Synthesis and Physical Properties of Cuphea–Oleic Estolides and Esters

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ABSTRACT: Cuphea–oleic estolides and esters were synthesized from cuphea and oleic FA with various amounts of perchloric acid (0.01 to 0.40 equiv) at 60°C. Estolide yields ranged from 30 to 65% after Kugelrohr distillation. Estolide number (EN), the average number of FA units added to a base FA, varied with reaction conditions. Cuphea–oleic estolides were esterified with 2-ethylhexanol to obtain high yields of the corresponding ester. A streamlined, one-pot process was used to synthesize the estolide and its ester with 0.05 equiv of $HClO_4$, with esterification incorporated into an *in situ* second step to provide a functional fluid at a very reasonable cost. The physical properties of the cuphea–oleic estolides and estolide esters, including their viscosities, pour points, and cloud points, were related directly to the amount of oligomerization (EN), i.e., viscosity increased with higher oligomerization. The viscosity index ranged from 132 to 166 cSt for the free-acid estolides, whereas the complex estolide 2-ethylhexyl esters had slightly higher viscosity indices that ranged from 165 to 181 cSt. These new cuphea–oleic estolide esters displayed good low-temperature properties (pour point –42°C and cloud point –41°C).

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KEY WORDS: Cloud point, cuphea, estolides, oleic acid, pour point, PSR-23, viscosity.

Cuphea (Lythraceae) is an annual plant that produces a small seed rich in saturated medium-chain TAG. The initial oil characterization of a number of cuphea species was done at the U.S. Department of Agriculture (USDA) Research Center in Peoria, Illinois, in the early 1960s (1). To address the need for higher seed yields, a higher oil content, and less seed shattering, Steve Knapp (2) at Oregon State University began developing promising cuphea crosses. One of these new crosses, PSR-23 (where PSR refers to partial seed retention), was developed at the University of Oregon and planted in the Midwest. This cross has been mechanically harvested by researchers at the USDA in Morris, Minnesota, and Peoria, Illinois, for the past 3 yr. PSR-23 is a cross that is high in C_{10}, decanoic acid (65%; see Table 1).

Coconut and palm kernel oils provide about 5.5 million tons (5.6 million metric tons) of lauric acid to the global market, where it is used mainly for detergents, shampoos, and toothpastes (3). Many species of cuphea contain lauric acid as the major FA. Obtaining the correct species of cuphea or cuphea cross with high levels of lauric acid may provide farmers with a strong economic incentive to incorporate cuphea as a new rotation crop. Once such a cross has been developed, it could become a viable source of lauric acid in the United States and would lessen our demand for foreign imports of coconut and palm kernel oils.

TABLE 1
FA Compositions[a]

	FA (%)							
	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2
Cuphea[b]	0.6	65.6	3.2	6.5	7.2	0.8	9.1	5.9
Coconut	5.1	4.9	48.3	21.7	10.6	7.0	2.4	–

[a]Determined by GC (SP-2380 column, 30 m × 0.25 mm i.d.; Supelco, Bellefonte, PA). Dash indicates not detected.
[b]Cross PSR-23.

One of the challenges in introducing a new crop such as cuphea into the marketplace is that so-called intermediate products must also be developed. For farms to produce enough cuphea to meet detergent manufacturers' demands for lauric acid, farmers would need to plant several million acres. Since it is unfeasible to go from research plots today to millions of acres in the next season, farmers must become interested in growing new crops, and there has to be a guaranteed economic advantage in doing so. One way this is accomplished is with the use of high end products that do not require large initial plantings. The cuphea crop of the future will have a FA profile similar to those of coconut and palm kernel oils (Table 1).

The most promising intermediate products for the cuphea crop are estolides, which would be used as a lubricant. Estolides are formed when a carbo-cation undergoes nucleophilic addition, with or without carbo-cation migration along the length of the chain. The carboxylic acid functionality of one FA links to the site of unsaturation of another FA to form oligomeric esters (Fig. 1). The estolide number (EN) is defined as the average number of FA added to the base FA (Fig. 1, where EN = n + 1).

