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# ESTOLIDE ESTER FROM *RICINUS COMMUNIS L.* SEED OIL FOR BIOLUBRICANT PURPOSE

## (Ester Estolida dari Minyak Biji *Ricinus Communis L* untuk Kegunaan Biolubrikan)

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### Abstract

Product of 2-ethylhexyl estolide ester formed from acid catalyst reaction was characterized by using Fourier Transform Infrared (FTIR) in conjunction to determine the functional groups presence. Meanwhile, Nuclear Magnetic Resonance (NMR) has been used to determine the structure's compounds. The present of ester group at 1738.23 cm$^{-1}$ indicated that the formation of estolide ester has been occurred. The vibration peak of C-O occurred at 1174.60 cm$^{-1}$ and 1117.10 cm$^{-1}$ confirmed the formation of ester. Present of $CH_2$ bending indicated the existence of long-chain compounds. Existent of ester methine signal at 3.8669 ppm indicated the estolide linkage in the $^{1}$H-NMR spectrum. On the other hand, two signals have been notified in the $^{13}$C-NMR spectrums. One signal appeared at 173.41 ppm indicated the existence of carbonyl acid compound while carbonyl ester's signal appeared at 173.56 ppm. Chemical shift of $^{1}$H and $^{13}$C for stimulation and experiment were matched with estolide structure. Result of pour point, flash point and viscosity indicated that estolide 2-ethylhexyl ester meet the lubricant criteria as they possesses low pour points (-6 °C), high flash point (246 °C) and optimum viscosity (179 cps).

**Keywords**: Castor oil, estolide ester, biolubricant, pour point, flash point, viscosity

### Abstrak

Hasil 2-etilheksil ester estolida yang terhasil dari tindakbalas bermangkinkan asid katalis telah dianalisa dengan menggunakan Spektroskopi Infra Merah (FTIR) bagi tujuan mengenal pasti kumpulan berfungsi yang hadir. Manakala Resonan Magnetik Nuklear (RMN) digunakan untuk pengecaman formula struktur sebatian. Kumpulan ester telah didapati hadir pada regangan 1738.23 cm$^{-1}$ dan ini menandakan pembentukan ester estolide telah berlaku. Puncak getaran C-O pada 1174.60 cm$^{-1}$ dan 1117.10 cm$^{-1}$ mengesahkan pembentukan ester. Kehadiran bengkokan regangan $CH_2$ menunjukkan kehadiran rantai panjang di dalam kompaun. Isyarat methine ester yang muncul pada 3.8669 ppm melalui spectrum RMN $^{1}$H menandakan kehadiran rangkaian estolida manakala melalui spektrum RMN $^{13}$C didapati dua isyarat karbonil telah muncul. Isyarat karbonil pada at 173.41 ppm mengesahkan kehadiran karbonil asid manakala isyarat pada 173.56 ppm mengesahkan kehadiran karbonil ester. Spektrum RMN $^{1}$H dan $^{13}$C telah membuktikan nilai simulasi dan eksperimen berpadanan dengan struktur molekul estolida. Hasil ujian takat tuang, takat kilat dan kelikatan menunjukkan estolida 2-etilheksil ester sesuai digunakan sebagai pelincir kerana mempunyai takat tuang yang rendah (-6 °C), takat kilat yang tinggi (246 °C) dan kelikatan optimum (179 cps).

