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Modification of Epoxidized Ricinoleic Acid for Biolubricant Base Oil With Improved Flash and Pour Points

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Low-temperature properties need to be improved before lubricant oils can receive wider recognition as biodegradable base oil. In the present work in order to produce ricinoleic acid based biolubricants with good flash and low pour points, epoxidized ricinoleic acid (ERA) was chemically modified. Epoxidized ricinoleic acid was reacted with various fatty acids in the presence of *p*-toluenesulfonic acid (PTSA) as a catalyst to give a ring-opened intermediate product. Isobutanol was used to esterify the carboxylic acid hydroxyl groups of the ring-opened products. Some physical properties of each synthesized compound was determined through its pour point, viscocity and flash point values. Furthermore, the chemical structure for each one was confirmed through its FTIR, ^{1}H NMR and ^{13}C NMR spectra.

Key Words: Epoxidized ricinoleic acid oil, Biolubricant, Pour point, Ring-opening reaction.

INTRODUCTION

For utilization of vegetable oils as biolubricants, the major problems of inadequate oxidative stability and poor low-temperature properties need to be resolved[1-3]. The poor oxidative stability of a vegetable oil is typically attributed to the rapid reactions occurring at the double-bond functional groups in the molecule. Free radical oxidation and ionic reaction of the double bond, including hydrogen abstraction, addition reaction, fragmentation, rearrangement, disproportionation reaction and polymerization are the major processes cause the problem[4,5]. Many research groups have focused on adding commercially available antioxidants to the oil, preparing new antioxidants, or genetically modifying plants from which vegetable oils are derived in an attempt to solve this problem[6]. Poor low-temperature properties include cloudiness, precipitation, poor flowability and solidification at relatively high temperatures[7]. Efforts have been made to improve the low-temperature properties by blending the vegetable oils with diluents such as poly α-olefin, diisodecyl adipate and oleates[8]. The other possible way to control these obstacles is structural modification of the oils by chemical reactions[3]. It has been reported that triacylglycerols with more diverse chemical structures have lower solidification temperatures[9,10]. Chemical modifications of the vegetable oils to give more complex structures should improve the low-temperature properties.

Castor oil (CO) is a versatile vegetable oil because of its unique composition, in which the main component is 12-hydroxy-9-*cis*-octadecenoic acid, the so-called ricinoleic acid, which represents 90 % of its "fatty acid" content.

The rich chemistry of raw castor oil is attributed to its structure (one double C=C and one -OH group per fatty acid chain), which makes it a good starting material for a wide range of applications such as biolubricants, coatings, nylon and organic intermediates for several industries[11]. In general, one of the most important modifications in vegetable oils is epoxidation[12]. Fig. 1 shows castor oil and epoxidized castor oil (ECO) structures. Epoxidized castor oil (ECO) is a promising intermediate, since the epoxy group is readily functionalized with a variety of compounds or can be used as latent polyols[13,14].

