

Synthesis and Characterization of Esters Derived from Ricinoleic Acid and Evaluation of their Low Temperature Property

(Sintesis dan Pencirian Terbitan Ester daripada Asid Risinoleik dan Penilaian Sifat Suhu Rendah)

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ABSTRACT

A series of ester compounds derived from ricinoleic acid to be used as biolubricants base stock have been synthesized. The resulting products were confirmed by FTIR and NMR analyses. The synthesis was carried out in three stages: epoxidation of ricinoleic acid; synthesis of 10,12-dihydroxy-9-acyloxystearic acid from epoxidized ricinoleic acid with various fatty acids and esterification of the acyloxystearic acid products with octanol to yield octyl-10,12-dihydroxy-9-acyloxystearate. The viscosities, flash points and pour points behavior of the products were measured. The resulting esters had an increase in molar weight and viscosity and decrease in pour points as compared to ricinoleic acid.

Keywords: Biolubricants; chemical modification; epoxidation; ricinoleic acid

ABSTRAK

Suatu siri sebatian ester terbitan asid risinoleik untuk kegunaan minyak asas biolubrikan telah disediakan. Produk terhasil dikenal pasti melalui analisis FTIR dan NMR. Sintesis telah dilakukan melalui tiga langkah: pengepoksidaan asid risinoleik; sintesis 10,12-dihidroksi-9-asiloksistearik daripada asid risinoleik terepoksida dengan pelbagai asid lemak dan pengesteran asiloksistearik dengan oktanol untuk menghasilkan oktil-10,12-dihidroksi-9-asiloksistearat. Nilai kelikatan, takat kilat dan takat tuang produk yang terhasil telah ditentukan. Hasil kajian mendapati bahawa produk ester yang terhasil menunjukkan peningkatan dalam berat molekul dan nilai kelikatan serta penurunan dalam nilai takat tuang berbanding dengan asid risinoleik.

Kata kunci: Asid risinoleik; biolubrikan; modifikasi kimia; pengepoksidaan

INTRODUCTION

Recently, the world has been confronted with an energy crisis due to the depletion of natural resources and increased environmental threats. This situation has prompted the search for alternative fuels that are not only sustainable but also environmentally friendly. For developing countries, fuels of bio-origin (alcohol, plant oils, biomass, biogas & synthetic fuels) are of particular interest, as these fuels can be used directly as substitutes for conventional fuels, whereas others require modifications prior to use.

Plant oils primarily consist of triacylglycerols, the chemical structure of which is shown in Figure 1. Fatty acids found in natural plant oils differ in chain length and number of double bonds (Moser 2009; Salimon et al. 2011a). The composition of fatty acids is determined by the ratio and position of carbon-carbon double bonds. Long carbon chains is generally contain either one, two or three double bonds, which represent oleic, linoleic and linolenic fatty acid components, respectively (Metzger 2009).

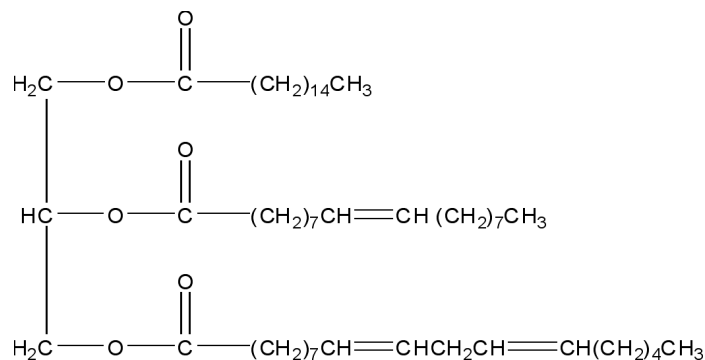


FIGURE 1. Structure of a typical triacylglycerol molecule

Most of plant-based oils contain at least four and up to twelve different types of fatty acids. The proportions of fatty acids in the oils depend not only on the type of plant, but also on the climate, weather and available nutrients. For example, castor bean oil consists of glycerol and several fatty acids with different physical and chemical properties. The main component of castor bean oil is ricinoleic acid, which constitutes up to 90% of the oil, while the remaining components consist of small amounts of saturated and unsaturated fatty acids (Table 1) (Salimon et al. 2010; 2011b). The high content of ricinoleic acid accounts for the versatile applications of castor oil in the chemical industry, which makes castor oil very valuable (Cermak et al. 2007; Matthew et al. 2007).