**Kata kunci**: Minyak jarak, ester estolida, biolubrikan, takat tuang, takat kilat, kelikatan

## Introduction

The development of the petroleum industry over the past few decades has enabled mineral or rather fossil oils to be used as efficient and cost-effective lubricants. Today, most of the lubricants used for industrial needs are made from non-biodegradable materials such as synthetic oils or petroleum derivatives. However, they pose a great deal of environmental hazards. Bio-lubricants or bio-based lubricants have begun to replace non-biodegradable fossil-based lubricants in industrial purposes [1]. A bio-lubricant can be available in two forms; either as vegetable oil-based or as synthetic esters manufactured from mineral oil-based products. Bio-based lubricants or bio-lubes contain biological materials or renewable domestic agricultural materials such as plant, animal and marine materials or forestry materials. From an environmental perspective, the use of bio-lubricants significantly reduces the carbon footprint than other non-biodegradable mineral oil based sources of crude oil or coal [2]. It is in fact a matter of great concern that millions of tons of hydraulic, machinery and industrial oils are discharged every year into water sources such as rivers and seas, thus leading to groundwater contamination [3]. This can ultimately inhibit the growth of plant life and prove extremely toxic to aquatic life.

The use of bio-based lubricants by industries is still in its infancy stage and there's much left to be done. The development of biolubricants based on estolides derivatives through oleic acid has been studies while only a limited number on ricinoleic acid being studied. Recent study showed *Ricinus communis* (castor bean) possessed high percentage of ricinoleic acid and can be used to produce estolides bio-based products [4]. Estolides are an oligomeric fatty acid produce from condensation of two different fatty acids with the presence of an acid catalyst [5]. Normally, they are found in triglycerides form in vegetable oils. Estolides have potential use as lubricants, plasticizers, cosmetic additives and printing ink components [6]. The aim of this study was to synthesize a new synthetic approach of producing estolide ester from a renewable resource which is later can be used as green-biolubricant.

## Materials and Methods

### Sample and Reagent

Samples of castor oil were collected from four difference areas; Meru-Kapar (Klang); Salak Tinggi(KL); Sungai Chua (Kajang) and Plant House (UKM, Bangi) in Selangor, Malaysia and solely synthesized. 2-ethylhexyl alcohol, lauric acid and percholoric acid were purchased from Sigma-Aldrich (USA). Hexane and potassium hydroxide were obtained from SYSTERM. All other chemicals and reagents were obtained from Aldrich Chemical (Milwaukee, WI). All materials were used without further purification. All organic extracts were dried using anhydrous magnesium sulfate (Aldrich Chemical).

### Synthesis

Samples went under pretreatment of drying (8[illegible] $^{o}$C, 8 h). Extraction was carried out for 6-12 h at 65°C in order to assure the oil was fully extracted. Collected oil was separated by using rotavapor. Synthesis of estolide 2-ethylhexyl ester were conducted based on Cermak et al., 2003 [7] with modification by using ricinoleic acid as first fatty acid reacted with lauric acid and capped with 2-ethylhexyl alcohol. Ricinoleic acid (50 g, 177 mmol) and lauric acid (17.75g, 88.5 mmol) were combined together and heated to 60 $^{o}$C under vacuum. Once the desired temperature was reached, 11.5 ml perchloric acid was added and stirred for 24 h. All the reactions were conducted in a three-neck round flask, connected to a circulating vacuum in a fume hood. After 24 h, 2-ethylhexyl alcohol (33.75 ml, 228.8 mmol, 29.8 g) was added to the vessel, vacuum was restored and the mixture was stirred for additional 2 h. The complete reaction was quenched by 25 g KOH in 90% ethanol/water (10 ml) solution. Solution was allowed to cool for 30 min. The organic layer was dried over sodium sulphate and filtered. The material was distilled at 105$^{o}$C to remove any excess alcohol and water contents.

