J Amer Oil Chem Soc (2007) 84:449–456
DOI 10.1007/s11746-007-1052-6

ORIGINAL PAPER

Synthesis and Physical Properties of Tallow-Oleic Estolide 2-Ethylhexyl Esters

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Received: 15 August 2006 / Accepted: 6 March 2007 / Published online: 20 April 2007

Abstract Tallow-oleic estolide 2-ethylhexyl (2-EH) esters were synthesized in a perchloric acid catalyzed one-pot process from industrial 90% oleic and tallow fatty acids at various ratios, while varying the ratio of tallow and oleic fatty acids, with the esterification process incorporated into an in situ second step to provide a functional fluid. Their viscosities ranged 57–80 cSt at 40 °C and 10.8–14.0 cSt at 100 °C with viscosity index (VI) 169–185. The 100% tallow estolide 2-EH ester had modest low-temperature properties (pour point = –15 °C and cloud point = –14 °C), while the 50:50 mixture of oleic and tallow fatty acids produced an estolide that had better low-temperature properties (pour point = –21 °C and cloud point = –21 °C) without a large negative effect on the oxidative stability. The oxidative stability increased as the amount of saturation increased (rotating pressurized vessel oxidation test (RPVOT) × 165–274 min). The tallow-oleic estolide 2-EH esters have shown remarkably low evaporative losses of only 1% loss compared to a 15–17% loss for commercial materials of similar viscosity grade. Along with expected good biodegradability, these tallow-oleic estolide 2-EH esters had acceptable properties that should provide a specialty niche.

Keywords Cloud point · Estolides · Evaporative loss · Oleic · Pour point · RPVOT · Tallow · Viscosity

Introduction

Estolides have been used to help develop new products from industrial crops [1, 2]. Estolides are formed by the formation of a carbocation that can undergo nucleophilic addition with or without carbocation migration along the length of the chain. The carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters. The extent of oligomerization is reported by estolide number (EN), which is defined as the average number of fatty acids added to the base fatty acid. The estolide carboxylic acid functionality can be converted in situ under esterification conditions with the addition of an alcohol to yield the corresponding estolide ester (Fig. 1).

Estolides have been developed to overcome some of the short falls associated with vegetable oils which are known to have poor thermal oxidative stability [3] and low temperature properties [4]. Some of these deficiencies can be improved with the use of additive packages, but usually at the sacrifice of biodegradability, toxicity, and cost.

Tallow is a fat primarily from cattle sources, but can also be from sheep and goats. The US production of beef tallow was about 1–2 million tons in 2005. Tallow has a wide range of applications, some of which date back to traditional soap making, as early as 2800 BC. Tallow is currently still being used as an edible oil but is slowly being replaced with other/healthier choice oils). With this slow trend from edible applications towards industrial applications, tallow is found in a wide range of products from plastics [5], lotions and softeners [6], soaps and

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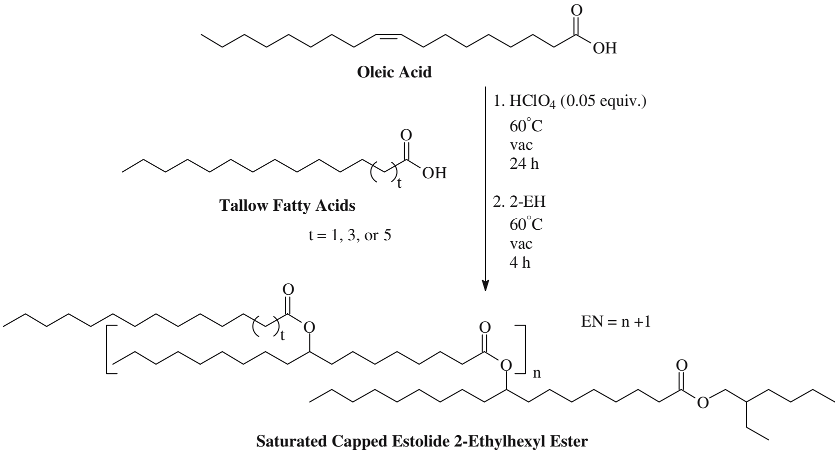

