J Am Oil Chem Soc (2010) 87:937–945
DOI 10.1007/s11746-010-1574-1

ORIGINAL PAPER

Synthesis and Physical Properties of Potential Biolubricants based on Ricinoleic Acid

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Received: 31 December 2009 / Revised: 3 March 2010 / Accepted: 10 March 2010 / Published online: 31 March 2010

Abstract The desire to replace petroleum-based materials with environmentally friendly and sustainable alternatives has stimulated the development of vegetable oil-based materials as biolubricants. Our studies have focused on molecules that might be produced by biosynthesis of genetically altered oilseed plants with limited post-harvest modification. Various ricinoleate and 12-hydroxystearate esters and estolides were synthesized and their melting points and viscosities were documented. The antifriction and antiwear properties of some esters were evaluated with a microtribometer. The purities of all the products were >98–99% by gas chromatography. Some of these compounds showed melting points, viscosities, and lubricity suitable for uses as biolubricants. Various ricinoleate esters acylated at the 12 positions with short-chain acids were particularly promising.

Keywords 12-Acetylricinoleate esters · Friction · 12-Hydroxystearate · Melting point · Ricinoleate · Viscosity · Wear

Introduction

The use of vegetable oil-based lubricants to replace those based on petroleum has received significant attention recently because of environmental concerns and the highly variable price of crude petroleum. More than 60% of the lubricants currently used in the United States are reported to become pollutants through spillage, evaporation, and loss to the environment [1]. Lubricants that are produced from natural fats and oils can be biodegradable and non-toxic as well as reducing America's dependence on foreign oil. But some properties of conventional vegetable oils limit their use as biolubricants even though they can have excellent lubricity and viscosity indices [2]. Long-chain fatty acids have high melting points if saturated or poor oxidative stability if polyunsaturated, and these traits are particularly undesirable in lubricant applications. Branched and monounsaturated esters, such as oleates, can exhibit acceptable oxidative stability and have melting points acceptable for many lubricant applications [3–5].

Although chemical modifications of conventional vegetable oils can improve their performance in lubrication application [1, 2], fatty acid derivatives with desirable lubrication properties might be produced in oilseeds that have been modified by genetic engineering techniques [6, 7]. Potentially, the latter approach could bring about major savings [Dowling A, Zakharenko O (2005) Assessing biodiesel's cold flow limitation and gains from re-engineered soybeans, Unpublished data].

The development of biolubricants based on estolides derivatives from castor, lesquerella, and meadowfoam oils through chemical modifications has been studied thoroughly [8–10]. While only a limited number of plant species synthesize oxygenated fatty acids, such as hydroxy and epoxy acids, in their seed oils, all higher plants produce a variety of oxygenated fatty acids and fatty acid derivatives during the synthesis of surface waxes. These plant surface waxes contain a variety of hydroxy and epoxy fatty acids. Li and Beisson [11] have reviewed the

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use of plant surface waxes as possible sources of high value-added lipids.

The general goal of our work has been to design and identify molecules that might be biosynthesized in oilseed crops and that would possess properties suitable for lubrication, including excellent low temperature properties, suitable viscosity, great stability to oxidation, and good lubricity. In our work, we have measured the physical properties of quite pure examples of these compounds to illustrate the best properties that could be achieved, although it is unlikely that such high purity can be expected in a biosynthetic product without further fractionation. This comparison of pure targets also facilitates comparisons among various candidates for the usually long genetic and biological process of molecular alteration. In this paper, we explore the synthesis, melting, viscosity, and lubricity properties of several pure ricinoleate and 12-hydroxystearate derivatives.

Materials and Methods

Materials

Castor oil was purchased from a local pharmacy (Walgreen, Ames, IA). Potassium isopropylate (19% in isopropanol) and potassium propylate (20% in propanol) were purchased from BASF Corp. (Evans City, PA). Silica gel (40–140 Mesh) was from J. T. Baker (Phillipsburg, NJ). Light mineral oil was from Fisher Scientific (Pittsburgh, PA). Other chemicals including 12-hydroxystearate, were purchased from Sigma-Aldrich (St Louis, MO).

Synthesis and Purification of Ricinoleate Esters with Free Hydroxy Groups

About 20 g of castor oil was dissolved in 300 mL of methanol containing 6 mL of 5 N sodium methoxide. The mixture was vigorously stirred overnight at room temperature. The methyl esters were extracted with hexane and washed with 2% aqueous acetic acid and with water, and weighed about 18–20 g after solvent removal. The GC response factor of methyl ricinoleate (MeR, see Table 1 for a key to abbreviations) relative to methyl stearate was found to be 0.86. Applying this factor and assuming the other fatty acids had the same response as methyl stearate, GC showed that the resulting methyl esters contained 88.0% MeR, 4.6% methyl linoleate, 3.2% methyl oleate, 0.6% methyl palmitate, 0.6% dihydroxystearate, 0.3% methyl eicosanoate and additional minor impurities.