### Characterization

NMR spectroscopy been used to detect $^{1}$H proton and carbon $^{13}$C in the estolide structure 1H and 13C NMR spectra were recorded using a JEOL JNMECP 400 spectrometer operating at 400.13MHz and 100.61 MHz, respectively. The spectrometer used a 5-mm broadband inverse Z-gradient probe in DMSO-d6 solvent (Cambridge Isotope Laboratories, Andover, MA) as solvent. Each spectrum was Fourier-transformed, phase-corrected, and integrated using a MestRe-C 2.3a software (Magnetic Resonance Companion, Santiago de Compostela, Spain). FTIR spectra were recorded neat on a Perkin Elmer GX FTIR Spectrophotometer. FTIR spectroscopy analysis was carried out to determine the functional group presence in estolide ester based on the spectrum peaks. Samples which were in liquid form were sandwiches between two sodium chloride (NaCl) plates while samples in solid form were diluted before being placed between two potassium bromide (KBr) plates. The functional group to be monitored for is ester carbonyl (1735 cm$^{-1}$), hydroxyl –OH (2900-3300 cm$^{-1}$), sp$^{3}$ stretching carbon (2800-3000cm$^{-1}$), long chain (720cm$^{-}$

$^{1}$) and other functional groups which may appear as a characteristic of the product. Spectrums for all raw materials (ricinoleic acid and 2-ethylhexyl alcohol) were compared to product's to observe the differences between each spectrum.

**Low temperature operability**

The pour point of a liquid is the lowest temperature at which it becomes semi solid and loses its flow characteristics. This method is routinely used to determine the low temperature flow properties of fluids [8]. Pour point values were measured according to ASTM D5949, a Standard Test Method for Pour Point of Petroleum Products (Automatic Pressure Pulsing Method). It uses automatic apparatus and yields pour point results in a format similar to the manual method (ASTM D97).

The D5949 test method determines the pour point in a shorter period of time than manual method D97. Less operator time is required to run the test using this automatic method. Additionally, no external chiller bath or refrigeration unit is needed. D5949 is capable of determining pour point within a temperature range of -57°C to +51°C. Results can be reported at 1°C or 3°C testing intervals. Generally, materials with low pour point exhibit improved fluidity at lower temperature than those in higher temperature. This test method has better repeatability and reproducibility than manual method D97. Each sample was run in triplicate and the reported average values are rounded to the nearest whole degree.

**Flash point value**

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the source of ignition is removed. The flash point is often used as a descriptive characteristic of liquid fuel, and it is also used to help characterize the fire hazards of liquids. "Flash point" refers to both flammable liquids and combustible liquids. The greater the flash point is, the greater the fire hazard [8]. Flash point determination was measured according to ASTM Standard D 56-79 using a Tag Closed Tester. Each sample was run in triplicate and the reported average values are rounded to the nearest whole degree.

**Viscosity index measurement**

Viscosity index (VI) is an arbitrary measure for the change of viscosity with temperature. It is used to characterize lubricating oil in the automotive industry. Viscosity was measured by using automated multi range viscometer tubes HV M472 obtained from Walter Herzog (Germany). Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at both 40°C and 100°C. The viscosity and viscosity index were calculated using ASTM method D 445-97 (ASTM D 445-97) and ASTM D 2270-93 (ASTM D 2270-93), respectively. The measurements were taken in triplicate and the average values were reported. The viscosity of liquids decreases as temperature increases. The viscosity of a lubricant is closely related to its ability to reduce friction. Generally, the least viscous lubricant which still forces the two moving surfaces apart is desired. If the lubricant is too viscous, it will require a large amount of energy to move (as in honey); if it is too thin, the surfaces will rub and friction will increase.

## Results and Discussion

### Synthesis of estolide 2-ethylhexyl ester

Acid-catalyzed transesterification reactions were conducted with solvent 2-ethylhexyl alcohol, in a three-neck round bottom flask under vacuum. Generally, formation of estolide ester is influences by two major factors; acid catalyst and the reaction temperature used. In this reaction, perchloric acid was chosen as catalyst due it provides significantly faster rate (5-8 times) of estolide formation compare to sulphuric acid and produce more yield of estolide [9]. Addition of sulphuric acid to unsaturated fatty acid will produce sulfated oils. The sulfated oil is stable at low temperature (≤ 20°C) in the presence of acid, but at elevated temperature (50°C), the sulphate esters quickly decompose, estolides and lactones are observed.

