SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF NEW ESTOLIDE ESTERS AS POTENTIAL BIOLUBRICANT BASE OIL

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ABSTRACT

In this study, plant oil-derived oleic acid was modified chemically to generate estolide esters that displayed low pour points and good oxidation stability. Specifically, oleic acid was reacted with hydrogen peroxide (H_2O_2) to yield estolide with hydroxyl groups, which were then end-capped with various organic acids of different chain lengths and structures, while the carboxylic acid group of estolide was esterified with 2-ethylhexanol (2EH). Analysis results revealed that products end-capped with lauric acid (C12) and 2-ethylhexanoic acid, respectively recorded the best pour point at -36°C, while other products made with shorter or longer chain length organic acids showed higher pour points. Additionally, product end-capped with longer chain length organic acid exhibited better anti-wear properties and lower kinematic viscosity than product made with shorter chain length organic acid. Furthermore, the oxidation stability of products end-capped with linear organic acid were higher than those end-capped with branched organic acids and the oxidation onset temperature (OOT) of products were between 193°C-200°C, which is an improvement in comparison with starting material. Physicochemical properties evaluation revealed that most of the prepared estolides esters have lubricant properties comparable to commercial product, which suggested that they are suitable to be used as base oil for lubricants.

INTRODUCTION

Most of lubricants that we use today are made with non-renewable petrochemicals, which have poor biodegradability and consequently are harmful to the environment. These undesirable traits of petrochemical-based lubricants make them a great threat to the environment because of their disposal and inadvertent release to the environment (Nowak *et al.*, 2019; Luther, 2007). As a countermeasure to this problem, some countries have implemented regulations that favour the use of biolubricants such as the 2002 Farm Bill (Farm Security and Rural Investment Act) (Erhan *et al.*, 2006), California Senate

Bill 916 introduced in 2014 (Abi-Akar, 2017) and a Belgium law that imposes the use of biolubricants in all operations conducted near non-navigable waters (Salimon *et al.*, 2010).

Additionally, the German government had supported the use of biolubricants by implementation of 'Market Introduction Program' for biolubricants from year 2001 to 2008, in which financial grants, and technical advices were given to companies that adopted biolubricants (Theissen, 2010). Furthermore, current global consumers and lubricant industry players are shifting towards environment friendly lubricants by adopting biolubricants (Reeves *et al.*, 2017; Cecilia *et al.*, 2020). All these 'green' demand and initiatives have contributed to steadily increasing production of biolubricants as much as 10% annually (Chan *et al.*, 2018). Based on current development trend for lubricant market, the future of biolubricant is very promising.

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Biolubricants have been made from plant oils and animal fats such as palm oil, soyabean oil, rapeseed oil and tallow, which are sustainable and renewable resources. Plant oil-based biolubricants are known to be environmental-friendly because of their excellent biodegradability as compared to petrochemical-based lubricants (Parveez *et al.*, 2020; Borugadda and Dalai, 2018; Battersby *et al.*, 1992). Additionally, they also offer other beneficial properties such as low volatility, high flash point and high viscosity indices (Sammaiah *et al.*, 2016; Santos *et al.*, 2004). Furthermore, the polar ester group of plant oil-based biolubricant contributes to good boundary lubrication because of its attraction towards metal surface (Salimon *et al.*, 2010) and better solubility for polar contaminant as well as polar additives (Erhan *et al.*, 2006).

Nonetheless, plant oil-based biolubricant is not without drawbacks due to its triglycerides molecular structure. One of the main drawbacks is poor oxidation stability mainly because of the alkene group of unsaturated fatty acids that is susceptible to oxidation through free radical mechanism. Consequently, the viscosity of plant oil-based biolubricant will increase over time and form insoluble deposits that shorten the service lifespan of the biolubricant (Nowicki *et al.*, 2019; Soni and Agarwal, 2014). Another major weakness of plant oil-based biolubricant is the high melting point attribute of plant oil that translates to high pour point for corresponding biolubricant, which limits its usage in cold climate applications. As such, the plant oil-based biolubricants have high tendency to solidify in winter climate that make them unfavourable to consumer (Kim *et al.*, 2019; Kassfeldt and Goran, 1997).

The disadvantages of plant oil-based biolubricant can be resolved by chemical modification of the alkene group of plant oil or its derivatives such as fatty acids and methyl esters. One of the main methods to modify alkene group of unsaturated plant oil derivatives is through epoxidation of alkene with hydrogen peroxide (H_2O_2) and formic acid to generate epoxidised plant oil derivatives (Chen *et al.*, 2019; Hoong *et al.*, 2008; Armylisas *et al.*, 2017). The purified epoxidised plant oil derivatives were then subjected to epoxide-ring opening reaction with various nucleophiles such as fatty acids (Salih *et al.*, 2011), alcohols (Salimon *et al.*, 2011) and water (Lv *et al.*, 2017; Adhvaryu *et al.*, 2005) to yield modified plant oil derivatives. Subsequent reactions conducted to convert all functional groups of modified plant oil derivatives to ester functionality, significantly lower the pour point and improved the oxidation stability of plant oil-based biolubricants. Nevertheless, the main drawback of this method is the multi-steps process including purification steps required to produce biolubricants with commercially acceptable properties, which

contribute to high production cost that may not be economically attractive to consumer.

Alternatively, the properties of plant oil-based lubricants can be improved through a simpler method known as transesterification, in which plant oils can be reacted with various polyhydric alcohols to generate polyol esters that exhibited improved lubricant properties. For example, Heikel *et al*. (2017) reported a two-steps synthesis of trimethylolpropane (TMP) esters from palm oil and jatropha oil. Both plant oils were first converted to methyl esters through transesterification with methanol and subsequently the methyl esters were further transesterified with TMP to yield TMP esters that exhibited improved cold flow properties in comparison with starting materials. Additionally, the prepared TMP esters also showed better viscosity indices and improved flash points. However, the prepared TMP esters still contain alkene groups that are prone to oxidation degradation, which could reduce the service life of the lubricants. Hence, it is beneficial to make biolubricants with minimal amount of alkene group and simultaneously display good cold flow properties.

Another renowned approach to improve the lubricant properties of plant oil-based lubricant is through formation of estolide from unsaturated fatty acids that generally show good cold flow properties with minimal alkene group in resultant biolubricants (Chen *et al*., 2020). Estolide is formed when the carboxylic acid group of a fatty acid reacts with the alkene group of another unsaturated fatty acid to form an ester linkage between the two fatty acids, in which the reaction requires the use of strong acids such as perchloric acid as the catalyst (Cermak and Isbell, 2001). Further reaction of the estolide with a branched alcohol afforded estolide ester that achieved desirable low pour point (Cermak *et al*., 2015; Cermak and Isbell, 2003a; 2003b). Nonetheless, the disadvantage of this approach is the need to use corrosive and hazardous perchloric acid that is known to form explosive mixture, which poses significant threats to human and the environment (Everett and Graf, 1971). Therefore, an alternative method to make estolide without the use of perchloric acid would be a way forward.

An alternative method to make estolide is through esterification of hydroxy fatty acid such as ricinoleic acid with other fatty acids (Salih *et al*., 2013) or diacids (Sammaiah *et al*., 2016). Similarly, the prepared estolide esters originated from hydroxy fatty acids displayed excellent cold flow properties and good thermal oxidation stability. Nonetheless, the main drawback of this approach is that the prepared estolides still contain significant amount of alkene groups that require further chemical modification in order to improve the oxidation stability of the prepared estolides, which will incur

higher production cost that may hinder commercial acceptance (Greco-Duarte *et al*., 2019; Cermak *et al*., 2006). Additionally, global production of hydroxy fatty acids is substantially less than commodity fatty acid and the cost of hydroxy fatty acid is significantly higher than commodity fatty acid such as oleic acid (Mubofu, 2016), which makes hydroxy fatty acid less attractive to be used as raw material for estolide-based biolubricant.

After taking into consideration the advantages and weaknesses of disclosed methods for chemical modification of plant oils and fatty esters, we have reported a direct one-pot method to synthesis polyhydroxy estolide (PE) from oleic acid (Hoong *et al*., 2017). The reported method did not require the use of purified epoxidised methyl esters or hydroxy fatty acids as starting material, which simplify the process to produce estolides. The process also did not use hazardous perchloric acid as catalyst, instead it used only H_2O_2 as the reactant. Additionally, the prepared PE had minimal alkene group that imparted good oxidation stability to lubricant made from it. Nevertheless, the prepared PE has multiple hydroxyl groups that need to be converted to ester group in order to further enhance its oxidation stability and low temperature properties.

A thorough search of relevant literature revealed that no previous study has investigated the structure-properties relationship between organic acids employed to end-cap the hydroxyl groups of PE and the physicochemical properties of the resultant estolide esters. Therefore, the objective of this study is to prepare various organic acids end-capped PE and their respective 2-ethylhexyl estolide esters. Another objective is to examine the structure-properties relationship between the end-capping organic acids and the physicochemical properties of the prepared estolide esters. The findings of this study will help to establish the aptness of estolide esters made from organic acids end-capped PE as lubricant base oil.

