Synthesis and physical properties of estolide-based functional fluids

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Abstract

Biodegradable, vegetable oil-based lubricants must have better low temperature properties as well as comparable cost to petroleum oil before they can become widely acceptable in the marketplace. These include low pour point temperature, low viscosity and viscosity indices that do not change over a wide temperature range. Our objective was to synthesize estolides from various sources with improved lubricating physical properties. Oleic acid and lauric acid were treated with varying equivalents of perchloric acid at 60 °C to produce complex estolides. Yields ranged between 45 and 75% after purification by Kugelrohr distillation. The estolide number (EN), the average number of fatty acid units added to a base fatty acid, varied with reaction conditions. The saturate-capped, oleic estolides were esterified with 2-ethylhexanol to obtain high yields of the corresponding ester. Coconut–oleic 2-ethylhexyl estolide esters were produced by varying the ratio of oleic and coconut fatty acids with 0.05 equivalents of HClO4 to give estolides with excellent cold temperature properties. The amount of oligomerization (EN) played an important role on viscosity; viscosity increased with higher oligomerization. The free acid estolides were generally several hundred centistokes (cSt) more viscous than their corresponding esters. The viscosity index ranged from 141 to 170 for the free acid estolides, whereas the complex estolide 2-ethylhexyl esters had slightly higher viscosity indices, which ranged from 159 to 232. These new coco–oleic estolide esters displayed superior low temperature properties (−36 °C), were of reasonable cost, and were more suitable as a base stock for biodegradable lubricants and functional fluids than current vegetable oil-based commercial materials.

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1. Introduction

Extensive research have been conducted on biodegradable, renewable functional fluids. Many groups have tried to use the cheap commodity prices of soybeans to force this traditional US farmland oil into a functional fluid market (Tilton,
Several factors have contributed to this movement: namely, vegetable oil-based lubricants and derivatives have excellent lubricity and biodegradability properties (Mang, 1994, 1997; Legrand and Durr, 1998; Canter, 2001). Two major problems exist with vegetable oils as functional fluids related to low resistance to thermal oxidative stability (Becker and Knorr, 1996) and poor low temperature performance (Asadauskas and Erhan, 1999; Zehler, 2001). However, these properties sometimes can be improved with additives, but only at the expense of biodegradability, toxicity, and price.

Estolides and estolide esters from meadowfoam fatty acids (Isbell and Kleiman, 1996), oleic acid (Isbell et al., 2001), castor oil, or any source of hydroxy fatty acids (Zoleski and Gaetani, 1984) have been explored and show promise as cosmetics, coatings, and biodegradable lubricants. Estolides are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters (Fig. 1). The estolide number (EN) is defined as the average number of fatty acids added to the base fatty acid (Fig. 1, EN = $n$ + 1).

Complex estolides have been synthesized by Cermak and Isbell (2001a,b) where oleic acid and various saturated fatty acids, butyric through stearic, were treated with 0.4 equivalents of perchloric acid at either 45 or 55 °C to produce a new class of saturated estolides with superior low temperature properties (Fig. 2). Yields varied between 45 and 65% after Kugelrohr distillation. These new saturated complex estolides and the simple estolide esters showed very different physical properties. By varying the capping material on the estolide, the crystal lattice structure of the material was disrupted at low temperatures, which led to estolides with excellent low temperature properties.

These new, complex estolides have certain physical characteristics that could help eliminate common problems associated with vegetable oils as functional fluids (Cermak and Isbell, 2002). One of the concerns with vegetable oils is their oxidation stability. Simple homo-oleic estolides, when formulated with a small amount of oxidative stability package, show better oxidative stability than both petroleum and vegetable oil-based fluids (Cermak and Isbell, 2001a), but improvements can still be made. The oxidative stability of an oil can be improved by several ways. Akoh (1994) increased the oxidative stability index of refined soybean oil from 9.4 h at 110 °C to 15.3 h by partial hydrogenation. A similar approach was taken with the oleic estolides, where hydrogenation with 2% w/w of 10% palladium on activated carbon as catalyst gave completely saturated estolides (Isbell et al., 2001). The saturated oleic estolides are expected to be more oxidatively stable than the unsaturated estolides, assuming the same trend displayed by soybean oil holds true.

![Fig. 1. Reaction scheme for the formation of oleic estolides.](image-url)
Other low cost and relatively available sources of saturated fatty acids is necessary where coconut oil could serve this need. Coconut fatty acids are relatively cheap and readily available (Tilton, 2002). The fatty acid profile of coconut is primarily saturated fatty acids ranging from C8 to C18 with the majority being C12 and C14, Table 1. Cermak and Isbell (2002) reported that the C12 and C14 fatty acids made excellent low temperature estolides. Coconut oil would make an excellent fatty acid alternative source due to its fatty acid distribution (Table 1). It can be used to create a complex estolide mixture that would have even greater low temperature properties than the simple oleic estolide.