Estolide esters formation also influences by the temperature. At room temperature (27°C), the rate of reaction catalyzed by perchloric acid becomes slow. However, at higher temperature, the formation become too fast due to the rate is accelerated even though the concentration of perchloric acid is reduced and the side reactions begin to predominate, chiefly the formation of lactones [9]. Hence, an optimum temperature, 60°C has been applied in this study. Synthesis was carried out within 24 hours in order to assure all the reactions are complete.

Figure 1 shows ricinoleic acid tends to interact with OH group from lauric acid to form ester and capping the chain. Carbonyl group tends to form bonding with OH because carbonyl group are easier to disconnect compared to double bond, which is more stable. By capping the fatty ester, the compounds no longer had the opportunity to undergo either intra- or intermolecular hydrogen bond interaction [5]. Yield produced is about 82.25%.

**FTIR Characterization**

Synthesis of estolide 2-ethylhexyl ester was expected to produce unsaturated estolide as shown in Figure 1. FTIR spectrum in Figure 2 shown there is almost no OH peak appeared at region 3000-3400cm$^{-1}$ as water has been eliminated through hydrolysis process. A strong peak at 1738.23 cm$^{-1}$ indicates the presence of ester group in the compound as ester shows a strong peak at range 1750-1735 cm$^{-1}$ [10]. Precisely, C=O bands appear at 724.20 cm$^{-1}$ and 1738.23 cm$^{-1}$ .This assumption was supported by the presence of two C-O stretch bonds. At 1174.60 cm$^{-1}$ wave number which is more electronegative as the C-O group bonded to the acid backbone while ester with is less electronegative, which is C-O ester bonded to the ester backbone appeared at 1117.1[illegible] cm$^{-1}$. CH3 bands appear at range 1378.53-1559.43 cm$^{-1}$.

