J. SALIMON et al.: Synthetic Biolubricant Basestocks from Epoxidized Ricinoleic Acid, *Kem. Ind.* **60** (3) 127–134 (2011)

127

Synthetic Biolubricant Basestocks from Epoxidized Ricinoleic Acid: Improved Low Temperature Properties

J. Salimon,[a*] *N. Salih,*[a] *and E. Yousif* [b]

[a] School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43 600 Bangi, Selangor, Malaysia.
[b] Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq.

This paper presents a series of structural modifications of epoxidized ricinoleic acid for biolubricant to improve the cold flow behavior and oxidation stability of vegetable oils through measurement of pour point (PP) and oxidation onset temperature (OT) and signal maximum temperature (SMT) of each synthetic compound. The results showed that butyl 10,12-dihydroxy-9-behenoxystearate with bulky ester behenyl mid-chain exhibited the most favorable low-temperature performance ($\vartheta_{PP} = -47\ °C$). On the other hand, butyl 10,12-dihydroxy-9-octyloxystearate exhibited higher oxidation stability ($\vartheta_{OT} = 221\ °C$) than the other synthetic esters. It was discovered that increasing chain length of the mid-chain ester had a positive influence on the low temperature properties of synthesized compounds. Improved oxidation stability is achieved when the chain length of the mid-chain ester decreases. The synthesized ester structures were confirmed by NMR and FTIR analysis.

Key words: Vegetable oils, epoxidized ricinoleic acid, chemically modified biolubricants, pour point, oxidative stability.

Introduction

New technologies aimed at the development of products from renewable sources have emerged during the last decade, due to increased concerns over the use of petroleum-based products caused by the progressive depletion of the world reserves of fossil fuels, but also owing to concerns on their environmental impact.

In this regard, vegetable oils (VO) constitute a suitable alternative for replacing 'mineral oils', as they are wholly biodegradable, non-toxic, and 'Generally Regarded as Safe' (GRAS) products.[1,2] Indeed, VOs possess most of the desirable lubricity properties, such as good contact lubrication, high viscosity index (*i. e.*, minimum changes in viscosity with temperature), high flash-point and low volatility. They also have drawbacks, however, that must be overcome, including poor low-temperature properties (such as opacity, precipitation, poor flow ability and/or solidification at relatively moderate temperature), their susceptibility to oxidative degradation and their propensity to undergo hydrolysis in acid media. The latter, nevertheless, can be attenuated with relative ease through the use of additives.[3,4]

Deliberate modification of the chemical structure of VOs is a sound alternative to allow their direct use as lubricant basestocks. For instance, unsaturated alkene groups of the fatty acid chains in triglyceride molecules can be deliberately altered to give more complex structures that improve both the low-temperature and oxidative stability properties.[5–8]

Epoxidized vegetable oils are promising intermediates for the utilization of VO given that the epoxide, or oxirane, group can be easily functionalized. *Erhan and co-workers*[2–4,9] recently worked on the production of lubricant base stocks from acid-catalyzed oxirane ring-opening reactions using epoxidized soybean oil, employing several alcohols and later esterifying the resulting hydroxyl group with an acid anhydride. They also synthesized a biolubricant from di-hydroxylated soybean oil, obtained by acid hydrolysis of the epoxide group followed by esterification of said hydroxyl groups.[6,7] More recently, we also produced acyl derivatives of ricinoleic/oleic acid oil via the opening of the oxirane ring using fatty acids and employing *p*-toluenesulfonic acid as catalyst. These products appear to be promising biolubricants.[10,11]

In recent years, there has been an increased interest in the production of biodiesel (BD) as a more benign fuel. BD is usually produced by the transesterification of vegetable oil triglycerides with an aliphatic alcohol (such as, methanol) employing sodium hydroxide as a catalyst. Fatty acid methyl esters (FAME) are obtained as the main product of this reaction. Thus, FAMEs have become extensively available and are produced with high purity. This has open new pathways to the synthesis of oleochemical products, such as epoxidized FAMEs[12] and, also, lubricants[13–16] have recently been producing branched chain derivatives, partially hydrogenated and, also, diesters through the chemical modification of FAMEs and fatty acids.

* Corresponding author. Prof. Dr. Jumat Salimon, School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia; Tel.: +603 8921 3915; Fax: +603 8921 5410; e-mail address: jumat@ukm.my

In this work, we reported the oxirane ring opening reaction of epoxidized ricinoleic acid (ERA) by the nucleophilic addition of different carboxylic acids in the presence of PTSA as catalyst to give 10,12-dihydroxy-9-acyloxystearic acid (DHASA). Then esterification reaction of these products resulted in the formation of butyl 10,12-dihydroxy-9-acyloxystearate (BDHAS). We utilize both head group manipulation and branching strategies to impart favorable low-temperature behavior to these lipid-based materials. The paper discusses synthesis, characterization and some physical parameters of these products.

Experimental

Materials

Formic acid (88 %) was obtained from Fisher Scientific (Pittsburgh, PA) and ricinoleic acid (99 %) from Nu-Chek Prep, Inc. (Elysian, MN). 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).

Characterization

^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECP 400 spectrometer operating at a frequency of 400.13 and 100.77 MHz, respectively, using a 5-mm broadband inverse Z-gradient probe in DMSO-d$_6$ (Cambridge Isotope Laboratories, Andover, MA) as solvent. Each spectrum was Fourier-transformed, phase-corrected, and integrated using MestRe-C 2.3a (Magnetic Resonance Companion, Santiago de Compostela, Spain) software. FTIR spectra were recorded neat on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a Smart ARK accessory containing a 45 ZeSe trough in a scanning range of $\widetilde{v} = 650 - 4\,000$ cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1}.