Estolides and estolide esters have compared favorably to commercially available industrial products such as petroleum-based hydraulic fluids, soy-based fluids and petroleum oils. In this paper, we report the easy and cost effective synthesis of complex estolides and corresponding esters along with their physical properties, such as pour and cloud points, viscosity, and other low temperature properties. These new coco–oleic estolides, which should have superior biodegradability and lubricating properties than petroleum products, were compared with commercially available materials based on their low temperature properties.

2. Materials and methods

2.1. Materials

Oleic acid (90%) and N,O-bis(trimethylsilyl)acetamide (derivatization grade) were purchased
from Aldrich Chemical Co. (Milwaukee, WI). Ethyl acetate and hexanes (for extractions), acetone (for high performance liquid chromatography, HPLC), perchloric acid (70%), concentrated sulfuric acid (98%), methanol and 2-ethylhexyl alcohol, were purchased from Fisher Scientific Co. (Fair Lawn, NJ). Potassium hydroxide was obtained from J.T. Baker Chemical Co. (Phillipsburg, NJ). Filter paper was obtained from Whatman (Clifton, NJ). Acetonitrile and acetic acid (both for HPLC), charcoal, sodium dihydrogenphosphate and sodium hydroxide were obtained from EM Science (Gibbstown, NJ). Ethanol was purchased from AAPER Alcohol and Chemical Company (Shelbyville, KY). Pyridine was purchased from Mallinckrodt (Paris, KY). The fatty acid methyl ester (FAME) standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL). Solvents for chromatography and extraction were HPLC grade or equivalent, and were used without further purification. Petroleum oil: Mobil® 10W-30 and synthetic oil: Castrol Synthetic® 10W-30 were obtained from Wal-Mart Department Store® (Peoria, IL). Soy-based oil: Biosoy® was obtained as a free sample from University of Northern Iowa (Cedar Falls, IA). Hydraulic fluid: Traveler Universal Hydraulic Fluid® was obtained from Tractor Supply Company® (Peoria, IL).

2.2. Equipment and procedures

2.2.1. Gas chromatography

Gas chromatography (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. column (Supelco, Bellefonte, PA). Saturated C₈–C₃₀ FAMEs provided standards for calculating equivalent chain length (ECL) values, which were used to make fatty acid and by-product assignments.

Operating parameters for SP-2380 analysis were: column flow 3.3 ml/min with helium head pressure of 103.4 kPa; split ratio 22:1; programmed ramp 75–165 °C at 15 °C/min, 165–185 °C at 7 °C/min, 185–265 °C at 15 °C/min, hold 5 min at 265 °C; injector and detector temperatures set at 250 °C. Retention times for eluted peaks with ECL values in parentheses were: methyl oleate 9.73 min (18.36), hydroxy methyl oleate 14.10 (27.81), γ-stearalactone 15.31 min (30.39), and δ-stearalactone 15.72 min (31.59) (Cermak and Isbell, 2002).

2.2.2. GC–mass spectrometry

GC–mass spectrometry (GC–MS) was performed on a Hewlett-Packard 5890A GC with a 30 m × 0.20 mm i.d. SPB-1 column (Supelco) and a Hewlett-Packard 5970 mass selective detector. GC conditions: helium head pressure 103.4 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.

2.2.3. High performance liquid chromatography

Reverse phase HPLC, analyses were performed on a Thermo Separations Spectra System AS1000 autosampler/injector (Fremont, CA) with a P2000 binary gradient pump from Thermo Separation Products (Fremont, CA) coupled to a Alltech ELSD 500 evaporative light scattering detector (Alltech Associates). A C-8 reverse phase analysis used to separate reaction mixtures was carried out with a Dynamax column (250 mm × 4.5 mm, 5-μ particle size) from Rainin Instrument Co. (Woburn, MA).

Two methods for reverse phase analysis were used to separate the reaction mixtures. Method A (16 min run time) was used to follow the reaction. It provided information on the overall progress of the reaction. Method B (35 min run time) produced a more detailed separation of the reaction mixture, in particular a separation of estolides, lactones, fatty acids, and hydroxy fatty acids.