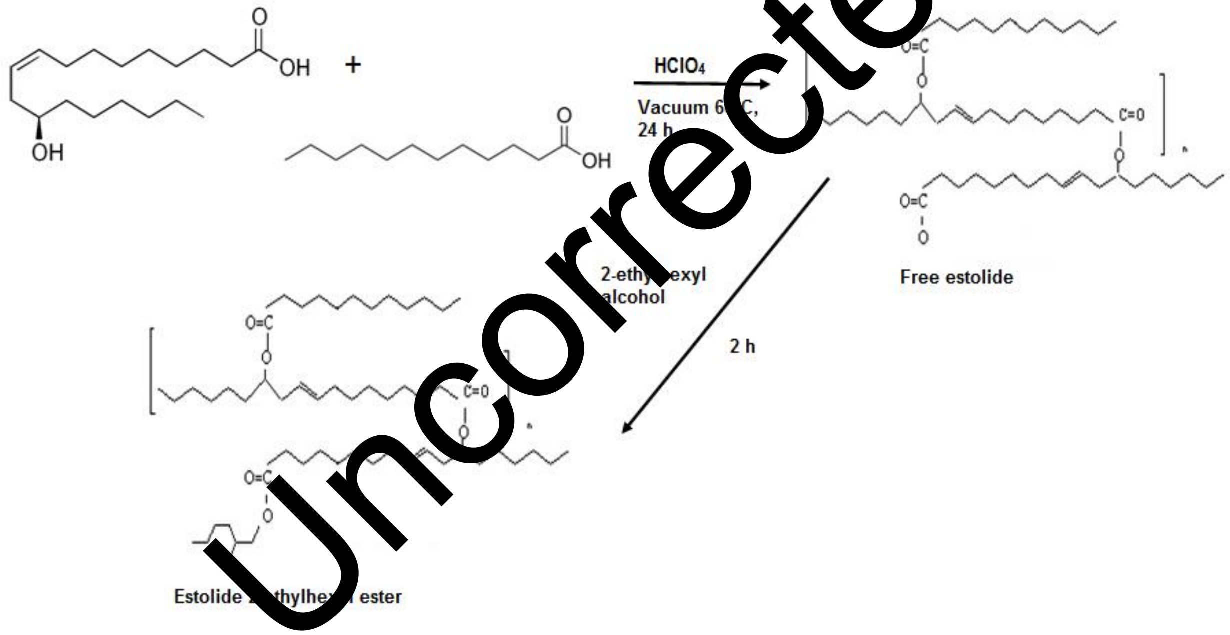

Figure 1: Synthesis of estolide 2-ethylhexyl ester

**NMR Characterization of estolide 2-ethylhexyl ester**

All synthesized compounds were verified by $^{1}$H and $^{13}$C NMR spectroscopy. The $^{1}$H-NMR spectrum for estolide 2-ethylhexyl ester shows in Figure 3 contains the expected estolide signals. The ester methine signal (Hm) at 2.157 ppm indicates the estolide linkage. Another distinctive feature is the α- methelyne proton shift at 4.5438 ppm adjacent to the acid and the α- methelyne proton shift at 3.8669 ppm adjacent to the ester (Table 1). The $^{13}$C NMR spectrum for estolide 2-ethylhexyl ester shows in Figure 4 contains some of the key features for a typical estolide and all the shift data are listed in Table 1. There are two carbonyl signals at 173.4091 ppm (acid) and 173.5697 ppm (ester). Methine carbons were appeared at 76.9122-77.5545 ppm which is common to estolides. Estolide ester is suggested to have ethylene peak at 130.6 ppm in the spectrum due to double bond from ricinoleic acid. However, spectrum of estolide 2-ethylhexyl ester shows inverse result where there is no ethylene peak or very small signal observed expected cause by the impurity of ricinoleic acid [5]

