Synthesis and physical properties of petroselinic based estolide esters

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A new series of petroselinic (\textit{Coriandrum sativum} L.) based estolide 2-ethylhexyl (2-EH) esters were synthesized, as the capping material varied in length and in degrees of unsaturation, in a perchloric acid catalyzed one-pot process with the esterification process incorporated into an \textit{in situ} second step to provide the coriander estolate 2-EH ester. The kinematic viscosities ranged from 53 to 75 cSt at 40 °C and 9.1 to 14.6 cSt at 100 °C with a viscosity index (VI) ranging from 151 to 165. The caprylic (C8) capped coriander estolate 2-EH ester had the lowest low-temperature properties (pour point = −33 °C and cloud point = −33 °C), while the coco-coriander estolate 2-EH ester produced an estolide with modest low-temperature properties (pour point = −24 °C and cloud point = −25 °C). The coco-coriander estolate 2-EH ester was explored for the ability to resist oxidative degradation with the use of a biodegradable additive package added in 1.5%, 3.5%, or 7.0% units based on weight. The oxidative stability increased as the amount of stability package increased (rotating pressurized vessel oxidation test (RPVOT) times 65–273 min). Along with expected good biodegradability, these coriander estolate 2-EH esters had acceptable properties that should provide a specialty niche in the U.S. as a biobased lubricant.

1. Introduction

\textit{Coriandrum sativum} L., belonging to the family Umbelliferae (Apiaceae), commonly known as Chinese parsley or cilantro is grown for its leaves (Zheljazkov et al., 2008; Kiralan et al., 2009). Coriander is native to southern Europe and North Africa and southwestern Asia (Ramadan and Mörsel, 2002). Coriander seeds have a lemony citrus flavor when crushed, due to the presence of the terpenes linalool and pinene. The seeds have many uses as a spice in food applications, in pickling vegetables, making sausages in Germany as well as used in brewing certain styles of beer, Belgian wheat beers in particular (Vanderhaegen et al., 2003).

Coriander seeds contain oil that is rich in petroselinic acid (18:1 n-12) (74%) with lesser amounts of oleic acid (18:1 n-9) (7%), Table 1. Petroselinic has many potential uses as an industrial raw base chemical with the most promising application supplying the chemical industry with adipic and lauric acids via oxidative cleavage of the Δ6 double bond in petroselinic acid (Isbell et al., 2006). Adipic acid is commonly used as a monomer for nylon synthesis and lauric acid is used in detergent applications. With the potential of coriander becoming a biobased feedstock in the near future other industrial applications of the oil must be explored and/or expanded. Most new crops require a high value of return, and thus initially may be developed for high value applications such as cosmetic or specialty lubricants. Estolides have allowed new crop oils to be easily incorporated into a variety of potential products. To date, the best performing estolides are produced from oleic (18:1) sources (Cermak and Isbell, 2000, 2003, 2004; Cermak et al., 2007) such as sunflower, canola, or soybean.

Estolides have been used to help develop new products from industrial crops (Cermak and Isbell, 2000; Isbell et al., 2000). Estolides are formed through the formation of a carboxylation at the carbon carbon double bond position that subsequently undergoes nucleophilic addition with or without carboxylation 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 \textit{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 (Cermak and Isbell, 2003) and low temperature properties (Asadauskas and Erhan, 1999). Some of these
Table 1
Chemical compositions of coriander and coconut fatty acids.

<table>
<thead>
<tr>
<th>FA (%)a</th>
<th>8:0</th>
<th>10:0</th>
<th>12:0</th>
<th>14:0</th>
<th>16:0</th>
<th>18:0</th>
<th>18:1</th>
<th>18:2</th>
<th>18:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coriander</td>
<td>–</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
<td>3.4</td>
<td>0.8</td>
<td>81.3</td>
<td>14.0</td>
<td>–</td>
</tr>
<tr>
<td>Coconut</td>
<td>5.1</td>
<td>4.9</td>
<td>48.3</td>
<td>21.7</td>
<td>10.6</td>
<td>7.0</td>
<td>2.4</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Dash indicates not detected.

a Determined by GC (SP-2380, 30 m × 0.25 mm i.d.).
b 73.5% n-12 (petroselinic), 6.9% n-9 (oleic), and 0.9% n-7 (vaccenic).

deficiencies inherent to vegetable oils can be reduced with the use of additive packages, but usually at the sacrifice of biodegradability, toxicity, and cost.