MATERIALS AND METHODS

Materials

Oleic acid (75%, PALMAC 750) was kindly provided by IOI Oleochemical Industries Bhd. (Pulau Pinang, Malaysia). H_2O_2 (50% in H_2O), acetic anhydride (99%), isovaleric acid (bC5) (98%), hexanoic acid (C6) (98%), octanoic acid (C8) (99%), lauric acid (C12) (98%), stearic acid (C18) (95%), 2-ethylhexanoic acid (bC8) (99%) and 2-ethylhexanol (2EH) (99%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Pentaerythritol tetraoleate was obtained from commercial sources. All chemicals were used as received without further purification.

Characterisation and Procedures

Fourier-transform infrared spectroscopy (FTIR) spectra of products were recorded neat on a Perkin-Elmer FTIR Spectrum 100 with 16 scans per sample at 4 cm^{-1} resolution in the range of 650-4000 cm^{-1}.

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy were recorded using JOEL JNM-ECZ600R at 600 MHz and 150 MHz, respectively. Sample (10 mg ml^{-1}) was prepared with deuterated chloroform.

Gel permeation chromatography (GPC) was carried out using Polymer Laboratories PL-GPC 50 Plus integrated GPC system furnished with differential refractive index (DRI)/viscometer detectors. Sample (2 mg ml^{-1}) was dissolved in tetrahydrofuran (THF) and was analysed through a set of Phenogel columns with molecular weight in the range of 10^2–10^6 Da. Sample was eluted in THF at a flow rate of 1 ml min^{-1}. The GPC was calibrated using polystyrene standards with range from 162 to 1×10^5 Da.

Wet chemistry analysis was conducted in accordance with American Oil Chemists' Society (AOCS) methods: Acid value (AV) Te 2a-64; Hydroxyl value (OHV) Cd 13-60; Iodine value (IV) Cd 1d-92; Oxirane oxygen content (OOC) Cd 9-57.

Kinematic viscosity measurement was carried out according to ASTM D445 in calibrated Ubbellohde tubes submerged in a Normalab NVB Classic viscosity bath. Viscosity index (VI) was calculated in accordance with American Society for Testing and Materials (ASTM) - ASTM D2270-93.

Pour point of sample was recorded using a Normalab CPP Classic test cabinet with integrated cooling system in accordance with ASTM D97.

The oxidation onset temperature (OOT) of sample was determined using DSC Q20P thermal analyser (TA Instruments) in accordance with ASTM E2009.

The anti-wear property of sample was assessed through wear scar diameter (WSD) test in accordance with ASTM 4172 (Four-ball method) by using a TR-30L four-ball equipment (DUCOM Instrument). Steel balls were acquired from SKF Malaysia Sdn. Bhd.

Synthesis of PE from Oleic Acid

Oleic acid (300 g, 1.06 mole) and H_2O_2 (50% in H_2O) (360 g, 5.3 mole) were weighed into a 1 litre three-neck round bottom flask equipped with a condenser, thermometer and magnetic stirrer. The mixture was stirred (500 rpm) and heated at 80°C for 24 hr. Then, reaction mixture was poured into a separating funnel and left to separate. Next, the aqueous layer was discharged from the organic layer. Subsequently, ethyl acetate (200 ml) and water (200 ml) were added to the organic layer. Again, the

aqueous layer was discharged from the separating funnel. The organic layer was washed with more water (2 x 200 ml). The organic layer was dried with anhydrous magnesium sulphate (MgSO$_4$) and ethyl acetate was removed to yield a viscous colourless liquid labeled as PE (321 g, 76% yield). v$_{max}$/cm^{-1} 3440 (OH) 2924, 2854 (C-H) 1733, 1708 (C=O) 1465 (C-H) 1241, 1176 (C-O) 723 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ$_H$=4.80-4.76 (1H, m, HCOC=O), 3.57-3.52 (1H, m, HCO) 3.39-3.34 (2H, m, HCO), 2.29 (4H, t, J=7.5 Hz, O=CCH$_2$CH$_2$), 1.62-1.53 (4H, m, O=CCH$_2$CH$_2$), 1.46-1.32 (8H, m, CH$_2$COH), 1.33-1.17 (40H, m, CH$_2$CH$_2$), 0.84 (6H, t, J=7.0 Hz, CH$_2$CH$_3$); ^{13}C NMR (150 MHz CDCl$_3$): δ$_C$=179.0, 174.0 (C=O), 76.3 (HCOC=O), 74.6, 72.5 (HC-O), 34.5 (O=CCH$_2$), 25.1 (O=CCH$_2$CH$_2$), 31.9, 29.4, 24.7, 22.7 (CH$_2$CH$_2$), 14.2 (CH$_2$CH$_3$).

Synthesis of Acetylated Estolide (C2E)

PE (230 g, 0.70 mole of OH, OHV=170 mg KOH g^{-1}), acetic anhydride (60 g, 0.59 mole) and xylene (60 ml) were charged into a 500 ml round bottom flask equipped with a Dean-Stark apparatus and magnetic stirrer. The mixture was stirred (300 rpm) and heated to 150°C for 16 hr. Thereafter, excess acetic anhydride and xylene were distilled from the reaction product at 140°C under vacuum of 20 mbar. The product was left to cool to room temperature and chloroform (200 ml) was added to the product. The diluted product was dried with anhydrous MgSO$_4$ and chloroform was removed to yield a viscous yellowish liquid labeled as C2E (229 g, 97% yield). v$_{max}$/cm^{-1} 2925, 2855 (C-H) 1736, 1709 (C=O) 1464 (CH$_2$) 1372 (CH$_3$) 1235, 1167 (C-O) 723 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ$_H$=4.97-4.92 (2H, m, HCOC=O), 2.3-2.2 (4H, m, O=CCH$_2$), 2.02 (3H, s, O=CCH$_3$), 1.6-1.52 (4H, m, O=CCH$_2$CH$_2$), 1.47-1.41 (4H, m, CH$_2$CHO), 1.32-1.14 (44H, m, CH$_2$CH$_2$), 0.81 (6H, t, J=6.9 Hz, CH$_2$CH$_3$); ^{13}C NMR (150 MHz CDCl$_3$): δ$_C$=179.6, 173.4, 170.7 (C=O), 73.9, 73.5 (HCOC=O), 34.3, 34.1 (O=CCH$_2$), 25.1 (O=CCH$_2$CH$_2$), 31.8, 29.7, 29.4, 29.2, 25.2 24.6, 20.9 (CH$_2$CH$_2$), 22.6 (O=CCH$_3$), 14.1 (CH$_2$CH$_3$).

General Procedure for Synthesis of Organic Acid-capped Estolide (OAE)

Synthesis of isovaleric acid-capped estolide (bC5E) as an example. PE (250 g, 0.76 mole of OH, OHV=170 mg KOH g^{-1}), bC5 (102 g, 1 mole) were charged into a 500 ml round bottom flask equipped with a Dean-Stark apparatus and magnetic stirrer. The mixture was stirred (300 rpm) and heated to 210°C for 8 hr. Thereafter, excess bC5 was removed from the reaction product at 200°C under vacuum of 20 mbar. The product was left to cool to room temperature and chloroform (200 ml) was added to the product. The diluted product was dried with

anhydrous MgSO$_4$ and chloroform was removed to yield a viscous yellowish liquid labeled as bC5E (298 g, 95% yield). v$_{max}$/cm^{-1} 2925, 2855 (C-H) 1735, 1709 (C=O) 1465 (CH$_2$) 1371 (CH$_3$) 1240, 1166 (C-O) 723 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ$_H$=4.99-4.91 (2H, m, HCOC=O), 2.31-2.26 (2H, m, O=CCH$_2$), 2.25-2.20 (2H, m, O=CCH$_2$), 2.18-2.11 (2H, m, O=CCH$_2$), 2.08-2.01 (1H, m, (CH$_3$)$_2$CH), 1.62-1.53 (6H, m, O=CCH$_2$CH$_2$), 1.52-1.42 (4H, m, CH$_2$CHO), 1.32-1.16 (44H, m, CH$_2$CH$_2$), 0.93-0.90 (6H, m, CH$_3$CH) 0.83 (6H, t, J=6.0 Hz, CH$_2$CH$_3$); ^{13}C NMR (150 MHz CDCl$_3$): δ$_C$=179.7, 173.5, 172.8 (C=O), 74.1, 73.5 (HCOC=O), 43.6 (O=CCH$_2$), 34.5, 34.0 (O=CCH$_2$), 25.7 (O=CCH$_2$CH$_2$), 31.9, 29.7, 29.4, 29.2, 25.5, 25.1, 24.6 (CH$_2$CH$_2$), 22.7, 22.4 (CHCH$_3$), 14.1 (CH$_2$CH$_3$).