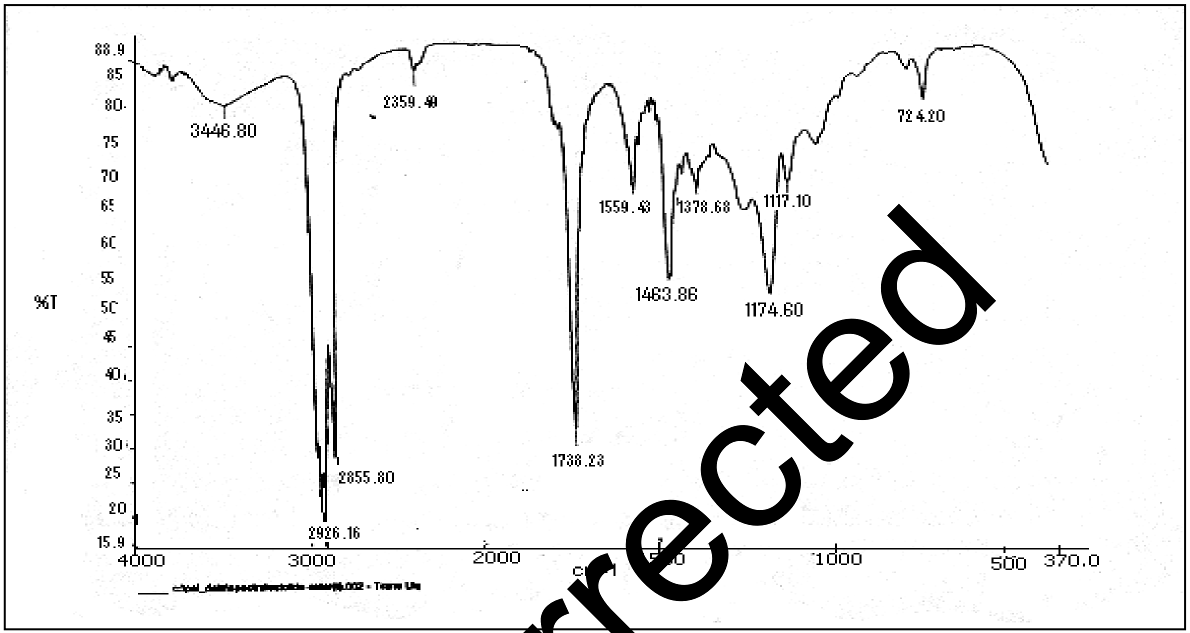

Figure 2: FTIR spectrum of estolide 2-ethylhexyl ester

Table 1: Data elucidation of $^{1}H$ & $^{13}C$ NM

| Node | Shift (ppm) | Group |
|---|---|---|
| **$^{1}H$ NMR** | | |
| $CH_3$ | 0.7710 | Methyl |
| $CH_2$ | 1.1641 | Methylene ($CDCl_3$ peak) |
| | 1.4929 | Methylene |
| | 4.5438 | Methylene (α- acid) |
| CH | 2.1570 | Methine (ester linkage) |
| | 3.8669 | Methine (α-ester) |
| **$^{13}C$ NMR** | | |
| $CH_3$ | 10.8630 - 13.9675 | Methyl |
| $CH_2$ | 22.9137 - 30.4300 | Methylene |
| | 64.7010 - 66.3602 | Methylene |
| CH | 38.7722 | Methine |
| | 76.9122 - 77.5545 | Methine ($CDCl_3$ peak) |
| C-O | 173.4091 | Carbonyl (acid) |
| | 173.5697 | Carbonyl (ester) |

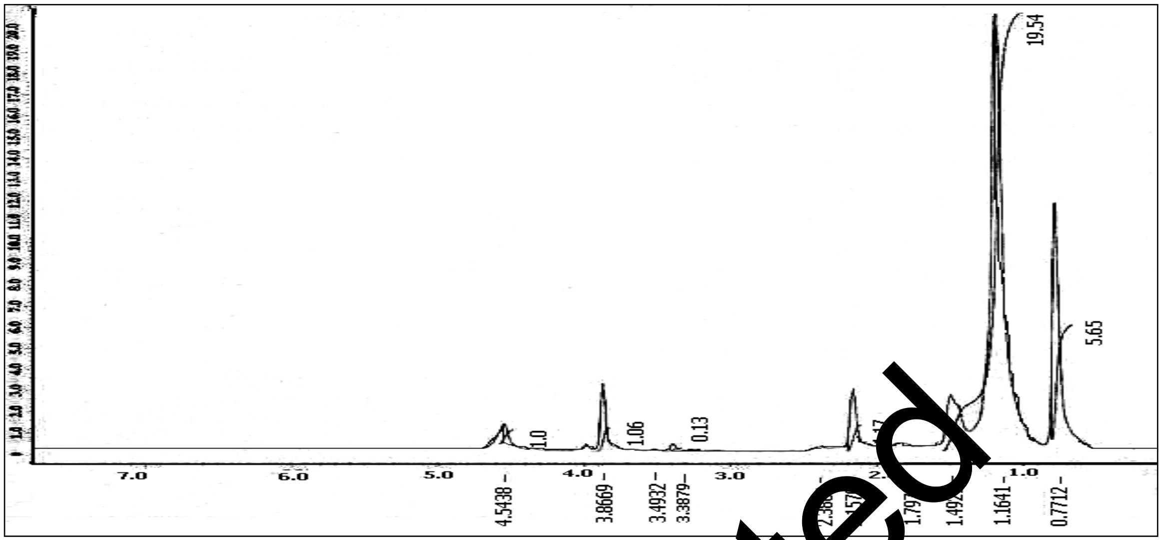

Figure 3: Spectrum of NMR $^1H$ estolide 2-ethylhexyl ester.