MeR was freed of non-hydroxy FAMEs by a countercurrent fractionation method adapted from Berdeaux et al. [12]. The crude castor oil FAMEs (30 g) was dissolved in 200 mL of hexane and washed with 100 mL of methanol–water–acetic acid (90:10:1, by vol). The methanol-rich phase was transferred to a second funnel and washed with 200 mL of fresh hexane. After being washed with another 200 mL of fresh hexane in a third funnel, the methanol-rich phase was collected as fraction 1. The MeR was equilibrated successively with the same hexane washes until 12 fractions of the methanol–water–acetic acid phase had been collected. Then 1 mL of each of the 12 methanol fractions was partitioned between hexane (2 mL) and water (5 mL), and the hexane layer was analyzed by gas chromatography (GC). Fractions with >98.5 GC % of MeR were combined and 1 part of the combined fractions was mixed with 1 part of hexane and 3 parts of 2% aqueous acetic acid by volume. The >98.5% pure MeR was now in the hexane layer. The hexane was removed and the MeR (about 16 g) was stored at −5 °C.

Alternatively, about 3 g of crude castor oil FAMEs was purified using a 30-g silica column so that non-hydroxy FAMEs and MeR were eluted separately with hexane-diethyl ether at ratios of 95:5 (v/v) and 80:20 (v/v), respectively. The purity of the resulting MeR was >99% (by GC). Less than 0.5% of methyl dihydroxystearate was present in the MeR. MeR obtained from silica gel purification was used in melting point determinations, whereas that obtained from countercurrent-solvent fractionations was used in the synthesis of other derivatives and viscosity and lubricity measurements.

Ethyl, propyl, butyl, pentyl, and isopropyl ricinoleates were synthesized via the same procedure as MeR in 5–8 g amounts using the metal alkoxide corresponding to the esterifying alcohol. The catalysts for producing esters with alcohols longer than propyl were generated by reacting sodium metal with the appropriate alcohols [4]. The resulting esters were purified with silica gel using the same procedure used for MeR.

Enzymatic methods were used for the synthesis of methyl and isopropyl 12-hydroxystearate. The reaction was carried out with a molar ratio of 12-hydroxystearic acid to the alcohol of 50:1 and Novozyme 435 at 5% of the weight of the alcohol for 24 h.

Synthesis and Purification of 12-Acylated Ricinoleate and 12-Acylated Hydroxystearate Esters with Alcohols of Various Chain Lengths

Acetyl esters of various alcohols were used to place acetyl groups on the 12-position of ricinoleate in instances where the alcohol group on ricinoleate was also available as an ester of acetic acid we wished to place on the 12 position of ricinoleate. Thus, MeR (6 mM) was reacted with methyl acetate (300 mM) catalyzed by sodium methoxide (2% by weight of methyl acetate) for 3 h at 25 °C with stirring. The

Table 1 Melting points and reaction conversion rate of various ricinoleate and 12-hydroxystearate esters

Compounds	Melting point of unstable polymorphs[a] (°C)	T_{com}[b] (°C)	Reaction conversion[c] (%)
Methyl ricinoleate (MeR)		−3.5	98
Ethyl ricinoleate (EtR)		−15.7	98
Propyl ricinoleate (PrR)		−19.4	98
Butyl ricinoleate (BuR)	−35.5	−29.4	98
Pentyl ricinoleate (PeR)		−22.2	98
Isopropyl ricinoleate (*i*-PrR)	−50.6, −42.6	−20.3	98
Methyl 12-hydroxystearate (MeHS)	35.3, 52.6	59.4	95
Isopropyl 12-hydroxystearate (*i*-PrHS)	43.8	49.0	95
Methyl 12-acetylricinoleate (MeR-Ac)		−50.0[e]	85(95)[d]
Ethyl 12-acetylricinoleate (EtR-Ac)		−50.0[e]	85
Propyl 12-acetylricinoleate (PrR-Ac)		−50.0[e]	85
Butyl 12-acetylricinoleate (BuR-Ac)		−50.0[e]	85
Isopropyl 12-acetylricinoleate (*i*-PrR-Ac)		−50.0[e]	85
Methyl 12-butyrylricinoleate (MeR-Bu)		−50.0[e]	34
Isopropyl 12-butyrylricinoleate (*i*-PrR-Bu)		−50.0[e]	25
Methyl 12-hexanoylricinoleate (MeR-Hx)		−50.0[e]	95
Methyl 12-octanoylricinoleate (MeR-Oc)		−50.0[e]	95
Methyl 12-decanoylricinoleate (MeR-10)	−45.0, −33.5	−12.1	81(86)[d]
Methyl 12-undec-10-enylricinoleate (MeR-11u)	−23.8	−18.7	80
Methyl 10-undecylenate[f] (C11:1 FAME)		−19.8	99
Methyl 12-acetylstearate (MeHS-Ac)	−24.0	−5.7	45
Methyl 12-butyryl stearate (MeHS-Bu)	−14.1, −3.7	4.9	7
Isopropyl 12-acetylstearate (*i*-PrHS-Ac)	−31.2	−9.8	71
Isopropyl 12-butyryl stearate (*i*-PrHS-Bu)		−15.0	24