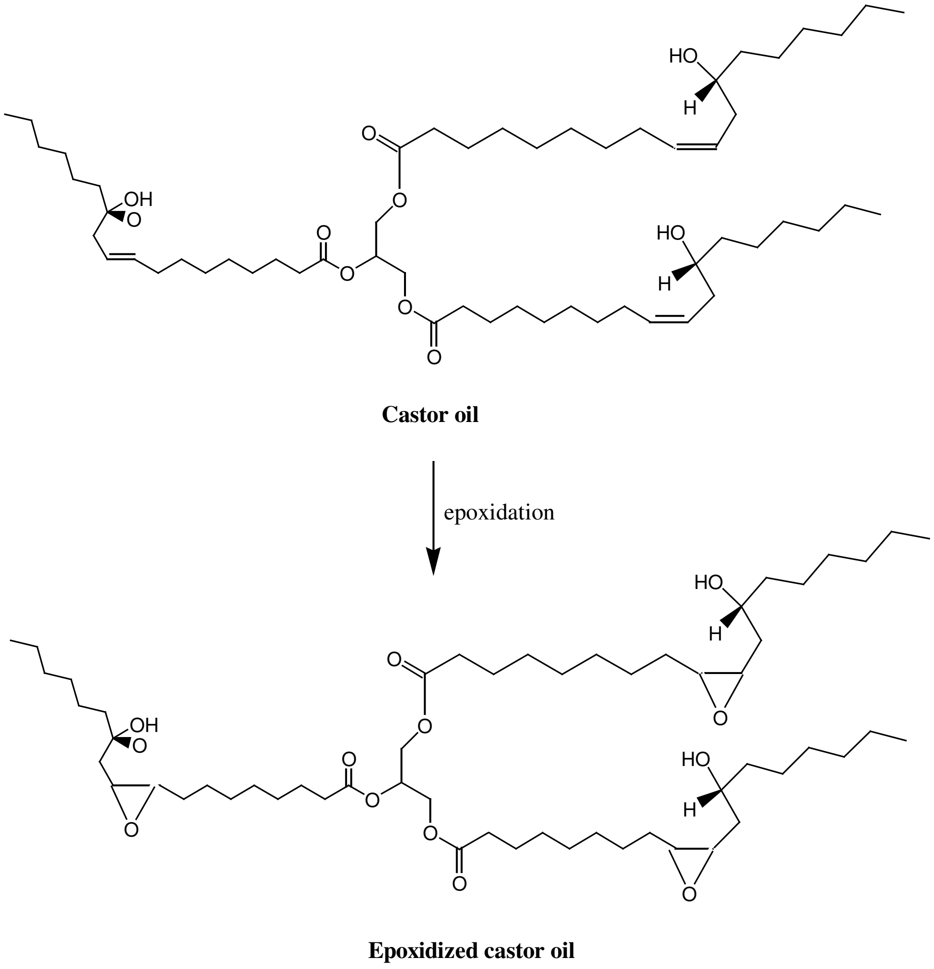


Fig. 1. Castor oil and epoxidized castor oil structures

On the other hand, another important modifications of the carboxyl group of the fatty acid chain is the esterification of the fatty acids hydroxyl group. Esters in particular have better lubricity than mineral oils or polyalphaolefins (PAO) since they have high polarity due to the presence of lone pair electrons on the oxygen atom of the ester group. Such polar molecules are very effective as boundary lubricants, as they tend to form stable physical bonds with metal surfaces. In spite of their many advantages, the application of plant oil esters as lubricants at present is limited by their high price[15].

In the present work we focused on the development of ester-based biolubricants from epoxidized ricinoleic acid (ERA) and found that the ring opening reaction of epoxidized ricinoleic acid followed by esterification of fatty acids hydroxyl group gave good biolubricant candidates with improved flash and pour points.

EXPERIMENTAL

Ricinoleic acid (80 %), formic acid (88 %) and hydrogen peroxide (30 % solution) were obtained from Fluka (Germany). All other chemicals and reagents were obtained from Aldrich Chemicals Company (USA) and used without further purification.

General procedure

Epoxidation of ricinoleic acid: Hydrogen hydroxide solution (30 % in H_2O, 8.0 mL) was added slowly into a stirred solution of ricinoleic acid (90 %, 15 g) in formic acid (88 %, 14 mL) at 4 ºC (ice bath). The reaction proceeded at room temperature with vigorous stirring (900 rpm) until the formation of a powdery solid was noticed in the reaction vessel (2-5 h). The solid was collected *via* vacuum filtration, washed with H_2O (chilled, 3 × 10 mL) and placed for 12 h under high vacuum to provide epoxidized ricinoleic acid (ERA) as a white, powdery solid (14.7 g, 93 %).

Preparation procedure of 10,12-dihydroxy-9-acyloxystearic acid (2-8): To a mixture of epoxidized ricinoleic acid (31 g), 5 g of *p*-toluene sulfonic acid (PTSA) and toluene, fatty acids (6 g) was added and the mixture was stirred under the reaction conditions shown in Table-1. After reaction termination, the heating was stopped and the mixture was left to stand overnight at ambient room temperature. The mixture was washed with the water next day. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using the vacuum evaporator.