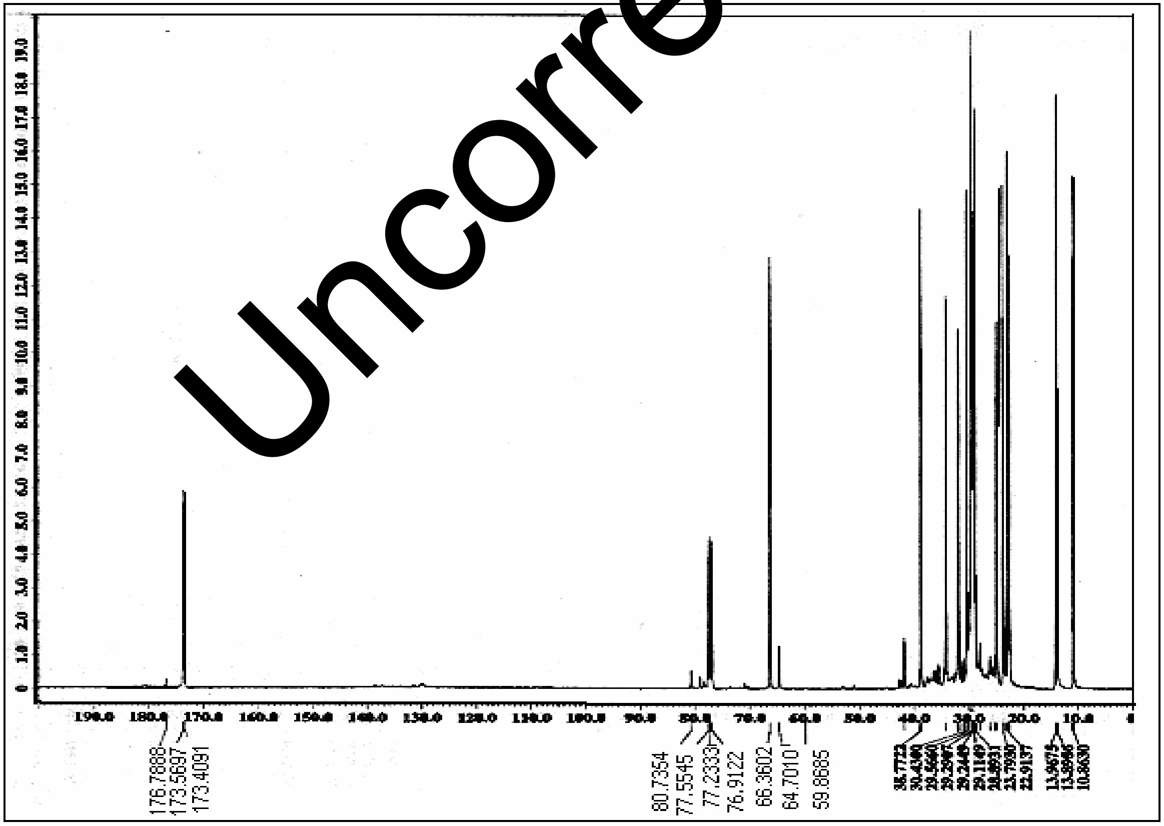

Figure 4: Spectrum of NMR $^{13}C$ estolide 2-ethylhexyl ester.

**Biolubricant Parameter**

The ability of a substance to remain as a liquid at low temperatures is an important attribute for a number of industrial materials, such as biolubricant, surfactants and fuels. The cold flow property of plant oils is extremely poor and this limits their use at low operating temperature especially as automotive and industrial fluids [8]. Plant oils have a tendency to form macrocrystalline structures at low temperatures through uniform stacking of the 'bend' triglyceride backbone. Such macrocrystals restrict the easy flow of the system due to loss of kinetic energy of individual molecules during self-stacking [11]. Cold flow properties of these samples were determined using their pour points. In practice, synthetic base stocks are produced from carefully-chosen and well-defined chemical compounds and by specific chemical reactions. The final base stocks are designed to have optimized properties and significantly improved performances features [12].

Even though vegetable based-lubricant possesses effective lubricant and great biodegradation properties, they are failing to meet lubricity need at cold temperature. To ensure quality of estolide lubricant achieve the market standards, pour point, flash point and viscosity test have been done. Lubricity properties of prepared compounds are summarized in Table 2.