TABLE 1. Composition of castor oil

Fatty acid	Molecular formula	Percentage (%) *
Palmitic	$C_{16}H_{32}O_2$	0.8– 1.1
Stearic	$C_{18}H_{36}O_2$	0.7– 1.0
Oleic	$C_{18}H_{34}O_2$	2.2– 3.3
Linoleic	$C_{18}H_{32}O_2$	4.1– 4.7
Linolenic	$C_{18}H_{30}O_2$	0.5– 0.7
Ricinoleic	$C_{18}H_{34}O_3$	87.7–90.4

*Salimon (2010)

The triacylglycerol structure, which contains long, polar fatty acid chains, is desirable for boundary lubrication because it is capable of forming biolubricant films that interact strongly with metallic surfaces, reducing both friction and wear. Fatty acids, which contain triacylglycerols, are therefore thought to be key substances involved in lubricity (Salih et al. 2011a; Salimon et al. 2011c).

The use of renewable feedstocks, such as plant oils, to obtain industrial products has become increasingly important (Salih et al. 2011b). The development of efficient and environmentally benign pathways that can produce valuable products is desirable (Joseph 2007). This strategy can decrease our dependence on non-renewable and limited resources such as mineral oil. The presence of one or more double bonds in plant oils serves as a handle for chemical modifications (Salimon et al. 2010a; Salimon & Salih 2010b). The oxidative stability of plant oil can be improved by saturating the double bond functionality and thereby produce a class of biolubricants. Moreover, double bonds can undergo additional reactions such as acylation, isomerization, metathesis, hydroxylation, oxidative cleavage, carboxylation and epoxidation (Sharma et al. 2006).

Due to the reactivity of the oxirane ring, which results from the epoxidation of double bonds, a wide range of synthetic reactions can be carried out under mild reaction conditions. For example, the epoxide can react

with different nucleophiles to produce alcohols, diols, alkoxyalcohols, hydroxyl esters, *N*-hydroxyalkylamides, mercaptoalcohols and aminoalcohols (Campanella et al. 2008). Among these products, hydroxy esters, which resemble the structure of castor oil, can be used as biolubricants, polyurethane foams or casting resins. The physical properties of biolubricants derived from hydroxy esters can be further altered using different carboxylic acids that modify the length and size of the carbon chain and the molecular structures of mid acyloxy groups (Salimon et al. 2010c).

Here, we report the ring opening reaction of epoxidized ricinoleic acid (ERA) by the nucleophilic addition of different carboxylic acids in the presence of PTSA as a catalyst to give 10,12-dihydroxy-9-acyloxystearic acid (DHASA). Esterification of DHASA resulted in the formation of octyl-10,12-dihydroxy-9-acyloxystearate (ODHAS). This paper discusses the synthesis, characterization and physical parameters of these products.

MATERIALS AND METHODS

Ricinoleic acid, formic acid (88%) and hydrogen peroxide (30% solution) were obtained from ChemR (Poland). Octanoic, nonanoic and lauric acids were obtained from Fisher Scientific. Myristic, palmitic, stearic and behenic acids were obtained from Merck. PTSA, octanol and sulfuric acid were obtained from Aldrich. All materials were used without further purification. All organic extracted were dried using anhydrous magnesium sulfate.

SYNTHESIS OF EPOXIDIZED RICINOLEIC ACID (ERA)

A solution of hydrogen peroxide solution (30% in H_2O , 8.0 mL) was slowly added to a stirred solution of ricinoleic acid (RA) (90%, 15 g) dissolved in formic acid (88%, 14 mL) at 4°C (ice bath). The reaction proceeded at room temperature with vigorous stirring (900 rpm) until a powdery solid formed in the reaction vessel (2-5 h). The solid was collected via vacuum filtration, washed with H_2O (chilled, 3×10 mL) and dried for 12 h under high vacuum to provide epoxidized ricinoleic acid (ERA) as a white, powdery solid (14.7 g, 93%).