Synthesis of hexanoic acid-capped estolide (C6E). The experiment was conducted according to the general procedure for synthesis of OAE. PE (250 g, 0.76 mole of OH, OHV=170 mg KOH g^{-1}), C6 (116 g, 1 mole), viscous yellowish liquid labeled as C6E (274 g, 97% yield). v$_{max}$/cm^{-1} 2925, 2855 (C-H) 1735, 1709 (C=O) 1465 (CH$_2$) 1377 (CH$_3$) 1242, 1166 (C-O) 756 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ$_H$=5.01-4.91 (2H, m, HCOC=O), 2.34-2.28 (2H, m, O=CCH$_2$), 2.28-2.20 (4H, m, O=CCH$_2$), 1.64-1.55 (6H, m, O=CCH$_2$CH$_2$), 1.51-1.43 (4H, m, CH$_2$CHO), 1.35-1.17 (48H, m, CH$_2$CH$_2$), 0.89-0.83 (9H, m, CH$_3$CH); ^{13}C NMR (150 MHz CDCl$_3$): δ$_C$=179.8, 173.5 (C=O), 74.0, 73.6 (HCOC=O), 34.4, 34.0 (O=CCH$_2$), 25.5 (O=CCH$_2$CH$_2$), 31.9, 31.4, 29.7, 29.4, 29.2, 25.2, 24.8, 22.7, 22.4 (CH$_2$CH$_2$), 14.1, 13.9 (CH$_2$CH$_3$).

Synthesis of octanoic acid-capped estolide (C8E). The experiment was conducted according to the general procedure for synthesis of OAE. PE (200 g, 0.61 mole of OH, OHV=170 mg KOH g^{-1}), C8 (100 g, 0.69 mole), viscous yellowish liquid labeled as octanoic acid-capped estolide (C8E) (239 g, 98% yield). v$_{max}$/cm^{-1} 2923, 2854 (C-H) 1735, 1708 (C=O) 1464 (CH$_2$) 1377 (CH$_3$) 1162 (C-O) 723 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ$_H$=4.94-4.86 (2H, m, HCOC=O), 2.27-2.20 (2H, m, O=CCH$_2$), 2.20-2.14 (4H, m, O=CCH$_2$), 1.58-1.47 (6H, m, O=CCH$_2$CH$_2$), 1.45-1.36 (4H, m, CH$_2$CHO), 1.29-1.09 (52H, m, CH$_2$CH$_2$), 0.81-0.74 (9H, m, CH$_3$CH); ^{13}C NMR (150 MHz CDCl$_3$): δ$_C$=179.4, 173.3 (C=O), 73.8, 73.5 (HCOC=O), 34.4, 33.9 (O=CCH$_2$), 25.1 (O=CCH$_2$CH$_2$), 31.8, 31.6, 29.7, 29.4, 29.2, 25.2, 24.6, 22.7, 22.6 (CH$_2$CH$_2$), 14.1 (CH$_2$CH$_3$).

Synthesis of 2-ethylhexanoic acid-capped estolide (bC8E). The experiment was conducted according to the general procedure for synthesis of OAE. PE (200 g, 0.61 mole of OH, OHV=170 mg KOH g^{-1}), 2-ethylhexanoic acid (100 g, 0.69 mole), viscous yellowish liquid labeled as 2-ethylhexanoic acid-capped estolide (bC8E) (235 g, 97% yield).

v_{max}/cm^{-1} 2925, 2855 (C-H) 1733, 1709 (C=O) 1460 (CH_2) 1377 (CH_3) 1167 (C-O) 724 (CH_2); ^1H NMR (600 MHz, $CDCl_3$): δ_H=5.05-4.88 (2H, m, HCOC=O), 2.33-2.29 (2H, m, O=CCH_2), 2.28-2.17 (4H, m, O=CCH_2), 1.63-1.53 (8H, m, O=CCH_2CH_2), 1.53-1.41 (4H, m, CH_2CHO), 1.29-1.09 (44H, m, CH_2CH_2), 0.91-0.82 (12H, m, CH_3CH); ^{13}C NMR (150 MHz $CDCl_3$): δ_C=179.7, 175.9, 173.5 (C=O), 74.0, 73.5 (HC OC=O), 44.7 (HC C=O), 34.5, 34.1 (O=CC H_2), 25.6, 25.1 (O=CCH_2C H_2), 31.9, 31.7, 29.7, 29.5, 29.2, 25.0, 24.6, 22.7, 22.6 (CH_2C H_2), 14.1, 11.9 (CH_2C H_3).

Synthesis of lauric acid-capped estolide (C12E). The experiment was conducted according to the general procedure for synthesis of OAE. PE (200 g, 0.61 mole of OH, OHV=170 mg KOH g^{-1}), C12 (120 g, 0.6 mole), viscous yellowish liquid labeled as lauric acid-C12E (247 g, 96% yield). v_{max}/cm^{-1} 2923, 2854 (C-H) 1737, 1709 (C=O) 1465 (CH_2) 1377 (CH_3) 1235, 1166 (C-O), 723 (CH_2); ^1H NMR (600 MHz, $CDCl_3$): δ_H=5.01-4.92 (2H, m, HCOC=O), 2.32-2.29 (2H, m, O=CCH_2), 2.28-2.21 (4H, m, O=CCH_2), 1.63-1.54 (6H, m, O=CCH_2CH_2), 1.52-1.43 (4H, m, CH_2CHO), 1.33-1.16 (54H, m, CH_2CH_2), 0.86-0.82 (9H, m, CH_3CH); ^{13}C NMR (150 MHz $CDCl_3$): δ_C=180.0, 173.5 (C=O), 74.0, 73.6 (HC OC=O), 34.5, 34.1 (O=CC H_2), 24.7 (O=CCH_2C H_2), 31.9, 29.6, 29.4, 29.2, 25.6, 25.0, 22.7 (CH_2C H_2), 14.1 (CH_2C H_3).

Synthesis of stearic acid-capped estolide (C18E). The experiment was conducted according to the general procedure for synthesis of OAE. PE (200 g, 0.61 mole of OH, OHV=170 mg KOH g^{-1}), C18 (100 g, 0.35 mole), viscous yellowish liquid labeled as stearic acid-capped estolide (C18E) (285 g, 98% yield). v_{max}/cm^{-1} 2917, 2850 (C-H) 1736, 1707 (C=O) 1464 (CH_2) 1371 (CH_3) 1234, 1166 (C-O) 721 (CH_2); ^1H NMR (600 MHz, $CDCl_3$): δ_H=5.02-4.95 (2H, m, HCOC=O), 2.35-2.31 (2H, m, O=CCH_2), 2.31-2.23 (4H, m, O=CCH_2), 1.65-1.57 (6H, m, O=CCH_2CH_2), 1.53-1.45 (4H, m, CH_2CHO), 1.36-1.21 (66H, m, CH_2CH_2), 0.87 (9H, t, CH_3CH); ^{13}C NMR (150 MHz $CDCl_3$):δ_C=180.1, 173.6 (C=O), 74.1, 73.7 (HC OC=O), 34.5, 34.1 (O=CC H_2), 25.2 (O=CCH_2C H_2), 32.0, 29.8, 29.5, 29.3, 25.6, 24.8, 22.8 (CH_2C H_2), 14.2 (CH_2C H_3).

General Procedure for Synthesis of 2-ethylhexyl Ester of OAE

Synthesis of 2-ethylhexyl ester of octanoic acid-capped estolide (2EH-C8E). Octanoic acid-capped estolide (C8E) (182 g, 0.32 mole of CO_2H, AV = 100 mg KOH g^{-1}) and 2EH (102 g, 0.78 mole) were weighed into a reaction flask connected to a Dean-Stark apparatus. The mixture was stirred (300 rpm) and heated at 210°C for 8 hr. Thereafter, the excess 2EH was removed through distillation at 210°C under 10 mbar vacuum. The product was diluted

with 200 ml chloroform and dried with anhydrous $MgSO_4$. Then, solvent was removed to yield a yellowish liquid known as 2-ethylhexyl ester of octanoic acid-capped estolide (2EH-C8E) (215 g, 98% yield). v_{max}/cm^{-1} 2924, 2855 (C-H) 1735 (C=O) 1463 (CH_2) 1378 (CH_3) 1244, 1165 (C-O) 723 (CH_2); ^1H NMR (600 MHz, $CDCl_3$): δ_H= 4.97-4.87 (2H, m, HCOC=O), 3.95-3.88 (2H, m, H$_2$COC=O), 2.29-2.16 (6H, m, O=CCH_2), 1.59-1.51 (6H, m, O=CCH_2CH_2), 1.51-1.46 (1H, m, CHCHO), 1.46-1.40 (4H, m, CH_2CHO), 1.33-1.10 (60H, m, CH_2CH_2), 0.85-0.76 (15H, m, CH_3CH); ^{13}C NMR (150 MHz $CDCl_3$): δ_C=173.9, 173.2 (C=O), 73.9, 73.5 (HC OC=O), 66.5 (H_2C OC=O) 38.8 (HCC H_2O) 34.4, 34.3 (O=CC H_2), 25.5 (O=CCH_2C H_2), 31.8, 31.7, 30.4, 29.7, 29.4, 29.3, 28.9, 25.0, 23.8, 22.9, 22.7 (CH_2C H_2), 14.1, 10.9 (CH_2C H_3).