Operating parameters for method A were: flow rate of 1 ml/min; 0–4 min 80% acetonitrile, 20% acetone; 6 to 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 137.9 kPa N₂, providing a flow rate of 2.0 standard liters per minute (SLPM). Retention times for eluted...
peaks: estolides, 9.8–13.0 min; methyl oleate, 6.3 min; oleic acid, 5.1 min; lactones, 4.8 min; and hydroxy acids 4.1 min.

Operating parameters for method B were: flow rate of 1 ml/min; 0–2 min 60% acetonitrile 40% acetone; 20–25 min 100% acetone; 30–35 min 60% acetonitrile 40% acetone. The ELSD drift tube was set at 55 °C with the nebulizer set at 137.9 kPa N₂, providing a flow rate of 2.0 SLPM. Retention times for eluted peaks: estolides, 8.2–25.6 min; methyl oleate, 5.5 min; oleic acid, 4.8 min; γ-lactones, 4.5 min; δ-lactones, 4.1 min; and hydroxy acids 3.8 min.

Normal phase HPLC analyses were performed using a Spectra-Physics 8800 ternary pump (San Jose, CA) with a Spectra System AS3000 autosampler/injector from Thermo Separation Products coupled to a Varex ELSD III light scattering detector (Alltech Associates). A silica normal phase analysis was carried out with a Dynamax column (250 mm x 4.6 mm, 8 μm) from Rainin Instrument Co. Components were eluted isocratically from the column with a 80:20 mixture hexanes/acetone at a flow rate of 1 ml/min with the ELSD drift tube set at 45 °C and nebulizer set at 69.0 kPa N₂, flow rate 1.50 SLPM.

Normal phase HPLC was used to separate esterification reaction mixtures. Retention times for eluted peaks: 2-ethylhexyl estolide ester, 2.6–2.8 min; and estolide, 3.5–3.7 min depending on the capping fatty acid.

2.2.4. Gardner color

Gardner color was measured on a Lovibond 3-Field Comparator from Tintometer Ltd (Salisbury, England) using AOCS method Td 1a-64 (Firestone, 1994b). 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 or, in the case of the residue, an 18+ represented a color darker than the upper limit of 18.

2.2.5. Viscosity

Viscosity was determined with calibrated Cannon–Fenske viscometer tubes purchased from Cannon Instrument Co. (State College, PA). Viscosity measurements were made 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 D445-97 (ASTM, 1997) and ASTM D2270-93 (ASTM, 1998), respectively. Duplicate measurements were made and the average value was reported.

2.2.6. Pour point

Pour points were measured by ASTM method D97-96a (ASTM, 1996) 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. The sample no longer poured 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.

2.2.7. Cloud point

Cloud points were determined by ASTM method D2500-99 (ASTM, 1999) 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 any 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. All cloud points were run in duplicate and average values were reported.
2.2.8. Acid value

The acid values were measured on a 751 GPD Titrino from Metrohm Ltd (Herisau, Switzerland). Acid values were determined by the AOCs Method Te 2a-64 (Firestone, 1994a) 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.

2.2.9. Iodine values and EN

Iodine values (IV) were calculated from GC data using AOCS Method Cd 1c-85 (Firestone, 1994c). ENs were determined by GC from the SP-2380 column analysis described by Isbell and Kleiman, (1994).

2.2.10. GC analysis of hydroxy fatty acids

Analytical estolide samples for GC were prepared by heating a 10 mg sample of estolide or estolide 2-ethylhexyl ester in 0.5 ml of 0.5 M KOH/MeOH to reflux on a heating block for 60 min in a sealed vial. After cooling to room temperature, 2 ml of 1 M H2SO4/MeOH was added to the vial, the vial was resealed and heated to reflux on a heating block for 30 min. The solution was transferred to a separatory funnel with water (1 ml) and washed with hexanes (2/C29/2 ml), dried over sodium sulfate, gravity filtered, placed in a GC vial with hexanes, sealed, and injected into the GC and/or GC/MS.

2.2.11. TMS derivatization of hydroxy fatty esters

Hydroxy FAMEs (10 mg) (prepared as described) were dissolved in 0.1 ml of pyridine and 0.05 ml N,O-bis(trimethylsilyl)acetamide. This solution was then placed in a sealed vial for 10 min at 100 °C. After this time hexanes (1 ml) were added, and the resulting solution was filtered through a silica plug. The filtered sample was placed in a sealed GC vial with hexanes and injected onto the GC and/or GC/MS.