Abbreviations for each molecule are in parentheses

[a] Melting points of polymorphic peak were the peak temperatures of the DSC curves

[b] T_{com} is the temperature at completion of melting

[c] The conversion standard deviation were about 2

[d] The value in the parenthesis is from the reaction catalyzed by DMAP and DCC; the value without parenthesis is from the reaction catalyzed by sodium methoxide

[e] Approximate gelling temperatures

[f] Methyl 10-undecylenate (C11:1 FAME) was prepared by methylating a commercial sample of 10-undecenoic acid

product, methyl 12-acetylricinoleate (MeR-Ac), was washed with 2% aqueous acetic acid and water and extracted with hexane. Excess methyl acetate was removed by distillation and the product was purified by chromatography on silica gel. The non-polar MeR-Ac was eluted with 5% diethyl ether in hexane, and the yield after purification was ∼67%. Other 12-acetylricinoleate esters with longer alcohol chains, were synthesized by the same procedure using the corresponding acetate esters, appropriate ricinoleate ester and sodium alkoxide. Ethyl 12-acetylricinoleate, for example, was obtained from the reaction of ethyl acetate and ethyl ricinoleate and catalyzed by sodium ethoxide.

Traditional methods also were used to synthesize MeR-Ac in order to avoid some of the side products that occurred with alkoxide catalysts. Pyridine was used to catalyze the reactions between MeR and acetic anhydride at a molar ratio of 1:1.2:2.4 of MeR:acetic anhydride:pyridine according to Sharma et al. [13]. The excess acid anhydride was removed under vacuum after the reaction was complete. The residual mixture of MeR-Ac and unreacted MeR was separated by silica gel chromatography. The desired product was eluted with 5% diethyl ether in hexane. Similar synthesis strategies were applied for methyl 12-butyrylricinoleate (MeR-Bu), isopropyl 12-butyrylricinoleate (*i*-PrR-Bu), methyl 12-acetylstearate (MeHS-Ac), methyl 12-butyryl stearate (MeHS-Bu), isopropyl 12-acetylstearate (*i*-PrHS-Ac) and isopropyl 12-butyryl stearate (*i*-PrHS-Bu).

Methyl 12-hexanoylricinoleate (MeR-Hx), and methyl 12-octanoylricinoleate (MeR-Oc) were synthesized by esterification of MeR with hexanoic acid and octanoic acid, respectively, catalyzed by 4-dimethylaminopyridine (DMAP) and 1,1-dicyclohexylcarbodiimide (DCC), following the procedure of Kodali et al. [14].

Methyl 12-decanoylricinoleate (MeR-10) was synthesized by reacting methyl ricinoleate with methyl decanoate at a molar ratio of 1:5, and catalyzed by 2% sodium methoxide. The excess methyl decanoate was removed by distillation. GC analysis showed that the product contained ~80% MeR-10 and small amounts of MeR (10%), methyl ricinoleate estolide dimer (MeR-Estolide, 2%) and methyl 12-decanoylricinoleate estolide dimer (MeR-Estolide-10, 8%). The polar constituents, MeR and MeR-Estolide were removed by silica gel chromatography with a gradient elution of hexane/diethyl ether (95:5 to 80:20, v/v). The non-polar MeR-Estolide-10 was removed by silver ion-silica gel chromatography.

The preparation of silica gel containing 20–30% silver nitrate for use in chromatography was adapted from a procedure of Ghebreyessus et al. [15]. About 140 g silica gel was added to a 300 mL of 22% aqueous solution of silver nitrate. The mixture was well stirred for 10 min and dried at 110 °C for ~5 h. The powder was protected from light. A gradient elution of 45–60% diethyl ether in hexane washed out MeR-10 that had one double bond, and left MeR-Estolide-10, which had two double bonds, on the column.

The synthesis and purification of methyl 12-undec-10-enoylricinoleate (MeR-11u) were similar to those for MeR-10. A gradient elution of 85–90% ether/hexane collected MeR-11u from the silver ion-silica gel column.

The reaction conversion percentages of various esters are given in Table 1.

Instrumental Analysis

GC analysis was done on an HP 5890 Series II instrument (Hewlett-Packard, PA) with a SPB-1 fused silica column (15 m × 0.25 mm × 0.25 μm) (Supelco, Bellefonte, PA). The carrier gas (helium) flow rate was 1.9 mL/min, and the split ratio was 2.64. The injector and flame ionization detector were at 300 °C. The oven temperature was programmed from 100 to 300 °C at a rate of 10 °C/min, and then held at 300 °C for 10 min.

The structures of various esters in $CDCl_3$ solution were confirmed by ^1H NMR with a Varian VXR-400 NMR spectrometer (Varian Inc., Palo Alto, CA) and compared with chemical shifts predicted by ACD/ChemSketch Predictor software (Advance Chemistry Development, Inc., Toronto, Ontario, Canada).