Synthesis of 2-ethylhexyl ester of acetic acid-capped estolide (2EH-C2E). The experiment was conducted according to the general procedure for synthesis of 2-ethylhexyl ester of OAE. Acetic acid-capped estolide (C2E) (195 g, 0.27 mole of CO_2H, AV=80 mg KOH g^{-1}) and 2EH (75 g, 0.57 mole). A yellowish liquid known as 2-ethylhexyl ester of acetic acid-capped estolide (2EH-C2E) (224 g, 98% yield). v_{max}/cm^{-1} 2925, 2855 (C-H) 1735 (C=O) 1463 (CH_2) 1373 (CH_3) 1234, 1169 (C-O) 724 (CH_2); ^1H NMR (600 MHz, $CDCl_3$): δ_H=4.95-4.87 (2H, m, HCOC=O), 3.93-3.85 (2H, m, H$_2$COC=O), 2.26-2.15 (4H, m, O=CCH_2), 1.97 (3H, s, O=CCH_3) 1.56-1.49 (4H, m, O=CCH_2CH_2), 1.49-1.44 (1H, m, CHCHO), 1.43-1.37 (4H, m, CH_2CHO), 1.33-1.10 (52H, m, CH_2CH_2), 0.84-0.73 (12H, m, CH_3CH); ^{13}C NMR (150 MHz $CDCl_3$): δ_C=173.9, 173.2, 170.4 (C=O), 73.8, 73.4 (HC OC=O), 66.5 (H_2C OC=O) 38.7 (HCC H_2O) 34.3 (O=CC H_2), 25.4 (O=CCH_2C H_2), 31.8, 30.4, 29.6, 29.3, 28.9, 25.0, 23.8, 22.9, 22.6 (CH_2C H_2), 20.9 (H_3C C=O) 14.1 (CH_2C H_3).

Synthesis of 2-ethylhexyl ester of isovaleric acid-capped estolide (2EH-bC5E). The experiment was conducted according to the general procedure for synthesis of 2-ethylhexyl ester of OAE. bC5E (200 g, 0.31 mole of CO_2H, AV=86 mg KOH g^{-1}) and 2EH (120 g, 0.92 mole). A yellowish liquid known as 2EH-bC5E (224 g, 96% yield). v_{max}/cm^{-1} 2925, 2855 (C-H) 1735 (C=O) 1464 (CH_2) 1370 (CH_3) 1245, 1167 (C-O) 724 (CH_2); ^1H NMR (600 MHz, $CDCl_3$): δ_H=4.99-4.90 (2H, m, HCOC=O), 3.97-3.90 (2H, m, H$_2$COC=O), 2.29-2.20 (4H, m, O=CCH_2), 2.19-2.11 (2H, m, O=CCH_2), 2.10-2.01 (1H, m, (CH$_3$)$_2$CH), 1.61-1.54 (4H, m, O=CCH_2CH_2), 1.53-1.49 (1H, m, CHCHO), 1.49-1.42 (4H, m, CH_2CHO), 1.37-1.15 (52H, m, CH_2CH_2), 0.94-0.89 (6H, m, HCCH_3), 0.88-0.80 (12H, m, CH_3CH); ^{13}C NMR (150 MHz $CDCl_3$): δ_C=173.9, 173.3, 172.6 (C=O), 74.0, 73.8 (HC OC=O), 66.6 (H_2C OC=O) 43.6 (O=CC H_2), 38.8 (HCC H_2O), 34.5, 34.4 (O=CC H_2), 25.7

(O=CCH$_2$CH$_2$), 31.8, 30.5, 29.7, 29.4, 29.2, 28.9, 25.0, 23.8, 23.0 (CH$_2$CH$_2$), 22.7, 22.4 (CHCH$_3$), 14.1, 11.0 (CH$_2$CH$_3$).

Synthesis of 2-ethylhexyl ester of hexanoic acid-capped estolide (2EH-C6E). The experiment was conducted according to the general procedure for synthesis of 2-ethylhexyl ester of OAE. C6E (200 g, 0.32 mole of CO$_2$H, AV=90 mg KOH g^{-1}) and 2EH (100 g, 0.77 mole). A yellowish liquid known as 2-ethylhexyl ester of hexanoic acid-capped estolide (2EH-C6E) (232 g, 98% yield). v_{max}/cm^{-1} 2925, 2856 (C-H) 1734 (C=O) 1463 (CH$_2$) 1378 (CH$_3$) 1242, 1168 (C-O) 725 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ_H=4.99-4.90 (2H, m, HCOC=O), 3.98-3.91 (2H, m, H$_2$COC=O), 2.32-2.21 (6H, m, O=CCH$_2$), 1.63-1.55 (6H, m, O=CCH$_2$CH$_2$), 1.55-1.49 (1H, m, CHCHO), 1.49-1.43 (4H, m, CH$_2$CHO), 1.37-1.17 (56H, m, CH$_2$CH$_2$), 0.89-0.82 (15H, m, CH$_3$CH); ^{13}C NMR (150 MHz CDCl$_3$): δ_C= 174.0, 173.4 (C=O), 73.9, 73.5 (HCOC=O), 66.7 (H$_2$COC=O) 38.8 (HCCH$_2$O) 34.5 (O=CCH$_2$), 25.5 (O=CCH$_2$CH$_2$), 31.8, 31.4, 30.5, 29.7, 29.4, 29.2, 28.9, 25.2, 25.0, 24.8, 23.8, 23.0, 22.7 (CH$_2$CH$_2$), 14.1, 11.0 (CH$_2$CH$_3$).

Synthesis of 2-ethylhexyl ester of 2-ethylhexanoic acid-capped estolide (2EH-bC8E). The experiment was conducted according to the general procedure for synthesis of 2-ethylhexyl ester of OAE. 2-ethylhexanoic acid-capped estolide (bC8E) (188 g, 0.26 mole of CO$_2$H, AV=79 mg KOH g^{-1}) and 2EH (70 g, 0.54 mole). A yellowish liquid known as 2-ethylhexyl ester of 2-ethylhexanoic acid-capped estolide (2EH-bC8E) (210 g, 97% yield). v_{max}/cm^{-1} 2925, 2856 (C-H) 1734 (C=O) 1464 (CH$_2$) 1378 (CH$_3$) 1238, 1167 (C-O) 724 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ_H=5.04-4.86 (2H, m, HCOC=O), 3.97-3.90 (2H, m, H$_2$COC=O), 2.30-2.17 (6H, m, O=CCH$_2$), 1.63-1.53 (8H, m, O=CCH$_2$CH$_2$), 1.52-1.49 (1H, m, CHCHO), 1.48-1.42 (4H, m, CH$_2$CHO), 1.35-1.12 (56H, m, CH$_2$CH$_2$), 0.89-0.79 (18H, m, CH$_3$CH); ^{13}C NMR (150 MHz CDCl$_3$): δ_C=175.8, 173.9 (C=O), 74.2, 73.9 (HCOC=O), 66.2 (H$_2$COC=O) 47.7(HCC=O), 38.8 (HCCH$_2$O) 34.4 (O=CCH$_2$), 25.5 (O=CCH$_2$CH$_2$), 31.9, 30.5, 29.7, 29.4, 29.2, 28.9, 25.0, 23.8, 23.0, 22.7 (CH$_2$CH$_2$), 14.1, 11.8, 11.0 (CH$_2$CH$_3$).

Synthesis of 2-ethylhexyl ester of lauric acid-capped estolide (2EH-C12E). The experiment was conducted according to the general procedure for synthesis of 2-ethylhexyl ester of OAE. Lauric acid-capped estolide (C12E) (200 g, 0.37 mole of CO$_2$H, AV=103 mg KOH g^{-1}) and 2EH (96 g, 0.74 mole). A yellowish liquid known as 2-ethylhexyl ester of lauric acid-capped estolide (2EH-C12E) (235 g, 97% yield). v_{max}/cm^{-1} 2924, 2855 (C-H) 1736 (C=O) 1464 (CH$_2$) 1378 (CH$_3$) 1236, 1169 (C-O) 724 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ_H=4.98-4.91 (2H, m, HCOC=O), 3.96-3.89 (2H, m, H$_2$COC=O), 2.30-2.18

(6H, m, O=CCH$_2$), 1.63-1.53 (6H, m, O=CCH$_2$CH$_2$), 1.52-1.47 (1H, m, CHCHO), 1.47-1.41 (4H, m, CH$_2$CHO), 1.35-1.11 (66H, m, CH$_2$CH$_2$), 0.88-0.78 (15H, m, CH$_3$CH); ^{13}C NMR (150 MHz CDCl$_3$): δ_C= 174.0, 173.3 (C=O), 73.9, 73.5 (HCOC=O), 66.6 (H$_2$COC=O) 38.8 (HCCH$_2$O) 34.5, 34.3 (O=CCH$_2$), 25.5 (O=CCH$_2$CH$_2$), 31.9, 31.7, 30.5, 29.6, 29.4, 29.2, 28.9, 25.1, 23.8, 23.0, 22.7 (CH$_2$CH$_2$), 14.1, 11.0 (CH$_2$CH$_3$).

