystearic acid compound as intermediate biolubricant products from oleic acid has done with reflux and hydroxylation method in basic solution. Reaction with reflux method needs 30 minutes while hydroxylation method only needs 5 minutes reaction. Elucidation of product's structure were determined by IR and MS. The products via reflux method was white powder solid with melting point 130-131 oC meanwhile 9.10-dihydroxystearic acid product via hydroxylation method was white powder solid with melting point 131.1-131.8 oC. Diol formation reaction with reflux method gave 9.10-dihydroxystearic acid with 80% yield meanwhile diol formation reaction via hydroxylation method gave 9.10-dihydroxystearic acid with 46.33% yield. Although, hydroxylation method gave lower yield but from purity degrees of products, amount steps of research, long time synthesis, temperature of reactions, chemical compounds is needed and toxicity of solvent in green chemistry view points, hydroxylation method is far better.

Keywords: 9,10-dihydroxystearic acid, biolubricant, hydroxylation, oleic acid, reflux

Introduction

Renewable raw materials are going to play a very noteworthy role in development of sustainable green chemistry. They offer a large number of possibilities for applications which can be rarely met by petrochemistry. A steady increase in the use of eco-friendly consumer products like lubricant has occured as a result of strict goverment regulation and increased public awareness for a pollution free environment (Anastopoulos et al., 2001).

There are wide ranges of lubricant base oil is in current use which includes mineral oils, synthetic oils, re-refined oils and vegetables oils. Among these, mineral oils are the most commonly used. They consist predominantly of hydrocarbons but also contain some sulfur and nitrogen compounds with traces of a number of metals. Due to their inherent toxicity and non-biodegradable nature, they pose a constant threat to ecology and vast ground water reserves (Jain and Suhane, 2013). Besides these, vegetable oil lubricant are preferred not only because they are renewable raw materials but also because they are biodegradable and non-toxic (Hassan et al., 2006). They also acquire most of the properties required for lubricants such as high index viscosity and low volatility however, they have poor oxidative and thermal stability, which is due to the presence of unsaturation (Adhvaryu et al., 2003).

Anastas and Warner (1998) have been reported the twelve principles of green chemistry for example waste prevention, less hazardous chemical synthesis, design for energy efficiency, real time analysis for pollution prevention,inherently safer chemistry for accident prevention and design for degradation.

Filley (2005) reported that acetal and ketal cyclic of methyl 9,10-dihydroxystearic from oleic acid good on active surface tension such as viscosity and their thermal stability. As their intermediate, 9.10-dihydroxystearic acid was synthesized by Filley via reflux method in 30 minutes and followed by reduced pressure distillation that consumed a lot of energy and steps of researches. Hence, it is worthwhile to develop a green and environmental friendly process based on hydroxylation method. In this research, will be compare between reflux and hydroxylation method to aims greener synthesis method.

Material and Method

Materials

Oleic acid ($C_{17}H_{33}COOH$) was purchased from Sigma-Aldrich. Formic acid (HCOOH), hydrogen peroxide (H_2O_2), ethanol 95% (C_2H_5OH), nitrogen gas (N_2), natrium hydroxide (NaOH), hydrochloric acid (HCl), sodium sulfate anhydride (Na_2SO_4), potassium permanganate ($KMnO_4$) and sodium sulfite (Na_2SO_3) were purchased from E Merck.

Methods

The infrared (IR) spectra were recorded on a Fourier transform IR Prestige 21 from Shimadzu and mass spectra (MS) analysis perform using an GC-MS QP 2010 S from Shimadzu with an HP-5MS capillary column (30 m x 0.25 mm x 0.5 μm) connected to an mass spectrophotometer at 70 eV (m/z 30-500) in the EI mode.