A number of in-depth studies on estolide structure versus physical properties have been conducted over the years (Isbell et al., 2001; Cermak and Isbell, 2009). The length of the base unit was determined with the optimization of low temperature properties. The capping fatty acids were modified to include different lengths and different levels of unsaturation into the capping of the estolide. The size or EN of the estolide was varied as the low temperature properties were measured. In all cases explored thus far, the estolide structure has a direct correlation to the physical properties of estolides.

With the ability to use fatty acids from coriander in the synthesis of estolides, the question we would like to explore is what effect the position of the estolide linkage point will have on estolide physical properties. The simple oleic estolide, oleic-oleic estolide 2-EH ester (Isbell and Kleiman, 1994), has the estolide linkage at primarily the (18:1 n-9) and (18:1 n-10) positions (Fig. 2). Petroselinic-based estolides would have the estolide linkage at primarily the (18:1 n-12) and (18:1 n-13) positions which would bring the two ester functional groups substantially closer together at the intramolecular level.

Strong correlations between estolide structure and physical properties have allowed for the ability to develop or synthesize estolides that exceed the properties of 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 and physical properties of a series of petroselinic-based estolide esters as well as relate estolide linkage position to the performance of these new petroselinic-based estolide esters to past oleic-based estolides and commercially available materials.

2. Materials and methods

2.1. Materials

Oleic acid (90%) was purchased from Aldrich Chemical Co. (Milwaukee, WI). Ethyl acetate, hexanes, acetone, perchloric acid (70%), and 2-ethylhexyl alcohol were purchased from Fisher Scientific Co. (Fairlawn, 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) were obtained from EM Science (Gibbstown, NJ). Ethanol was purchased from AAPER Alcohol and Chemical Company (Shelbyville, 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 an equivalent, and were used without further purification. Oxidative stability package, Lubrizol® 7652, was obtained from the Lubrizol Corporation (Wickliffe, OH). Soy based oil: Biosoy® was obtained from the University of Northern Iowa (Cedar Falls, IA). Petroleum oil: Mobil® 10W-30 and synthetic oil: Penzoil Synthetic® 10W-30, and hydraulic fluid: Traveler Universal Hydraulic Fluid® were obtained from local vendors.

Fig. 1. Synthesis of saturated-capped coriander estolide 2-ethylhexyl ester.
2.2. Coriander

2.2.1. Coriander seed production

Agronomic procedures for field production of coriander (C. sativum L.) followed standard procedures at Prosper, ND (46°58′N, 97°3′W; elevation 284 m) during the 2006 and 2007 growing seasons. A bulk seed increase of coriander was sown 2.5 cm deep at 22 kg/ha pure live seed near 27 May both years. Soil type at the Prosper location is a complex of Bearden/Perella silty-clay loam (Bearden: fine-silty, mixed, superactive, frigid Aeric Calciaqualis; Perella: fine-silty, mixed, superactive, frigid Typic Endoaquolls). The soil is of lacustrine origin and characterized with moderate organic matter levels, generally high cation exchange capacity, and high water holding capacity and plant available water.

The previous crop both years was hard red spring wheat (Triticum aestivum L.) grown under conventional tillage consisting of fall chisel plowing and a single spring cultivation/harrow operation prior to coriander seeding. Nitrogen fertility was adjusted to target a 2688 kg/ha hard red spring wheat yield. Soil phosphorus and potassium levels were adequate for the targeted wheat yield and did not require any additional fertilizer amendments. The coriander plot was approximately 0.3 ha each year and seeded with five rows per planter pass across the plot area.

Stand emergence was approximately 10 days after seeding and ranged from 65% to 90% among years. Flowering occurred 60 days after seeding; plant height was 103 cm; and plant lodging was high at 4.3 on a scale from 0 to 5. There were few pest issues other than some annual grass and broadleaf weeds that occurred later in the season when the pre-plant soil incorporated herbicide trifluralin began to lose effectiveness. Harvest was performed directly with a plot combine at harvest maturity with seed collected in cloth sacks and aerated in a grain dryer at ambient temperatures for 7 d. Seed yield was low to moderate at approximately 1000 kg/ha with a 1000-seed weight of 9.3 g.