Fig. 1 Reaction scheme for the formation of tallow-oleic estolide 2-ethylhexyl ester

detergents [7], tires [8], candles [9], paints and varnishes [10], lubricants and fuels [11], to even pharmaceuticals [12]. The tallow fatty acid profile depends highly on the tissue location as well as the diet of the animal. The typical fatty acid profile is oleic acid (18:1) at 43.3% as the major fatty acid with palmitic acid (16:0) at 24.6% as the second one (Table 1). Overall, saturated and unsaturated fatty acids were represented at almost a 1:1 split (47 and 53%, respectively).

Some of the estolides synthesized to date that best address cold temperature applications were made from a mixture of saturated and unsaturated fatty acids [13]. When saturated fatty acids are added to the estolide synthesis a saturated-capped estolide is formed. These estolides have an oleic acid backbone with a terminal saturated tallow fatty acid acting as a capping group. Cermak and Isbell [14] theorized that by varying the capping material on the estolide the crystal lattice structure of the material was disrupted as it approached its pour point, which lead to estolide esters with excellent low temperature properties, pour points of –36 °C and cloud points of –41 °C. These saturated-capped estolide 2-ethylhexyl (2-EH) estershave thus eliminated common problems associated with the use of vegetable oils as functional fluids.

Table 1 Chemical compositions of oleic and tallow fatty acids

FAME (fatty acid methyl ester)	Oleic (mass %)	Tallow (mass %)
14:0	–	2.4
14:1	–	0.5
15:0	–	0.4
16:0	0.3	24.6
16:1	–	3.3
17:0	–	1.1
17:1	–	0.7
18:0	2.3	18.0
18:1	90.1	43.3
18:2	3.9	5.3
18:3	0.4	–

Determined by GC (SP-2380, 30 m × 0.25 mm i.d.)

The second problem with vegetable oils as functional fluids is poor thermal oxidative stability [3]. Again estolides esters demonstrated dramatic improvements in oxidative stability over vegetable oils. Cermak and Isbell [3] reported that the saturated-capped estolide esters synthesized from coconut and oleic fatty acids provided a very oxidatively stable product and required very little oxidative stability package to provide suitable performance. These coco-oleic estolide esters had RPVOT times >400 min, which were double that of the simple oleic estolide esters as well as off-the-shelf commercial petroleum products.

The physical properties of estolides and estolide esters have compared favorably to commercially available industrial products such as petroleum-based hydraulic fluids, soy-based fluids, and petroleum oils thus far. In this paper we report the synthesis of potential commercially inexpensive estolide 2-EH esters from tallow along with a number of their physical properties. The physical properties of these new tallow-oleic estolide 2-EH esters were compared to commercially available materials.

Experimental Procedures

Materials

Oleic acid (90%) was purchased from the Aldrich Chemical Co. (Milwaukee, WI, USA). Ethyl acetate, hexanes, acetone, perchloric acid (70%), and 2-ethylhexyl alcohol were purchased from the Fisher Scientific Co. (Fairlawn, NJ, USA). Potassium hydroxide was obtained from the J. T. Baker Chemical Co. (Phillipsburg, NJ, USA). Filter paper was obtained from Whatman (Clifton, NJ, USA).

Acetonitrile and acetic acid (both for HPLC) were obtained from EM Science (Gibbstown, NJ, USA). Ethanol was purchased from the AAPER Alcohol and Chemical Company (Shelbyville, KY, USA). The fatty acid methyl ester (FAME) standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL, USA). Solvents for chromatography and extraction were HPLC grade or an equivalent, and were used without further purification. Tallow fatty acids were obtained from Cognis (Cincinnati, OH, USA). Soy based oil: Biosoy® was obtained from the University of Northern Iowa (Cedar Falls, IA, USA). Petroleum oil: Mobil® 10W-30 and synthetic oil: Penzoil Synthetic® 10W-30, and hydraulic fluid: Traveler Universal Hydraulic Fluid® obtained from local vendors.