Preparation procedure of isobutyl 10,12-dihydroxy-9-acyloxystearate (9-15): Sulphuric acid (conc. H_2SO_4, 10 mol %) was added into a stirred suspension of 10,12-dihydroxy-9-acyloxystearic acid (compound **2-8**, 3.35 mmol) in the isobutanol (3.35 mL). The suspension was heated with stirring at 60 ºC for 10 h. Hexanes (5 mL) was then added and the solution was washed with $NaHCO_3$ (sat. aq., 1 × 0.5 mL) and brine (2 × 1 mL), dried ($MgSO_4$), filtered, concentrated *in vacuo* and placed for 6 h under vacuum to yield the title products.

Identification: Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer GX FTIR spectrophotometer (USA). The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-ECP 400 spectrometer (400 MHz ^{1}H/100.61 MHz ^{13}C) using DMSO-d_6 as a solvent in all experiment. All the physical properties analyses were performed in duplicate according to the standard methods (AOCS official method) for flash point and pour point. Viscosity measurements were made using calibrated Brookfield Viscometer. The spindle size 4 was used with the speed of 100 rpm. Viscosity reading is in centipoise (cp) and the unit is in mPas (multipascal second).

RESULTS AND DISCUSSION

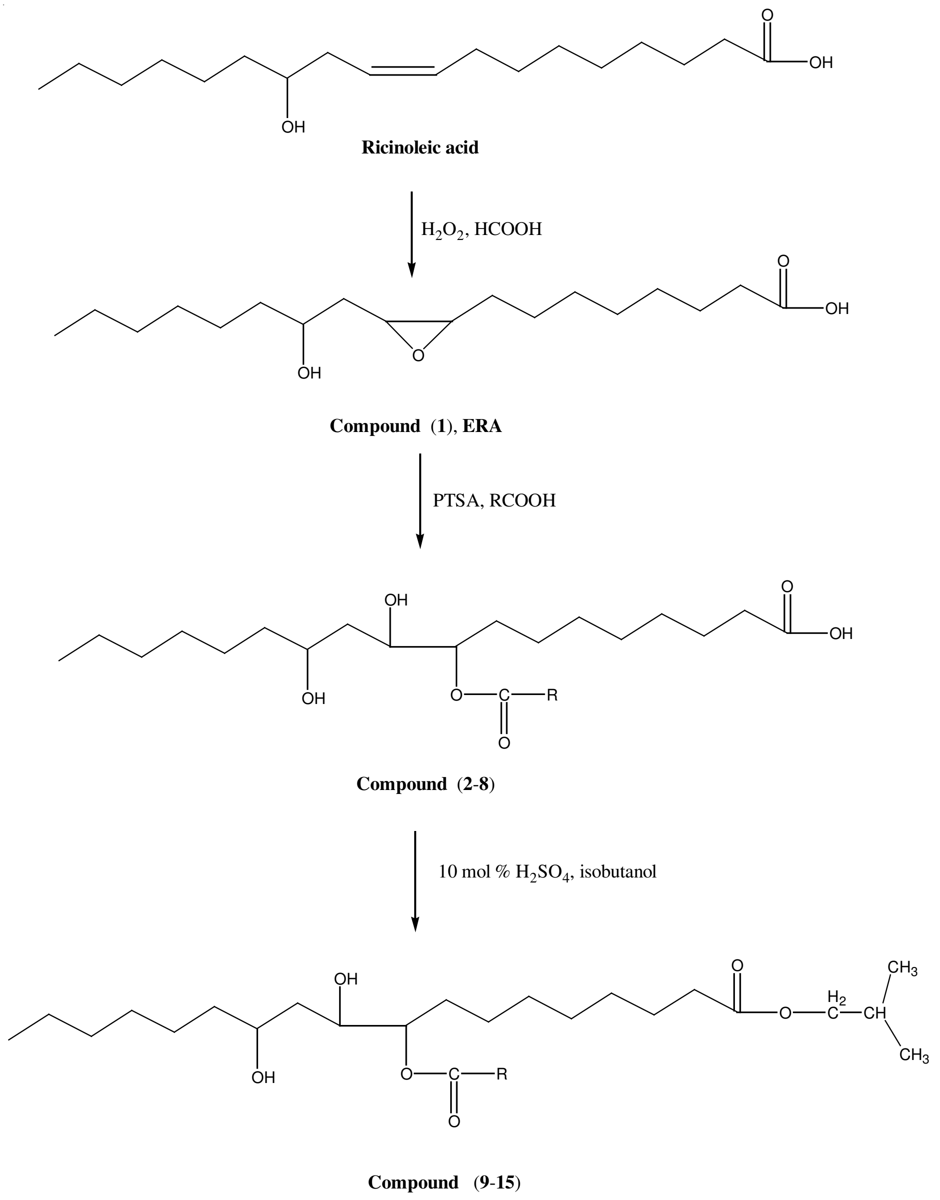
Synthesis: Reaction of epoxidized ricinoleic acid with fatty acids in the presence of a catalytic amount of *p*-toluene sulfonic acid gave the ring-opened products, as shown in **Scheme-I**. For investigation of the alkyl group effect on flash point and low-temperature properties, different fatty acids including octanoic, nonanoic, lauric, myristic, palmitic, stearic and behenic acids were used in the oxirane opening reaction.