Table 2: Pour point, flash point and viscosity of prepared products.

| Parameter | Value of estolide prepared | Reference value | Sources |
|---|---|---|---|
| Pour Point (°C) | -6 | -15 | Ref [13] |
| Flash point (°C) | 246 | 113 - 250 | Ref [14] |
| Viscosity (cps) | 179 | 1[illegible]2 - 1[illegible]6 | Ref [13] |

Pour point has been measured according to method 2.[illegible]. Branch chains of 2-ethylhexyl alcohol influenced the pour point value due to it will cause a dramatically decreasing of pour point. The more capping branches are, the higher potential of bond making thus will lowering the pour point value, In contrast, the shorter capping branches used will interrupt the interaction of bond making thus will increasing the pour point value [15]. Result in Table 2 shows pour point value of 2-ethylhexyl alcohol is -6 °C. This value has been compared with Ref [13] where they synthesized oleic acid with 2-ethylhexyl alcohol and has been capping with ricinoleic acid. At first, the obtained value before been capping with fatty acid was -3 °C and drop to -15 °C once has been capping with new fatty acid.

Ricinoleic acid from *Ricinus communis* oil is a unsaturated fatty acid which once it been capping with new fatty acid, the compound would not have any chances to interact either in inter or intramolecular forces with hydrogen bonds. This make the pour point value become even lower. The higher the unsaturated estolide is, the lower pour point obtained [5]. Estolide 2-ethylhexyl alcohol produced such a lower pour point as it was synthesized from unsaturated fatty acid.

Flash point is one of the important indicators in lubricant quality assurance. According to Ref [5], a good biolubricant posse's higher flash point values as the engine haven't set in fire even in higher flash point. This is an important criterion in major industrial machines as they involving high usage of temperature. Table 2 shows flash point of 2-ethylhexyl ester was 246 °C which is very high. There is no sudden increment has been recorded and this proven a good criteria of biolubricant.

The efficiency of the biolubricant in reducing friction and wear is greatly influenced by its viscosity. Generally, viscosity- temperature charts are available, making a good choice of a biolubricant operation temperature. The viscosity of a biolubricant is its tendency to resist flow. A biolubricant oil of high viscosity flows very slowly. The viscosity must always be high enough to keep a good oil film between the moving parts. Otherwise, friction will increase, resulting in power loss and rapid wear on the parts. The viscosity index, commonly designated as VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature. A low index means a steep slope of the curve, or a great variation of viscosity with change in temperature; high index means a flatter slope, or lesser variation of viscosity with the same changes in temperature [14].

Result in Table 2 shows a high value of viscosity index (VI). Vegetable oil and synthetic ester possesses way better viscosities compare to mineral oil and they are suitable to be used as lubricant [4]. However, due to the expensive price of derivatives synthetic ester, consumers are tends to choose vegetable oil as new alternative. According to Ref [13], viscosity increased with the increasing of oligomer amounts. In this context, viscosity index of estolide free acid were reported between 122-155 cps while viscosity of 2-ethylhexyl ester were recorded in higher range; 172-196 cps [13]. This is due to the existence of hydrogen bond with carboxylate group.

## Conclusion

Estolide 2-ethylhexyl ester was successfully synthesized between ricinoleic acid from castor oil and lauric acid with addition of 2-ethylhexyl alcohol. Perchloric acid has been used as catalyst. Data elucidation from FTIR and NMR described the characteristic of the product. Result shows significant value with the estimation and matched with the molecular structure, hence possibly been use as biolubricant material. Based on the results obtained, an increase in the chain length of the mid-chain ester had a positive influence on the low temperature properties of the products because they create a stearic barrier around the individual molecules and inhibits crystallization, resulting in lower pour point. The higher the unsaturated estolide is, the lower pour point obtained. Estolide 2-ethylhexyl alcohol produced such a lower pour point as it was synthesized from unsaturated fatty acid.

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