Synthesis of 2-ethylhexyl ester of stearic acid-capped estolide (2EH-C18E). The experiment was conducted according to the general procedure for synthesis of 2-ethylhexyl ester of OAE. Stearic acid-capped estolide (C18E) (200 g, 0.35 mole of CO$_2$H, AV=99 mg KOH g^{-1}) and 2EH (92 g, 0.71 mole). A yellowish liquid known as 2-ethylhexyl ester of stearic acid-capped estolide (2EH-C18E) (232 g, 97% yield). v_{max}/cm^{-1} 2923, 2854 (C-H) 1736 (C=O) 1464 (CH$_2$) 1378 (CH$_3$) 1242, 1169 (C-O) 723 (CH$_2$); ^{1}H NMR (600 MHz, CDCl$_3$): δ_H=5.03-4.91 (2H, m, HCOC=O), 3.99-3.91 (2H, m, H$_2$COC=O), 2.32-2.21 (6H, m, O=CCH$_2$), 1.61-1.56 (6H, m, O=CCH$_2$CH$_2$), 1.56-1.51 (1H, m, CHCHO), 1.49-1.44 (4H, m, CH$_2$CHO), 1.35-1.18 (80H, m, CH$_2$CH$_2$), 0.89-0.81 (15H, m, CH$_3$CH); ^{13}C NMR (150 MHz CDCl$_3$): δ_C=174.0, 173.4 (C=O), 74.0, 73.6 (HCOC=O), 66.6 (H$_2$COC=O) 38.8 (HCCH$_2$O) 34.5, 34.4 (O=CCH$_2$), 25.5 (O=CCH$_2$CH$_2$), 31.9, 31.8, 30.5, 29.7, 29.4, 28.9, 25.1, 23.9, 23.0, 22.7 (CH$_2$CH$_2$), 14.1, 11.0 (CH$_2$CH$_3$).

RESULTS AND DISCUSSION

One-pot Synthesis of Polyhydroxy Estolide from Oleic Acid

Estolide with multiple hydroxyl groups was prepared from oleic acid in accordance with a one-pot method that we have reported earlier (Hoong *et al.*, 2017) but with reaction time shortened to 24 hr instead of 72 hr. *Figure 1* illustrates the one-pot reaction between oleic acid and H$_2$O$_2$ that yielded PE. Generally, oleic acid was reacted with only H$_2$O$_2$ at 80°C for about 24 hr and *Figure 2* illustrates the experimental setup for the reaction. Oleic acid was converted to peroxy acid by H$_2$O$_2$, which subsequently converted oleic acid to epoxidised oleic acid. Thereafter, the epoxidised oleic acid was ring-opened by another oleic acid, which yielded estolide with hydroxyl groups. OOC analysis conducted on PE showed a value of 0.05%, which indicated that almost all the epoxide groups generated during the reaction were transformed to other functionalities.

Additionally, IV analysis performed on PE revealed that the product had IV of 3 g I$_2$ 100 g^{-1} sample, which indicated that almost all the alkene

groups of oleic acid were transformed to either ester or hydroxyl groups. The newly formed hydroxyl groups of PE were detected through OHV analysis that recorded a value of 170 mg KOH g^{-1}. Moreover, ^{1}H NMR analysis confirmed the formation of hydroxyl and ester groups of PE because similar ^{1}H NMR spectrum of PE was observed in literature (Hoong *et al.*, 2017). Furthermore, GPC analysis (*Figure 3*) showed that the prepared PE consisted of 72% estolide and 28% of 9,10-dihydroxystearic acid, which is the monomer of PE. The average molecular weight of PE was about 700 Da.

Synthesis of OAE

According to literature (Salih *et al.*, 2013), base oil that contain hydroxyl group is more susceptible to oxidation degradation than those without hydroxyl group. Consequently, the hydroxyl groups of the prepared PE were end-capped with organic acids to enhance the oxidation stability of the base oil. Various organic acids were employed to end-capped the hydroxyl groups of PE that included linear and branched organic acids as shown in *Figure 4*.
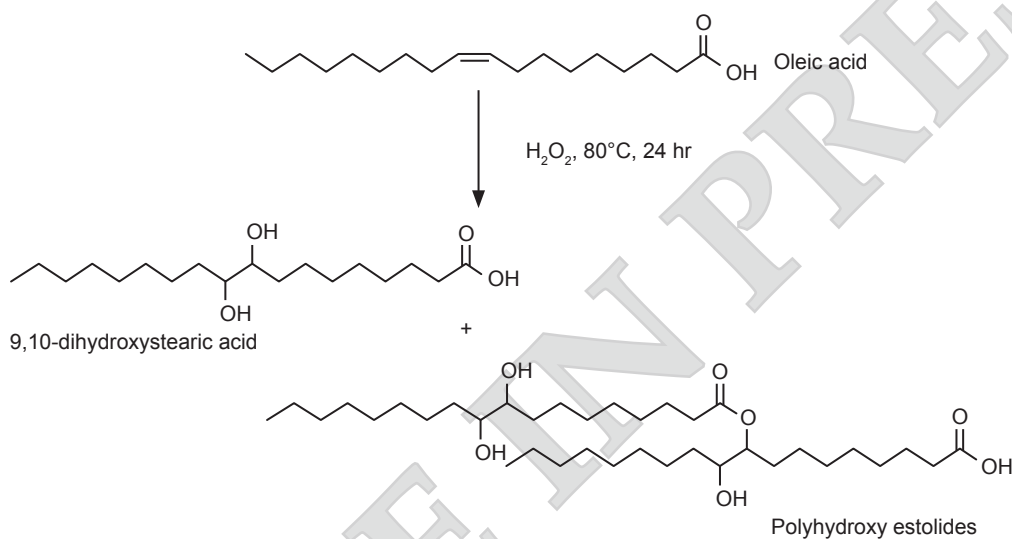
Figure 1. One-pot reaction between oleic acid and hydrogen peroxide (H$_2$O$_2$) that yielded polyhydroxy estolide.
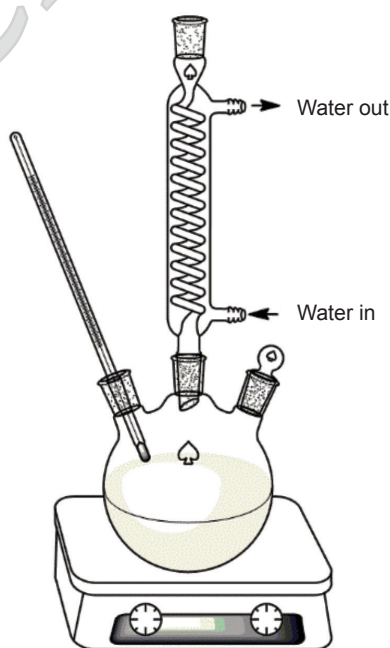
Figure 2. Experimental setup for synthesis of polyhydroxy estolide from oleic acid.
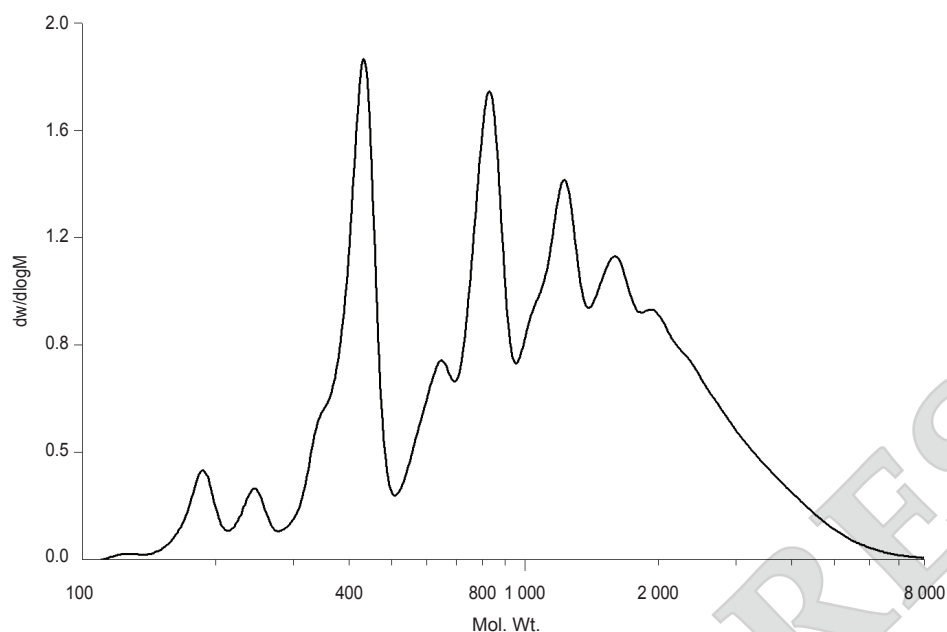
Figure 3. The gel permeation chromatography (GPC) of polyhydroxy estolide.
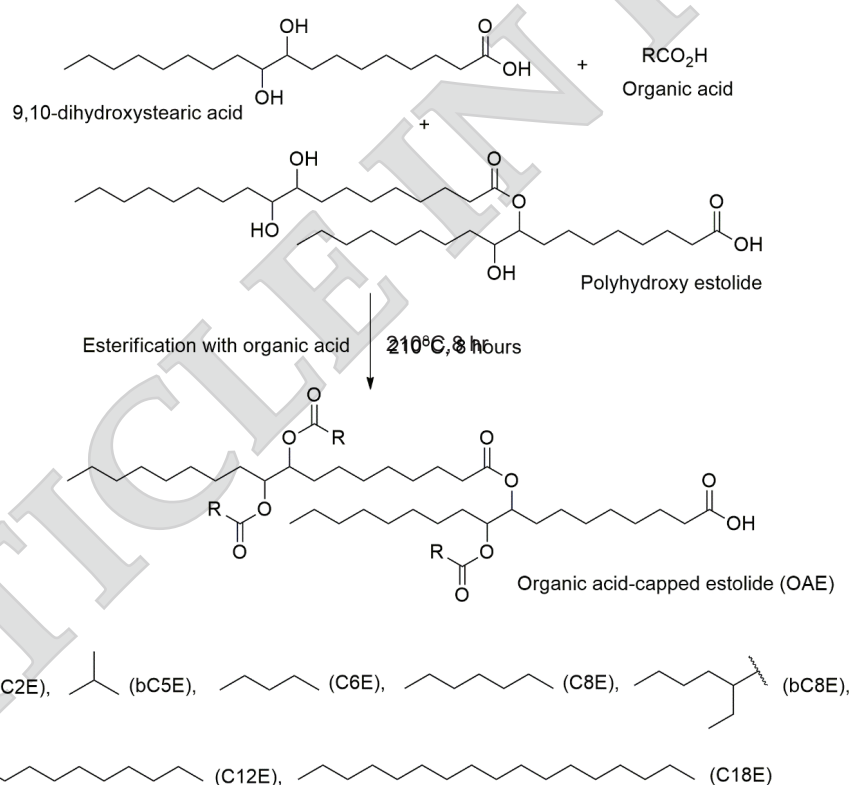
Figure 4. Esterification of polyhydroxy estolide with various organic acids.