SYNTHESIS OF 10,12-DIHYDROXY-9-ACYLOXYSTEARIC ACID (DHASA)

Fatty acids (6 g) were slowly added to a mixture of ERA (31 g) and *p*-toluenesulfonic acid (PTSA) (5 g) in toluene over 1.5 h and the temperature of the reaction mixture was kept under 70-80°C. The reaction mixture was subsequently heated to 90-100°C and refluxed for 3 h. After the reaction completed, the solution was allowed to cool to room temperature and stirred overnight. The next day, the mixture was washed with water, the organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using the vacuum evaporator.

SYNTHESIS OF OCTYL 10,12-DIHYDROXY-9-ACYLOXYSTEARATE (ODHAS)

The reaction scheme for the formation of the diesters is shown in Figure 2. Sulfuric acid (conc. H_2SO_4 , 10 mol-%) was added to a stirred suspension of DHASA (3.35 mmol) in octanol (3.35 mL). The suspension was stirred and heated at 60°C for 10 h. Next, hexane (5 mL) was added and the solution was washed once with saturated aqueous NaHCO_3 (0.5 mL) and brine (2×1 mL), dried (MgSO_4), filtered and concentrated under vacuum for 6 h to yield ODHAS.

PRODUCT CHARACTERIZATIONS

Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer GX FTIR spectrophotometer (USA). The ^1H - and ^{13}C -NMR spectra were recorded on a JEOL JNM-ECP 400 spectrometer (400 MHz and 100.61 MHz respectively) using DMSO-d_6 as a solvent in all experiments. Pour point values were measured according to the ASTM D5949 method using a Phase Technology Analyzer, Model PSA-70 S (Hammersmith Gate, Richmond, B.C., Canada). All analyses of the physical properties of these compounds were performed in duplicate according to standard methods (AOCS official methods) for determining flash points and pour points. The dynamic viscosity at 25°C was measured on a Brookfield, DV-III programmable rheometer (Middleboro, MA) equipped with a spindle (size 4) at a speed of 100 rpm. Viscosity was described in terms of centipoise (cp) with millipascal-second (mPa s) units.

RESULTS AND DISCUSSION

EPOXIDATION, RING OPENING AND ESTERIFICATION

The first step in the synthesis of ODHAS is the epoxidation of ricinoleic acid, as shown in Figure 2, using formic acid and hydrogen peroxide to produce epoxidized ricinoleic acid (ERA). Many nucleophilic reagents are known to add to and open oxirane rings. In this work, ring opening of ERA was achieved using octanoic, nonanoic, lauric, myristic, palmitic, stearic and behenic acids to give the respective 9(10)-hydroxy-10(9)-ester derivatives of ricinoleic acid (DHOSA, DHNSA, DHLA, DHMSA, DHPSA, DHSSA, DHBSA). Diesters-derivatives of 10,12-dihydroxy-9-acyloxystearate were prepared by the esterification of the seven corresponding acyloxy-derivatives using octanol and sulfuric acid. The yields of the synthesized compounds are summarized in Table 2.

The straight forward epoxidation of oleic acid was closely monitored to avoid the undesired synthesis of 9,10-dihydroxyoctadecanoate, which forms at elevated reaction temperatures or if the reaction is allowed to proceed for too long. During this synthesis, a mixture of positional isomers is always formed, with the hydroxy moiety positioned on either the 9 or 10 carbon and the ester functionality on other adjacent carbon (Moser & Erhan 2007). No attempt to separate the isomers was made due to

associated cost in terms of time and money. If this synthesis is eventually adopted for commercial use, the production costs relating to the synthesis and purification steps are of paramount importance. Therefore, the diesters here were tested for their low temperature behaviors without further purification.

NMR AND IR SPECTRA

All synthesized compounds were characterized by ^1H and ^{13}C NMR spectroscopy. Significant signals in the ^1H spectrum of ERA between 2.2 and 2.4 ppm correspond to protons on the quaternary carbons of the oxirane ring, whereas a doublet in the ^{13}C spectrum between 56.82 and 56.86 ppm corresponds to the carbons of the oxirane ring. Furthermore, the ^1H spectrum of ERA showed singlet signals at 9.15 and 9.32 ppm that represent protons of the OH groups (Campanella et al. 2010). Furthermore, a singlet at 9.12-9.29 ppm represents the OH, and the bands at 2.03-3.64 ppm correspond to $-\text{CH}_2$ groups in DHASA. The ^1H spectrum of ODHAS contains low intensity multiplet signals at 9.18-9.35 ppm and 2.05-3.60 ppm. The intense singlet at 3.68 ppm is attributed to the hydrogens of the methyl groups. Broad lines at 1.41-1.82 ppm and 1.3 ppm represent the hydrogens of CH_2 groups. In the ^{13}C NMR spectra, there were triplet peaks at 173.1 ppm, which were attributed to the ester groups (Adhvaryu et al. 2005).