Low temperature operability

The pour point is defined as the lowest temperature at which the sample still pours from a tilted jar. This method is routinely used to determine the low temperature flow properties of fluids. Pour point values were measured according to the ASTM D5949 method[17] using a phase Technology Analyzer, Model PSA-70 S (Hammersmith Gate, Richmond, B. C., Canada). Each sample was run in duplicate and average values rounded to the nearest whole degree are reported. For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment. Generally, materials with lower PP exhibit improved fluidity at low temperatures than those with higher PP.

Flash point values

The flash point is defined as the minimum temperature at which the liquid produces a sufficient concentration of vapor above it that it forms an ignitable mixture with air. The lower the flash point is, the greater the fire hazard. Flash point determination was run according to the American National Standard Method using a Tag Closed Tester

(ASTM D 56–79).[18] Each sample was run in duplicate and the average values rounded to the nearest whole degree are reported.

Viscosity index measurements

Automated multi range viscometer tubes HV M472 obtained from Walter Herzog (Germany) were used to measure viscosity. Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at $\vartheta = 40.0$ and 100.0 °C. The viscosity and viscosity index were calculated using ASTM methods D 445-97[19] and ASTM D 2270-93,[20] respectively. Triplicate measurements were made and the average values were reported.

Oxidation stability

Pressurized DSC (PDSC) experiments were accomplished using a DSC 2910 thermal analyzer from TA Instruments (Newcastle, DE). Typically, a 2 μL sample, resulting in a film thickness of $\delta_f < 1$ mm, was placed in an aluminum pan hermetically sealed with a pinhole lid and oxidized in the presence of dry air (Gateway Airgas, St Louis, MO), which was pressurized in the module at a constant pressure of $p = 1,378.95$ kPa (200 psi). A $\dot{\vartheta} = 10$ °C min^{-1} heating at the rate of temperature change from $\vartheta = 50$ to 350 °C was used during each experiment. The oxidation onset (ϑ_{OT} / °C) and signal maximum temperatures (ϑ_{SMT} / °C) were calculated from a plot of specific heat flow rate (ϕ / W g^{-1}) vs. temperature for each experiment. Each sample was run in triplicate and average values rounded to the nearest whole degree are reported (Table 1).

Epoxidized ricinoleic acid (ERA)

Hydrogen peroxide solution ($w = 30$ % in H$_2$O, 8.0 mL) was added slowly into a stirred solution of ricinoleic acid (RA) ($w = 90$ %, 15 g) in formic acid ($\varphi = 88$ %, $V = 14$ mL) at 4 °C (ice bath). The reaction proceeded at room temperature with vigorous stirring ($n = 900$ min^{-1}) 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$_2$O (chilled, 3 × 10 mL), and placed for 12 h under high vacuum to provide epoxidized ricinoleic acid (ERA) as a white, powdery solid ($m = 14.7$ g, $Y = 93$ %).

10,12-Dihydroxy-9-acyloxystearic acid (DHASA)

To a mixture of ERA (31 g), 5 g of *p*-toluenesulfonic acid (PTSA) and toluene, fatty acids (6 g) was added during $t = 1.5$ h in order to keep the reaction mixture temperature under $\vartheta = 70 – 80$ °C. The reaction mixture was subsequently heated to $\vartheta = 90 – 100$ °C and refluxed for $t = 3$ h. 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.

Butyl 10,12-dihydroxy-9-acyloxystearate (BDHAS)

The reaction scheme of diesters' formation is shown in Fig. 1. Sulfuric acid ($x(H_2SO_4) = 10$ %) was added into a stirred suspension of DHASA (3.35 mmol) in the butanol (3.35

mL). The suspension was heated with stirring at 60 °C for 10 h. Hexane (5 mL) was then added, and the solution was washed with saturated aqueous solution of NaHCO$_3$ (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.

Results and discussion

The first step in the synthesis is an epoxidation reaction of ricinoleic acid, as shown in Fig. 1, using formic acid and hydrogen peroxide to give epoxidized ricinoleic acid (ERA). Many nucleophilic reagents are known to add to an oxirane ring, resulting in ring opening. In this work, ring opening reaction of ERA was done using octanoic, nonanoic, lauric,

myristic, palmitic, stearic and behenic acids to give respective 9(10)-hydroxy-10(9)-ester derivatives of ricinoleic acid. The seven prepared acyloxy of 10,12-dihydroxy stearic acid derivatives were used as feed for the synthesis of modified diesters-derivatives of 10,12-dihydroxy-9-acyloxystearate by esterification of prepared dihydroxyesters with butanol in an protic solvent.