Melting points of the synthesized esters were measured with a DSC7 differential scanning calorimeter equipped with an Intracooler System I (Perkin Elmer, Norwalk, CT). The temperature programs and calibrations with indium and *n*-decane were described previously [4]. Visual observations of samples cooled with dry ice-acetone were used to determine the approximate gelation temperature for compounds that did not crystallize in the DSC.

The dynamic viscosities of the various ricinoleate esters in the temperature range −5 to 80 °C were determined with a Brookfield DV II + viscometer (Brookfield Inc., Stoughton, MA) using a CP42 cone spindle. The instrument condition, temperature calibration, and procedure for measurement were described previously [4]. The viscometer has an error of ±1% under the conditions used for our measurements.

The viscosities of 12-acetylricinoleate esters in the temperature range of −34 to 10 °C were determined with the same viscometer and spindle. The temperature was controlled with a Brinkmann RK 20 refrigerated circulator (Westbury, NY) and was monitored with a total immersion Fisherbrand ASTM thermometer (Fisher Scientific, Pittsburgh, PA) with the temperature of −38 to 2 °C, which was inserted in a glass tube on the return line of the circulating water bath. Data were collected between −34 and 0 °C at 5 °C intervals. Viscosities were recorded after equilibrating at the desired temperature for 5 min and at the maximum attainable torque.

The density of MeR was measured by a pycnometer with a 5-mL capacity (Ace Glass, Vineland, NJ) and water was used to verify the exact volume of the pycnometer.

The oxidative stability index (OSI) of MeR-Ac was measured using an ADM Oxidative Stability Instrument (Omnion, Rockland, MA) at 110 °C, according to AOCS Official Method Cd 12b-92 [16].

Friction and Wear Test

Friction and wear tests were performed on a custom-built ball-on-flat microtribometer, which has been previously described [17]. In both tests, a stainless steel ball rubbed against a polished stainless steel disk at specified speed for a specified time. The esters to be tested were mixed with light mineral oil at 10% (by wt).

Preliminary test had shown that the stainless steel disks were the major source of variance, so a balanced incomplete randomized block design was used in the friction tests. Twelve disks were treated as blocks, and each block was assigned randomly to three esters. Four repeated measurements were performed for each ester on different disks and averaged. A ramped load test was used to obtain the coefficient of friction (COF) in which the normal force was increased from 0.2 to 1,000 mN while the probe was sliding against the disk for 40 mm at 1 mm/s. The repeated measurements of each ester were performed in a parallel fashion and 0.9 mm apart. After each test, the stainless steel disk was cleaned with soapy water, and then sonicated for 10 min in acetone before the next ester was tested.

A completely randomized block design was used for the wear tests. Three disks were treated as blocks, and each ester was tested once on each disk. Reciprocal sliding of the probe against the disk under 800 mN normal load over a 30-mm distance for 500 cycles at 5 mm/s was used. Ten random locations on each wear track were selected, and wear depths were measured with a contact profilmeter Dektak IIA (Veeco Instruments, Santa Barbara, CA).

Data were fitted to a mixed linear model with SAS (Version 9.1, SAS Institute Inc. Cary, NC, USA) to test significant difference at $p = 0.05$.

Results and Discussion

Synthesis and Purification of Various Ricinoleate Esters

During the counter-current purification of MeR, the yield of the MeR in the collected fractions increased from fractions 1 through 3 and then slowly declined with successive fraction to low values. The purity of the MeR markedly increased from fraction 1 to 3 and remained above 99% through fraction 11, declining to 98% in fraction 12. The use of small amount of acetic acid prevents the production of free fatty acids. This proved to be a convenient method for obtaining pure MeR. The reaction conversions of 12-acetylricinoleate esters using the acetate esters transesterification were about 85%. A small amount (<2% by GC) of ricinoleate estolide dimer was inevitably produced during the synthesis of 12-acetylricinoleate esters by this method even though a large excess of the acetate esters were added to drive the reaction to completion and suppress the formation of ricinoleate estolide dimer. The MeR estolide dimer further reacted with the acetate esters to form 1–2% of non-polar acylated MeR estolide dimer that could not be removed from the desired product by silica gel chromatography. In spite of the presence of small amounts of impurities, this method provided an effective way to obtain acetylated ricinoleates with satisfactory reaction conversions. The acylation reactions catalyzed by DMAP generally gave higher conversion rate than those catalyzed by pyridine. Acylation with short chains acids tended to have higher conversion rate than long chain compounds when using the same methods. Reactions between MeR and a medium chain length fatty esters, such as methyl decanoate or methyl 10-undecylenate, had high conversion (>80%) when catalyzed by sodium methoxide, but silver ion-silica gel chromatography was not very efficient in separating these compounds from small amounts of accompanying acylated ricinoleate estolide dimer.

