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Physical properties of triglyceride estolides from lesquerella and castor oils[☆]

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Abstract

Lesquerella is a developing hydroxy oilseed crop suitable for rotation in the arid Southwestern United States. The hydroxy oil of lesquerella makes it suitable for esterification into triglyceride estolides. The estolide functionality imparts unique physical properties that make this class of materials suitable for functional fluid applications. Lesquerella and castor hydroxy triglycerides were converted to their corresponding estolides by reacting the oils with saturated fatty acids (C2–C18) in the presence of a tin 2-ethylhexanoate catalyst (0.1 wt.%) and utilizing the condensation of hydroxy with corresponding anhydride or heating under vacuum at 200 °C. Two homologous series of estolides for each triglyceride were synthesized for comparison, mono-capped (one hydroxy functionality per triglyceride molecule) and full-capped (all hydroxy functionalities per triglyceride molecule). Physical properties (pour point, cloud point, viscosity, and oxidative stability) were compared for this estolide series. The longer chain saturate capped estolides (C14–C18) had the highest pour points for both mono-capped (9 °C, C18:0) and full-capped (24 °C, C18:0) lesquerella estolides. Castor mono-capped (9 °C) and full-capped (18 °C) triglyceride estolides gave similar properties. However, pour points improved linearly when the shorter saturated fatty acid capping chain lengths were esterified with the hydroxy triglycerides. Lesquerella capped with a C6:0 fatty acid had pour points of −33 °C for the mono-capped and −36 °C for the full-capped and castor had −36 and −45 °C, respectively. Oxidative stabilities of the estolides were compared for oleic, lauric and lauric-hydrogenated mono- and full-capped materials by rotating bomb oxygen test (RBOT). RBOT times for oleic and lauric capped estolides were low and similar with times centered around 15 min. However, when antioxidant (4 wt.%) was added the RBOT times increased to 688 min for the hydrogenated full-capped lesquerella lauric estolide. The antioxidant had little effect on RBOT times when 2 wt.% or less antioxidant was added for all the estolides except those that were hydrogenated. The hydrogenated estolides showed improvements in oxidative stability at all concentrations of antioxidant tested. Viscosity index ranged from 130 to 202 for all estolides with the shorter chain length capped estolides gave the lower viscosity index values. Viscosity at 100 °C ranged from 13.9 to 26.6 cSt and the 40 °C viscosity ranged from 74.7 to 260.4 cSt where the longer chain length capped estolides gave the highest viscosities.
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1. Introduction

The genus *Lesquerella* is being developed as an alternative crop for the southwestern region of the U.S. The seed oil of *Lesquerella* contains 55–60% of 14-hydroxy-*cis*-11-eicosenoic acid (lesquerolic acid) a homologue of ricinoleic acid obtained from castor oil (Glaser et al., 1992). Lesquerella has not reached commercial production however, 16.2 hectare field plots have been grown in 2003 and 2004 for market development. The key aspects of lesquerella have centered on improving the agronomics of the crop through breeding (Dierig et al., 1993) and best management practices. Improved lesquerella breeding lines with seed oil contents of 35% compared with 30% are currently under development and seed yield of 2040 kg/ha versus current releases of 1360 kg/ha (Brahim et al., 1996) will help lesquerella to become competitive in the hydroxy oil market.

Chemical modifications of lesquerolic acid, thus far have closely duplicated derivatizations of ricinoleic acid. One of the more historic reactions of hydroxy fatty acids is the alkaline cleavage of lesquerolic and ricinoleic acid to 2-octanone and 12- or 10-hydroxydecanoic acid, respectively (Diamond et al., 1965; Naughton, 1974). In the presence of excess alkali and at higher temperatures (250–275 °C), an irreversible conversion of the ω-aldehydo acid to the 1,12-dodecanedioic acid occurs that could be used as the major ingredient in the synthesis of nylon-12,12, nylon-6,12, and other molded plastics.