2.2.2. Coriander seed cleaning, dehulling, press, and hydrolysis

The coriander seeds were cleaned by screening and aspirating and then dehulled using and impact huller (Model 15-D, Forsbergs Inc., Thief River Falls, MN). The dehulled seeds contained 26% oil (dry basis). The dehulled seed was cooked (180–200°F) and dried to around 5% moisture content using a laboratory seed conditioner/cooker (Model 324 French Oil Mill Machinery Company, Piqua, OH). The cooked and dried seed was pressed immediately using a heavy-duty laboratory screw press (Model L250, French Oil Mill Machinery Company, Piqua, OH). The crude oil was allowed to settle before it was filtered through No. 54 Whatman filter paper.

The crude coriander seed oil (350 g, 559 mmol) was hydrolyzed by the addition of 2.0 M KOH/EtOH (112 g of KOH in 1 L 95% ethanol) followed by heating to reflux for 60 min. After cooling to room temperature, the reaction mixture was placed in a 6 L Erlenmeyer with 1 L of hexane and cooled in an ice bath. A 1 M HCl solution (~2.1 L) was slowly added to the cooled hydrolysis mixture with overhead stirring. Addition was maintained until the solution was slightly acidic, as measured by pH paper. The mixture formed an emulsion as the transition occurred. 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 × 100 mL). The organic layer was removed, dried over sodium sulfate, and filtered. All reactions were concentrated under vacuum set to 6–13 kPa to remove any excess ethanol and 2-ethylhexyl alcohol. The residue was further distilled by kugelrohr-distillation at 160–190°C at 0.013–0.067 kPa to purify the fatty acids. A small sample of the fatty acids was then esterified to the corresponding methyl ester under conditions described above to yield the coriander fatty acid profile, Table 1.

2.3. General coriander estolide 2-ethylhexyl ester synthesis

An acid-catalyzed condensation reaction was conducted without solvent in a 500 mL round bottom flask that had been pre-treated with an acidic wash. Coriander fatty acids (100.0 g, 354.6 mmol) and capping fatty acids, i.e. oleic acid (50.0 g, 177.3 mmol) were combined together, heated to 60°C under house vacuum (7.5–10.9 kPa), and stirred with a Teflon coated stir bar. Once the desired temperature of 60 ± 0.1°C was reached, perchloric acid (26.6 mmol, 2.30 mL, 0.05 eq.) was added, vacuum restored, and stirred. After 24 h, 2-ethylhexyl alcohol (208.0 g, 1.60 mol, 235.4 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 (1.64 g, 29.2 mmol, 1.2 eq. based on HClO4) in 50% ethanol/water (10 mL) solution. The solution was allowed to cool with stirring for 45 min followed by filtration through a Buchner funnel with Whatman #1 filter paper. The organic layer was dried over sodium sulfate and filtered through a Buchner funnel with Whatman #1 filter paper. All reactions were concentrated in vacuo then kugelrohr-distilled 90–110°C at 6–13 kPa to remove any excess ethanol and 2-ethylhexyl alcohol. The residue was further distilled by kugelrohr-distillation 180–200°C at 6–13 kPa to remove any unre-
acted saturated and unsaturated fatty acids and by-products, such as lactones (Cermak and Isbell, 2001) and 2-EH esters (monomers). The percent yield of the estolide 2-EH esters reported in Table 2 were modest at 65–76% and similar to past synthesized estolides (Cermak and Isbell, 2001, 2004). Estolides for example when defined as an lauric capped oleic estolide, means that the estolides are capped with an lauric, oleic, and also some are capped with the saturates found in the oleic material as well as any fatty acid contaminates in the lauric material. This same purity issues are applicable to coriander.

2.4. Equipment and procedures

2.4.1. Characterization

2.4.1.1. Gas chromatography (GC). Hewlett-Packard 6890N Series gas chromatograph (Palo Alto, CA) equipped with a flame-ionization detector and an autosampler/injector was used for GC analysis. 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 making fatty acid and by-product assignments.

Parameters for SP-2380 analysis were: column flow 1.4 mL/min with a helium head pressure of 136 kPa; split ratio 50:1; injector temperature set at 250 °C; programmed ramp from 170 to 330 °C, hold 5 min at 265 °C; injector and detector temperatures set at 250 °C. Saturated C8–C30 FAME provided standards for calculating ECL values, which were used to make FAME assignments.