NMR Results

The ^{1}H-NMR results for all the purified compounds were compared with the NMR spectra predicted by ACD/ChemSketch Predictor software and in all instances they were in agreement with the relative size and location of the predicted peaks. There was no sign of peaks indicating extraneous impurities. Our results also agree with the ^{1}H-NMR spectra of MeR and MeR-Ac previously reported [18, 19].

Effects of Chemical Structures on Melting Points

The melting points (completion of melting) of ricinoleate and 12-hydroxystearate esters and acylated derivatives are shown in Table 1. Those who work with lubricants traditionally use parameters such as cloud point and pour point to characterize low temperature properties. For relatively pure compounds, such as those we are characterizing, the cloud and pour points are approximately the same as their melting point [20]. Among ricinoleate esters with a free hydroxy group, MeR had the highest melting point at −3.5 °C, which is slightly higher than the literature value [20]. BuR melted at the lowest melting temperature of −29.4 °C. For longer-chain esters of ricinoleate, the melting point increased with chain length. Such V-shaped plot of melting points versus chain length has been found for esters of oleate, stearate and for saturated free fatty acids [4, 21]. References 4 and 21 provide data and speculation about the causes of this phenomenon. The melting point of *i*-PrR, which melts at −20.3 °C, is very similar to that of the corresponding straight chain, PrR, which melted at −19.4 °C. In the oleate ester series, isopropyl oleate melted 6.2 °C lower than propyl oleate [4]. Presumably, this difference is because the isopropyl group interferes with the close packing of alkyl chains. The similar melting points of *i*-PrR and PrR suggest that the hydroxy group of the ricinoleate dominates its crystal packing pattern and makes the effect of the isopropyl branch negligible.

Figure 1 shows that the melting points of the ricinoleate esters of various chain lengths are slightly higher than those of the corresponding oleate esters. Similarly, the reported melting point for 12-hydroxystearic acid, 76 °C [22], is slightly higher than that of stearic acid, 70 °C. These observations suggest that a polar hydroxy group positioned in the middle of a carbon chain slightly increases the melting point of a fatty acid or its esters.

The ricinoleate esters whose 12-hydroxy groups were acylated with short-chain acids having carbon number 2 to 8, did not crystallize in the temperature range we measured (−60 to 0 °C). Instead, they formed transparent gel-like solids at about −50 to −55 °C.

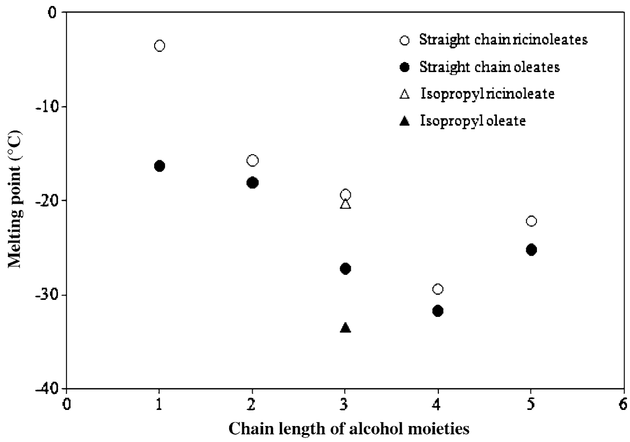

Fig. 1 Melting points of ricinoleate and oleate esters. The melting points of the oleate esters are from Ref. 4

In contrast to the shorter 12-acyl branches, the decanoyl and 10-undecenoyl derivatives of ricinoleates were able to crystallize at low temperatures. Seemingly, an acyl group that is a little longer than eight or nine carbons allows crystallization. The melting points of MeR-10 and MeR-11u were −12.1 and −18.7 °C, respectively. Compared with MeR, which possesses a free hydroxy group, the melting points were lowered considerably by adding these longer branches on the 12-position of MeR. The double bond on the 10-undecylenate moiety further depressed the melting point. Possibly the isopropyl esters of these compounds would have even lower melting points than their methyl ester counterparts.

Considering that there were small amounts of acylated estolide esters presented in these 12-acylated ricinoleates, we compared the melting profiles of MeR-Ac and MeR-10 of which the same compounds were alternatively synthesized with pyridine or DMAP. No differences were detected between the pure samples and those contaminated with acylated MeR estolide dimer.

The low temperature properties of 12-hydroxystearate esters also were studied. As shown in Table 1, MeHS and *i*-PrHS melt at 59.4 and 49.0 °C, respectively. Esterifying the 12-OH position with acetate or butyrate lowered the melting points by more than 50 °C for both the methyl and isopropyl esters.

During DSC measurements, most of the compounds showed polymorphism. Changing the temperature program and letting the compounds temper for 7–10 min at the temperature where the highest melting polymorph begins to melt, reduced or deleted the peaks of the low temperature polymorphs. All the melting points reported in Table 1 are from the polymorphic form with the highest melting temperature, which is the most stable form. The melting temperatures of other polymorphic forms that we encountered for each compound also are recorded.