Reflux method

Oleic acid (1.41 g, 5.00 mmol) and hydrogen peroxide (20.00 g, 0.588 mol) dissolved in 50 mL formic acid were refluxed for 30 minutes at 40^{o}C. After about 3 hours or after analysis has indicated that the peroxide has been consumed, the formic acid was removed by distillation under reduced pressure (b.p. 50°C/125 mm) in a stream of nitrogen gas. The residue in the flask, which consists of hydroxyformoxystearic acids was heated for 1 h at 100°C with an excess of 3*M* aqueous sodium hydroxide, and the hot, amber-colored soap solution was cautiously poured into an excess of 3*M* hydrochloric acid with stirring. The oil

ISBN: 978-602-73192-0-2

which separates was allowed to solidify, and the aqueous layer was discarded. The solid was remelted on the steam bath by addition of hot water and stirred well to remove residual salts and water-soluble acids. When the oil has solidified, the aqueous layer was discarded, and the solid was broken into small pieces and dissolved in 400 mL of 95% ethanol by heating on the steam bath. After 3 times crystallization at 0° for several hours, 9.10-dihydroxystearic acid was collected on a filter and dried under vacuum. Structure of product was elucidated by IR and MS spectra.

Hydroxylation Method. Oleic acid (3.14 g, 0.01 mol) and sodium hydroxyde (6 g, 0.15 mol) dissolved in 320 mL of distilled water were stirred mechanically for 10 minutes. Potassium permanganate solution (1%) was added into the mixture over a minute under 0-10 °C. After 5 minutes, sodium sulfite (7.00 g, 55.56 mmol) was added to reduced the excess of permanganate ions. The mixture was acidified with concentrated HCl. The product was collected via vacuum filtration, recrystallized with ethanol as solvent, yielding 9.10-dihydroxystearic acid as a white powdery solid. Structure of product was elucidated by IR and MS spectra.

Result and Discussion

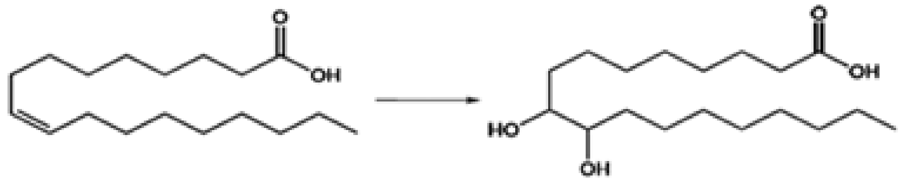

Fig. 1 Synthesis of 9.10-dihydroxystearic acid from oleic acid

Both method convert oleic acid to 9.10-dihydroxystearic acid via redox reaction.

Reflux method

At this method, oleic acid were hydroxylated by using in situ generated performic acid from hydrogen peroxide and formic acid. The excess of formic acid was removed by distillation under reduced pressure in a stream of nitrogen gas. Product was purified with several steps. After crystallization at 0°C for several hours, the product is collected on a filter and dried under vacuum. The yield of crude 9,10-dihydroxystearic acid is 1.45 g., m.p. 85–90°C. After a second recrystallization from 250 mL of 95% ethanol, the product weighs about 1.3 g. and melts at about 94–95°C. A third recrystallization may be necessary to produce a pure product melting at 130-131°C. The over-all yield is 1.26 g.