As summarized in Table-1, different fatty acids required different conditions to complete the reaction. Longer or bulkier fatty acids required longer reaction times and/or higher temperatures to complete the ring-opening reaction. For example, while 8 h at 100 ºC was required to complete the reaction with octanoic acid, a longer reaction time (15 h) at 130 ºC was required for the higher molecular weight fatty acids such as behenic acid.

TABLE-1
REACTION CONDITIONS FOR OXIRANE RING-OPENING STEP PRODUCTS OBTAINED FROM EPOXIDIZED RICINOLEIC ACID AND FATTY ACIDS

Compounds	Fatty acids	Reaction conditions
2	Octanoic acid	100 ºC, 8 h
3	Nonanoic acid	100 ºC, 8 h
4	Lauric acid	115 ºC, 10 h
5	Myristic acid	115 ºC, 12 h
6	Plamitic acid	120 ºC, 13 h
7	Stearic acid	125 ºC, 13 h
8	Behenic acid	130 ºC, 15 h

FTIR spectra: The reaction was monitored by following the disappearance of the epoxy group C-O-C stretching vibrations at 845 and 822 cm^{-1} in the IR spectrum and stopped when the ring-opening reaction was completed. Beside this, the FTIR spectra of ricinoleic acid and epoxidized ricinoleic acid show a C=O stretching bands at 1710, 1706 cm^{-1}, respectively. Compare to that of compounds **2** to **8**, the stretching band of C=O appear at about 1722 and 1705 cm^{-1} attributed to carbonyl stretching frequencies of ester and carboxylic acid moieties[16], respectively. While after esterification with isobutanol, FTIR spectra of compounds **9** to **15** show only one C=O stretching vibration at about 1718 cm^{-1} for ester group. Some characteristic data are recorded in Table-2.



Compound (9-15)

Scheme-I: Schematic reactions of epoxidation, ring opening and esterification of ricinoleic acid derivatives (ERA = epoxidized ricinoleic acid; PTSA = *p*-toluenesulfonic acid; RCOOH = octanoic, nonanoic, lauric, myristic, palmitic, stearic and behenic acids; H_2SO_4 = sulfuric acid)

^{1}H NMR spectra: The ring opening reaction's completion was further confirmed by checking disappearance of peaks at 2.8-3.0 ppm in the ^{1}H NMR spectrum corresponding to hydrogens in the epoxy ring[17]. Beside this, the ^{1}H NMR spectra for the products showed some of the key features for a typical ring opening and esterification