2.4.1.2. GC–mass spectrometry (GC–MS). Hewlett-Packard 5890A GC with a 30 m × 0.20 mm i.d. SPB-1 column (Supelco, Bellefonte, PA) and a Hewlett-Packard 5970 mass selective detector was used for GC–MS analysis. GC conditions were helium head pressure 15 psi (103 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. Saturated C8–C30 FAME provided standards for calculating ECL values, which were used to make FAME assignments.

2.4.1.3. High-performance liquid chromatography (HPLC). Thermo Separations Spectra System AS1000 autosampler/injector (Fremont, CA) with a P2000 binary gradient pump from Thermo Separation Products (Fremont, CA) coupled to an Alltech ELSD MKIII evaporative light scattering detector (Alltech Associates, Deerfield, IL) was used for normal phase–HPLC analysis of the esterification step. A silica normal phase analysis was carried out with a Dynamax column (250 mm × 4.6 mm, 8 μm) from Rainin Instrument Co. (Woburn, MA). 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 with the nebulizer set at 20 psi (138 kPa) N2, providing a flow rate of 2.0 standard liters per minute (SLPM). Retention times for eluted peaks: estolides, 2.8–2.9 min; free acid acetide, 3.8–3.9 min.

2.4.1.4. Iodine values (IVs) and estolide numbers (ENs). Iodine values (IVs) were determined from the GC results using AOCS Method Cd 1c–85 (Firestone, 1994). Estolide numbers (ENs) were determined by GC from the SP-2380 column analysis as described previously (Isbell and Kleiman, 1994).

2.4.1.5. GC analysis of hydroxy fatty acids. Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell (2001).

2.4.1.6. TMS derivatization of hydroxy fatty esters. Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell (2001).

2.4.1.7. Nuclear magnetic resonance (NMR). 1H and 13C NMR spectra were collected on a Bruker Avance 500 (Billerica, MA) spectrometer with a 5 mm BBI probe. All spectra were acquired at 300.0 K using CDCl3 as a solvent in all experiments. Chemical shifts are reported as parts per million from tetramethylsilane with an absolute frequency 500.11 MHz. The assignments of protons were by the data reported for the number of protons in the NMR reflect the actual numbers present in the reaction product.

Table 2

<table>
<thead>
<tr>
<th>Estolide</th>
<th>Capping fatty acid</th>
<th>Fatty acid # (EN)</th>
<th>(IV)</th>
<th>Capped (%)</th>
<th>Acid value (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>None</td>
<td>1.64</td>
<td>31.5</td>
<td>8.8</td>
<td>1.85</td>
</tr>
<tr>
<td>B</td>
<td>Caprylic</td>
<td>1.88</td>
<td>17.6</td>
<td>44.4</td>
<td>5.42</td>
</tr>
<tr>
<td>C</td>
<td>Lauric</td>
<td>1.93</td>
<td>45.4</td>
<td>4.22</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Myristic</td>
<td>1.11</td>
<td>53.4</td>
<td>3.85</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Palmitic</td>
<td>1.91</td>
<td>57.1</td>
<td>4.82</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Stearic</td>
<td>2.80</td>
<td>10.0</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Oleic</td>
<td>1.40</td>
<td>21.0</td>
<td>4.56</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Coco</td>
<td>5.42</td>
<td>1.85</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Estolide number—see Fig. 1.
b Iodine value.
c Percent of estolide saturated–capped.
d Mainly C12:0—see Table 1.
(m, 2.0 H, −O−CH2−CH(O−CH2−CH2−), 2.34−2.19 (m, 5.08 H, −CH2−(C=O)−O−CH2−, −CH2(=O)−O−CH−), 2.08−1.24 (m, 72.02 H, −CH2−), and 0.91−0.86 ppm (m, 13.50 H, −CH3). 13C NMR: δ 173.9 (s, C=O), 173.7 (s, C=O), 173.6 (s, C=O), 173.6 (s, C=O), 130.9−130.0 (d, −CH=CH−, very small signals, only a small amount of alkene present), 73.8 (d, −CH−O−C=O), 73.8 (d, −CH−O−C=O), 66.7 (t, −O−CH2−CH−), 66.6 (t, −O−CH2−CH−), 66.6 (t, −O−CH2−CH−), 38.8 (d, −CH2−CH(O−CH2−)−CH2−), 33.8 (t), 34.0 (t), 34.1 (t), 34.1 (t), 34.2 (t), 34.3 (t), 34.3 (t), 34.4 (t), 34.4 (t), 34.2 (t), 32.6 (t), 32.4 (t), 32.2 (t), 31.9 (t), 30.4 (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), 29.1 (t), 28.9 (t), 25.3 (t), 25.2 (t), 25.1 (t), 25.1 (t), 25.0 (t), 24.9 (t), 23.8 (t), 23.0 (t), 22.7 (t), 14.1 (q, −CH3), 14.0 (q, −CH3), and 11.0 ppm (q, −CH3).