GC

A Hewlett-Packard 6890N Series gas chromatograph (Palo Alto, CA, USA) equipped with a flame-ionization detector and an autosampler/injector used for GC analysis. Analyses were conducted on a SP-2380 30 m × 0.25 mm i.d. column (Supelco). Saturated C_8–C_{30} FAMEs provided standards for making fatty acid and by-product assignments.

Parameters for SP-2380 analysis were: column flow 1.4 ml/min with helium head pressure of 136 kPa; split ratio 50:1; programmed ramp 120–135 °C at 10 °C/min, 135–175 °C at 3 °C/min, 175–265 °C at 10 °C/min, hold 5 min at 265 °C; injector and detector temperatures set at 250 °C. Retention times for eluted peaks were: methyl stearate 12.3 min, methyl oleate 13.3 min, hydroxy methyl stearate 22.1 min, hydroxy methyl oleate 22.3 min, 14-hydroxy eicosanate 23.3 min, 14-hydroxy-*cis*-11-eicosanate 23.5 min, 14-hydroxy eicosanate 23.8 min, and 14-hydroxy-*cis*-17-eicosanate 24.0 min.

GC-MS

A Hewlett-Packard 5890A GC with a 30 m × 0.20 mm i.d. SPB-1 column (Supelco, Bellefonte, PA, USA) and a Hewlett-Packard 5970 mass selective detector was used for GC-MS analysis. GC conditions: helium head pressure 15 psi (103 kPa) at 170 °C set for constant flow with varying pressure; split ratio 50:1; injector temperature set at 250 °C; transfer line temperature set at 250 °C; programmed ramp from 170 to 270 °C at 3 °C/min. MS conditions: mass range 50–550 amu; electron multiplier 200 V relative.

HPLC

A Thermo Separations Spectra System AS1000 autosampler/injector (Fremont, CA, USA) with a P2000 binary gradient pump from Thermo Separation Products (Fremont) coupled to a Alltech ELSD 500 evaporative light scattering detector (Alltech Associates, Deerfield, IL, USA) was used for RP-HPLC analysis. A C-8 reverse phase analysis used to separate reaction mixtures was carried out with a Dynamax column (250 mm × 4.5 mm, 8-μ particle size) from Rainin Instrument Co. (Woburn, MA, USA).

A 16 min run time was used to follow the reaction which provided information on the overall progress of the reaction. The flow rate of 1 ml/min; 0 to 4 min 80% acetonitrile 20% acetone; 6–10 min 100% acetone; 11–16 min 80% acetonitrile 20% acetone. The ELSD drift tube was set at 55 °C with the nebulizer set at 20 psi (138 kPa) N_2, providing a flow rate of 2.0 standard liters per minute (SLPM). Retention times for eluted peaks: estolides, 10.3–13.9 min; oleic acid, 5.8 min; and tallow fatty acids, 5.7 min.

A Thermo Separations Spectra System AS1000 autosampler/injector (Fremont) with a P2000 binary gradient pump from Thermo Separation Products (Fremont) coupled to a Alltech ELSD MKIII evaporative light scattering detector (Alltech Associates, Deerfield, IL, USA) was used to carry out a silica normal phase analysis with a Dynamax column (250 mm × 4.6 mm, 8 μm) from Rainin Instrument Co. (Woburn, MA, USA). Components were eluted isocratically from the column with a 4:1 hexanes/acetone mixture at a flow rate of 1 ml/min with the ELSD drift tube set at 55 °C and nebulizer set at 20 psi (138 kPa) N_2, flow rate 2.0 standard liters per minute (SLPM). Normal phase HPLC was used to monitor theesterification step. Retention times for eluted peaks estolide-2-ethylhexyl esters, 2.8–2.9 min; and free acid estolide, 3.8–3.9 min.

Iodine Values (IV) and EN

IV were determined from the GC results using the AOCS Method Cd 1c-85 [15]. Estolide numbers (EN) were determined by GC from the SP-2380 column analysis as described previously [16].

GC Analysis of Hydroxy Fatty Acids

Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell [1].

TMS Derivatization of Hydroxy Fatty Esters

Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell [1].