Hydroxy fatty acids such as lesquerella can be readily converted to estolides (Penoyer et al., 1954; Hayes and Kleiman, 1995) either as triglycerides in the presence of free fatty acid or from homopolymerization of the split fatty acids. Lesquerella estolides have been synthesized using clays (Burg et al., 1995) and enzymes (Hayes and Kleiman, 1995) as catalysts. Castor oil estolides demonstrate that this reaction can be run in the absence of catalyst at high temperature under vacuum or carbon dioxide (Achaya, 1971). Estolide triglycerides have been reported to be useful as viscosity improvers in vegetable-based lubricants (Lawate, 1995) and as a base-stock for lubricants (Lawate, 1994). We recently reported a detailed study on the synthesis of triglyceride estolides from lesquerella and castor oils (Isbell and Cermak, 2002).

Examination of the triglyceride estolides from hydroxy oils for their basic physical properties has not been reported. However, estolides from non-hydroxy free fatty acids (i.e. oleic) have been shown to possess good cold temperature properties with pour points of −42 °C and yet maintain good oxidative stability (RBOT > 200 min with antioxidant additives) (Cermak and Isbell, 2003).

This manuscript will examine the two homologous series of estolides for the lesquerella and castor triglycerides and compare physical properties of the mono-capped (one hydroxy functionality per triglyceride molecule) with the full-capped (all hydroxy functionalities per triglyceride molecule).

2. Experimental procedures

2.1. Materials

Lesquerella oil was obtained from cold pressed *Lesquerella fendleri* seed and then subsequently alkali refined, bleached, and deodorized. Castor oil, concentrated sulfuric acid, hexanes, and methanol were obtained from Fisher Scientific Co. (Fair Lawn, NJ). Fatty acid methyl ester (FAMEs) standards were obtained from Alltech Associates (Deerfield, IL). Stannous, 2-ethylhexanoate was obtained from Sigma-Aldrich Chemical Co. (Milwaukee, WI).

2.2. Instrumentation

2.2.1. Gas chromatography

Gas chromatographic analysis (GC) was performed with a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA), equipped with a flame ionization detector and an autosampler/injector. Analyses were conducted on a SP 2380 30 m × 0.25 mm i.d. (Supelco, Bellefonte, PA) column. Saturated C_8 to C_{30} FAMEs provided standards for calculating equivalent chain length (ECL) values, which were used to make the fatty acid methyl ester assignments.

SP 2380 analysis was conducted as follows: column flow 3.3 ml/min with helium head pressure of 138 kPa; split ratio 22:1; programmed ramp 150–180 °C at 7 °C/min, 180–265 °C at 15 °C/min; injector and detector temperatures set at 250 °C.

2.2.2. Nuclear magnetic resonance (NMR)

^1H and ^{13}C NMR spectra were obtained on a Bruker ARX-400 (Karlsruhe, Germany) with a 5 mm dual proton/carbon probe (400 MHz ^1H/100.61 MHz ^{13}C) using $CDCl_3$ as a solvent in all experiments. Extent of estolide formation was determined by taking the ratio of the estolide methine resonance at 4.87 ppm to the hydroxy methine at 3.55 ppm (Isbell and Cermak, 2002).

Table 1
Physical properties of lesquerella triglyceride estolides

ID	Fatty acid	Estolide number	Pour Point (°C)	Cloud Point (°C)	Viscosity @ 40 °C (cSt)	Viscosity @ 100 °C (cSt)	Viscosity index
Lesquerella	NA	NA	−21	−22	127.7	15.2	123
L2-M	C2:0	0.90	−21	>r.t.	92.8	14.6	164
L2-F	C2:0	1.70	−30	−18	79.7	14.2	186
L4-M	C4:0	0.88	−27	<−27	86.7	14.4	173
L4-F	C4:0	1.50	−33	−30	74.7	13.9	194
L6-M	C6:0	0.78	−33	>r.t.	103.0	15.9	165
L6-F	C6:0	1.23	−36	>r.t.	87.9	15.2	183
L8-M	C8:0	0.75	−27	−25	115.7	15.1	187
L8-F	C8:0	1.41	−33	−27	76.0	14.8	205
L10-M	C10:0	0.66	−27	−26	118.5	17.2	159
L10-F	C10:0	1.51	−30	−17	99.9	16.7	182
L12-M	C12:0	1.00	−27	−23	110.8	17.4	173
L12-F	C12:0	1.60	−18	−28	101.0	17.2	186
H_2-L12-M	Hydrogenated L12-M	0.97	mp 28–38	NA	NA	NA	NA
H_2-L12-F	Hydrogenated L12-F	1.61	mp 20–32	NA	NA	NA	NA
L14-M	C14:0	1.29	−18	1	129.9	19.2	168
L14-F	C14:0	1.46	3	21	118.6	18.4	174
L16-M	C16:0	0.83	0	15	135.2	20.5	176
L16-F	C16:0	1.75	6	27	114.2	18.7	184
L18-M	C18:0	1.46	9	28	137.4	20.5	173
L18-F	C18:0	1.75	24	45	Solid	34.3	NA
L18:1-M	C18:1	0.97	−27	−16	119.6	18.7	176
L18:1-F	C18:1	1.56	−27	−16	95.1	17.0	195