Saturated/capped estolides (i.e., estolides to which a saturated FA has been added that terminates the oligomerization process) have been developed by Cermak and Isbell (4–6). These have physical properties that could help eliminate common problems associated with the use of vegetable oils as functional fluids. Vegetable oils as functional fluids have a lower resistance to

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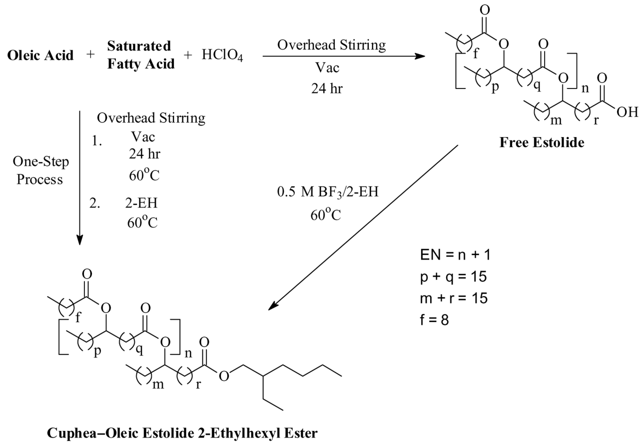

FIG. 1. Estolide synthesis. EN, estolide number; 2-EH, 2-ethylhexyl alcohol.

thermal oxidative stability than the petroleum products available (7), and they have poor low-temperature performance (8,9). By introducing additive packages, these properties can sometimes be improved, but usually by sacrificing biodegradability, toxicity, and cost-effectiveness. Cermak and Isbell (10) demonstrated that, by varying the capping material on the estolide, the crystal lattice structure of the material can be disrupted as it approaches its pour point, leading to estolides with excellent low-temperature properties, pour points of −36°C, and cloud points of −41°C without an additive package.

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

EXPERIMENTAL PROCEDURES

Materials. Cuphea seeds were harvested from USDA plots in Morris, Minnesota. Oleic acid (90%) was purchased from Aldrich Chemical Co. (Milwaukee, WI). Ethyl acetate and hexanes (for extractions), acetone (for HPLC), 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, acetic acid (both for HPLC), and sodium hydrogenphosphate were obtained from EM Science (Gibbstown, NJ). Ethanol was purchased from AAPER Alcohol and Chemical Company (Shelbyville, KY). FAME standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL). Solvents for chromatography and extraction were HPLC grade or the equivalent, and were used without further purification. Petroleum oil (Mobil® 10W-30) and synthetic oil (Castrol Synthetic® 10W-30) were obtained from the Wal-Mart Department Store (Peoria, IL). Soy-based oil (Biosoy®) was obtained as a free sample from the University of Northern Iowa (Cedar Falls, IA). Hydraulic fluid (Traveler Universal Hydraulic Fluid®) was obtained from the Tractor Supply Company (Peoria, IL).

GC. GC was performed with a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA) equipped with an FID and an autosampler/injector. Analyses were conducted on a 30 m × 0.25 mm i.d. SP-2380 column (Supelco, Bellefonte, PA). Saturated C_8–C_{30} FAME were used as standards to calculate ECL values, which were used to make FA and by-product assignments.

Parameters for SP-2380 analysis were as follows: column flow of 3.3 mL/min with helium head pressure of 15 psi; split ratio of 22:1; 50°C hold for 1 min, then programmed ramp to 165°C at 15°C/min, 165 to 185°C at 7°C/min, 185 to 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 decanoate, 6.14 min (10.00); methyl laurate, 7.46 min (12.00); methyl myristate, 8.63 min (14.00); methyl palmitate, 9.74 min (16.00); methyl stearate, 10.95 min (18.00); methyl oleate, 11.16 min (18.34); and methyl hydroxy stearate, 15.56 min (27.02).

GC–MS. GC–MS analyses was performed on a Hewlett-Packard 5890A gas chromatograph with a 30 m × 0.20 mm i.d. SPB-1 column (Supelco) and a Hewlett-Packard 5970 mass selective detector. GC conditions were: helium head pressure of 15 psi at 170°C set for constant flow with varying pressure; split ratio of 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 were: mass range, 50 to 550 amu; electron multiplier, 200 V relative.

HPLC. RP-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, coupled to an Alltech ELSD 500 ELSD (Alltech Associates). A C-8 reversed-phase analysis was used to separate reaction mixtures with a Dynamax column (250 × 4.5 mm, 8 µm particle size; Rainin Instrument Co., Woburn, MA).

Two methods for reversed-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, FA, and hydroxy FA.

The parameters for method A were: flow rate of 1 mL/min; 0 to 4 min 80% acetonitrile/20 acetone; 6 to 10 min 100% acetone; 11 to 16 min 80% acetonitrile/20% acetone. The ELSD drift tube was set at 55°C with the nebulizer set at 20 psi N_2, providing a flow rate of 2.0 standard liters per minute (SLPM). Retention times for eluted peaks were: estolides, 9.8–13.0 min; methyl oleate, 6.3 min; oleic acid, 5.1 min; and hydroxy acids, 4.1 min.