Gardner Color

A Lovibond 3-Field Comparator from Tintometer Ltd (Salisbury, England) using the AOCS method Td 1a-64 [15] was used for Gardner color measurements. The

Gardner color of both the residue and distillate materials was measured throughout the distillation. The ''+'' and ''–'' notation was employed to designate samples that did not match one particular color.

Viscosity and Viscosity Index

Calibrated Cannon-Fenske viscometer tubes obtained from Cannon Instrument Co. (State College, PA, USA) were used to measure viscosity. Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at 40.0 and 100.0 °C. The viscosity and viscosity index were calculated using ASTM methods D 445-97 and ASTM D 2270-93, respectively. Duplicate measurements were made and the average values were reported.

Pour Point

The ASTM method D 97-96a was used to measure pour points to an accuracy of ±3 °C. The pour points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged in a cooling medium. The sample temperature was measured in 3 °C increments at the top of the sample until the material stopped pouring. This point is determined when the material in the test jar did not flow when held in a horizontal position for 5 s. The temperature of the cooling medium was chosen based on the expected pour point of the material. 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. The pour point was defined as the coldest temperature at which the sample still poured. All pour points were run in duplicate and average values were reported.

Cloud Point

The ASTM method D 2500-99 was used to measure cloud points to an accuracy of ±1 °C. The cloud points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged into a cooling medium. The sample temperature was measured in 1 °C increments at the bottom of the sample until some cloudiness was observed at the bottom of the test jar. The temperature of the cooling medium was chosen based on the expected cloud point of the material. Samples with cloud points that ranged from (room temperature to 10, 9 to –6, and –6 to –24, –24 to –42 °C) were placed in baths of temperature (0, –18, –33, and –51 °C), respectively. The cloud point was defined as the coldest temperature at which the sample remained opaque. All cloud points were run in duplicate and average values were reported.

Acid Value

A 751 GPD Titrino titrator from Metrohm Ltd (Herisau, Switzerland) was used for measurements. Acid values were determined by the official AOCS method [15] with ethanol substituted for methanol to increase the solubility of the estolide ester during the titration. All acid values were run in duplicate and average values were reported.

Rotating Pressurized Vessel Oxidation Test

Tests determinations were conducted on a rotating pressurized vessel oxidation test (RPVOT) apparatus manufactured by Koehler (Bohemia, NY, USA) using the ASTM method D 2272-98. Estolides, free research samples, and commercial products were run at 150 °C. Samples were measured to 50.0 ± 0.5 g with 5.0 ml of reagent water added to the sample. 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, USA) and was used immediately. The wire was wound to have an outside diameter of 44–48 mm and a weight of 55.6 ± 0.3 g and to a height of 40–42 mm. The bomb was assembled and slowly purged with oxygen twice. The bomb was charged with 90.0 + 0.5 psi (620 kPa) of oxygen then tested for leaks by immersing in water. The test was complete after the pressure dropped more than 175 kPa below the maximum pressure. All samples were run in duplicate and the average time was reported.

Noack Evaporative Loss Test

Evaporative loss determinations were conducted on a non-woods metal Noack evaporative tester apparatus manufactured by Koehler (Bohemia) using the ASTM Method D 5800-00a. Estolides, free research samples, and commercial products were run at 250 °C. Samples were measured to 65.0 ± 0.1 g to a precision of 0.01 g. The test was complete after 60 min at which time the extraction tube was disconnected within 15 s. The sample crucible was placed in a cold-water bath to a minimum depth of 30 mm for 30 min. All samples were run in duplicate and the average evaporative losses were reported.