Ester functional group structures were also confirmed by IR spectral analysis. Bands representing ester $\text{C}=\text{O}$ group (1740 cm^{-1}), CH_3 group (1376 cm^{-1}), OH group ($3478\text{-}3443\text{ cm}^{-1}$) and $\text{C}-\text{O}-\text{C}$ functionality ($1000\text{-}1100\text{ cm}^{-1}$) were clearly visible in the spectra (Sliverstien et al. 2005). However, the applied spectroscopic methods were not able to determine whether the diester derivatives contain hydroxyl or acyloxy groups at the 9 and 10 positions.

PRODUCTS PARAMETERS

The physico-chemical properties of synthetic products are summarized in Table 2. Due to the poor low temperature flow property of plant oils, this oil has limited use as an automotive or industrial fluid. The pour point (PP) of a biolubricant is a good indicator of its low temperature fluidity. Plant oils have a tendency to form macro-crystalline structures at low temperatures due to uniform stacking of the 'bent' triglyceride backbone. These macro-crystals restrict the flow of the system due to a loss in kinetic energy of individual molecules during self-stacking (Hwang & Erhan 2001).

Seven different fatty acids, namely octanoic, nonanoic, lauric, myristic, palmitic, stearic and behenic acids, were chosen to investigate the effect of various alkyl groups on the low temperature properties of diester fluids. These fatty acids were chosen based on the length of their backbone carbon chains, which were medium ($\text{C}_8\text{-C}_{12}$) to long ($\text{C}_{14}\text{-C}_{22}$). The presence of long saturated fatty acids in the compounds does not allow individual molecules easily stack due to disruption in the symmetry