The hydrocarbon chain length of linear organic acid used to end-capped PE was varied from short to long chain length. This exercise was meant to evaluate the effect of hydrocarbon chain length of organic acid on the physicochemical properties of resultant lubricant base oil. Selected linear organic acids were acetic acid (C2), C6, C8, C12 and C18.

Literature reported that base oils made of branched molecule showed lower pour point in comparison with linear molecule (Liu *et al.*, 2019). Therefore, branched organic acids were included in this study to evaluate the effect of branched moiety on the properties of base oil. Branched organic acids selected for this study are bC5 and bC8.

The esterification between PE and organic acids that generate OAE was conducted without catalyst at temperature between 150°C-210°C, depending on the boiling point of the organic acid and *Figure 5* illustrates the experimental setup for the reaction. For esterification with acetic anhydride, the reaction was carried out at 150°C with xylene as the solvent to remove water from the reaction system. While for esterification with the rest of organic acids, reaction temperature was set at 210°C to accelerate the reaction. For most of the reaction, an excess amount of organic acid in regard to hydroxyl groups of PE was used in the reaction, in order to end-cap all the hydroxyl groups to form ester groups. The targeted OHV of the OAE should be less than 10 mg KOH g^{-1} and all the prepared OAE achieved OHV less than the targeted value, which indicated that almost all the hydroxyl groups were end-capped with organic acid. For reaction conducted with lauric and stearic acids, the amount of organic acid employed was 50% w/w of PE because excess lauric and stearic acids were difficult to be removed from the product through vacuum distillation.
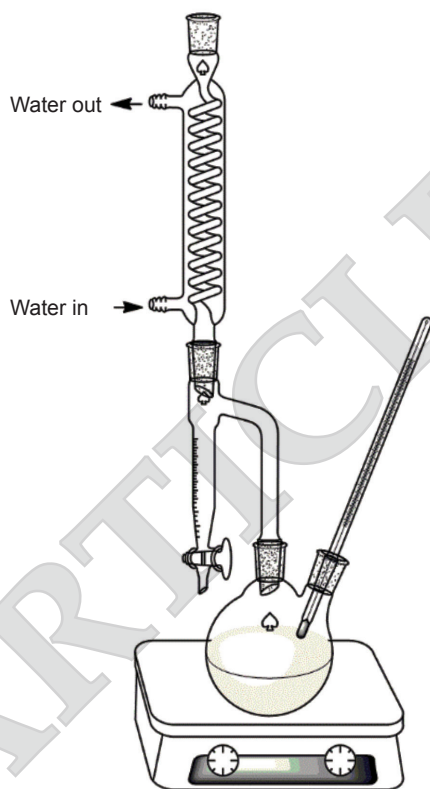

Figure 5. Experimental setup for esterification of between PE and organic acids.

Labels in figure: Water out, Water in

^{1}H NMR analysis of product supported the results of OHV analysis that almost all the hydroxyl groups of PE were end-capped by organic acid to form ester groups. For example, ^{1}H NMR spectrum

of hexanoic end-capped estolide (*Figure 6a*) showed a new peak at 4.97 ppm, which correlated to a methine proton attached to an ester group that was formed when hexanoic acid end-capped the hydroxyl group of PE. Additionally, two peaks at 3.57-3.33 ppm in the ^{1}H NMR spectrum of PE (*Figure 6b*) that correlated to methine protons attached to hydroxyl groups of PE were not observed in the ^{1}H NMR spectra of OAE, which clearly suggested that almost all the hydroxyl groups were converted to ester groups.

Synthesis of 2-ethylhexyl Ester of Organic Acid-capped Estolides

The synthesised OAE have carboxylic acid groups that are weak acid and may cause corrosion problem to metallic surfaces they intend to protect especially at high operating temperature (Owuna *et al.*, 2020). Therefore, carboxylic group of OAE need to be transformed to ester group in order to impart better qualities to the lubricant base oil. The conversion of carboxylic acid group of OAE to ester group was conducted through esterification with an alcohol. The alcohol selected for the esterification reaction was 2EH because literature reported (Moser *et al.*, 2007) that branched alcohols such as 2EH imparted lower pour points to lubricant made with them as compared to linear alcohols.

The esterification between OAE and 2EH was carried out without catalyst at 210°C for about 8 hr as shown in *Figure 7*. The experimental setup as shown in *Figure 5* was used for the esterification reaction. The 2EH was used in excess relatively to carboxylic acid group of OAE with the aim of converting all the carboxylic acid groups to esters and to push the reaction forward. The reaction was followed by monitoring the AV of reaction mixture and the targeted AV of product should be less than 2 mg KOH g^{-1} to ensure that the resultant base oil has good lubricant properties. AV analysis performed on all the prepared 2-ethylhexyl ester of organic acid-capped estolides (2EH-OAE) showed AV less than 2 mg KOH g^{-1}, which indicated that the reaction was successful.