2.2.12. Synthesis

2.2.12.1. Free-acid estolide. Acid-catalyzed condensation reactions were conducted without solvent in a 500 ml, baffled, jacketed reactor with a three-neck reaction kettle cover. The reactor was connected to a recirculating constant temperature bath maintained at 45±0.1 °C. All reactions described were mixed with an overhead stir motor using a glass shaft and a Teflon blade. The reactions were conducted at atmospheric pressure in a sealed flask. Reactions were performed under the general conditions described previously while varying the equivalents of perchloric acid as reported in Table 2. In most cases, oleic acid (100.0 g, 354.0 mmol) and saturated fatty acids, i.e. lauric, (35.5 g 177.0 mmol) were combined together and heated to the desired temperature as outlined in Table 2. Once the temperature was reached, perchloric acid was added and the flask was stoppered. Product distribution was monitored by HPLC, GC and/or GC/MS. Completed reactions were quenched by the addition of 0.5 M Na2HPO4 (212.4 mmol, 424.8 ml) to the reaction vessel. The reactor was disconnected from the circulating bath and the solution was allowed to cool with stirring for 30 min. The material was transferred to a separatory funnel followed by the addition of 200 ml of a 2:1 ethyl acetate:hexanes solution. The pH of the organic layer was adjusted to 5.3–6.0 with the aid of a pH 5 buffer (NaH2PO4, 519 g in 4 l H2O, 2/C29/50 ml) followed by saturated NaCl (2/C29/50 ml). The organic layer was dried over sodium sulfate and filtered. All reactions were concentrated in vacuo then Kugelrohr-distilled at 160–90 °C at 0.0131–0.067 kPa to remove any lactones, saturated and unsaturated fatty acids.

2.2.12.2. Estolide 2-ethylhexyl ester. The distilled, free acid estolides were combined with a 0.5 M BF3/2-ethylhexyl alcohol solution (3 × estolide wt, w/v) in a 500 ml round bottom flask. The reactions were conducted at 60 °C with magnetic stirring and were monitored hourly by normal phase HPLC (Table 3). Esterification reactions were run until >99% complete then were transferred to a separatory funnel and were washed with saturated NaCl (2 × 75 ml). The pH of the organic layer was adjusted to 5.3–6.0 with pH 5 buffer (NaH2PO4, 519 g in 4 l H2O, 2 × 50 ml). The oil was dried over sodium sulfate and filtered. All reactions were concentrated in vacuo, then Ku-
2.2.12.3. Estolide 2-ethylhexyl ester (one step).

Acid-catalyzed condensation reactions were conducted without solvent in a 500 ml, baffled, jacketed reactor with a three-neck reaction kettle cover. The reaction was connected to a recirculating, constant temperature bath maintained at ± 0.1 °C of the set point. All reactions described were mixed with an overhead stir motor using a glass shaft and a Teflon blade as reported in Table 5 and Table 6. In most cases, oleic acid (100.0 g, 354.0 mmol) and saturated fatty acids, lauric, (35.5 g, 177.0 mmol) were combined together and heated to 60 °C under house vacuum, as in Table 6. Once the desired temperature was reached, perchloric acid (0.05 eq., 26.5 mmol, 2.3 ml, Table 5) was added and the flask was placed under vacuum and stirred for 24 h. After 24 h, 2-ethylhexyl alcohol (59.6 g, 457.6 mmol, 67.5 ml) was added to the vessel, vacuum was restored, and the mixture was stirred for 2 additional h. The completed reactions were quenched by the addition of KOH (22.3 mmol, 1.25 g, 1.2 equivalent based on HClO₄) in 90% ethanol/water (10 ml) solution. The reactor was disconnected from the circulating bath and the solution was allowed to cool with stirring for 30 min. The material was filtered through a Buchner funnel with Whatman #1 filter paper. The organic layer was dried over sodium sulfate and filtered. All reactions were concentrated in vacuo then Kugelrohr-distilled at 160–190 °C at 0.013–0.067 kPa to remove any lactones, saturated and unsaturated fatty acids, and any excess 2-ethylhexyl alcohol.

2.2.12.4. Decolorization of 2-ethylhexyl estolide esters.

Gardner color was measured on a Lovibond 3-Field Comparator from Tintometer Ltd. Gardner color of the 2-ethylhexyl estolide esters was measured before and after decolorization. To remove color, the estolides were placed in a 500-ml Erlenmeyer flask with 2% w/w of activated carbon (Table 3) then stirred with a magnetic stirrer for 4 h at room temperature. Upon completion, hexanes (100 ml) were added and the mixture was filtered through a silica plug. The
Table 3
Esterification of lauric–oleic estolides with 2-ethylhexyl alcohol