2.4.2. Properties

2.4.2.1. Gardner color. Lovibond 3-Field Comparator from Tintometer Ltd. (Salisbury, England) using AOCS Method Td 1a-64 (Firestone, 1994) was used for Gardner color measurements. Gardner color, of both the residue and distillate materials, was measured. The “+” and “−” notation was employed to designate samples that did not match one particular color.

2.4.2.2. Viscosity and viscosity index. Calibrated Cannon-Fenske viscometer tubes obtained from Cannon Instrument Co. (State College, PA) were used to measure kinematic viscosity. Measurements were run 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 D 2270-93, respectively. Duplicate measurements were made and the average values were reported.

2.4.2.3. Pour point. ASTM Method D97-96a 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 test 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 sample. Samples with pour points that ranged from (+9 to −6, −6 to −24, and −24 to −42 °C) were placed in baths at different temperatures (−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.

2.4.2.4. Cloud point. 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 test 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, −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.

2.4.2.5. Acid value. 751 GPD Titrino from Metrohm Ltd. (Herisau, Switzerland) was used for measurements. Acid values were determined by the official AOCS Method Te 2a-64 (Firestone, 1994) with ethanol substituted for methanol to increase the solubility of the estolide esters during the titration. All acid values were run in duplicate and average values were reported.

2.4.2.6. Rotating pressurized vessel oxidation test. Test determinations were conducted on a rotating pressurized vessel oxidation test (RPVOT) apparatus manufactured by Koehler (Boehma, NY) using the ASTM Method D2272-98. Estolides 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) 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.

2.4.3. Statistical analysis

Standard curves were developed for the GC to determine the response factors for the different fatty acid chain lengths. Standard deviations for all the GC data were less than ±0.05. ORIGIN 7.0 was used to make bar graphs.

3. Results and discussion

Estolides are formed from the cationic homo-oligomerization of unsaturated fatty acids resulting from the addition of a fatty acid carboxyl moiety across the olefin (Isbell et al., 1994). 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) (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 since the saturate provides no additional reaction site to further the oligomerization. Consequently, the estolide is stopped at this point from further rapid growth, thus we term the estolide as being “capped” (Cermak and Isbell, 2001). As the estolides increase in size, the ability for individual polyestolides to link to each other becomes less likely based on stearic interactions, therefore estolides do not have rapid growth from the carboxylic acid site of the estolides.

Coriander seeds were pressed for oil which was hydrolyzed followed by distillation to yield the corresponding petroselinic fatty acids, shown in Table 1. Table 2 outlines a series of reactions (Fig. 1) that explored the formation of a new series of petroselinic (coriander) based estolide 2-EH esters. The type of capping material was varied (chain length) to include examples of both saturated and unsaturated capping materials as all other reaction parameters were 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 to yield the estolide 2-EH esters in modest yields. The final products underwent vacuum distillation to remove any excess 2-ethylhexyl alcohol, fatty acids, fatty esters, and other by-products, providing estolide 2-EH ester samples. The EN, iodine value (IV), percent of estolide saturated-capped, and the acid value for the petroselinic estolides are reported in Table 2. These new coriander based estolide 2-EH esters have a petroselinic acid backbone with a terminal saturated capping group. Fig. 2 shows one such example of a saturated-capped petroselinic estolide 2-EH ester where the terminal saturated capping group, saturated (C12:0) lauric (Table 2, Estolide E).

The saturated-capped % values in Table 2 were obtained from GC analysis of the estolide 2-EH esters which were saponified and
Capped oleic estolide 2-EH esters had the best cold temperature properties when compared to caprylic (C8:0) or capric (C10:0) fatty acids such as those present in estolides. Previously, caprylic-capped coriander estolide 2-EH esters had the best low temperature properties when capped with saturated fatty acids as reported by Cermak and Isbell (2001, 2004). Thus, the position on the base unit influence on the low temperature properties of these coriander based estolide 2-EH esters.