The result of AV analysis was supported by FTIR analysis conducted on 2EH-OAE. As an example, the FTIR spectrum of 2-ethylhexyl ester of octanoic acid-capped estolide (2EH-C8E) (*Figure 8*) showed a narrow band at 1735 cm^{-1} that indicated the presence of ester group in the product, while no band associated with carboxylic acid group at 1710 cm^{-1} was observed, which suggested that all the carboxylic acid groups were transformed to ester groups. Additionally, ^{13}C NMR analysis on products also did not detect peak associated with carboxylic acid group at 179 ppm but instead it detected peak at 174 ppm, which indicated the presence of ester group.
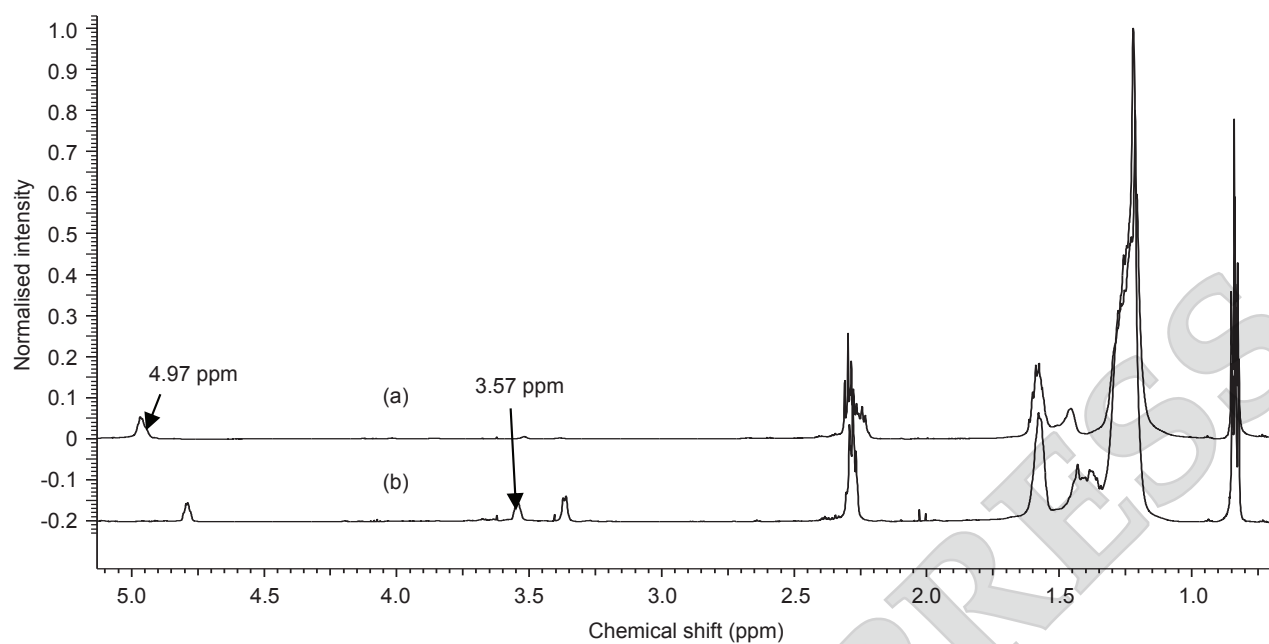
Figure 6. ¹H NMR spectrum of (a) hexanoic acid-capped estolide, and (b) polyhydroxy estolide (PE).
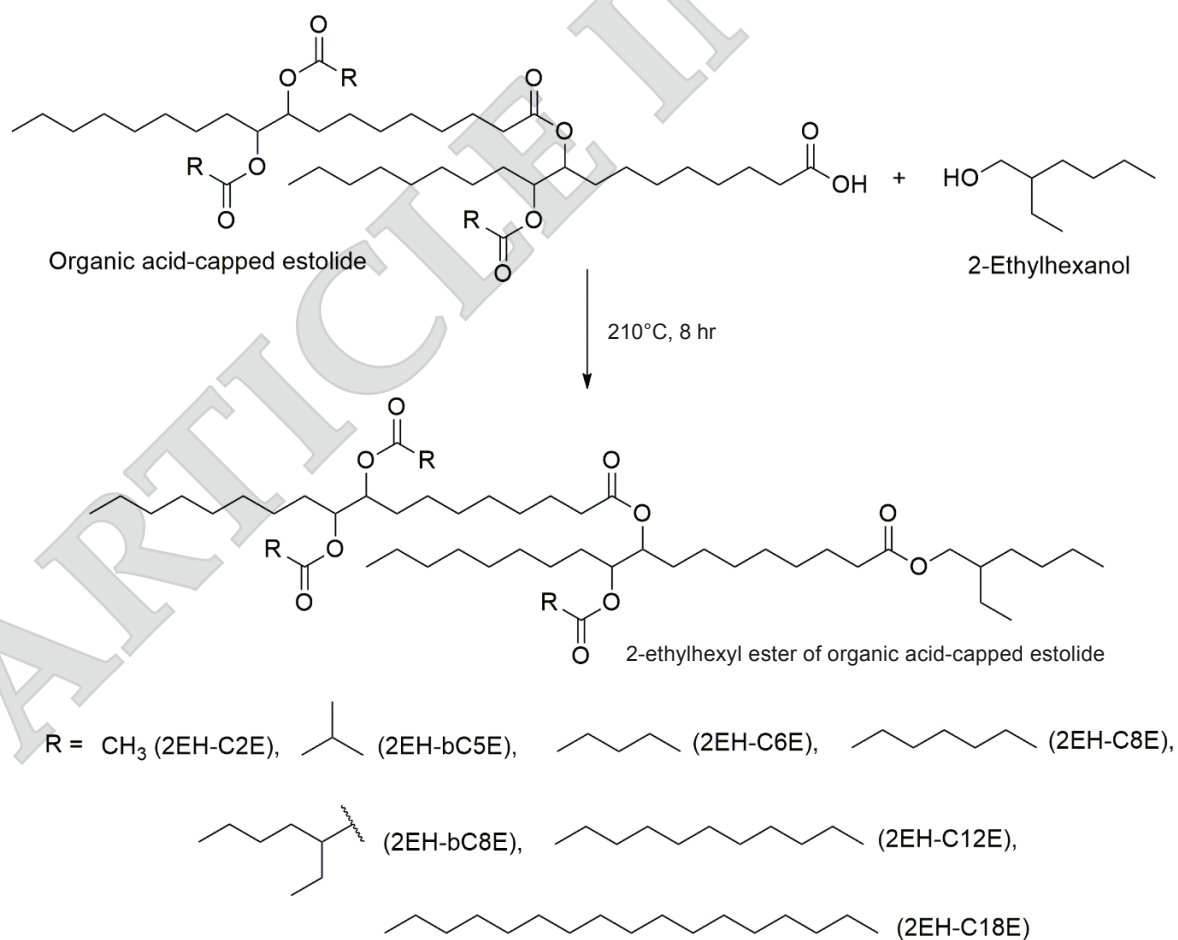

Figure 7. Esterification of organic acid-capped estolide with 2-ethylhexanol (2EH).
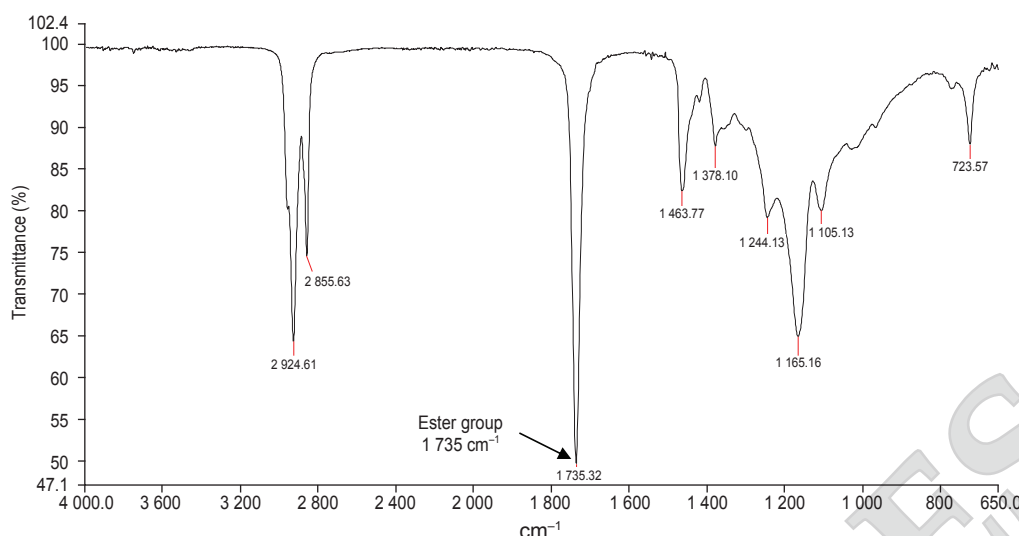
Figure 8. FTIR spectrum of 2-ethylhexyl ester of octanoic end-capped estolide (2EH-C8E).

Evaluation of 2-ethylhexyl Ester of Organic Acid-capped Estolides as Lubricant Base Oil

The synthesised 2EH-OAE were evaluated as lubricant base oil in accordance with typical specifications of commercial lubricant base oil which included kinematic viscosity, pour point, oxidation stability and wear prevention. For the evaluation, a commercial product was included in the study, which served as a benchmark for commercially acceptable lubricant properties. The commercial product was a biolubricant base oil consisted of pentaerythritol tetraoleate, prepared from esterification between pentaerythritol and oleic acid. The results of the physicochemical evaluation of all prepared 2EH-OAEs are shown in *Table 1*.

One of the main purposes of chemical modification performed on plant oils is to improve the pour point of plant oil-based lubricants to a level comparable to synthetic lubricants that they can be used in arctic condition. As a result of chemical alteration performed on oleic acid, majority of the synthesised 2EH-OAE products showed improved low temperature properties with pour points that were lower than most of commoditised plant oils such as soyabean oil and canola oil. For example, 2EH-C2E recorded a pour point of -21°C, which was lower than the pour point of canola oil at -18°C (Asadauskas and Erhan, 1999).

Referring to pour points of 2EH-OAE in *Table 1*, we noticed there was a strong correlation between the chain length of organic acid employed to end-cap the hydroxyl group of PE and the pour point of the resultant 2EH-OAE. For example, when organic acid with longer chain length such as C8 was used to make 2EH-C8E, the product showed a pour point of -33°C, which was lower than pour point of 2EH-C2E (-21°C) that was made with C2. This observation suggested that the longer chain length of C8 contributed to the lower pour point. Thus, as anticipated, 2EH-C12E displayed even lower pour point of -36°C as it was made with longer chain organic acid namely C12 in comparison with C8.