<table>
<thead>
<tr>
<th>Estolide ester</th>
<th>GC (EN&lt;sup&gt;b&lt;/sup&gt;)</th>
<th>GC Iodine value</th>
<th>Capped (%)</th>
<th>Gardner color</th>
<th>Decolorized Gardner color</th>
<th>Gardner color improvement</th>
<th>Acid value (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-2EH</td>
<td>2.26</td>
<td>12.0</td>
<td>61.5</td>
<td>9</td>
<td>5</td>
<td>4</td>
<td>1.01</td>
</tr>
<tr>
<td>B-2EH</td>
<td>1.69</td>
<td>18.5</td>
<td>60.9</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>1.27</td>
</tr>
<tr>
<td>C-2EH</td>
<td>1.48</td>
<td>20.4</td>
<td>59.9</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>1.35</td>
</tr>
<tr>
<td>D-2EH</td>
<td>1.47</td>
<td>21.8</td>
<td>63.3</td>
<td>12</td>
<td>10</td>
<td>2</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Esterification reactions were run with magnetic stirring and 0.5 M BF<sub>3</sub> at 60 °C.

<sup>a</sup> Estolide 2-ethylhexyl ester.

<sup>b</sup> Estolide number.

<sup>c</sup> Ratio of estolide capped with saturated fatty acids determined by GC (SP-2380, 30 m × 0.25 mm i.d.).

organic layer was dried over sodium sulfate and gravity filtered. All reactions were concentrated in vacuo to remove excess hexanes.

2.2.13. Nuclear magnetic resonance

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker ARX-400 (Karlsruhe, Germany) with a 5 mm dual proton/carbon probe (400 MHz <sup>1</sup>H/100.61 MHz <sup>13</sup>C) using CDCl<sub>3</sub> as a solvent in all experiments. The assignment of protons was not to the whole number. The representative nuclear magnetic resonance (NMR) contained a compound that had an average EN of 1.99 for the free estolide (I-2EH) and 1.94 for the estolide ester (OC-EH-DD), which made whole number assignment impossible. The data reported for the number of protons in the NMR reflected the actual numbers. The numbers could be multiplied by a factor to obtain whole numbers that correspond to a whole number EN.

2.2.13.1. <sup>1</sup>H and <sup>13</sup>C NMR of free acid estolide D (Table 2). <sup>1</sup>H NMR: δ 5.37–5.33 (m, 0.5H, –CH<sub>2</sub>–CH<sub>–</sub>), 4.86–4.83 (m, 1.7H, –CH–OC=O–CH<sub>2</sub>–), 2.32 (t, J = 7.4 Hz, 2H, –CH<sub>2</sub>(C=O)–OH), 2.28–2.23 (m, 3.4H, –CH<sub>2</sub>(C=O)–O–CH<sub>–</sub>), 1.96–1.20 (m, 74.3H), and 0.88–0.84 ppm (m, 8.3H, –CH<sub>3</sub>). <sup>13</sup>C NMR: δ 179.7 (s, HO–C=O), 173.6 (s, –CH–O–(C=O)–CH<sub>2</sub>–), 130.5 (d, –CH=CH<sub>–</sub>–, very small signal, only a small amount of alkene present), 74.1 (d, –CH–O–C=O), 34.7 (t), 34.2 (t), 34.0 (t), 32.5 (t), 31.8 (t), 31.8 (t), 31.5 (t), 29.8 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.5 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 29.1 (t), 29.0 (t), 27.2 (t), 2.23 (m, 3.4H, –CH<sub>2</sub>(C=O)–O–CH<sub>–</sub>), 1.96–1.20 (m, 74.3H), and 0.88–0.84 ppm (m, 8.3H, –CH<sub>3</sub>).

2.2.13.2. <sup>1</sup>H NMR and <sup>13</sup>C of estolide 2-ethylhexyl ester OC-EH-DD (Table 7). <sup>1</sup>H NMR: δ 5.37–5.34 (m, 0.3H, –CH=CH<sub>–</sub>–), 4.87–4.81 (m, 1.0H, –CH–OC=O–), 3.96 (d, J = 5.7 Hz, 1.9H, –OCH<sub>2</sub>–CH(CH<sub>2</sub>)–CH<sub>–</sub>–), 2.29–2.24 (m, 4.1H, –CH<sub>2</sub>(C=O)–O–CH<sub>–</sub>–), 1.96–1.24 (m, 55.7H), and 0.89–0.85 ppm (m, 10.7H, –CH<sub>3</sub>), <sup>13</sup>C NMR: δ 174.0 (s, C=O), 173.5 (s, C=O), 130.0 (d, –CH=CH<sub>–</sub>–, very small signals, only a small amount of alkene present), 73.9 (d, –CH–O–C=O), 66.5 (t, –O–CH<sub>2</sub>–CH<sub>–</sub>–), 38.6 (d, –CH<sub>2</sub>–CH(CH<sub>2</sub>)–CH<sub>–</sub>–), 34.3 (t), 34.0 (t), 31.8 (t), 30.3 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.4 (t), 29.3 (t), 29.2 (t), 29.1 (t), 29.0 (t), 28.8 (t), 25.2 (t), 24.9 (t), 23.7 (t), 22.8 (t), 22.5 (t), 14.0 (q, –CH<sub>3</sub>), 13.9 (q, –CH<sub>3</sub>), and 10.9 ppm (q, –CH<sub>3</sub>).