The parameters for method B were: flow rate of 1 mL/min; 0 to 2 min 60% acetonitrile/40% acetone; 20 to 25 min 100%

acetone; 30 to 35 min 60% acetonitrile/40% acetone. The ELSD drift tube was set at 55°C with the nebulizer set at 20 psi N_2, providing a flow rate of 2.0 SLPM. Retention times for the eluted peaks were: estolides, 8.2–25.6 min; methyl oleate, 5.5 min; oleic acid, 4.8 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 × 4.6 mm, 8 µm; Rainin Instrument Co.). Components were eluted isocratically from the column with a 4:1 hexane/acetone mixture at a flow rate of 1 mL/min with the ELSD drift tube set at 45°C and the nebulizer set at 10 psi N_2, with a flow rate of 1.50 SLPM. Normal-phase HPLC was used to separate the esterification reaction mixtures. Retention times for the eluted peaks were: 2-ethylhexyl estolide ester, 2.6–2.8 min; and estolide, 3.5–3.7 min.

Gardner color. Gardner color was measured on a Lovibond 3-Field Comparator (Tintometer Ltd., Salisbury, England) using AOCS method Td 1a-64 (11). The notations + and – were used to designate samples that did not match one particular color.

Viscosity. Viscosity measurements were made by using calibrated Cannon-Fenske viscometer tubes purchased from the 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 the viscosity index were calculated using ASTM methods D 445-97 (12) and ASTM D2270-93 (13), respectively. All viscosity measurements were run in duplicate, and the average value was reported.

Pour point. Pour points were measured by ASTM method D97-96a (14) 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 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.

Cloud point. Cloud points were determined by ASTM method D2500-99 (15) 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 in 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, and –24 to –42°C were placed in baths of temperatures 0, –18, –33, and –51°C, respectively. All cloud points were run in duplicate, and average values were reported.

Acid value. The acid values were measured on a 751 GPD Titrino from Metrohm Ltd. (Herisau, Switzerland). Acid values were determined by AOCS Method Te 2a-64 (11), 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.

Iodine values (IV) and EN. IV were calculated from GC data using AOCS Method Cd 1c-85 (11). EN were determined by GC from the SP-2380 column analysis as described previously (12).

GC analysis of hydroxy FA. Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell (4).

Trimethylsilyl derivatization of hydroxy fatty esters. Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell (4).

Cuphea seed extraction and hydrolysis. Cuphea seeds were collected from a test plot in Morris, Minnesota. Seeds (10 g) were ground in a Black and Decker SmartGrind^{TM} coffee bean mill. The milled seeds were placed in a Soxhlet extractor with petroleum ether (750 mL) and heated on a steam bath for 48 h. The organic layer was dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield 2.3 g of a green/brown oil.

The crude cuphea seed oil (350 g, 559 mmol) was hydrolyzed by the addition of 2.0 M KOH/EtOH followed by heating to reflux temperature for 60 min. After cooling to room temperature, the reaction mixture was placed in a 6-L Erlenmeyer flask with 1 L of hexane and cooled in an ice bath. A 1-M HCl solution was slowly added to the cooled hydrolysis mixture with overhead stirring. The addition was continued 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 (NaH_2PO_4, 519 g in 4 L H_2O, 2 × 100 mL). The organic layer was removed, dried over sodium sulfate, and filtered. All reactions were concentrated *in vacuo*, then Kugelrohr-distilled at 160–190°C and 0.1–0.5 mm Hg to purify the FA (331.3 g). A small sample of the FA was then esterified to the corresponding methyl esters under the conditions described above to yield the FA profile shown in Table 1.

Free-acid estolide. Acid-catalyzed condensation reactions were conducted without solvent in a 500-mL, baffled, jacketed reactor with a three-necked reaction kettle cover that had been pretreated with an acidic wash. All reactions described were mixed with an overhead stir motor using a glass shaft and a Teflon blade. Reactions were performed under the general conditions described above while varying the equivalents of perchloric acid, as reported in Table 2. In most cases, oleic acid (100.0 g, 354.0 mmol) and cuphea FA (35.5 g, 177.0 mmol) were combined and heated to 60°C ± 0.1°C under house vacuum. Once the desired temperature was reached, perchloric acid was added, vacuum was restored, and the mixture was stirred for 24 h. Product distribution was monitored by HPLC,

TABLE 2
Acid-Catalyzed Condensation Reaction with Oleic and Cuphea FA with Varying Amounts of $HClO_4$[a]