General Tallow Estolide 2-Ethylhexyl Ester Synthesis

An acid-catalyzed condensation reaction was conducted without a solvent in a 1,500 ml, baffled, jacketed reactor with a three-neck reaction kettle cover that had been pretreated with an acidic wash. The reaction solution was mixed with an overhead stir motor using a glass shaft and a Teflon blade. Oleic acid (211.8 g, 750.0 mmol) and tallow fatty acids (205.5 g, 750.0 mmol) were combined together and heated to 60 °C under house vacuum. Once the desired temperature of 60 ± 0.1 °C was reached, perchloric acid (75.0 mmol, 6.5 ml, 0.05 equiv) was added and the flask was placed under vacuum (7.5–10.9 kPa) and stirred. After 24 h, 2-ethylhexyl alcohol (609.0 g, 4.67 mol, 689.6 ml) was added to the vessel, vacuum was restored, and the mixture was stirred for an additional 3–4 h. The completed reactions were quenched by the addition of KOH (5.04 g, 90.0 mmol, 1.2 eq based on $HClO_4$) in 90% ethanol/water (20 ml) solution. The solution was allowed to cool with stirring for 45 min followed by filtration through a Buchner funnel with a Whatman no.1 filter paper. The organic layer was dried over sodium sulfate and filtered through a Buchner funnel with a Whatman no.1 filter paper. All reactions were concentrated in vacuo then kugelrohr-distilled at 90—110 °C and 6–13 Pa to remove any excess ethanol and 2-ethylhexyl alcohol. The residue was further distilled by kugelrohr-distillation at 180–200 °C and 6–13 Pa to remove any unreacted saturated and unsaturated fatty acids and by-products, such as lactones [1], 2-EH stearate ester, and 2-EH palmitate ester. All 2-ethylhexyl estolide esters (Table 2, A–G) were carried out under the same conditions with just the ratio of oleic and tallow fatty acids changing. The percent yield of the estolide 2-EH esters as shown in Table 2 were very modest at 65–72% and very similar to past synthesized estolides [1, 13].

NMR

^{1}H- and ^{13}C-NMR spectra were collected on a Bruker Avance 500 (Billerica, MA, USA) spectrometer with a 5 mm BBI probe. All spectra were acquired at 300.0 K using $CDCl_3$ as a solvent in all experiments. Chemical shifts are reported as parts per millions from tetramethylsilane with an absolute frequency 500.11 MHz. The assignments of protons were not to the whole number. The representative NMR sample contained a compound that had an average estolide number of 1.40 for the estolide ester (D, Table 2), which made whole number assignment impossible. The data reported for the number of protons in the NMR reflect the actual numbers present in the reaction product.

^{1}H and ^{13}C NMR of Tallow-Oleic Estolide 2-Ethylhexyl Ester D (Table 2)

^{1}H NMR: δ 5.38–5.36 (*m*, 0.86 H, –C*H*=C*H*–), 4.88–4.85 (*m*, 1.50 H, –C*H*–O–(C=O)–CH_2–), 3.98 (*d*, *J* = 6.0 Hz, 2.0 H, –O–CH_2–CH(CH_2–)CH_2–), 2.30–2.25 (*m*, 5.1 H, –CH_2–(C=O)–O–CH_2–, –CH_2(C=O)–O–CH–), 1.96–1.26 (*m*, 75.6 H), and 0.91–0.86 ppm (*m*, 13.6 H, –CH_3). ^{13}C NMR: δ 173.9 (*s*, *C*=O), 173.9 (*s*, *C*=O), 173.6 (*s*, *C*=O), 130.4–130.3 (*d*, –*C*H=*C*H–, very small signals, only a small amount of alkene present), 74.0 (*d*, –*C*H–O–C=O), 66.6 (*t*, –O–CH_2–CH–), 38.7 (*d*, –CH_2–*C*H(CH_2–)–CH_2–), 34.7 (*t*), 34.4 (*t*), 34.3 (*t*), 32.5 (*t*), 31.9 (*t*), 31.9 (*t*), 31.9 (*t*), 31.8 (*t*), 31.7 (*t*), 30.4 (*t*), 29.7 (*t*), 29.6 (*t*), 29.6 (*t*), 29.6 (*t*), 29.5 (*t*), 29.5 (*t*), 29.5 (*t*), 29.4 (*t*), 29.3 (*t*), 29.3 (*t*), 29.2 (*t*), 29.2 (*t*), 29.1 (*t*), 29.0 (*t*), 28.8 (*t*), 25.3 (*t*), 25.3 (*t*), 25.2 (*t*), 25.1 (*t*), 25.0 (*t*), 24.9 (*t*), 23.8 (*t*), 23.0 (*t*), 22.7 (*t*), 22.6 (*t*), 14.1 (*q*, –CH_3), 14.0 (*q*, –CH_3), and 11.0 ppm (*q*, –CH_3).