3. Results and discussion

A series of reactions (Fig. 2) that explored the formation of new complex estolides when the amount of HClO<sub>4</sub> varied and all other variables were held constant are listed in Table 2. Vacuum distillation removed any excess fatty acids and by-products providing neat estolide samples. The equivalents of HClO<sub>4</sub>, percent yields, ENs, pour and cloud points, viscosity, viscosity index, and color are reported in Table 2. These new estolides have an oleic acid backbone with a
terminal saturated fatty acid. Estolides are formed from the carbocationic homo-oligomization of unsaturated fatty acids (Isbell et al., 1994) resulting from the addition of a fatty acid carboxyl adding across the olefin. This condensation can continue, resulting in oligomeric compounds where the average extent of oligomerization is defined as the EN (EN = n + 1, Fig. 2) (Isbell and Kleiman, 1994). When saturated fatty acids are added to the reaction mixture, the oligomerization terminates upon addition of the saturated fatty acid to the olefin because the saturate pro-vides 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’ (Cermak and Isbell, 2002).

Yield decreases as the amount of HClO₄ is decreased from 0.4 to 0.01 equivalents. At 0.01 equivalents of HClO₄, no estolide was detected by HPLC. There is a darkening of the free acid estolide as well as a decrease in the EN as the amount of HClO₄ is decreased. The physical properties listed in Table 2 are similar to each other in terms of functional fluids.

The alcohol portion of the ester functionality was determined by Isbell et al. (2001) to play a significant role in pour point reductions as branched chain alcohols dramatically lower the pour point. Thus, these estolides were converted into their corresponding 2-ethylhexyl estolide esters by the addition of 0.5 M 2-ethylhexanol/BF₃ at 60 °C for 2–4 h for enhanced pour point capability. Samples were vacuum distilled to remove any excess 2-ethylhexanol, providing neat estolide 2-ethylhexyl ester samples. The physical properties of the estolide 2-ethylhexyl esters were evaluated and general trends, such as the EN, were noted as with the free acid estolides. The expected increase in Gardner color (Table 3) caused by the estolide undergoing an additional treatment with acid. This was easily resolved by the decolorization of the estolides. The Gardner colors improved in all cases, resulting in colors similar to commercially available material. The estolides esters were also evaluated in terms of structure. The estolides ranged from 63 to 49% capped with a saturated fatty acid (Table 3).

Effects on the other physical properties of these estolide 2-ethylhexyl esters were noted as the amount of HClO₄ varied (Table 4). These physical property differences were not readily noticeable in the free acid estolides. As the amount of HClO₄ decreased, a dramatic decrease in the pour and cloud points of the lauric–oleic estolide 2-ethylhexyl esters occurs (Table 4). The best pour point improvements were observed between Estolide D, (Table 2, PP –24 °C) and the corresponding Estolide ester D-2EH (Table 4, PP –41 °C). These complex estolides also showed improvements in viscosities and viscosity indexes.

A new series of reactions (Fig. 2) that explored the complex estolides formed when the amount of HClO₄ was varied as the reaction was stirred under vacuum is listed in Table 5. The free estolides were converted to their corresponding esters in situ under vacuum, to improve the progress of the reaction. One of the by-products of the esterification reaction is water. By conducting the reaction under vacuum and at a higher temperature 60 °C, the water was removed to help drive the reaction to completion. The final products underwent vacuum distillation to remove any excess fatty acids, by-products, and 2-ethyl-

### Table 4
Physical properties of lauric–oleic estolide 2-ethylhexyl esters

<table>
<thead>
<tr>
<th>Estolide estera</th>
<th>Pour point (°C)</th>
<th>Cloud point (°C)</th>
<th>Vis@40 °C (cSt)</th>
<th>Vis@100 °C (cSt)</th>
<th>Viscosity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-2EH</td>
<td>–33</td>
<td>–30</td>
<td>89.5</td>
<td>14.5</td>
<td>169</td>
</tr>
<tr>
<td>B-2EH</td>
<td>–27</td>
<td>–32</td>
<td>69.6</td>
<td>12.6</td>
<td>183</td>
</tr>
<tr>
<td>C-2EH</td>
<td>–36</td>
<td>–33</td>
<td>52.2</td>
<td>9.8</td>
<td>176</td>
</tr>
<tr>
<td>D-2EH</td>
<td>–41</td>
<td>–40</td>
<td>52.2</td>
<td>10.0</td>
<td>182</td>
</tr>
</tbody>
</table>

Esterification reactions were run with magnetic stirring and 0.5 M BF₃ at 60 °C.

a Estolide 2-ethylhexyl ester.
hexyl alcohol, providing neat estolide ester samples.