ISBN: 978-602-73192-0-2

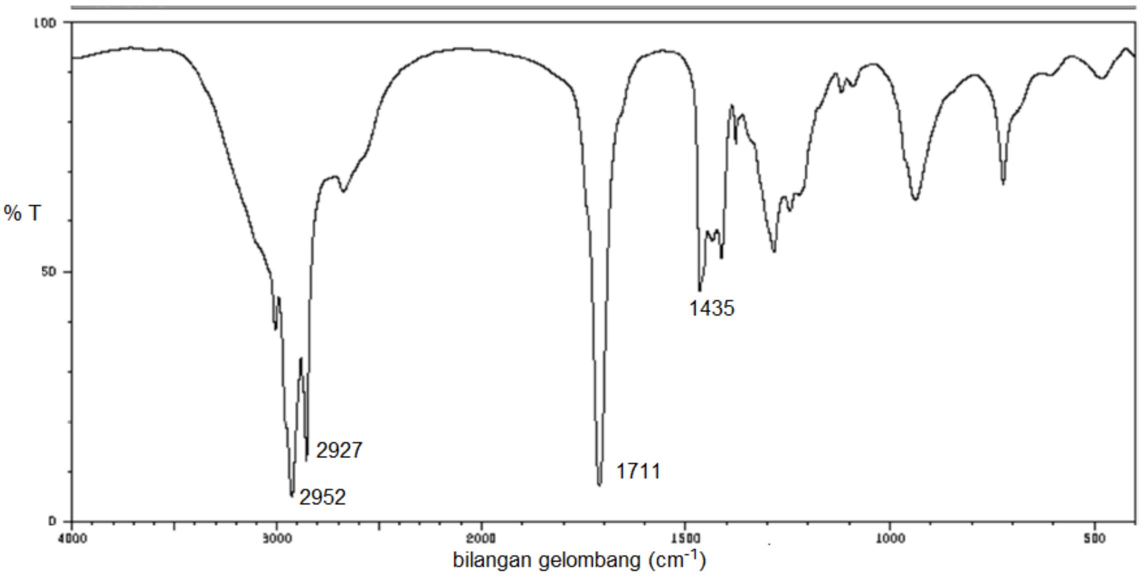

Fig. 2. IR spectra of oleic acid (SDBS)

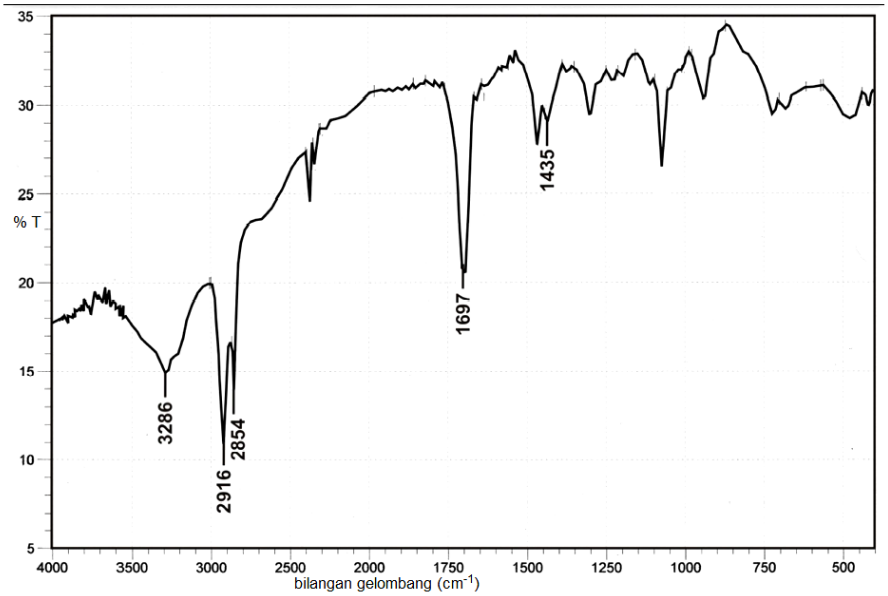

Fig. 3. IR spectra of 9.10-dihydroxystearic acid via reflux method

The FTIR spectra of oleic acid (Figure 2) did not exhibit hydroxy bands at 3286 cm^{-1} so the diol group in 9.10-dihydroxystearic acid was confirmed by the increase in peak intensity at 3286 cm^{-1} (-OH asymmetric stretching). The FTIR spectra of the products have some common peaks at 2916 and 2854 cm^{-1} (methylene asymmetric stretching), 1697 cm^{-1} (C-O stretching of carboxylic acid) and 1435 cm^{-1} ($-CH_2-$ bending vibration). The MS spectra also indicated the presence of diol group in 9.10-dihydroxystearic acid.