Additionally, the coco-oleic estolides synthesized in the past by Cermak and Isbell (2001) had outstanding low temperature properties as well as outstanding oxidative stabilities. The coco-coriander estolide 2-EH esters (Estolide J, Table 3) had a PP of −24 °C as compared to −33 °C for the corresponding coco-oleic based-estolide 2-EH ester. If the results from Table 3 are plotted against the oleic based-estolide 2-EH ester PP data reported by Cermak and Isbell (2002) the advantage of one over the other is obvious (Fig. 3). In almost all cases the oleic based estolide 2-EH esters had superior to equal PP as compared to the coriander based estolide 2-EH esters. The position of the estolide linkage must play an active role in the determination of the low temperature properties of these estolide esters.

Table 3 shows no general trend of the Gardner color of the estolides produced from coriander. Previous work reported by Cermak and Isbell (2009) showed that the same general results were observed, with the caprylic, C6:0, producing the darkest capped estolide. In all cases the estolide 2-EH esters produced were from coriander fatty acids that came from oil that was not refined. The extra color bodies could have come from the underfined oil or impurities carried over in distillation. Generally, the Gardner colors of the estolides could be improved by a double distillation of the coriander fatty acids prior to estolide formation. Color improvements have been accomplished via an additional costly distillation step for estolides previously synthesized. Estolides 2-EH esters where improved from a Gardner color in the 10–11 range to a −6 (Cermak et al., 2007).

Not only are low temperature properties important for a biobased material to be considered a lubricant, they must also be good color bodies.

### Table 3

<table>
<thead>
<tr>
<th>Estolide</th>
<th>Capping fatty acid</th>
<th>Fatty acid #</th>
<th>Pour point (°C)</th>
<th>Cloud point (°C)</th>
<th>Visc. @ 40 °C (cSt)</th>
<th>Visc. @ 100 °C (cSt)</th>
<th>Vis. index</th>
<th>Gardner color</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>None</td>
<td>None</td>
<td>−27</td>
<td>−27</td>
<td>74.5</td>
<td>12.2</td>
<td>162</td>
<td>11−</td>
</tr>
<tr>
<td>B</td>
<td>Caproic</td>
<td>6:0</td>
<td>−30</td>
<td>−33</td>
<td>58.0</td>
<td>10.2</td>
<td>165</td>
<td>15</td>
</tr>
<tr>
<td>C</td>
<td>Caprylic</td>
<td>8:0</td>
<td>−33</td>
<td>−33</td>
<td>60.9</td>
<td>10.3</td>
<td>158</td>
<td>11−</td>
</tr>
<tr>
<td>D</td>
<td>Capric</td>
<td>10:0</td>
<td>−30</td>
<td>−33</td>
<td>54.4</td>
<td>9.6</td>
<td>162</td>
<td>9+</td>
</tr>
<tr>
<td>E</td>
<td>Lauric</td>
<td>12:0</td>
<td>−27</td>
<td>−23</td>
<td>53.4</td>
<td>9.1</td>
<td>151</td>
<td>10+</td>
</tr>
<tr>
<td>F</td>
<td>Myristic</td>
<td>14:0</td>
<td>−21</td>
<td>−14</td>
<td>62.9</td>
<td>10.8</td>
<td>163</td>
<td>10+</td>
</tr>
<tr>
<td>G</td>
<td>Palmitic</td>
<td>16:0</td>
<td>−15</td>
<td>−9</td>
<td>58.1</td>
<td>10.1</td>
<td>162</td>
<td>9+</td>
</tr>
<tr>
<td>H</td>
<td>Stearic</td>
<td>18:0</td>
<td>−12</td>
<td>−3</td>
<td>53.7</td>
<td>9.6</td>
<td>165</td>
<td>9+</td>
</tr>
<tr>
<td>I</td>
<td>Oleic</td>
<td>18:1</td>
<td>−30</td>
<td>−32</td>
<td>92.8</td>
<td>14.6</td>
<td>164</td>
<td>7+</td>
</tr>
<tr>
<td>J</td>
<td>Coco</td>
<td>−9</td>
<td>−24</td>
<td>−25</td>
<td>55.9</td>
<td>9.8</td>
<td>162</td>
<td>12−</td>
</tr>
</tbody>
</table>

*Mainly C12:0—see Table 1.