When the reaction was conducted under vacuum, the yields of the estolide conversions were increased. In the case of J-2EH (Table 5), the reaction produced estolide, whereas when the reaction was not under vacuum, no product was formed. There were other problems in obtaining completely esterified material with the 0.01 equivalent HClO₄. Under normal reaction times, the product showed a very high acid value for the distilled product. A longer reaction time may improve the low conversion rate conditions for the reaction. J-2EH was changed to allow the esterification reaction to proceed four times the normal time, which made only a minimal change in the overall conversion. Due to low amounts of acid, this conversion could not be carried out completely.

The previous data (Tables 2–5) suggested that the optimal conditions, in terms of properties, yields, and cost, for the synthesis of a complex estolide is 0.05 equivalents of HClO₄ at 60–80 °C for 24 h followed by the direct conversion to the corresponding esters. Based on these results, a cheap and readily available source of saturated fatty acids is important. Coconut fatty acids are an excellent source based on cost (Tilton, 2002) and fatty acid profile (Table 1). The coconut fatty acids contain the same fatty acids that Cermak and Isbell (2002) used to synthesize complex estolides, as individual saturated fatty acids, and have demonstrated their excellent cold temperature properties. Thus, the mixture of fatty acids might have an even greater effect on the cold temperature properties due to the increased disruption of the crystal lattice structure.

The physical properties of new complex estolides (Fig. 3) synthesized by varying the amounts of saturated fatty acids are listed in Table 6. The material represented in Table 6 has not had any of the excess 2-ethylhexyl monomer ester removed. This material represented in Table 6 is the most cost-effective material because there is no additional costs from distillation or decolorization. Estolide OC-EH-D is the best performing estolide and compares with the simple oleic estolide in terms of its cold temperature properties (Isbell et
However, it should have increased oxidative stability over the homo-oligomeric estolides. When larger ratios of coconut to oleic fatty acids are used, cold temperature performance is reduced, cloud and pour points increased, because of an increase in saturated fatty esters. This potential savings from these cost effective materials were limited by the need of a cold weather performer. After the removal of the coco and oleic monomers through a second distillation, there was a dramatic improvement in the cold temperature properties (Table 7). The best improvements were observed with the cloud points where improvements of 41 °C were noted. These results were not surprising because the literature notes that the cold temperature properties of fatty acid esters are poor, particularly the saturated fatty acid esters. The OC-EH-DD gave the best cold temperature properties, although, the yield was modest.

The physical properties of various commercial materials were compared with the better performing estolide 2-ethylhexyl esters (Table 8). The two estolide 2-ethylhexyl esters selected for comparison with the commercial products were based on price and best cold weather performance (Tables 6 and 7, OC-EH-D and OC-EH-DD). These estolide 2-ethylhexyl 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 8 have cold weather-functional pour points except the soy-based oil. Soy-based products have been demonstrated to have pour points too high for cold weather climates (Erhan and Asadauskas, 2000). All of the commercial products listed had higher cloud points than the estolide 2-ethylhexyl esters. A high cloud point could lead to filter plugging and poor pumpability in cold weather applications. The high cloud point of commercially available oils demonstrates a need for a better cold weather performing oil.

The proton NMR for the free acid estolides in Table 2, specifically estolide ester D, shows some key features of a typical estolide. The ester methine signal at 4.85 ppm is indicative of an estolide linkage. Another distinctive feature is the \( \alpha \)-methylene proton shift (2.32 ppm) adjacent to the acid and the \( \alpha \)-methylene proton shift (2.25 ppm) adjacent to the ester. Integration of these signals provides a ratio for the number of ester bonds to acid functionalities. This ratio of \( \alpha \)-ester/\( \alpha \)-acid can be used as another means to determine the EN complementary to the GC method. The NMR analysis indicates some presence of alkene in the estolide by the appearance of an alkene signal at 5.37–5.33 ppm. The alkene signal indicates that some of the estolide is capped with unsaturated material, i.e. oleic acid. The alkene signal in the proton NMR supports the 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 signals. Two different carbonyl signals are present at 179.7 ppm (acid) and 173.6 ppm (ester). The other distinctive signal is the methine carbon at 74.1 ppm, which is common to estolides. These major peaks in the carbon