ISBN: 978-602-73192-0-2

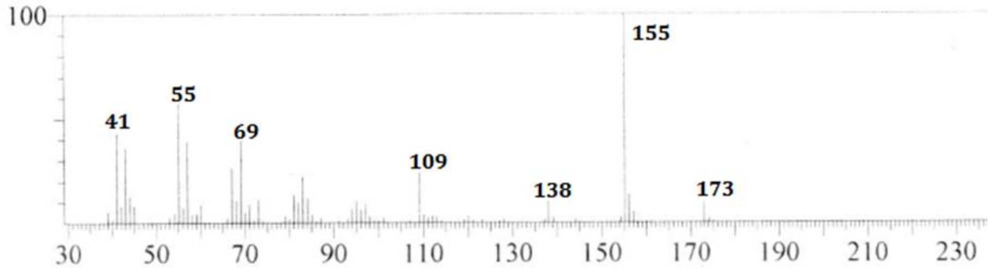

Fig. 4. Mass spectra of 9.10-dihydroxystearic acid

Hydroxylation Method

First of all, oleic acid was dissolved in basic solution to form sodium oleic salt. After this, temperature of oxidation reaction was keep at 0 – 10°C to prevent from contamination from side products. Sodium sulfite was added to reduce the excess of permanganate ion to form manganese dioxide (MnO_2). Solution was acidified by concentrate hydrochoric acid to protonate the anion of carboxylate from products. Differ from reflux method, products only need one time recrystallization because melting point of products nearby the references.

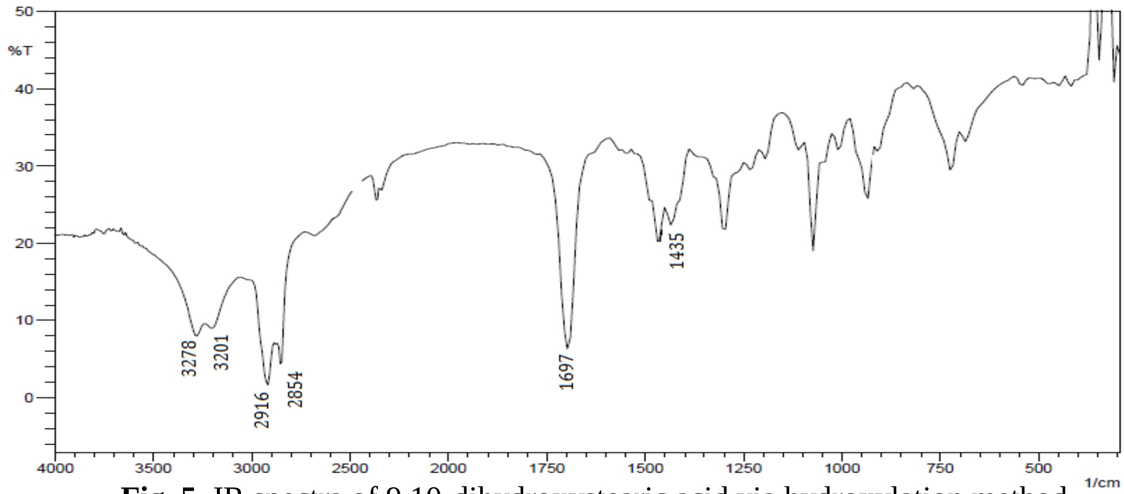

Fig. 5. IR spectra of 9.10-dihydroxystearic acid via hydroxylation method

The FTIR spectra of oleic acid (Figure 2) did not exhibit diol bands at 3286 cm^{-1} so the diol group in 9.10-dihydroxystearic acid was confirmed by the increase in peak intensity at 3278 and 3201 cm^{-1} (-OH asymmetric stretching). The FTIR spectra of the products have some common peaks at 2916 and 2854 cm^{-1} (methylene asymmetric stretching), 1697 cm^{-1} (C-O stretching of carboxylic acid) and 1435 cm^{-1} ($-CH_2-$ bending vibration). The MS spectra also indicated the presence of diol group in 9.10-dihydroxystearic acid.