The straightforward epoxidation of ricinoleic acid was closely monitored to avoid the synthesis of the undesired 9,10-dihydroxyoctadecanoate, which will form if the reaction temperature is elevated or the reaction is allowed to progress for too long. With this synthesis, a mixture of positional isomers is always formed, with the hydroxy moiety on either the 9 or 10 carbon, and the ester functionality on the other carbon.[16]
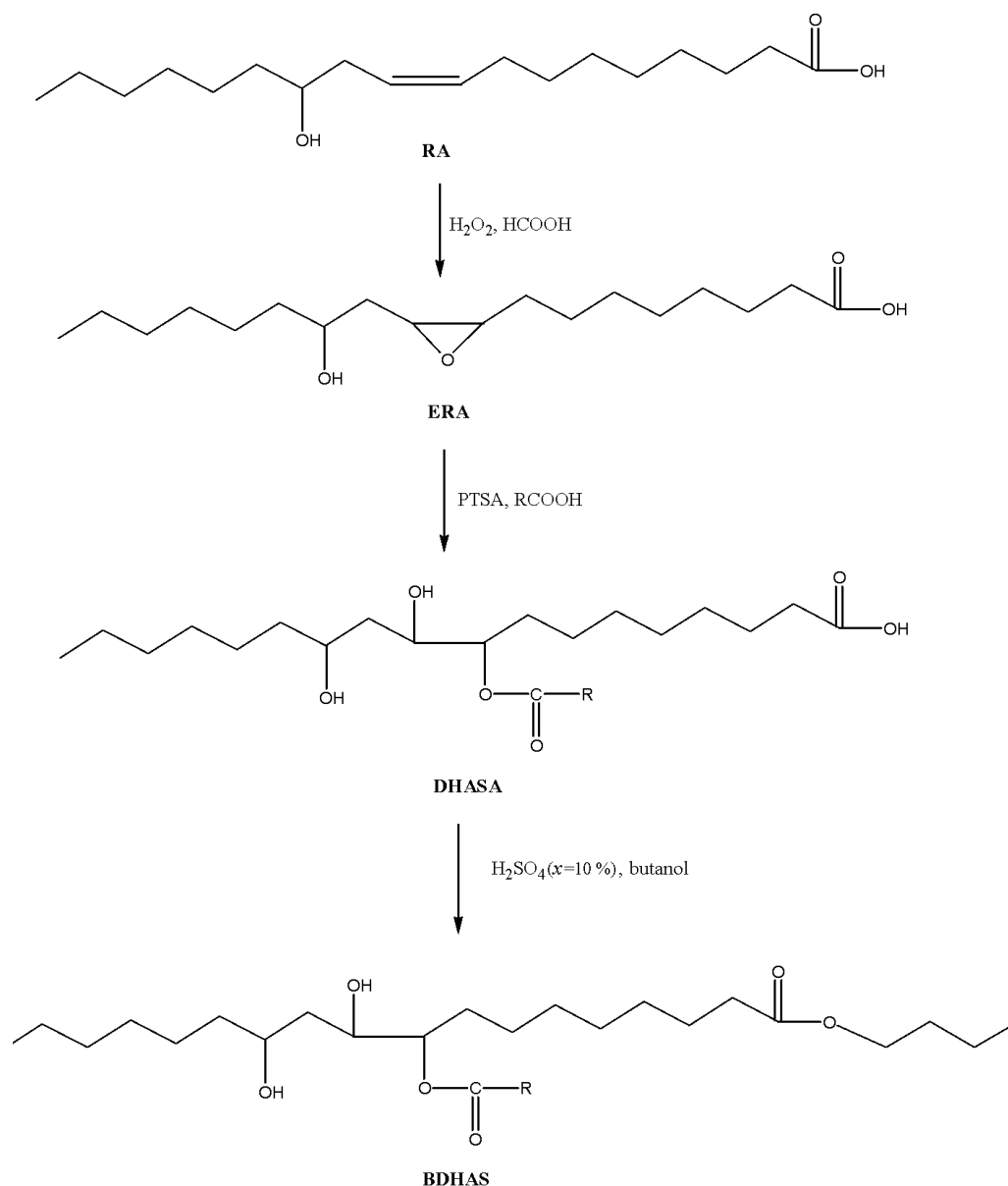

F i g. 1   – Schematic reactions of epoxidation, ring opening and esterification of ricinoleic acid derivatives (ERA = epoxidized ricinoleic acid; PTSA = p-toluenesulfonic acid; RCOOH = octanoic, nonanoic, lauric, myristic, palmitic, stearic, and behenic acids)

S l i k a 1 – Shematski prikaz reakcija epoksidacije, otvaranja prstena i esterifikacije ricinolne kiseline (ERA = epoksidirana ricinolna kiselina; PTSA = p-toluensulfonska kiselina; RCOOH = oktanska kiselina, nonanska kiselina, laurinska kiselina, miristinska kiselina, palmitinska kiselina, stearinska kiselina i behenska kiselina)

All synthesized compounds were verified by ^{1}H and ^{13}C NMR spectroscopy. Significant signals in the ^{1}H spectrum of ERA between $\delta = 2.50$ and 2.70 ppm correspond to quaternary carbons of the oxirane ring and the doublet in the ^{13}C spectrum between $\delta = 56.89$ and 56.90 ppm correspond to carbons of the oxirane ring. Furthermore ^{1}H spectrum of ERA showed singlet signals at $\delta = 9.20$ and 9.35 ppm due to OH groups. A multiplet in the area around $\delta = 9.15 - 9.27$ ppm, representing an OH group, and the bands at about $\delta = 2.05 - 3.66$ ppm, corresponding to $-CH_2-$ groups, are present in the ^{1}H spectra of DHASA (Fig. 2).