The melting points of ricinoleate esters with free hydroxy groups and those acylated at the C-12 position by medium-chain fatty acids, i.e. MeR-10 and MeR-11u, ranged from −3.5 to −29.4 °C. The compounds in Table 1 that did not crystallize upon cooling to −50 °C included all the 12-acylated ricinoleate esters with an acyl side chain of eight carbons or less. These are promising candidates for biolubricants; however, Knothe [20] has suggested that ricinoleate ester may be considerably less stable to oxidation than oleate esters. A preliminary study in our laboratory showed that for samples that had been stripped of tocopherols, MeR-Ac had an OSI time longer than MeR. Esters derived from 12-hydroxystearic acid had fairly high melting points except for *i*-PrHS-Bu, which melted at −15.0 °C, but they should have high stability because of the absence of double bonds.

Effect of Chemical Structures on Viscosities

The dynamic viscosities between −5 and 80 °C of most of the products synthesized in this study are shown in Table 2. As usual, the viscosities of the compounds we examined increased with carbon numbers and decreased with temperature. At temperatures below 40 °C, ricinoleate esters with a free hydroxy group had higher viscosities than 12-acylated ricinoleate esters. Indeed, a free 12-hydroxy group on MeR gave a higher viscosity than MeR acylated with a 10 or 11-carbon chain. Above 40 °C, the differences in viscosity among these compounds became relatively small.

The viscosity at 40 °C of compounds in Table 2 are considerably lower than biolubricants made from triacylglycerol estolides, or oils with ether-linked side chains chiefly because of the difference in molecular sizes [8]. Their viscosities were slightly lower than ricinoleate estolide dimers esterified with monohydroxy alcohols [9]; but comparable to other straight or branched-chain monoesters [2].

The viscosities of some 12-acetylricinoleate esters also were measured in the range of −10 to −34 °C, and the results are shown in Table 3. Their viscosities at −34 °C were not particularly high, which indicated that the 12-acetylricinoleates still flow freely at −34 °C. Our equipment was unable to achieve temperatures below −34 °C. As expected, the longer the carbon chain of the esterifying alcohol, the greater the viscosity of the ester.

The viscosity of isopropyl esters showed some interesting changes with temperature relative to other ricinoleate derivatives. In our previous work on branched esters [4], we found that the isopropyl ester gave viscosities similar to *n*-propyl esters. Of the ricinoleate esters shown in Table 2, the isopropyl ester had a higher viscosity than the *n*-propyl ester and butyl ester at −5 °C. The isopropyl ester continued to have slightly higher viscosity than the

Table 2 Dynamic viscosities of various ricinoleate esters

Temperature (°C)	Viscosity (cp)											
	MeR[a]	EtR	PrR	BuR	*i*-PrR	MeR-Ac	EtR-Ac	PrR-Ac	BuR-Ac	*i*-PrR-Ac	MeR-10	MeR-11u
−5	130.8	145.6	162.3	171.6	182.6	55.0	59.2	66.4	68.9	73.7	65.4	96.8
0	95.1	105.1	117.1	124.1	130.2	40.9	45.4	50.0	52.4	54.8	50.4	76.7
5	70.2	77.8	84.9	90.8	94.2	31.5	35.1	38.3	40.3	41.6	39.5	56.6
10	52.7	58.1	63.1	67.6	69.1	24.7	27.4	29.9	31.4	32.0	31.0	45.3
15	40.0	43.8	47.9	51.3	51.8	20.2	22.1	23.9	25.1	25.2	25.4	35.9
20	31.2	34.0	37.0	39.6	39.8	16.9	18.1	19.6	20.3	20.2	20.4	28.0
25	25.9	27.0	29.0	31.4	31.3	14.0	14.8	16.1	16.8	16.7	17.3	22.8
30	20.0	21.5	23.1	24.9	24.7	12.0	12.3	13.3	14.0	13.8	14.5	19.0
35	16.8	17.3	18.6	20.1	19.7	10.1	10.4	11.2	11.8	11.6	12.4	15.9
40	13.8	14.2	15.2	16.5	16.1	8.84	8.89	9.54	10.0	9.79	10.7	13.5
45	11.5	11.8	12.8	13.6	13.2	7.57	7.65	8.20	8.64	8.38	9.27	11.6
50	9.70	9.87	10.8	11.4	11.0	6.59	6.65	7.12	7.48	7.23	8.06	9.97
55	8.25	8.40	9.10	9.71	9.28	5.75	5.85	6.25	6.55	6.31	7.10	8.71
60	7.05	7.15	7.76	8.30	7.92	5.06	5.15	5.48	5.77	5.54	6.27	7.63
65	6.09	6.19	6.70	7.13	6.81	4.50	4.58	4.86	5.12	4.91	5.59	6.74
70	5.30	5.39	5.81	6.21	5.89	4.01	4.09	4.35	4.57	4.38	5.03	5.98
75	4.67	4.72	5.11	5.43	5.15	3.61	3.68	3.90	4.11	3.91	4.54	5.34
80	4.11	4.19	4.51	4.80	4.55	3.27	3.33	3.54	3.71	3.54	4.11	4.79
100[b]	2.77	2.80	3.06	3.21	3.06	2.37	2.44	2.59	2.72	2.55	3.04	3.46
VI[c]	22	19	53	53	29	100	115	123	134	105	171	157