Table 1. A comparation between reflux and hydroxylation method for synthesis of 9.10-dihydroxystearic acid

Properties	Reflux method	Hydroxylation method
Yield	80%	46.33%
Melting point*	130-131^oC	131.1-131.8^oC
Time of reaction	30 minutes	5 minutes
Total time in synthesis and purification	410 minutes	90 minutes
Amount of process stage	7 steps : - Reflux at 40^oC - Reduced pressure distillation - Heating at 100^oC in basic solution - Neutralization with HCl - Recrystallisation (3 times)	5 tahapan yaitu: - Dissolution of oleic acid in basic solution - Reaction with $KMnO_4$ - Addition of Na_2SO_3 - Acidification with concentrated HCl - Recrystallisation (1 time)
Temperature of reaction	40-100^oC	0-10^oC
Chemical compounds needed	Oleic acid ($C_{17}H_{33}COOH$) Formic acid (HCOOH), Hydrogen peroxyde (H_2O_2) Nitrogen (N_2) gas Sodium hydroxyde (NaOH) Hydrochloric acid (HCl) Ethanol (C_2H_5OH) Sodium sulfate anhydrous (Na_2SO_4)	Oleic acid ($C_{17}H_{33}COOH$) Potassium permanganate ($KMnO_4$) Sodium sulfite (Na_2SO_3) Sodium hydroxyde (NaOH) Hydrochloric acid (HCl) Ethanol (C_2H_5OH)
Solvent	Formic acid (HCOOH)	Distillated water

*References melting point of 9.10-dihydroxystearic acid is 132 ^oC (Young, 2002)

As summarized in Table 1, hydroxylation method is greener than reflux method because hydroxylation method gain products with higher purity, less steps of research, lower shorter synthesis time, temperature of reactions, less chemical compounds is needed and non-toxic solvent.

Conclusions

Oxidation reaction of oleic acid to form 9.10-dihidroxystearic acid was successfully synthesized by reflux and hydroxylation method. Although, hydroxylation method gave lower yield but from purity degrees of products, amount steps of research, long time synthesis, temperature of reactions, chemical compounds is needed and toxicity of solvent in green chemistry view points, hydroxylation method is far better.

References

Adhvaryu, A., Liu, Z., Erhan, S.Z. 2005. Synthesis of Novel Alkoxylated Triacylglicerols and Their Lubricant Base Oil Porperties, *Industrial Crops and Products* 21: 113-119.

Anastas, P., Warner, J.C. 1998. *Green Chemistry, Theory and Practice*, Oxford University Press, Oxford, hal. 99.

Anastopoulos, G., Lois, E., Serdari, A., Zanikos, F., Stournas, S., Kaligeros, S. 2001. Lubrication Properties of Low-Sulfur Diesel Fuels in the Presence of Specific Types of Fatty Acid Derivates, *Energy Fuels*, 15: 106-112.

Filley, J. 2005. New Lubricants from Vegetable Oil : Cyclic Acetals of Methyl-9,10-dihiroxystearate, *Bioresource Technology*, 96(5): 551-555.

Hassan, A.B., Abolarin, M.S., Nasir, A. Ratchel, U. 2006. Investigation on the Use of Palm Olen as Lubrcation Oil, *Leonardo Electronic Journal Practices & Technology* 8: 1-8.

Jain, A.K., and Suhane, A. 2013. Capability of Biolubricants as Alternative Lubricant in Industrial and Maintenance Applications, *International Journal of Current Engineering and Technology*, 3(1): 179-183.

Young, J.A. 2002. Chemical Laboratory Information Profile: Oleic Acid, *Journal of Chemical Education* 79: 24.

ISBN: 978-602-73192-0-2