Furthermore, the ^{13}C NMR spectra of DHASA showed the signals at $\delta = 72.11$ and 74.36 ppm due to $-CH(OH)$ and $-CH(OCOR)$ groups beside other characteristic signals (Fig. 3).[7] The ^{1}H spectrum of synthesized diesters, BDHAS, consists of multiplet signals of low intensity at $\delta = 9.20 - 9.38$ ppm and $\delta = 2.08 - 3.64$ ppm. Broad lines at $\delta = 1.40 - 1.78$ ppm represent the CH_2 groups' hydrogen peaks (Fig. 4). In the ^{13}C NMR spectra significant bands at about $\delta = 175$ ppm are present, which exhibit the characteristic triplet attributed to ester groups (Fig. 5).[21]
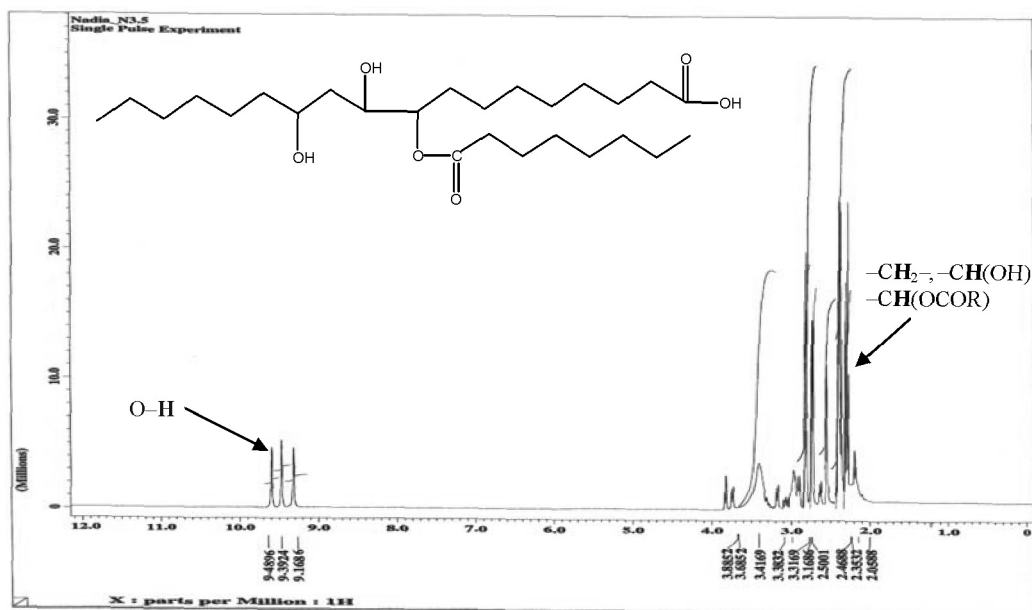

F i g. 2　 – *^{1}H NMR spectrum for 10,12-dihydroxy-9-octyloxystearic acid (DHOSA)*
S l i k a 2 – *^{1}H NMR-spektar 10,12-dihidroksi-9-oktiloksistearinske kiseline (DHOSA)*

F i g. 3　 – *^{13}C NMR spectrum for 10,12-dihydroxy-9-octyloxystearic acid (DHOSA)*
S l i k a 3 – *^{13}C NMR-spektar 10,12-dihidroksi-9-oktiloksistearinske kiseline (DHOSA)*
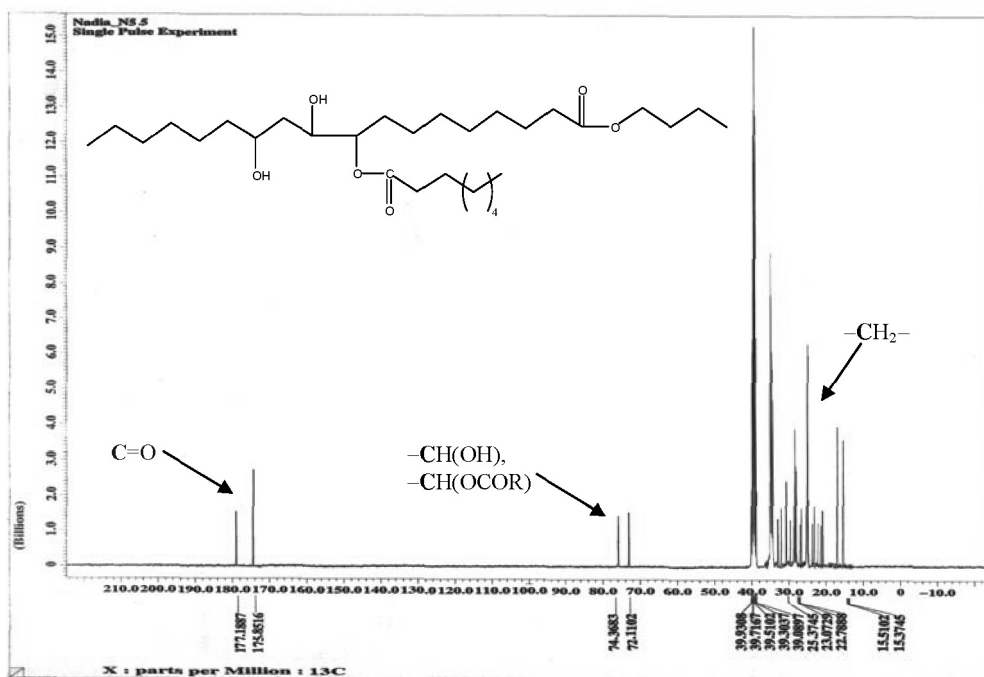
The types of esters were also confirmed by IR spectra. Bands representing C=O groups ($\tilde{\nu}$ = 725, 1743 cm^{-1}), CH$_3$ groups ($\tilde{\nu}$ = 1373 – 1461 cm^{-1}), OH groups ($\tilde{\nu}$ = 3475 – 3440 cm^{-1}) and also C–O–C bands in esters ($\tilde{\nu}$ = 998 – 1100 cm^{-1}) are clearly visible in the spectra.[22]