Estolide numbers were determined by NMR of the ratio of the estolide methine resonance at 4.87 ppm to the hydroxy methine resonance at 3.55 ppm.

2.3. Methods

2.3.1. Preparation of methyl esters for GC

Estolides, oils, and fatty acid methyl esters were prepared by treating a 10 mg sample with 0.5 ml of 0.5 M KOH/MeOH in a sealed vial for 1 h at 100 °C in a heating block. After cooling to room temperature, 1.5 ml of 1 M H_2SO_4/MeOH was added and then the vial was resealed and heated to 100 °C in a heating block for 15 min. The mixture was transferred into a 2 dram vial and 1 ml of water was added. The solution was extracted with 1 ml of hexane. The hexane layer was dried over sodium sulfate and than injected onto the GC for FAMEs analysis. Comparison of the normalized area percent of the hydroxy containing FAMEs to the non-hydroxy FAMEs gave the estolide numbers for synthesized triglyceride estolides.

2.3.2. Synthesis of lesquerella and castor estolides C2 and C4

For the synthesis of mono-capped triglyceride estolides, refined lesquerella oil (63.4 g, 65.8 mmol) or castor oil (61.2 g, 65.9 mmol) was combined with an equimolar amount of the corresponding acid anhydride as listed in Tables 1 and 2. Pyridine (0.98 g, 12.4 mmol) was added as a catalyst. Reactants were combined in a three-neck round bottom flask equipped with magnetic

stirrer, cold water condenser, and temperature probe. For the synthesis of full-capped lesquerella estolides, refined lesquerella oil (63.5 g, 65.9 mmol) was combined with a 2.5 molar equivalent of the corresponding acid anhydride as listed in Tables 1 and 2. For the synthesis of full-capped castor triglyceride estolides, castor oil (60.2 g, 64.8 mmol) was combined with a 4 molar equivalent of the corresponding acid anhydride as listed in Tables 1 and 2. Pyridine (0.98 g, 12.4 mmol) was added as a catalyst. The round bottom flask was set up as previously described. All acetic anhydride reactions were run at 50 °C for 24–26 h then dissolved in hexane and washed with 5% H_2SO_4(aq), saturated NaCl, and NaH_2PO_4 (pH 5) solutions. Butyric anhydride reactions were run at 60 °C for 4–6 h then dissolved in hexane and washed with 1 M KOH, saturated NaCl, NaH_2PO_4 (pH 5), Na_2HPO_4 (pH 9) solutions. Ethanol (85%) was added to break the emulsions. The crude estolides had acid values of 2.68 mg/g or lower.

2.3.3. Synthesis of lesquerella and castor estolides C6–C12

For the mono-capped triglyceride estolides, refined lesquerella oil (1.33 kg, 1.38 mol) or castor oil (1.25 kg, 1.35 mol) and an equimolar amount of the corresponding fatty acid listed in Tables 1 and 2 were combined