<table>
<thead>
<tr>
<th>Estolide(^a)</th>
<th>Oleic to coconut ratio</th>
<th>Pour point (°C)</th>
<th>Cloud point (°C)</th>
<th>Vis@40 °C (cSt)</th>
<th>Vis@100 °C (cSt)</th>
<th>Viscosity index</th>
<th>Gardner color</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-EH-A</td>
<td>1:3</td>
<td>18</td>
<td>23</td>
<td>28.8</td>
<td>6.1</td>
<td>165</td>
<td>11</td>
</tr>
<tr>
<td>OC-EH-B</td>
<td>1:1</td>
<td>–21</td>
<td>–13</td>
<td>21.3</td>
<td>5.1</td>
<td>173</td>
<td>10</td>
</tr>
<tr>
<td>OC-EH-C</td>
<td>1:2</td>
<td>–18</td>
<td>16</td>
<td>21.3</td>
<td>5.0</td>
<td>175</td>
<td>10</td>
</tr>
<tr>
<td>OC-EH-D</td>
<td>2:1</td>
<td>–33</td>
<td>–26</td>
<td>52.2</td>
<td>9.6</td>
<td>169</td>
<td>11</td>
</tr>
<tr>
<td>OC-EH-E</td>
<td>3:1</td>
<td>–24</td>
<td>–21</td>
<td>58.8</td>
<td>13.2</td>
<td>232</td>
<td>11</td>
</tr>
</tbody>
</table>

Reactions were run for 24 h with overhead stirring under vacuum, oleic:coconut fatty acids with 0.05 equivalents of perchloric acid, then 1.2 equivalents of 2-ethylhexanol at 60 °C for 2 h followed by distillation at 90–110 °C.

\(^a\) (Coco–oleic)-(2-ethylhexyl ester)-(sample #).
NMR are also confirmed by a DEPT experiment. The alkene carbons are only slightly noticeable, as these signals are about the same as the signal-to-noise ratio.

The proton NMR for the estolide esters in Table 7, specifically estolide ester OC-EH-DD, gives some predictable signal changes in the proton NMR as compared with the free acid estolides. The \( \alpha \)-carbonyl methylene protons have similar shifts, resulting in a multiplet from 2.29–2.24 ppm. As before, the alkene signal is noticeable at 5.37–5.34 ppm, confirming the IV determined by GC. The carbon NMR signals are indicative of the estolide 2-ethylhexyl ester and confirmed by a DEPT experiment.

Estolides D and OC-EH-DD (Tables 2 and 7) were saponified in 0.5 M KOH/MeOH then esterified with 1 M H\(_2\)SO\(_4\)/MeOH to give the corresponding hydroxy and non-hydroxylated fatty esters. The isolated mixtures of fatty acid esters were then silylated and analyzed by GC–MS (Erhan and Kleiman, 1992). The main mass spectral features were \( m/e \) 371 (M\(_+\) 15, 1.2%), 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 estolide data (Cermak and Isbell, 2001b). The estolide position was distributed from positions 5–13 with the original D9 and 10 positions having the largest abundances in the mass spectrum, which also was very similar to complex estolide data of Cermak and Isbell (2001b). This method demonstrated that during the estolide reaction a migration of the double bond occurs.

4. Conclusions

Estolides have been synthesized with low amounts of HClO\(_4\) to produce lauric–oleic estolides that have great cold temperature properties. The esterification was incorporated into an in situ second step, and thus, the estolide and estolide ester reactions have been modified to produce functional fluids of different grades at a very reasonable cost.
Estolides from oleic and coconut fatty acids and their 2-ethylhexyl esters have excellent low temperature properties. The coco–oleic estolides synthesized at 60 °C and a 2:1 oleic to coconut fatty acids ratio produced materials that had especially good low temperature properties with pour point of −33 °C. The reaction produced a functional fluid with great properties at a reasonable cost. This material can be further refined to produce a high-value estolide with even superior cold temperature properties.

Viscosity is also controlled by the amount of oligomerization, with higher oligomerization providing higher viscosity. Many applications are available for materials with the viscosity range of these estolides. Thus, as the amount of HClO₄ is reduced, the degree of oligomerization decreases. These new saturated, coconut fatty acid-capped, oleic estolides and corresponding 2-ethylhexyl esters have outperformed commercial products in cold temperature properties even though the estolides remained unformulated.

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References