TABLE-2
CHARACTERISTIC FTIR DATA OF PREPARED PRODUCTS

Compd.	ν(O-H)	ν(C-H) aliphatic	ν(C=O)	C=C	ν(C-O-C)
1	3420	2930, 2835	1706	1623	845, 822
2	3422	2924, 2832	1718, 1706	-	-
3	3418	2934, 2837	1721, 1706	-	-
4	3416	2928, 2842	1722, 1705	-	-
5	3418	2929, 2853	1718, 1706	-	-
6	3323	2915, 2824	1720, 1705	-	-
7	3421	2930, 2832	1723, 1708	-	-
8	3326	2932, 2839	1724, 1705	-	-
9	3427	2931, 2829	1718	-	-
10	3425	2934, 2827	1720	-	-
11	3430	2938, 2834	1722	-	-
12	3427	2931, 2834	1719	-	-
13	3426	2935, 2827	1718	-	-
14	3429	2937, 2854	1717	-	-
15	3428	2948, 2842	1720	-	-

reactions. By analogy, the shift value for aliphatic protons appeared at about 1.30-2.53 ppm. However, the methine proton signal was shifted upfield at about 4.62-5.33 ppm which indicative the presence of this type of protons[18]. Another distinctive features are the three hydroxyl proton shift at about 8.13 (C_{12}(OH)), 8.43 (C_{10}(OH)) and 8.67 (C_1(OH)) ppm which confirmed the presence of three different -OH groups in the structure of compounds **2** to **8**. Furthermore, the most important features for the success of esterification reaction are the presence of only two hydroxyl signals at about 8.54 (C_{12}(OH)) and 8.86 (C_{10}(OH)) ppm in the ^{1}H NMR spectra for compounds **9** to **15**. Table-3 shows the most characteristic ^{1}H NMR data for these compounds.

^{13}C NMR spectra: The ^{13}C NMR data of the prepared compounds are presented in Table-4. The ^{13}C NMR confirmed two carbonyl resonances at about 167.53 ($-C_9-O-\underline{C}-R$) and 172.48 ($-C_1-$) ppm for compounds **2** to **15**. The ^{13}C NMR spectra indicate the existence of carbonyl groups in their structure. The other distinctive signals were methine carbons at about 62.29 and 66.43 ppm, which are common for these types of compounds[19].

Physical properties of the prepared compounds: The ability of a substance to remain liquid at low temperatures is an important attribute for a number of industrial materials, such as biolubricants, surfactants and fuels. The pour points (PP) of the ring-opened and esterification products were measured by using a standard method (ASTM D 97)[20] and the results are shown in Table-5. The relatively high pour point of the ring-opening reaction products may be attributed to hydrogen bonding of the three hydroxy groups present in the products produced after the ring-opening reaction. For transformation of the hydroxyl groups to ester groups, the products were reacted

TABLE-3
CHARACTERISTIC ^{1}H NMR DATA OF PREPARED PRODUCTS

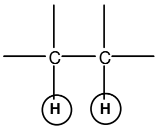
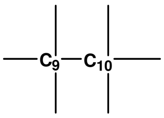
Compd.	Aliphatic protons		O-H
2	1.30-2.54	4.60-5.33	8.14, 8.42, 8.65
3	1.32-2.53	4.63-5.36	8.13, 8.44, 8.68
4	1.31-2.55	4.62-5.31	8.11, 8.45, 8.69
5	1.29-2.53	4.61-5.32	8.12, 8.42, 8.66
6	1.28-2.54	4.60-5.32	8.12, 8.40, 8.65
7	1.30-2.52	4.62-5.34	8.13, 8.42, 8.67
8	1.32-2.54	4.63-5.32	8.10, 8.43, 8.68
9	1.30, 2.53	4.61-5.31	8.53, 8.87
10	1.27-2.53	4.60-5.28	8.54, 8.85
11	1.32-2.54	4.62-5.33	8.52, 8.84
12	1.28-2.52	4.60-5.32	8.55, 8.87
13	1.33-2.55	4.63-5.34	8.53, 8.88
14	1.29-2.53	4.61-5.32	8.52, 8.87
15	1.30-2.53	4.60-5.31	8.56, 8.84