Table 2
Physical properties of castor triglyceride estolides

ID	Fatty acid	Estolide number	Pour point (°C)	Cloud point (°C)	Viscosity @ 40 °C (cSt)	Viscosity @ 100 °C (cSt)	Viscosity index
Castor	NA	NA	−15	−34	260.4	20.1	89
C2-M	C2:0	0.82	−24	<−24	147.4	16.8	122
C2-F	C2:0	2.59	−27	<−27	110.0	15.6	150
C4-M	C4:0	0.93	−27	<−27	117.4	15.4	138
C4-F	C4:0	2.70	−33	−30	82.2	14.0	177
C6-M	C6:0	0.80	−36	<−36	133.0	19.4	167
C6-F	C6:0	1.67	−45	<−45	79.0	17.0	234
C8-M	C8:0	0.98	−21	<−21	203.0	21.1	123
C8-F	C8:0	2.54	−36	<−36	105.9	16.8	172
C10-M	C10:0	1.04	−27	<−27	183.8	21.0	135
C10-F	C10:0	2.34	−36	<−36	91.8	16.2	191
C12-M	C12:0	0.92	−27	<−27	193.1	21.4	132
C12-F	C12:0	2.36	−33	<−33	120.0	19.1	181
H_2-C12-M	Hydrogenated C12-M	1.19	mp 24–36	NA	NA	NA	NA
H_2-C12-F	Hydrogenated C12-F	2.35	−3	21	161.2	22.1	164
C14-M	C14:0	1.11	−24	−17	223.4	25.6	146
C14-F	C14:0	2.69	−18	−7	155.9	23.2	179
C16-M	C16:0	0.81	−18	−3	220.6	24.1	137
C16-F	C16:0	2.69	3	21	177.8	26.1	182
C18-M	C18:0	2.10	9	27	226.8	26.6	151
C18-F	C18:0	2.42	18	24	174.5	25.7	182
C18:1-M	C18:1	1.55	−33	<−50	186.9	23.5	154
C18:1-F	C18:1	2.69	−27	−27	131.8	21.9	195

Estolide numbers were determined by NMR of the ratio of the estolide methine resonance at 4.87 ppm to the hydroxy methine resonance at 3.55 ppm.

in a three-neck round bottom flask. For the synthesis of full-capped lesquerella estolides, refined lesquerella oil (1.33 kg, 1.38 mol) and a 2.5 molar equivalent of the corresponding fatty acid listed in Table 1 were combined in a three-neck round bottom flask. For the synthesis of full-capped castor estolides, castor oil (1.25 kg, 1.35 mol) and a 4 molar equivalent of the corresponding fatty acid listed in Table 2 were combined in a three neck round bottom flask of sufficient size. In all of the reactions, the flask was equipped with a magnetic stir bar, temperature probe, and two condensers connected in series (this condenser set up was necessary to recirculate all the unreacted fatty acids back into the flask). The first condenser was connected to a recirculating water bath and maintained at a temperature slightly above the melting point of the fatty acid. The second condenser was connected to the first with a 75° distilling head and cooled with cold tap water. The outlet of the second condenser was fitted with a vacuum distillation adapter and round bottom flask to collect the water of reaction. The reaction was catalyzed with 0.1 wt.% tin(II) 2-ethylhexanoate (1.30 g, 3.21 mmol) per gram of oil. Reactants and catalyst were heated to 130 °C under vacuum (12–18 Pa) for 24 h. At the conclusion of the reaction, saturated NaCl was added followed by ethanol (85%) to break any emulsion that

formed. Unreacted fatty acids were removed using a Kügelrohr distillation unit with a vacuum of 6–13 Pa and a temperature of 140–160 °C, distillation required 3–5 h for complete removal of excess fatty acids. When precipitated salts were observed in the finished product, the material was taken up in hexane and gravity filtered.

2.3.4. Synthesis of triglyceride-estolides C14–C18

For mono-capped triglyceride estolides, lesquerella oil (1.33 kg, 1.38 mol) or castor oil (1.25 kg, 1.35 mol) and an equimolar amount of the corresponding fatty acid listed in Tables 1 and 2 were placed in a three-neck round bottom flask. For the synthesis of the full-capped lesquerella estolides, refined lesquerella oil (1.33 kg, 1.38 mol) and a 2.5 molar equivalent of the corresponding fatty acid listed in Table 1 were combined in a three-neck round bottom flask. For the synthesis of full-capped castor estolides, castor oil (1.25 Kg, 1.35 mol) and a 4 molar equivalent of the corresponding fatty acid listed in Table 2 were combined in a three neck round bottom flask of sufficient size. In all of the reactions, the flask was fitted with a temperature probe, vacuum adapter, and stopper. The reaction was performed under vacuum (20 Pa) and held at 200 °C for 24 h using a heating mantle controlled by a J-Kem Gemini-2 (St Louis, MO)