Results and Discussion

Table 2 outlines a series of reactions (Fig. 1) that explored the formation of a new series of saturated-capped estolide 2-EH esters as the amounts of tallow and oleic fatty acids were varied and all other reaction parameters held constant. The acid catalyzed process converted the fatty acids to the free acid estolides under vacuum at 60 °C followed by an in situ esterification under similar conditions. The final products underwent vacuum distillation to remove any excess fatty acids, fatty esters, by-products, and 2-ethylhexyl alcohol providing neat estolide ester samples. The ratio of oleic to tallow, pour and cloud points, viscosity, viscosity index, acid values, estolide numbers, iodine values, saturated-capped estolide, and color are reported in Table 2. These new tallow based estolide 2-EH esters have an oleic acid backbone with a terminal saturated tallow fatty acid. Estolides are formed from the cationic homo-oligomerization of unsaturated fatty acids resulting from the addition of a fatty acid carboxyl adding across the olefin [17]. This condensation can continue, resulting in oligomeric compounds where the average extent of oligomerization is defined as the estolide number (EN = $n + 1$, Fig. 1) [16]. When saturated fatty acids are added to the reaction mixture, the oligomerization terminates upon addition of the saturated fatty acid to the olefin since the saturate provides no additional reaction site to further the oligomerization. Consequently, the estolide is stopped at this point from further growth, thus we term the estolide as being ‘‘capped’’ [1].

As the amount of tallow was decreased from 100 to 0%, a decrease (lower temperatures) in the pour and cloud points were observed. As the amount of tallow increased the low temperature properties were less impressive where pour points ranged from –33 to –15 °C. Table 2 shows that at a 1–1 ratio of tallow to oleic acid had a pour point of –21 °C for Estolide C while the straight tallow estolide (Estolide A) had a pour point of –15 °C. Both pour points compare favorably to current commercially available bio-based materials but were not as low as past estolides [18]. The cloud points were very close to the pour points in all cases (Table 2).

Table 2 Characterization of estolides 2-ethylhexyl esters prepared with varying amounts of oleic and tallow acids fatty acids

Estolide	Fatty acid[b] ratio	Pour point (°C)	Cloud point (°C)	Viscosity at 40 °C (cSt)	Viscosity at 100 °C (cSt)	Viscosity index	Acid value (mg/g)	(EN)[c]	(IV)[d]	Capped[e] (%)	Gardner color
A	0:1	–15	–14	57.8	10.8	182	1.77	1.02	15.7	77.4	12+
B	1:2	–15	–12	70.3	12.5	179	3.88	1.26	26.3	58.5	14+
C	1:1	–21	–21	68.1	12.2	179	2.78	1.20	30.3	45.4	12+
D[a]	2:1	–24	–26	74.5	12.6	169	1.07	1.40	32.4	32.2	6–
E	3.5:1	–27	–20	67.7	12.4	185	4.16	1.58	34.4	25.1	10–
F	5:1	–27	–23	80.1	14.0	182	4.63	1.42	37.6	10.0	11–
G	1:0	–33	–27	79.6	13.4	172	2.01	1.30	42.1	8.1	8+

Reactions were run for 24 h with overhead stirring under vacuum, oleic: tallow fatty acids with 0.05 equivalents of perchloric acid at 60 °C, then 1.2 equivalents of 2-ethylhexanol at 60 °C for 2–3 h followed by distillations at 90–110 °C and 180–200 °C

[a] Tallow fatty acids distilled twice prior to use

[b] Oleic to tallow

[c] Estolide number—see Fig. 1

[d] Iodine value

[e] Percent of estolide saturated-capped

Cermak and Isbell [1] previously showed that complex estolides had the best low temperature properties when capped with very short chain, saturated fatty acids such as those present in cuphea and coconut. Decanoic acid based estolides had the best cold temperature properties, with a pour point of –39 °C. The tallow estolides did not compete with the cuphea estolide 2-EH esters synthesized in the past in terms of cold temperature properties [13]. Cuphea contains much shorter fatty acids while the tallow contained longer fatty acids i.e. the reason for the less desirable pour points.