TABLE-4
CHARACTERISTIC ^{13}C NMR DATA OF PREPARED PRODUCTS

Compd.	Aliphatic carbons		C=O
2	21.87-38.32	62.30, 65.40	166.50, 173.46
3	20.76-39.44	63.32, 66.44	167.68, 172.50
4	21.84-38.31	61.28, 67. 42	168.57, 173.38
5	22.21- 39.32	64.27, 65. 39	168.41, 173.24
6	23.14-38.31	62.33, 65. 74	166.50, 172.46
7	20.34-38.30	63.30, 67. 02	167.54, 171.98
8	22.87-38.31	62.76, 67. 13	168.18, 171.39
9	22.82-39.29	61.30, 66. 69	166.54, 173.10
10	20.94-39.31	62.46, 66. 41	167.56, 173.08
11	21.96-39.29	62.29, 66. 43	166.78, 171.92
12	22.42-39.36	62.45, 66. 50	168.23, 172.14
13	22.36-39.31	62.37, 66. 39	167.53, 173.79
14	20.75-38.30	63.28, 65. 40	166.87, 173.63
15	22.84-38.82	63.29, 65. 41	166.46, 173.15

with isobutanol at 60 °C for 10 h. An improvement in the cold flow behaviour of diesters for compound **9** to **15** was obtained over that of the precursors **2** to **8**. In general, as the chain length of the mid-chain ester is increased, a corresponding improvement in the pour point of a biolubricant oil[21] was observed. This is due to the greater ability of the longer chain esters to disrupt crystalline formation at reduced temperatures. For example, comparison between of compound **12** (R = myristyl; PP = -30 ºC) and compound **13** (R = palmityl; PP = -37 ºC) (**Scheme-I**) reveals an improvement in pour point as the mid-chain ester length (R) was increased. A similar trend was exhibited when comparing compounds **9**, **10**, **11**, **14** and **15**, which can be expressed as R: octanoyl to behenyl. It can be assumed that the presence of a large branching point on the fatty acid molecule create a steric barrier around the individual molecules and inhibits crystallization, resulting in lower pour point. Furthermore, the nature of the end-chain ester group also plays a role in the cold flow behaviour of diesters, branching in the end-chain ester lowers pour point[22]. The results confirmed that increases in viscosity corresponded to longer chain of the mid-chain group. This result can attribute to an overall increase in the molecular weights of the products resulting from the increased chain length introduced by the ester functionality. Table-5 summarized the physical properties and the yields for the above mentioned compounds.

TABLE-5
POUR POINT, FLASH POINT, VISCOSITY AND PERCENTAGE YIELD OF PREPARED PRODUCTS

Compd.	Pour point (ºC)	Flash point (ºC)	Viscosity (cp)	Yield (%)
2	-10	145	65	87
3	-13	189	87	65
4	-15	163	110	63
5	-17	202	132	97
6	-18	192	157	74
7	-20	264	174	69
8	-23	295	185	83
9	-25	258	213	90
10	-26	134	211	87
11	-29	115	226	63
12	-30	160	230	77
13	-37	231	246	82
14	-40	188	258	80
15	-43	223	273	91

Conclusion

The key step in the three step synthesis of oleochemical diesters entails a ring opening esterification of epoxyoleic acid using aliphatic fatty acids in toluene and in the presence of *p*-toluenesulfonic acid as catalyst. The ring opening products (compounds **2-8**) have relatively high pour points due to the high interaction between the hydroxyl groups (hydrogen bonding) of these compounds and this may attributed to the crystal growth process at low temperature. On the other hand, increasing chain length of the mid-chain ester and branching in the end-chain ester had a positive influence on the low temperature properties of diester compounds **9-15**.

At low temperature, biolubricant oils have a tendency to form macro-crystalline structures through uniform stacking. The presence of long chains in the middle and branching at the end of the molecule will disrupt this stacking process and results in improved low temperature properties.

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