temperature controller utilizing a temperature probe immersed below the liquid surface in the flask. Reactions with lesquerella oil turned from a light red color to pale yellow as the temperature passed beyond 175 °C. For reactions with castor oil, the material changed from colorless to pale yellow over the course of the experiment. When the reaction time was reached the solution was allowed to cool to room temperature under vacuum. The crude reaction mixture was placed in a 2-l distilling flask and connected to a Kügelrohr distillation unit (Aldrich Chemical Co., Milwaukee, WI) and fitted with a 500 ml receiving flask. The material was distilled at 150–170 °C at 6–13 Pa. A colorless distillate of fatty acid was obtained with a yellow residue of triglyceride estolide.

2.3.5. Hydrogenation of triglyceride estolides

Hydrogenation was performed by combining neat estolide and 0.25 wt.% Pd on carbon into a stainless steel pressure reactor (Pressure Products Industries, Warminser, PA). The reactor was charged to 1379 kPa hydrogen after purging with hydrogen. A temperature of 80 °C was maintained and the reaction was stirred for 2.5–5 h until hydrogen consumption ceased. The product was separated from catalyst by vacuum filtration through Celite and #50 Whatman filter paper in a jacketed funnel heated with steam. A 10 mg sample was converted into its methyl ester as described previously and injected onto the GC to confirm saturation of the estolide.

2.3.6. Viscosity measurements

Viscosity was measured using a calibrated Cannon-Fenske viscometer tube (Cannon Instrument Co., State College, PA) in a Temp-Trol (Precision Scientific, Chicago, IL) viscometer bath set at 40.0 and 100.0 °C. Viscosity and viscosity index were calculated using ASTM methods D 445-97 and ASTM D2270-93 (American Society for Testing Materials, 1997, 1998a), respectively. All viscosity measurements were run in duplicate and the average values are reported.

2.3.7. Pour point

Pour points were measured by the ASTM method D97-96a (American Society for Testing Materials, 1996) to an accuracy of ±3 °C. The pour point was defined as the coldest temperature at which the sample still poured. The pour points were determined by placing a test jar with 50 ml of the sample submerged into a cooling medium. The sample temperature was measured in 3 °C increments at the top of the sample until liquid stopped pouring. This point is defined when the sample did not flow when the jar is held in a horizontal position for 5 s. The set point temperature of the cooling media was

determined based on the expected pour point of the sample. Samples with pour points that ranged from +9 to −6, −6 to −24 and −24 to −42 °C were placed in baths of temperature −18, −33, and −51 °C, respectively. All pour points were run in duplicate and the average values were reported.

2.3.8. Cloud point

Cloud points were determined by the ASTM method D2500-99 (American Society for Testing Materials, 1999) to an accuracy of ±1 °C. The cloud points were determined by placing a test jar with 50 ml of the sample submerged into a cooling media. The cloud point is defined as the coldest temperature at which the sample remained opaque. The sample temperature was measured in 1 °C increments at the bottom of the sample until cloudiness was observed. The set point temperature of the cooling media was determined based on the expected cloud point of the sample. Samples with pour points that ranged from +9 to −6, −6 to −24, and −24 to −42 °C were placed in baths of temperature −18, −33, and −51 °C, respectively. All cloud points were run in duplicate and the average values were reported.

2.3.9. Oxidative stability by RBOT

Rotating bomb oxidation tests were conducted on a RBOT apparatus (Koehler, Bohemia, NY) using the ASTM method D 2272-98 (American Society for Testing Materials, 1998b). Samples were run at 150 °C by measuring 50 ± 0.5 g of estolide into the bomb and adding 5.0 ml of reagent water. The copper catalyst was measured to 3 m and sanded with 220 grit silicone carbide sand paper produced by Abrasive Leaders and Innovators (Fairborn, OH) and was used immediately. The wire was wound to have an outside diameter of 44–48 mm, height of 40–42 mm and a mass of 55.6 ± 0.3 g. The bomb was assembled and purged twice with oxygen. The bomb was then charged with 620 kPa of oxygen then tested for leaks by immersion in water. The bomb was placed in the hot oil bath and rotated until the pressure dropped more than 175 kPa below the maximum pressure. All samples were run in duplicate and the average time reported. Samples were run with 0, 0.1, 0.5, 1.0, 2.0, and 4.0 wt.% of a Lubrizol 7652 antioxidant dissolved in the oil prior to the test.