The increase in Gardner color with an increased ratio of tallow (Table 2, A–C) was expected since tallow was not refined to the same low color as the oleic acid. Gardner colors could be improved by a double distillation of the tallow fatty acids prior to estolide formation. Color improvement was demonstrated for (Table 2, Estolide D) where the color was improved from a 10–11 range to a –6 range but was accomplished via an additional costly distillation step.

The saturated-capped percentage values in Table 2 were obtained from GC analysis of the estolide esters, which were saponified and esterified. The components of the GC were classified as one of the following: unsaturated, saturated, and hydroxy fatty acids. The percent saturated-capped was calculated from Eq. 1:

$$[(\text{Saturated fatty acids})/(100 - \text{hydroxy fatty acids})] \times 100 = \text{percent saturated} - \text{capped}$$

As the amount of tallow increased the amount of saturated-capped estolides also increased (Table 2). A simple homo-oleic estolide (Estolide G) was 8% capped with saturated while the tallow estolide (Estolide A) was 77% saturated-capped. Figure 2 shows that as the percentage oleic decreases the amount of saturate increases in a nearly linear fashion. With this type of response, a producer would be able to customize an estolide to meet certain applications based on amount of saturation needed.

The iodine values (IV) have shown themselves to play a critical role in the physical properties of the estolide. By lowering the iodine values of the estolides, dramatic improvements in oxidative stability were observed [3]. As the amount of tallow was increased, i.e. the amount of saturation in the estolide, the oxidative stability increased which was demonstrated with the RPVOT. Estolide A was about 77% capped with saturated fatty acids, which provide a material with outstanding RPVOT time (274 min) when small amounts of anti-oxidant (<2%) were added. Estolide F had only 10% capped with saturates and had an average RPVOT time (165 min) when a small amount of anti-oxidant (<2%) was added. Overall as the amount of unsaturation decreased there was a dramatic improvement in the oxidative stability of the estolides as previously reported by Cermak and Isbell [3].

Another important fact in determining how well an oil will behave as a potential lubricant is to evaluate the oils volatility or evaporative loss. In most applications where oil is used as a lubricant, heat is generated due to friction. As the oil heats it can and does become very volatile, as in the case of air-cooled gas engines (i.e. water pumps, lawnmowers, etc.). As the oil evaporates, the engine has less lubricating material, which increases the operating temperatures until engine failure or damage occurs. There are a number of ways to correct this current volatility problem. The first would be to develop lubricating oil that

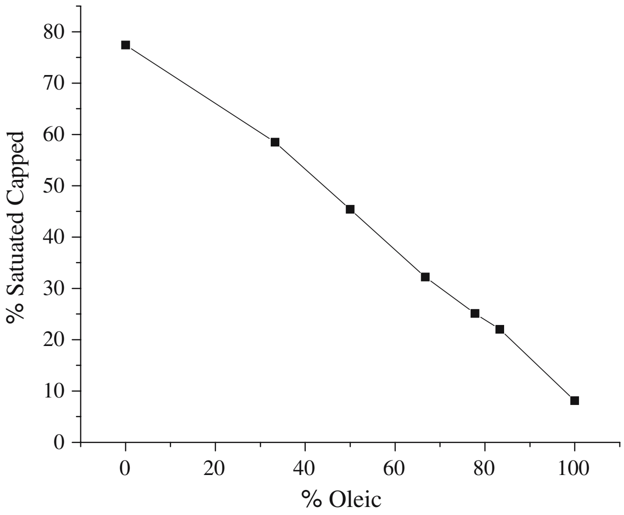

Fig. 2 Percentage of saturated-capped material versus percentage of the oleic capped material

would either dissipate the heat rapidly, or create an excellent lubricant that would not generate heat. The simplest and most cost-effective method would be to produce oil that would have very low or no evaporative losses. Current oils have evaporative loss requirements of about 15% using the Noack method. Table 3 shows that all the commercial samples have evaporative losses very close to 15%. While the tallow estolide esters have evaporative losses of only 1%, this would allow the estolides to last longer in the very hot running engines, thus potentially extending engine life and reducing wear.