[a] See Table 1 for the key to abbreviated names

[b] Calculated from Eq. 1 with E_a in Table 4

[c] VI was calculated by assuming the density of these esters were 0.9

Table 3 Dynamic viscosities of 12-acetylricinoleates at −10 to −34 °C

Temperature (°C)	Viscosity (cP)		
	MeR-Ac[a]	BuR-Ac	*i*-PrR-Ac
−10.0	88.0	91.5	81.1
−15.2	124.0	126.1	112.3
−20.4	177.8	186.0	165.0
−24.6	257.6	263.9	234.2
−30.8	398.9	413.5	355.5
−34.9	620.9	635.9	556.1

[a] See Table 1 for the key to abbreviated names

n-propyl ester throughout the temperature range studied, but the difference in the viscosity of the isopropyl and butyl esters became smaller as the temperature increased, and at 25 °C and higher, the butyl esters had a greater viscosity. Table 2 shows a similar relationship among the propyl, butyl and isopropyl esters of the 12-acetylricinoleates. The isopropyl ester had a greater viscosity at −5 °C but was surpassed by the butyl ester at 20 °C. This observation is further complicated by data in Table 3, which shows that at −10 °C, the viscosity of isopropyl 12-acetylricinoleate was well below, not only that of the corresponding butyl ester, but also that of the methyl ester. Seemingly, the branched isopropyl group and the branch on the 12 position of ricinoleate caused complex changes in the relative viscosities of these esters.

The viscosities of the esters examined in this paper were fitted with the Eq. 1 developed by Yao and Hammond [4] for oleate esters,

$$\ln \eta = \ln\left(\frac{R}{Nh}\right) + \ln T - \left[\frac{B + CT + DT^2}{RT}\right] \qquad (1)$$

where η is the dynamic viscosity, N is Avogadro's number, h is Planck's constant, T is the temperature in degrees Kelvin, R is the gas constant, and B, C, and D are constants such that $\mathrm{B} + \mathrm{CT} + \mathrm{DT}^2 = E_a$, the energy of activation or the energy required for sliding one molecule past another.

The results gave good fits of the data, which generally are within the experimental error of the measurements ($\leq \pm 1\%$) when temperature is above 5 °C. However, larger variations between calculated and observed viscosities were observed at low temperature measurements where the viscosity increased greatly with temperature decreases. The

Table 4 Equations for calculating E_a with Eq. 1

Compounds[a]	E_a calculations[b]
MeR	$E_a = -0.2609T^2 + 531.95T - 58996$
EtR	$E_a = -0.2899T^2 + 552.85T - 62790$
PrR	$E_a = -0.3101T^2 + 565.30T - 64908$
BuR	$E_a = -0.2920T^2 + 553.58T - 63202$
i-PrR	$E_a = -0.3231T^2 + 576.31T - 67199$
MeR-Ac	$E_a = -0.2053T^2 + 481.71T - 47511$
EtR-Ac	$E_a = -0.2489T^2 + 511.33T - 52584$
PrR-Ac	$E_a = -0.2597T^2 + 518.69T - 54016$
BuR-Ac	$E_a = -0.2565T^2 + 516.09T - 53644$
i-PrR-Ac	$E_a = -0.2474T^2 + 512.28T - 53284$
MeR-10	$E_a = -0.2286T^2 + 493.75T - 49538$
MeR-11u	$E_a = -0.2582T^2 + 517.92T - 54829$

[a] See Table 1 for the key to abbreviated names

[b] T is in Kelvin

equations for E_a and values for B, C, and D are given for each compound in Table 4.

In lubricants studies, it is customary to determine the kinematic viscosity of a fluid at 40 and 100 °C and use this data to calculate the viscosity index (VI) [23]. The kinematic viscosity can be obtained by dividing the dynamic viscosity of a fluid by its density. The density of fatty acid esters are typically about 0.9 g/mL. For example, we found MeR's density to be 0.928 g/mL at 25 °C and 0.913 g/mL at 40 °C. We have calculated the approximate VI of the compounds listed in Table 2 according to ASTM D2270 [23] by assuming the density of all these compounds was 0.9 and calculating the viscosity at 100 °C of each compound with our Eq. 1 using the appropriate E_a from Table 4. As shown in Table 2, the 12-acylated ricinoleate esters gave VIs in the range of 100 to 171 whereas ricinoleate esters with a free hydroxy group had VIs below 100. The ricinoleate esters with long acyl groups, i.e. MeR-10 and MeR-11u, had a greater VIs than 12-acetylricinoleates. MeR-11u had a lower VI than that of MeR-10 possibly because of MeR-11u's terminal double bond. In general, the VI increased with molecular weight but decreased with branching, i.e. the isopropyl ester. The VI of simple fatty esters usually was about 200 [2]. Having a branch in the carbon chain (such as 12-acyl ricinoleates) decreased the VI in agreement with Hwang et al. [24]. But the VI reduction could be reduced by increasing the chain length of the branch. The VI of 12-acylated ricinoleate esters are comparable to those of synthetic oil and superior to those of mineral oil with similar kinematic viscosities at 100 °C [25].