Physico-chemical properties of prepared compounds are summarized in Table 1. The cold flow property of vegetable oils is extremely poor and this limits their use at low operating temperature especially as automotive and industrial fluids. Vegetable oils have a tendency to form macro crystalline structures at low temperature through uniform stacking of the 'bend' triglyceride backbone. Such macro crystals restrict the easy flow of the system due to loss of kinetic energy of individual molecules during self-stacking. Cold flow properties of these samples were determined using their pour point. The ERA and synthetic esters (DHASA and BDHAS) described above were screened for low temperature behavior through determination of their pour point (PP). PP determinations were made in agreement with ASTM D5949.[17]
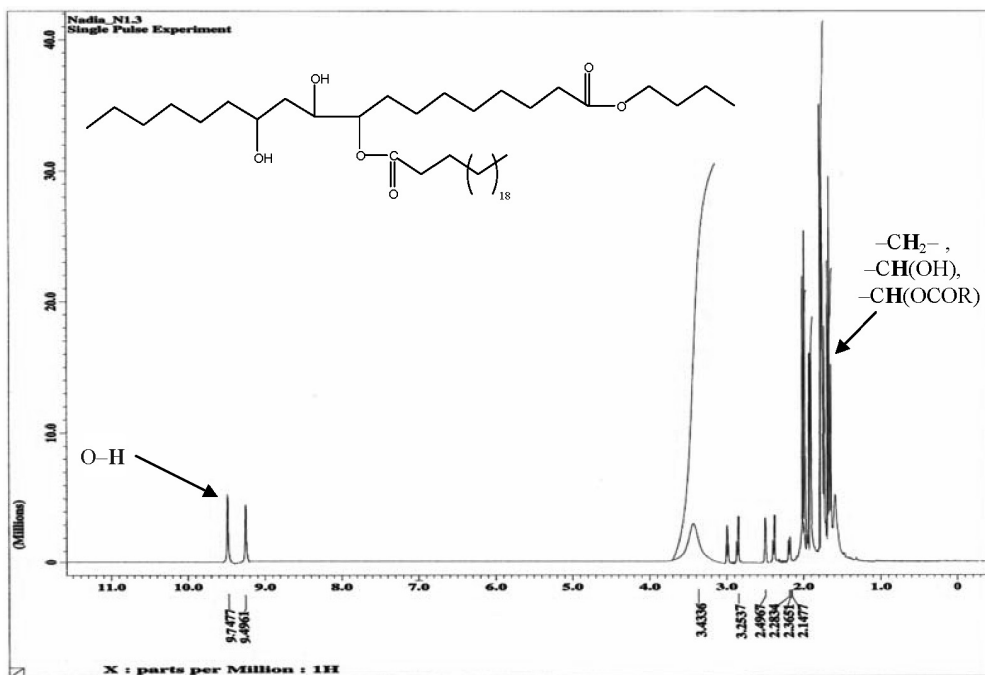

F i g. 4   – *^{1}H NMR spectrum for butyl 10,12-dihydroxy-9-behenoxystearate (BDHBS)*
S l i k a 4 – *^{1}H NMR-spektar butil-10,12-dihidroksi-9-behenoksistearata (BDHBS)*
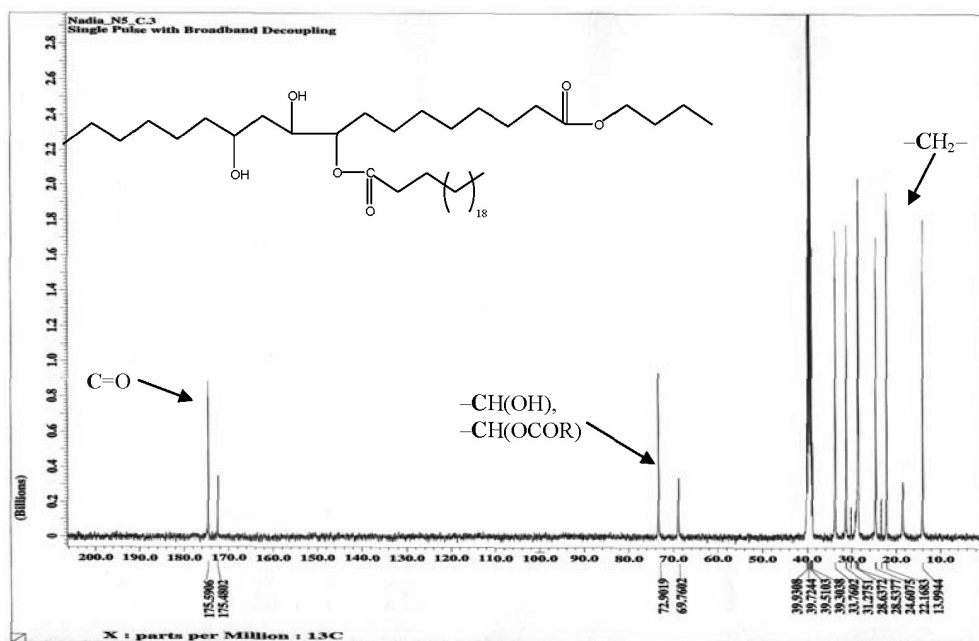

F i g. 5   – *^{13}C NMR spectrum for butyl 10,12-dihydroxy-9-behenoxystearate (BDHBS)*
S l i k a 5 – *^{13}C NMR spektar butil-10,12-dihidroksi-9-behenoksistearata (BDHBS)*

An improvement in the cold flow behavior of diesters BDHAS was obtained over that of their precursors DHASA. Actually there are two reasons for this behavior. The first reason is that as the chain length of the mid-chain ester is increased, a corresponding improvement in the pour point of biolubricant oil was observed. This is due to the greater ability of the longer chain esters to disrupt crystalline formation at reduced temperatures. Secondly, the lack of one hydroxyl group means the number of hydrogen bonds decrease, which could cause the molecules to stack together.