As the chain length increased, the percent of saturated-capped estolide also increased. Caproic, C6:0, exhibited the least amount of saturated capped material with only 28.3% while myristic, C14:0, had 61.9% of the estolides capped with saturated materials while the palmitic, C16:0, and stearic, C18:0, percentages decreased. The saturated fatty acids were added to the reaction in a 2:1 excess as compared to the coriander base material. This trend suggests that during estolide formation, the fatty acids added preferred to be of similar chain length regardless of the degrees of saturation due to either steric effects or solubility issues.

The IVs have shown to play a critical role on the physical properties of the estolide. The IVs reported provide information on the amount of unsaturation located in the molecule. A number of factors influence the IVs of the estolide samples with the two greatest influences are from the amount of unsaturation and the EN of the estolide 2-EH ester. As the amount of saturation and/or estolide number increases the IV decreases; as unsaturation or possible unsaturation is removed from the reaction sample. Past demonstrations have proven that lowering the iodine values of the estolides dramatically improves the oxidative stability of the estolide 2-EH esters as reported by Cermak and Isbell (2003).

Table 3 outlines the physical properties, viscosity, color, pour point (PP) and cloud points (CP) of these new coriander based estolides. As the chain length of the saturated capped material decreased, the PP and CP were also decreased. With coriander as the base unit of the estolide, the lowest PP material was capped with caprylic, C8:0, fatty acid (Estolide C, Table 3). The caprylic-capped coriander estolide 2-EH ester had a PP of −33 °C and CP of −33 °C. As the chain length increased the low temperature properties for the coriander based estolides became less desirable (Estolide H, stearic capped estolide, PP −12 °C and CP −3 °C).

Cermak and Isbell (2001, 2004) showed that complex oleic based estolides had the best low temperature properties when capped with short chain, saturated fatty acids such as those present in cuphea and coconut. Previously, caprylic (C8:0) or capric (C10:0) capped oleic estolide 2-EH esters had the best cold temperature properties, with a PP of −39 °C. The coriander based estolide 2-EH esters did not follow the same general trend as the cuphea-capped oleic estolide 2-EH esters synthesized in the past in terms of what saturated capping material maximized the cold temperature properties (Cermak and Isbell, 2004). Thus, the position on the base unit where the estolide linkage (Fig. 2) is located has some degree of influence on the low temperature properties of these coriander based estolide 2-EH esters.

\[
\text{molar \% saturated fatty acids} \times 100 = \% \text{ saturated-capped}
\]

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\text{molar \% saturated fatty acids} \times 100 = \% \text{ saturated-capped}
\]

\[
\text{molar \% saturated fatty acids} \times 100 = \% \text{ saturated-capped}
\]
have some degree of thermal stability towards oxidation (Isbell et al., 1999). The RPVOT times were determined for the coco-coriander estolide 2-EH ester (Tables 2 and 3, Estolide J), with varying amounts of an oxidative stability package, Lubrizol® 7652, at 150 °C (Isbell and Kleiman, 1994), with et al., 1999). The RPVOT times were determined for the coco-coriander estolide 2-EH ester, Estolide J, showed the expected low RPVOT time of 16 min (Table 4) as is typical for most unformulated vegetable oils (Cermak and Isbell, 2003). The oxidative stability package, Lubrizol® 7652, was added in 1.5%, 3.5%, or 7.0% units based on weight. As 1.5% of the oxidative stability package was added, there was four times the improvement in the RPVOT value to 65 min (Table 4, Estolide J). Addition of a 3.5% oxidative stability package produced an RPVOT value of 212 min for the coco-coriander estolide 2-EH ester (Table 4, Estolide Jb), which was comparable with petroleum and synthetic crankcase fluids (Table 4). This was an improvement of more than 13 times over the original stability time. Addition of a 7.0% oxidative stability package produced an RPVOT value of 273 min for the coco-coriander estolide 2-EH ester (Table 4, Estolide Jc), which exceeded the performance of commercial petroleum and synthetic crankcase fluids (Table 4). This was an improvement of more than 17 times over the original stability time. Due to a limited supply of coriander oil, RPVOT sample destruction and RPVOT method required a sample size that we did not have available. The oxidative stability package was not added in increments of 1% weight units as in previous studies (Cermak and Isbell, 2003) to determine the optimum concentration in terms of min of oxidative stability. Previous data have shown that estolide 2-EH esters reached this maximum RPVOT range after 3% and any additional oxidative stability package greater than 10.0% showed a destructive effect on the overall RPVOT values (Cermak and Isbell, 2003).