2.3.10. Melting points

Melting points were determined on a Fisher-Johns melting point apparatus set to heat at a rate of 1 °C per min. Samples were placed on a plastic disk and melting points were reported from the first liquid appearance until no solid material remained.
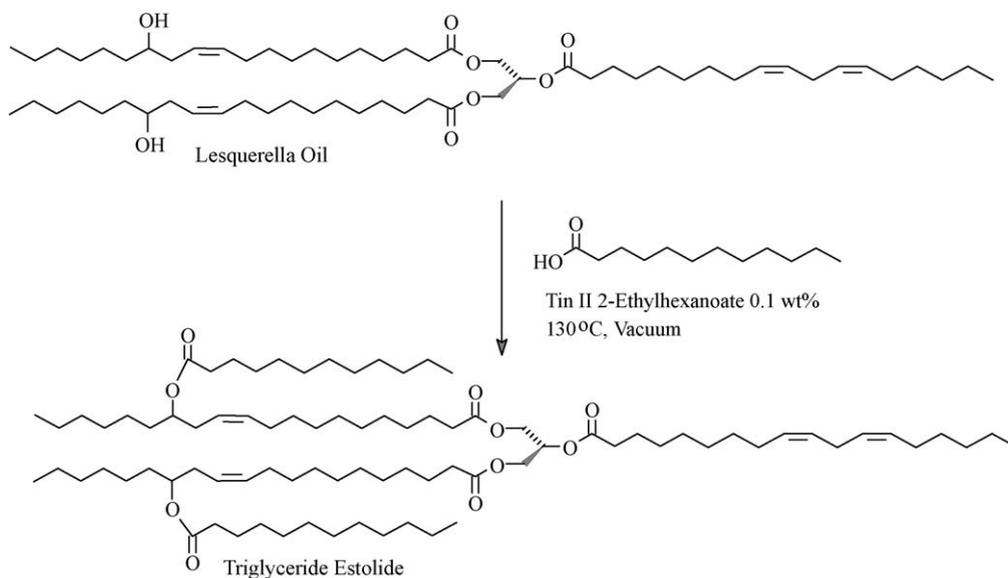
Fig. 1. Reaction scheme for the synthesis of triglyceride estolides (full-capped lesquerella triglyceride estolide shown).

3. Results and discussion

3.1. Synthesis of triglyceride estolides

The hydroxy triglycerides of lesquerella and castor oil were converted into their corresponding mono- and full-capped estolides according to the reaction depicted in Fig. 1. Triglyceride estolides were synthesized from a series of even-numbered carbon saturated fatty acids from acetic to stearic plus oleic. Tin(II) 2-ethylhexanoate served as a catalyst for the capping fatty acids between C6:0 to C12:0 and C18:1. Triglyceride estolides with the shorter chain capping groups (less than C6:0) were reacted with the corresponding acid anhydrides because the tin(II) 2-ethylhexanoate catalyzed reaction only worked at temperatures greater than the boiling point of these shorter chain acids and reaction temperatures could not be achieved. Estolides with longer chain (C14:0–C18:0) were made under vacuum with no catalyst at 200 °C as previously described by Isbell and Cermak (2002). The basic physical properties (pour point, cloud point, viscosity and viscosity index are reported in Tables 1 and 2.

3.2. Effect of esterification on pour points

Lesquerella and castor oils have pour points of −21 and −15 °C, respectively. The full-capped lesquerella triglyceride estolides had slightly lower pour points for all cases than the mono-capped estolides. The lowest pour points were observed for both the mono- (pp = −33 °C) and full-capped lesquerella triglyceride estolides (pp = −36 °C) when the capping group was hexanoic (Table 1). When the saturate capping chain was stearic the materials were semi solids. The full-capped castor triglyceride estolides also had lower pour points than the mono-capped materials for all saturated fatty acid groups below lauric. The lowest pour points observed for both mono- (pp = −36 °C) and full-capped castor triglyceride estolides (pp = −45 °C) were also when the capping group was hexanoic (Table 2). The stearic full-capped castor triglyceride estolides were also solids at room temperature as well. The oleate capped triglyceride estolides for both lesquerella and castor had pour points about −30 °C.