TABLE 1. PHYSICOCHEMICAL PROPERTIES OF 2-ETHYLHEXYL ESTER OF ORGANIC ACID-CAPPED ESTOLIDES

Product	KV		VI	PP (°C)	OOT (°C)	WSD (mm)
	40ºC, cSt	100°C, cSt				
2EH-C2E	295	40	189	-21	200	0.715
2EH-bC5E	269	35	177	-24	196	0.757
2EH-C6E	285	37	180	-24	198	0.692
2EH-C8E	274	35	175	-33	198	0.663
2EH-bC8E	222	28	163	-36	193	0.734
2EH-C12E	129	20	177	-36	197	0.631
2EH-C18E	124	19	173	-6	196	0.612
C1	63	12	190	-21	150	0.648

Note: KV - kinematic viscosity; VI - viscosity index; PP - pour point; OOT - oxidation onset temperature;
WSD - four-ball wear scar diameter.
C1 = commercial biolubricant (pentaerythritol tetraoleate).

The reason for this outcome was due to the ability of C12 to fully cover the alkyl chain of PE beyond the hydroxyl group that it end-capped and thus, disrupted the intermolecular stacking of estolide molecules, which inhibited crystal formation, and consequently contributed to the low pour point of the product. Conversely, when shorter chain organic acid such as C2 was used to end-cap the hydroxyl group of PE as in 2EH-C2E, the short chain length of C2 was not able to cover the entire alkyl chain length of PE and this allowed alkyl stacking interaction to occur, which eventually resulted in crystal formation and higher pour point value of 2EH-C2E at -21°C.

This observation is contrarily to general knowledge on ester-based lubricants, which dictates that longer alkyl chain length will impart higher pour point to ester-based lubricant because longer chain length has higher efficiency to pack and form wax-like material than shorter chain length (Stepina *et al.*, 1992). The observed divergence from the norm occurred because the molecular structure of prepared 2EH-OAE is a branched ester unlike mostly linear ester-based lubricant, and the end-capping of hydroxyl group of PE with an organic acid of proper chain length, further disrupted crystal formation that resulted in lower pour point. Similar observation was reported in literature (Isbell, 2011).

Nonetheless, when C18 was used to end-cap hydroxyl groups of PE, the resultant product 2EH-C18E exhibited the highest pour point (-6°C) among prepared products. This was due to the long alkyl chain of C18 that exceeded the length of alkyl chain beyond the hydroxyl group of PE that it end-capped and the extra length of C18 encouraged intermolecular stacking and crystal formation, which led to higher pour point of the product.

The use of branched organic acids had significant effect on the pour point of products made with them, in which products made with branched acids recorded lower pour points than their linear counterpart. This observation was made evidence when comparing pour point of 2EH-bC8E with 2EH-C8E. The branched structure of bC8 has higher efficacy to obstruct stacking of molecules and avert crystal formation, which resulted in lower pour point than linear C8 (Isbell, 2011). Overall, all the prepared 2EH-OAE exhibited pour points lower or equivalent to commercial product except for 2EH-C18E, which suggested that most of the 2EH-OAE are good candidates for lubricant base oil.

Another objective of chemical modification conducted on plant oil derivatives is to improve the oxidation stability of plant oil-based lubricants, which is considered inferior in comparison with mineral oil-based lubricants. The oxidation stability of base oil can be evaluated by measuring the OOT of base oil by using pressure differential scanning calorimetry (PDSC) method. Referring to *Table 1*, the PDSC analysis results showed that the prepared 2EH-OAE had OOT values between 193°C-200°C, which were remarkably higher than OOT value of the commercial sample. This indicated that the chemical modification performed on the alkene group of oleic acid was able to substantially improve the oxidation stability of resultant base oils, in comparison with commercial samples that contain alkene groups. The observation suggested that conversion of alkene group to ester group can enhance the oxidation stability of base oil made from plant oil derivatives that contain unsaturation sites. Furthermore, the OOT results showed that products made with branched organic acid such as 2EH-bC8E registered a lower OOT value (193°C) than product made with linear organic acid (2EH-C8E, 198°C), which indicated that products made with linear organic acids were more stable oxidatively.

One of the important attributes of lubricant is its ability to reduce friction and prevent wear on surfaces, which contributes to longer lifespan of machineries. The anti-wear properties of lubricants can be measured by a four-ball method in accordance with ASTM 4172 and usually test result is reported as WSD, in which lubricant with better anti-wear properties would exhibit smaller WSD. As shown in *Table 1*, product 2EH-C18E exhibited the smallest WSD among all prepared 2EH-OAE, which suggested that it had the best anti-wear properties. The good anti-wear attribute of 2EH-C18E was most likely contributed by the long chain linear C18 employed to end-cap the hydroxyl group of PE as similar observation was reported by Salih *et al.* (2011).

Thus, for products that were made with shorter chain linear organic acids such as 2EH-C12E and 2EH-C8E, the WSD recorded for these products were slightly larger (0.631–0.663 mm) than 2EH-C18E, which reflected the negative effect of shorter chain organic acids on the anti-wear properties. For product made with even shorter chain fatty acid namely 2EH-C6E, the WSD was even larger (0.692 mm). Eventually, the product 2EH-C2E prepared with the shortest chain length organic acid (C2) exhibited the largest WSD among 2EH-OAE made with linear organic acids.

In comparison to products made with linear organic acids, the WSD for products made with branched organic acids were even larger, which suggested that they provided less wear prevention than products made with linear organic acids. This observation was made evidence when comparing WSD of 2EH-bC8E with 2EH-C8E, in which 2EH-bC8E showed larger WSD due to its branched moiety as reported in literature (Sharma and Erhan, 2013). Nevertheless, three products namely 2EH-C8E, 2EH-C12E and 2EH-C18E exhibited anti-wear properties similar or better than the commercial product used as benchmark.

Viscosity is a crucial physical property of base oil for lubricant. In the context of lubrication, viscosity of lubricant is commonly measured by kinematic viscosity and can be classified according to ISO VG system, which uses the kinematic viscosity of a fluid at 40°C as the reference point for classification. Referring to *Table 1*, the viscosity of 2EH-OAE was inversely proportionate to the chain length of organic acid employed in their syntheses. For example, product 2EH-C2E, which was made with the shortest chain length organic acid showed the highest kinematic viscosity of 295 cSt, while product made with the longest chain length organic acid (2EH-C18E) exhibited the lowest viscosity of 124 cSt. Additionally, product made with branched acid exhibited slightly lower viscosity when compared with its linear counterpart and this was made evidence when comparing product 2EH-bC8E to 2EH-C8E. Similar observation on the effect of alkyl chain length on the viscosity of OAE was reported by Isbell (2011).

The prepared 2EH-OAE can be divided into two groups based on their kinematic viscosity at 40°C. The first group consisted of product 2EH-C12E and 2EH-C18E, which recorded kinematic viscosity between 124-129 cSt and can be classified as ISO VG 150 base oil. The second group consisted of the rest of the 2EH-OAE that were made with C2 to C8 organic acids, which displayed kinematic viscosity between 200-300 cSt at 40°C. Product 2EH-bC8E can be classified as ISO VG 220 base oil while the rest of products can be classified as ISO VG 320 base oil. All the prepared products with viscosity between ISO VG 150 and ISO VG 320 can be used as lubricant for gears and bearings, which require base oil with relatively high viscosity (Pirro *et al.*, 2016).

VI is an indication of a lubricant change in viscosity relative to temperature change. It is a classification to describe the viscosity-temperature relationship of lubricant. Lubricant with higher VI indicates that the viscosity of the lubricant is less affected by temperature fluctuations. Generally, any base oil with VI more than 100 is considered to have good viscosity-temperature consistency profile (Tanveer and Prasad, 2006). As shown in *Table 1*, all the prepared products exhibited VI between 163-189 and this result suggested that all the prepared 2EH-OAE have excellent VI quality.

CONCLUSION

The present study has shown that estolides esters can be made from oleic acid through chemical modification performed on alkene group of oleic with H_2O_2 that generated PE. Subsequently, the hydroxyl groups of PE were end-capped by various organic acids in order to evaluate the effect of organic acid moiety on the lubricant properties of resultant base oil. Afterward, the carboxylic acid group of OAE was converted to ester group with 2EH to further enhanced its lubricant properties.

Generally, the chemical modifications conducted on oleic acid that eventually generated estolides esters, not only significantly improved the low temperature properties of estolide esters but also remarkably enhanced the oxidation stability of estolide esters in comparison with the starting material and a commercial product. These results highlighted that the two major drawbacks associated with plant oil-based lubricants namely high pour point and poor oxidation stability can be resolved by converting oleic acid to estolide esters.

In particular, the chain length of organic acid that end-capped the hydroxyl group of PE strongly affected the properties of base oil. Products made with linear lauric acid (2EH-C12E) and branched 2-ethylhexanoic acid (2EH-bC8E), respectively exhibited the best pour point (-36°C), while products made with shorter or longer chain length organic acids showed higher pour points. Furthermore, products made with longer chain organic acid recorded better anti-wear properties and lower kinematic viscosity than products made with shorter chain length organic acid. Additionally, the oxidation stability of products made with linear organic acid were higher than those made with branched organic acids.

Most of the 2EH-OAE prepared in this study have physicochemical properties that comply with standard specifications of hydraulic oil, gear oil and stern tube lubricants, which indicated that most of the prepared 2EH-OAE are suitable to be used as base oil for lubricants.

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