The physical properties of various commercial materials and two tallow-oleic estolide 2-EH esters were compared (Table 3). Estolide A was picked for comparison due to the fact that it was 100% tallow based while estolide C was picked based on its physical properties as well as its estimated low production costs. Both of the estolide 2-EH esters were completely unformulated, unlike the commercial products, which contained up to 40% additives designed to improve cold temperature properties. All the commercial products in Table 3 have cold temperature-functional pour points and cloud point depending on the application. The two estolides A and C competed well with the soybean-based material with pour points in the upper teens and lower twenties. Another common cold temperature problem is oil havinga cloud point that is too high, thus potentially leading to filter clogging and poor pumpability in cold weather applications. The two estolide esters exceed the soybean-based material in terms of cloud point as the soybean material has a cloud point above 0 °C.

The proton NMR for the estolide esters in Table 2, specifically estolide 2-EH ester D, shows some key features of typical estolide 2-EH esters. The ester methine signal at 4.88–4.85 ppm is indicative of an estolide linkage. Another distinctive feature is the multiplet α-methylene proton shift (2.30–2.25 ppm) adjacent to the two esters. The NMR indicates the presence of alkene in the estolide by the appearance of an alkene signal at 5.38–5.36 ppm. The alkene signal indicated that some of the estolide was capped with unsaturated material, i.e. oleic acid. The alkene signal in the proton NMR supports the iodine value (IV) determined by GC, as the intensity of the NMR signals is comparable to the reported IV.

The carbon NMR spectrum contains the expected estolide 2-EH ester signals. There are three different carbonyl signals present in the 173 ppm region (estolide esters and 2-EH ester). The lack of the shift in the 179 ppm region indicates the estolides have been converted to the 2-EH ester which supports the acid value number in Table 2. The other distinctive signal was the methine carbon at 74.0 ppm, which is common to estolide 2-EH esters. These major peaks in the carbon NMR are also confirmed by a DEPT experiment.

Estolide 2-EH ester D (Table 2) was saponified in 0.5 M KOH/MeOH then esterified with 1 M H_2SO_4/MeOH to

Table 3 Comparison of physical properties of tallow-oleic estolide 2-EH esters to those of commercial lubricants

Lubricant	Pour point (°C)	Cloud point (°C)	Viscosity at 40 °C (cSt)	Viscosity Index	RPVOT (min)	Noack (loss %)
Commercial petroleum oil[a]	–27	2	65.0	155	208	14.1
Commercial synthetic oil[a]	–45	<–45	60.2	156	161	16.2
Commercial soy based oil[a]	–18	1	49.6	220	28	–[d]
Commercial hydraulic fluid[a]	–33	1	56.6	146	464	17.6
Estolide A[b]	–15[b]	–14[b]	57.8[b]	182[b]	274[c]	1.1[b]
Estolide C[b]	–21[b]	–21[b]	68.1[b]	179[b]	207[c]	1.1[b]

[a] Commercial, fully-formulated material from local vendors

[b] Unformulated

[c] Formulated with 2.0% Lubrizol® 7652 additive

[d] Sample not available

give the corresponding hydroxy and non-hydroxylated fatty esters. The isolated mixture of fatty acid esters was then silylated and analyzed by GC-MS [13]. The main mass spectral features were *m/e* 371 (M + –15, 2.96%), 73 (TMS+, 100%), and a Gaussian fragment representing cleavage at the C–C bond adjacent to the silyloxy positions (masses 173–315). The fragments and abundances were very similar to previously reported complex saturated estolide data [1]. The estolide position was distributed from positions 5–13 with the original Δ9 and Δ10 positions having the largest abundances in the mass spectrum, which also was very similar to previously reported complex estolide data [1]. This method demonstrated that during the estolide reaction there was a migration of the double bond and the estolides are indeed complex molecules.

Acknowledgments Kendra B. Brandon, Benjamin A. Lowery, Jonathan L. A. Phillips, and April M. Stanley assisted in the synthesis of these estolides. The authors are grateful to Karl E. Vermillion for performing all the NMR experiments.

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