The longer chain capping groups provided sufficient alkyl stacking to yield pour points that were higher than the original oils. The shorter chain groups appear to disrupt the triglyceride stacking interactions to yield pour points that are considerably lower than the underivatized oils. Interestingly, the acetate capped estolides with their two carbon unit do not appear to significantly disrupt the stacking interactions in the oil where the mono-capped estolide has the same pour point as lesquerella oil. Fully capping the lesquerella oil removed both the intra- and intermolecular hydrogen bond interactions yielding a lower pour point. When oleate was used as the capping fatty acid, the unsaturation of the oleate improved the pour point compared with the stearates, 24 °C for stearate full-capped to −27 °C for the oleate full-capped lesquerella estolides.

3.3. Effect of esterification on viscosity

The two main factors in this series of homologous compounds that affect viscosity are hydrogen bonding by the hydroxyl groups and the steric bulk of the molecules. Intermolecular hydrogen bonding between the hydroxy triglycerides increases the steric bulk of the solution by creating weakly associated dimers, trimers, etc. of the original triglycerides, therefore increasing the viscosity of the oil. In all cases, the full-capped triglyceride estolides have lower viscosities for all chain-lengths than the mono-capped estolides. Capping of the hydroxyl moiety reduces or eliminates the hydrogen bonding and consequently reduces the viscosity of the oil. The viscosity trend across the chain-length series follows a linear relationship with increasing viscosity correlated to increasing chain length.

3.4. Oxidative stability

The oxidative stabilities of vegetable oils are very poor due to the amount of unsaturation inherently present in the molecule. The formation of estolides from oleic acid not only improved pour point performance, but reduced the amount of unsaturation in the molecule which resulted in improved oxidative stability (Cermak and Isbell, 2003). The estolides in this study however, do not remove the unsaturation during the course of the derivatization. Consequently, the RBOT times for the estolides are still poor, approximately 15 min (Table 3). The addition of an antioxidant package can improve the performance of the triglyceride estolides in the RBOT however, even when 4% additive was incorporated the triglyceride estolides only gave RBOT times in the 200 min range (RBOT times of 200 min are typical of most mineral oil based automotive crankcase fluids). Hydrogenation of the lauric capped estolides from both lesquerella and castor greatly improved their performance for even the neat oils (no antioxidant added) where the lesquerella mono-capped estolide had an RBOT of 56 min. When 1% anti oxidant was added to this material the RBOT time was extended to 439 min. The castor triglyceride estolides performance were also improved at the same anti oxidant incorporation levels, but the improvement in RBOT time was less. Unfortunately, the pour points of these materials were negatively impacted because these materials were solids at room temperature.

4. Conclusions

Lesquerella and castor triglyceride estolides improved the physical properties (pour point, viscosity and oxidative stability) of the original oils. Full-capped estolides (all hydroxyl moieties within the triglyceride are esterified) gave better pour points and viscosity index values than the mono-capped estolides. Hexanoic acid when used as a capping group provided the best pour points of all the fatty acids studied. Reduction or elimination of hydrogen bonding in the parent oil improved the viscosity properties of all the oils studied. Hydrogenation of the resulting triglyceride estolides improved the oxidative stability of the oils, but decreased the cold temperature properties of the oil.

Table 3
Oxidative stabilities of lesquerella and castor triglyceride estolides

ID	Lubrizol anti oxidant added (wt.%)				
	0	0.5	1	2	4
L12-M	13	17	29	66	118
L12-F	14	22	47	106	158
H_2-L12-M	56	nd	439	559	541
H_2-L12-F	37	nd	476	688	668
L18:1-M	16	18	29	34	121
L18:1-F	14	20	31	60	127
C12-M	18	30	44	102	241
C12-F	16	32	46	124	318
H_2-C12-M	47	nd	142	289	396
H_2-C12-F	28	nd	242	410	515
C18:1-M	15	23	52	90	197
C18:1-F	14	26	48	103	180

All RBOT times are reported in minutes.

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