In general the coco-coriander estolide 2-EH esters had RPVOT values that were highly comparable to commercial products, but did not perform to similar high levels exhibited by the saturated and unsaturated estolides (coco-oleic estolide 2-EH esters) previously reported by Cermak and Isbell (2003). The oxidative stability difference in the coco-coriander versus coco-oleic systems may be caused by some residual higher unsaturates in the coriander (Table 1) since it is a mixture and the oleic was presumably a pure starting material. Oxidative stability is known to be readily dependent on the amount of unsaturation in a molecule (Isbell et al., 1999). The coco-coriander 2-EH estolide esters had an IV of 212 d), which was superior. The low CP is one of the estolides' strongest selling points as a cold weather lubricant.

The carbon NMR spectrum contained the expected estolide 2-EH ester signals. There were three different carbonyl signals at 4.89–4.82 ppm is indicative of an estolide linkage. Another distinctive feature is the multiplet α-methylene proton shift (2.34–2.19 ppm) adjacent to the two esters. The NMR indicates the presence of alkene in the estolide by the appearance of an alkene signal at 5.40–5.32 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 IV determined by GC, as the intensity of the NMR signals is comparable to the reported IV.

The carbon NMR spectrum contained the expected estolide 2-EH ester signals. There were three different carbonyl signals present in the 173 ppm region (estolide esters, estolide 2-EH ester and 2-EH ester). The lack of the shift in the 179 ppm region (Cermak and Isbell, 2001) indicated the estolides had been converted to the 2-EH ester which supported the AV number in Table 2. The other distinctive signal was the methine carbon at 73.8 ppm, which is common to estolide 2-EH esters. These major peaks in the carbon NMR are also observed by GC, as the intensity of the NMR signals is comparable to the reported IV.

In general the coco-coriander estolide 2-EH esters had RPVOT values that were highly comparable to commercial products, but did not perform to similar high levels exhibited by the saturated and unsaturated estolides (coco-oleic estolide 2-EH esters) previously reported by Cermak and Isbell (2003). The oxidative stability difference in the coco-coriander versus coco-oleic systems may be caused by some residual higher unsaturates in the coriander (Table 1) since it is a mixture and the oleic was presumably a pure starting material. Oxidative stability is known to be readily dependent on the amount of unsaturation in a molecule (Isbell et al., 1999). The coco-coriander 2-EH estolide esters had an IV of 21 while the simple oleic 2-EH estolide esters, oleic-oleic estolide 2-EH ester (Isbell and Kleiman, 1994), had an IV of 42 (Cermak et al., 2007). Contrary to our predictions the reverse was found in terms of oxidative stability. Thus, the position of the estolide linkage must influence to some degree the amount of thermal and hydrolytic stability this new class of compounds possesses.

The physical properties of various commercial materials versus a coco-coriander estolide 2-EH ester were compared (Table 4).
distributed from positions 2–12 with the original Δ6 and Δ7 positions having the largest abundances in the mass spectrum, which also followed the very similar trend displayed with oleic based material in the complex estolide data (Cermak and Isbell, 2001). This method demonstrated that during the estolide reaction there was migration of the double bond and the estolides were indeed complex molecules.

4. Conclusions

A new series of petroselinic (coriander) based estolide 2-EH esters were synthesized, as the capping material varied from caproic (C6) to stearic (C18) chain lengths and degrees of unsaturation, in a perchloric acid catalyzed one-pot process. Thus, followed by an in situ esterification second step to provide the coriander estolide 2-EH esters. In general, the low temperature properties of the synthesized estolide 2-EH esters were comparable to other synthesized oleic based estolide 2-EH esters. The C8 or caprylic-coriander estolide 2-EH ester had lowest low-temperature properties (pour point = –33 °C and cloud point = –33 °C), while the coco-coriander estolide 2-EH ester produced an estolide that had modest low-temperature properties (pour point = –24 °C and cloud point = –25 °C). Of all the estolides reports to date, the oleic based materials produced the best low temperature “estolide” material which was the decanolic-oleic estolide 2-EH esters. The coco-coriander estolide 2-EH ester was explored for the ability to maintain oxidative stability with the use of an biodegradable additive package added in 1.5%, 3.5%, or 7.0% units based on weight. The oxidative stability increased as the amount of stability package increased (RPVOT times 65–273 min). Along with expected good biodegradability, these coriander estolide 2-EH esters had acceptable properties that should provide a specialty niche in the U.S. as a bio-based lubricant.

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References