Friction and Wear Test

The COF was calculated as the slope of the linear regression line of normal force versus lateral force. There was no significant difference in the COFs among mineral oil and mineral oil containing 10% MeR, BuR, or *i*-PrR. The COFs ranged from 0.20 to 0.24. The COFs of unlubricated disks were significantly different ($p = 0.0194$) under our microscale conditions, which is not surprising [26] but is frequently overlooked in the statistical design of tribological tests. We overcame this problem with a statistical block design.

The wear depths for various lubrication conditions are shown in Fig. 2. A low value indicates better wear protection. Disks lubricated with MeR-Ac had significantly less wear depth than those of an unlubricated surface or a surface lubricated with mineral oil. Disks lubricated with MeR-10, BuR, *i*-PrR and MeR showed significant less wear depths than an unlubricated surface, but were not different from surfaces lubricated with mineral oil. Apparently, adding 10% of MeR-Ac to mineral oil enhanced the protection against wear damage. Again a significant effect for disk blocks ($p < 0.0001$) suggested that variation in the surface of the unlubricated disks should not be ignored in the statistical design.

We confirmed that the locations of each wear track on a particular disk, which were randomly selected to test for wear depths, had no significant difference.

In conclusion, 12-acylated ricinoleate esters, and some acylated 12-hydroxystearate esters reported in this study have shown considerable potential for use in lubrication applications because of their low melting temperatures, viscosities and lubricity. Isopropyl 12-hydroxystearate acylated with acetate and butyrate melted, respectively, at −9.8 and −15 °C. They should be quite stable to oxidation. The 12-acylated ricinoleate esters with acyl chain lengths of 8 or less all melted below −50 °C. In addition, MeR-Ac promises to reduce the wear of metal surfaces compared with petroleum-based lubricants. The oxidative stability of MeR seems to be less than that of methyl oleate [20], but

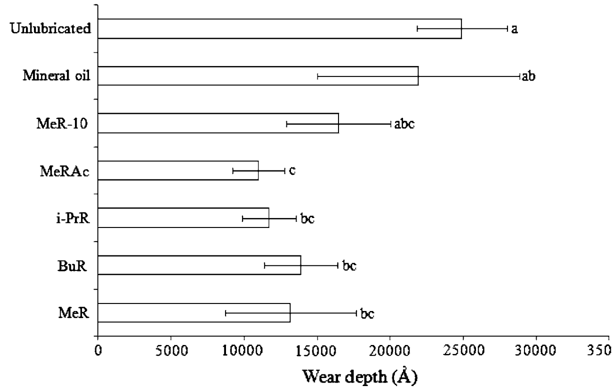

Fig. 2 The wear depths observed for unlubricated surfaces and surfaces lubricated with mineral oil or mineral oil with 10% of various esters. Treatments with the same *letter* had no significant difference ($p < 0.05$)

preliminary data from our laboratory suggests that MeR-Ac is considerably more stable to oxidation than MeR. Kortenska and Yanishlieva [27] have found that long-chain alcohols accelerate oxidation presumably by hydrogen bonding antioxidants as well as a direct effect on the oxidation reaction. Most of their work has been done with primary alcohols, and they found that the longer the chain, the greater the prooxidant effect. Methyl ricinoleate has been reported to exhibit a similar prooxidant effect [28]. If this mechanism is correct, then MeR-Ac might have a stability comparable to oleate because its 12-hydroxy group is acylated. Further work is needed on the oxidative stability of these compounds.

The isolation and acylation of pure ricinoleate esters can be accomplished by fairly simple chemistry. The ricinoleate esters can be isolated in a pure form by the counter-current distribution process described in this report. This step is critical to the removal of long-chain saturated and monounsaturated esters that would elevate the melting point of the product. The acylation can be accomplished by the sodium alkoxide process we used with suitable recycling and drying of the large amount of acetate ester required. The unacylated product of the reaction can be recovered and recycled by the counter-current method used to isolate the original ricinoleate esters. The formation of esters of ricinoleate or other hydroxy alkyl esters in oilseed plants that had probably been modified by molecular genetics would probably reduce the expense of this sort of lubricant significantly. Smith [6] and Li and Beisson [11] have discussed ways in which this could be accomplished, although such a process has yet to be achieved.

Acknowledgments We thank the Plant Science Institute and Center for Crop Utilization Research at Iowa State University for funding, and A. Pintar for statistics advice.

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