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 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 VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature. Each oil has a viscosity index based on the slope of the temperature-viscosity curve. The viscosity index depends on the rate of change in viscosity of given oil with a change in temperature. A low index means a steep slope in the curve, or a great variation of viscosity with a change in temperature; high index means a flatter slope, or lesser variation of viscosity with the same changes in temperature. If we are using biolubricant oil with a high viscosity index, its viscosity or body will change less when the temperature of the engine increases. The viscosity index of oil is crucial when selecting a lubricant for an application, and is especially critical in extremely hot or cold climates. Failure to use oil with the proper viscosity index when temperature extremes are expected may result in poor lubrication and equipment failure.

In general, from the viscosity index data of compounds ERA, DHASA and BDHAS (Table 1) we can see that the viscosity index increases with chain length (number of carbons). A high viscosity index indicates small oil viscosity changes with temperature. Therefore, biolubricant oil that has a high viscosity index can be expected to undergo very little change in viscosity with temperature extremes and is considered to have stable viscosity.

Another important fact in determining how well oil will behave as a potential biolubricant is to evaluate the oils flash point. Flash point values are a function of the apparatus design, the condition of the apparatus used, and the operational procedure carried out. The flash point can be used to determine the transportation and storage temperature requirements for biolubricants. Biolubricant producers can also use the flash point to detect potential product contamination. Biolubricants exhibiting low flash point will be suspected of contamination with a volatile product and usually require special precautions for safe handling.

The ability of a substance to resist oxidative degradation is another important attribute for a number of industrial materials, such as lubricants, surfactants, and fuels. Therefore, ERA, DHASA and BDHAS were screened for oxidation stability using PDSC through determination of OT and SMT, Table 1. PDSC is an effective method for measuring oxidation stability of oleochemicals in an accelerated mode.[23] The OT is the temperature at which a rapid increase in the rate of oxidation is observed at a constant, high pressure (1.378 kPa). A high OT would suggest high oxidation stability of the material. The SMT is the temperature at which maximum heat output is noted from the sample during oxidative degradation. A higher SMT does not necessarily correlate with improved oxidation stability. Both OT and SMT were calculated from a plot of specific heat flow rate (ϕ / W g^{-1}) vs. temperature that was generated by the sample upon degradation and, by definition, SMT > OT.

In the present study, as the chain length of the mid-chain ester decreased, a corresponding improvement in oxidation stability was observed, due to the fact that longer chains are more susceptible to oxidative cleavage than shorter chains. These results are in agreement with other studies on synthetic esters.[24] For example, when comparing mono esters (DHASA) and di esters (BDHAS), an improvement in OT was noticed as the mid-chain ester length (R) decreased, as shown by mono esters DHOSA (ϑ_{OT} = 105 °C, R = octyl) and DHNSA (ϑ_{OT} = 98 °C, R = nonyl). A similar trend was exhibited when comparing DHLSA to DHMSA, DHPSA to DHSSA and DHBSA; BDHOS to BDHNS, BDHLS to BDHMS, BDHPS to BDHSS and BDHBS (Table 1).

On the other hand, from the results we can see that another important effect on oxidation stability is the number of hydroxyl group in the synthetic esters. For example, comparing the mono esters DHOSA (ϑ_{OT} = 105 °C) and BDHOS (ϑ_{OT} = 221 °C), an improvement in the oxidation stability occurs. A similar trend was exhibited when comparing DHNSA to BDHNS, DHLSA to BDHLS, DHMSA to BDHMS, DHPSA to BDHPS, DHSSA to BDHSS and DHBSA to BDHBS (Table 1), in this case the trend of PP and OT are consistent with each other.

Conclusions

Based on the results obtained, an increase in chain length of the mid-chain ester had a positive influence on the low temperature properties of diesters because they create a steric barrier around the individual molecules and inhibit crystallization, resulting in lower pour point. However, the trends for PP run counter to that of OT, *i. e.*, increasing chain length is a beneficial to PP, but a detrimental to OT. From these results, a future study will aim to strike a balance between two opposing properties through investigation of a greater variety of mid-chain ester groups. From the present study, it is evident that hydrogen bonding is a critical parameter influencing the low temperature properties and oxidation stability of synthetic esters. Increased hydrogen bond amount will lead to increased pour point (PP) and decreased oxidation stability of these compounds for this we can see that DHASA have higher PP and lower oxidation stability than BDHAS. Furthermore, the viscosity index and flash point of ERA, DHASA and BDHAS are significantly influenced by compound structure.