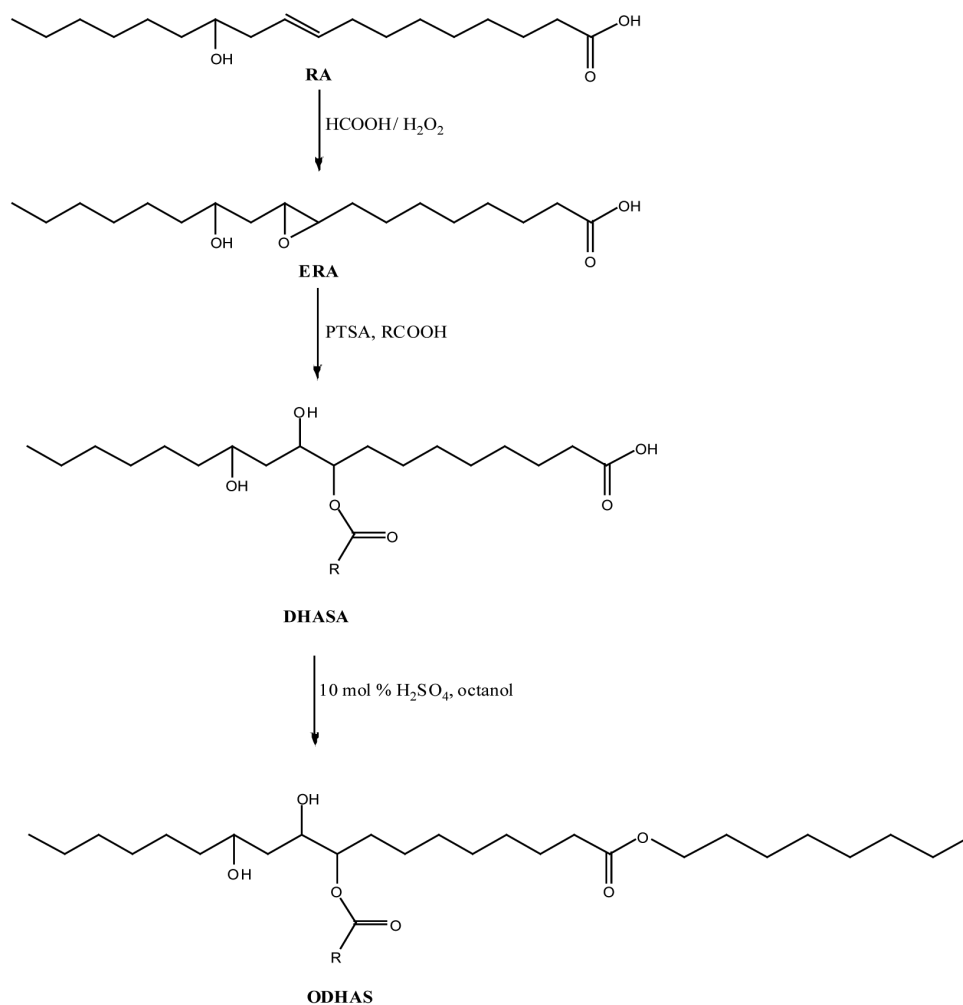


FIGURE 2. Schematic reactions of epoxidation, ring opening and esterification of ricinoleic acid (RA) derivatives (ERA = epoxidized ricinoleic acid; PTSA = *p*-toluenesulfonic acid; RICOOH = octanoic, nonanoic, lauric, myristic, palmitic, stearic and behenic acids; H₂SO₄ = sulfuric acid; DHASA = 10,12-dihydroxy-9-acyloxystearic acid; ODHAS = octyl 10,12-dihydroxy-9-acyloxystearate)

TABLE 2. Pour point, flash point, viscosity and percentage yield of prepared products

Samples	Pour point (°C)	Flash point (°C)	Dynamic viscosity 25°C (mPa s)	% Yield
ERA	9	78	38	78
DHOSA	-10	145	65	83
DHNSA	-13	189	87	77
DHLSA	-15	163	110	86
DHMSA	-17	202	132	75
DHPSA	-18	192	157	90
DHSSA	-20	264	174	85
DHBSA	-23	295	185	78
ODHOS	-26	113	191	92
ODHNS	-28	128	196	72
ODHLS	-33	176	210	65
ODHMS	-39	223	245	94
ODHPS	-44	118	267	86
ODHSS	-48	254	278	70
ODHBS	-53	270	283	84

ERA: epoxidized ricinoleic acid, DHOSA: 10,12-dihydroxy-9-octylxystearic acid, DHNSA: 10,12-dihydroxy-9-nonanoxystearic acid, DHLSA: 10,12-dihydroxy-9-lauroxystearic acid, DHMSA: 10,12-dihydroxy-9-myristoxystearic acid, DHPSA: 10,12-dihydroxy-9-palmitoxystearic acid, DHSSA: 10,12-dihydroxy-9-stearoxystearic acid, DHBSA: 10,12-dihydroxy-9-behenoxystearic acid, ODHOS: octyl 10,12-dihydroxy-9-octylxystearate, ODHNS: octyl 10,12-dihydroxy-9-nonanoxystearate, ODHLS: octyl 10,12-dihydroxy-9-lauroxystearate, ODHMS: octyl 10,12-dihydroxy-9-myristoxystearate, ODHPS: octyl 10,12-dihydroxy-9-palmitoxystearate, ODHSS: octyl 10,12-dihydroxy-9-stearoxystearate, ODHBS: octyl 10,12-dihydroxy-9-behenoxystearate

of the molecules. As a result, microcrystalline structures form instead of macro-structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another enhancing the fluidity of the liquid.

The results confirmed that increases in viscosity correspond 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.

We hypothesize that this phenomenon was due to the increased ability of longer chain esters to disrupt crystalline formation at reduced temperatures. The diesters can be prepared easily with high yields. Domestic renewable sources were utilized in this synthesis and no environmentally toxic by-products were produced.

CONCLUSION

Seven octyl ester derivatives of 10,12-dihydroxy-9-acyloxystearic acid were successfully prepared from ricinoleic acid by epoxidation of the double bond, ring opening of the resulting oxirane and esterification of the carboxylic hydroxyl group. Removal of the unstable double bonds from this fatty acid increased the molecular weight and produced diesters with decreased pour points and increased viscosity. As the chain length of the mid-chain ester (acyloxy group) increased, a corresponding improvement in the low temperature behavior was observed due to the increased ability of longer chain esters to disrupt crystalline formation at reduced temperatures. The diesters can be prepared easily with high yields.

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