T a b l e 1 – *Pour point, flash point, viscosity index, OT, SMT and percentage yield of prepared products*
T a b l i c a 1 – *Vrijednosti stiništa, plamišta, indeksa viskoznosti, oksidacijske postojanosti (OT, SMT) i iskorištenje priređenih proizvoda*

Samples Uzorci	Pour point[a] ϑ_{PP} / °C Stinište[a] ϑ_{PP} / °C	Flash point[a] ϑ / °C Plamište[a] ϑ / °C	Viscosity index[b] Indeks viskoznosti[b]	OT[b] ϑ_{OT} / °C	SMT[b] ϑ_{SMT} / °C	Yield Y / % Iskorištenje Y / %
ERA	9	80	67	60	228	80
DHOSA	−10	63	110	105	214	64
DHNSA	−13	134	117	98	232	75
DHLSA	−15	112	125	95	239	85
DHMSA	−17	135	146	90	200	67
DHPSA	−18	180	155	82	256	92
DHSSA	−20	142	163	75	223	90
DHBSA	−23	192	171	64	240	78
BDHOS	−30	163	180	221	250	80
BDHNS	−34	214	189	205	234	66
BDHLS	−36	220	194	193	246	68
BDHMS	−38	136	205	185	248	79
BDHPS	−41	212	222	178	205	93
BDHSS	−45	282	239	167	220	91
BDHBS	−47	180	243	155	225	80

ERA: epoxidized ricinoleic acid, DHOSA: 10,12-dihydroxy-9-octyloxystearic 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, BDHOS: butyl 10,12-dihydroxy-9-octyloxystearate, BDHNS: butyl 10,12-dihydroxy-9-nonanoxystearate, BDHLS: butyl 10,12-dihydroxy-9-lauroxystearate, BDHMS: butyl 10,12-dihydroxy-9-myristoxystearate, BDHPS: butyl 10,12-dihydroxy-9-palmitoxystearate, BDHSS: butyl 10,12-dihydroxy-9-stearoxystearate, BDHBS: butyl 10,12-dihydroxy-9-behenoxystearate.

ERA: epoksidirana ricinolna kiselina, DHOSA: 10,12-dihidroksi-9-oktiloksistearinska kiselina, DHNSA: 10,12-dihidroksi-9-noniloksistearinska kiselina, DHLSA: 10,12-dihidroksi-9-lauroiloksistearinska kiselina, DHMSA: 10,12-dihidroksi-9-miristiloksistearinska kiselina, DHPSA: 10,12-dihidroksi-9-palmitiloksistearinska kiselina, DHSSA: 10,12-dihidroksi-9-steriloksistearinska kiselina, DHBSA: 10,12-dihidroksi-9-beheniloksistearinska kiselina, BDHOS: butil-10,12-dihidroksi-9-oktiloksistearat, BDHNS: butil-10,12-dihidroksi-9-noniloksistearat, BDHLS: butil-10,12-dihidroksi-9-lauroiloksi stearat, BDHMS: butil-10,12-dihidroksi-9-miristiloksistearat, BDHPS: butil-10,12-dihidroksi-9-palmitiloksistearat, BDHSS: butil-10,12-dihidroksi-9-steariloksistearat, BDHBS: butil-10,12-dihidroksi-9-beheniloksistearat.

[a] Two measurements, $\sigma = \pm 1$ °C; dva mjerenja, $\sigma = \pm 1$ °C

[b] Three measurements, $\sigma = \pm 1$ °C; tri mjerenja, $\sigma = \pm 1$ °C

References
Literatura

1. *S. Z. Erhan, S. Asadauskas*, Lubricant basestocks from vegetable oils, Ind. Crops Prod. **11** (2000) 277–282.

2. *S. Z. Erhan, J. M. Perez* (Eds.), Biobased industrial fluids and lubricants. AOCS Press, Champaign, IL, 2002, pp. 14–30.

3. *H. S. Hwang, S. Z. Erhan*, Modification of epoxidized soybean oil for lubricant formulations with improved oxidative stability and low pour point, J. Am. Oil Chem. Soc. **78** (2001) 1179–1184.

4. *H. S. Hwang, A. Adhvaryu, S. Z. Erhan*, Preparation and properties of lubricant basestocks from epoxidized soybean oil and 2-ethylhexanol, J. Am. Oil Chem. Soc. **80** (2003) 811–815.

5. *P. S. Lathi, B. Mattiasson*, Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil, Appl. Catal. B: Environ. **69** (2006) 207–212.

6. *A. Adhvaryu, Z. Liu, S. Z. Erhan*, Synthesis of novel alkoxylated triacylglycerols and their lubricant base oil properties, Ind. Crops Prod. **21** (2005) 113–119.

7. *B. K. Sharma, A. Adhvaryu, Z. Liu, S. Z. Erhan*, Chemical modification of vegetable oils for lubricant applications, J. Am. Oil Chem. Soc. **83** (2006) 129–136.

8. *B. K. Sharma, Z. Liu, A. Adhvaryu, S. Z. Erhan*, One-pot synthesis of chemically modified vegetable oils, J. Agric. Food Chem. **56** (2008) 3049–3056.

9. *S. Z. Erhan, B. K. Sharma, Z. Liu, A. Adhvaryu*, Lubricant base stock potential of chemically modified vegetable oils, J. Agric. Food Chem. **56** (2008) 8919–8925.

10. *J. Salimon, N. Salih, E. Yousif*, Biolubricants: Raw materials, chemical modifications and environmental benefits, Eur. J. Lipid Sci. Technol. **112** (2010) 519–530.

11. *J. Salimon, N. Salih*, Modification of epoxidized ricinoleic acid for biolubricant base oil with improved flash and pour points, Asian J. Chem. **22** (2010) 5468–5476.

12. *A. Campanella, C. Fontanini, M. A. Baltanás*, High yield epoxidation of fatty acid methyl esters with performic acid generated in-situ, Chem. Eng. J. **144** (2008) 466–475.

13. *B. R. Moser, S. Z. Erhan*, Branched chain derivatives of alkyl oleates: tribological, rheological, oxidation, and low temperature properties, Fuel **87** (2008) 2253–2257.

14. *B. R. Moser, B. K. Sharma, K. M. Doll, S. Z. Erhan*, Diesters from oleic acid: synthesis, low temperature properties, and oxidation stability, J. Am. Oil Chem. Soc. **84** (2007) 675–680.

15. *B. R. Moser, M. J. Haas, J. K. Winkler, M. A. Jackson, S. Z. Erhan, G. R. List*, Evaluation of partially hydrogenated methyl esters of soybean oil as biodiesel, Eur. J. Lipid Sci. Technol. **109** (2007) 17–24.

16. *B. R. Moser*, *S. Z. Erhan*, Preparation and evaluation of a series of α-hydroxy ethers from 9,10-epoxystearates, Eur. J. Lipid Sci. Technol. **109** (2007) 206–213.

17. ASTM Standard D5949: Standard test method for pour point of petroleum (automatic pressure pulsing method). ASTM, West Conshohocken, PA (USA).

18. ASTM Standard D 56-79: Standard test method for flash point of liquids with a viscosity less than, 45 Saybolt Universal Seconds (SUS) at 37.8 °C (that don't contain suspended solids and don't tend to form a surface film under test).

19. ASTM D 445-97: Standard test method for kinematic viscosity of transparent and opaque liquids. ASTM, West Conshohocken, PA (USA).

20. ASTM D 2270-93: Standard practice for calculating viscosity index from kinematic viscosity at 40 and 100 °C. ASTM, West Conshohocken, PA (USA).

21. *A. Adhvaryu*, *Z. Liu*, *S. Z. Erhan*, Synthesis of novel alkoxylated triacylglycerols and their lubricant base oil properties, Ind. Crops Prod. **21** (2005) 113–119.

22. *R. Silverstein*, *G. Bassler*, *T. Morrill*, Spectrometric identification of organic compounds. 7th ed., John-Wiley, New York, 2005, pp. 25–27.

23. *D. Du*, *S.-S. Kim*, *W.-S. Moon*, *S.-B. Jin*, *W.-S. Kwon*, Oxidation performance of oils containing ZnDTC, ZnDDP and their mixture after oxidation test by PDSC, Thermochim. Acta **407** (2003) 17–23.

24. *S. J. Randles*, Esters, in L. R. Rudnick and R. L. Shubkin (eds), Synthetic lubricants and high-performance functional fluids. 2nd ed., Marcel Dekker, New York, 1999, pp. 63–102.

Abbreviations
Kratice

BD   – biodiesel
     – biodizel

FAME – fatty acid methyl esters
     – metilni ester masne kiseline

OT   – oxidation onset temperature
     – početna oksidacijska temperatura

PP   – pour point
     – stinište

SMT – signal maximum temperature
     – maksimalna početna temperatura

VO   – vegetable oil
     – biljno ulje

List of symbols
Popis simbola

m – mass, g
     – masa, g

n – stirring speed, min^{-1}
     – brzina vrtnje miješala, min^{-1}

p – pressure, kPa
     – tlak, kPa

t – time, h
     – vrijeme, h

V – volume, mL, L
     – obujam, mL, L

w – mass fraction, %
     – maseni udjel, %

x – mole fraction, %
     – množinski udjel, %

Y – yield, %
     – iskorištenje, %

δ – chemical shift, ppm
     – kemijski pomak, ppm

δ_f – film thickness, μm
     – debljina tankog sloja, μm

ϑ – Celsius temperature, °C
     – Celzijeva temperatura, °C

$\dot{\vartheta}$ – rate of temperature change, °C min^{-1}
     – brzina temperaturne promjene, °C min^{-1}

$\tilde{\nu}$ – wavenumber, cm^{-1}
     – valni broj, cm^{-1}

σ – standard error
     – standardna pogreška

φ – volume fraction, %
     – obujamski udjel, %

ϕ – specific heat flow rate, W g^{-1}
     – specifični toplinski tok, W g^{-1}

SAŽETAK

Sintetička biomaziva bazna ulja od epoksidirane ricinolne kiseline poboljšanih niskotemperaturnih svojstava

J. Salimon,[a] N. Salih,[a] and E. Yousif[b]*

Opisan je veći broj strukturnih preinaka epoksidirane ricinolne kiseline kojima se poboljšavaju neka uporabna svojstva kada služe kao biomaziva ulja. Posebice su poboljšana svojstva niskotemperaturne tečljivosti i oksidacijske postojanosti. Također su utvrđeni indeksi viskoznosti, plamišta i iskoristivosti pri sintezi opisanih estera. Dobiveni rezultati ukazuju da je poboljšanje niskotemperaturnih svojstava izravno razmjerno povećanju veličine esterskih skupina središnjeg dijela molekula, dočim je suprotni utjecaj na njihovu oksidacijsku postojanost. Tako, najbolja niskotemperaturna svojstva (stinište –47 °C) posjeduje butil-10,12-dihidroksi-9-behenoktilstearat, zahvaljujući velikim sterički ometanim esterskim skupinama središnjeg dijela molekula. S druge strane, najveću oksidacijsku postojanost posjeduje butil-10,12-dihidroksi-9-oktilstearat (ϑ_{OT} = 221 °C), zahvaljujući maloj veličini središnje esterske skupine. Struktura priređenih estera potvrđena je spektroskopskim metodama prvenstveno spektrima NMR i FTIR.

^a *Zavod za kemijske znanosti i prehrambenu tehnologiju*
Fakultet znanosti i tehnologije
Sveučilište Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
^b *Odjel kemije, Fakultet znanosti*
Sveučilište Al-Nahrain Baghdad, Iraq