Estolide	Equiv $HClO_4$	Estolides (%)[b]	GC EN[c]	Pour point (°C)	Cloud point (°C)	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)	Viscosity index	Gardner color
A	0.40	64	2.13	−3	15	356.9	33.0	132	14−
B	0.20	63	2.02	−6	0	283.4	29.9	143	13−
C	0.10	60	1.88	−27	−11	220.1	28.2	166	12
D	0.05	55	1.75	−27	−23	213.4	24.0	140	14+
E	0.01	31	1.47	−27	−30	123.4	16.7	146	18

[a] Reactions were run for 24 h with overhead stirring under vacuum in a 2:1 molar ratio of oleic acid/cuphea FA at 60°C, followed by distillation at 180–200°C.
[b] Yield based on the mass of pure estolides obtained *via* distillation.
[c] EN, estolide number.

GC, and/or GC–MS as described above. The completed reactions were quenched by the addition of KOH (22.3 mmol, 1.25 g, 1.2 equiv based on $HClO_4$) in 90% ethanol/water (10 mL) solution. The solution was allowed to cool with stirring for 30 min. The material was filtered through a Büchner 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 180–200°C at 0.1–0.5 mm Hg to remove any lactones, saturated FA, and unsaturated FA.

Estolide 2-ethylhexyl ester. The distilled, free-acid estolides were combined with a 0.5-M BF_3/2-ethylhexyl alcohol solution (3 × estolide wt, vol/wt) in a 500-mL round-bottomed flask. The reactions were conducted at 60°C with magnetic stirring and were monitored hourly by normal-phase HPLC as described above (see Table 3). Esterification reactions were run until >99% complete, then were transferred to a separatory funnel and washed with saturated NaCl (2 × 75 mL). The pH of the organic layer was adjusted to 5.3–6.0 with the aid of the pH 5 buffer (NaH_2PO_4, 519 g in 4 L H_2O, 2 × 50 mL). The oil was dried over sodium sulfate and filtered. All reactions were concentrated *in vacuo*, then Kugelrohr-distilled at 100–120°C and 0.1–0.5 mm Hg to remove any excess 2-ethylhexyl alcohol.

Estolide 2-ethylhexyl ester (one step). An acid-catalyzed condensation reaction was conducted without solvent in a 500-mL, baffled, jacketed reactor with a three-necked 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. Reactions were run for 24 h with overhead stirring under vacuum in a 2:1 molar ratio of oleic acid/cuphea FA at 60°C, followed by distillation at 180–200°C. Oleic acid (100.0 g, 354.0 mmol) and cuphea FA (35.5 g, 177.0 mmol) were combined and heated to 60°C under house vacuum. Once the desired temperature of 60°C ± 0.1°C was reached, perchloric acid (0.05 equiv, 26.5 mmol, 2.3 mL) was added, and the flask was placed under vacuum and stirred. 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 an additional 2 h. The completed reactions were quenched by the addition of KOH (22.3 mmol, 1.25 g, 1.2 equiv based on $HClO_4$) in a 90% ethanol/water (10 mL) solution. The solution was allowed to cool with stirring for 30 min. The material was filtered through a Büchner 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 180–200°C and 0.1–0.5 mm Hg to remove any lactones, saturated FA, unsaturated FA, and any excess 2-ethylhexyl alcohol.

NMR. ^1H and ^{13}C NMR spectra were obtained on a Bruker ARX-400 (Karlsruhe, Germany) with a 5-mm dual proton/carbon probe (400 MHz ^1H/100.61 MHz ^{13}C) using $CDCl_3$ as a solvent in all experiments. The assignment of protons was not to the whole number. The representative NMR sample contained a compound that had an average EN of 1.75 for the free-acid estolide (D) and 1.50 for the estolide ester (A-2EH), which made whole-number assignment impossible. The data reported for the number of protons in the NMR spectra reflect the actual numbers.

^1H and ^{13}C NMR of free-acid estolide D (Table 2). ^1H NMR: δ 5.38–5.33 (*m*, 1.0H, –C*H*=C*H*–), 4.87–4.83 (*m*, 1.7H, –C*H*–OC=O–CH_2–), 2.33 (*t*, *J* = 7.5 Hz, 2.4H, –CH_2–(C=O)–OH), 2.29–2.23 (*m*, 3.5H, –CH_2(C=O)–O–CH–), 2.00–1.20 (*m*, 77.1H), and 0.88–0.84 ppm (*m*, 8.7H, –CH_3). ^{13}C

TABLE 3
Esterification of Cuphea–Oleic Estolides with 2-Ethylhexyl Alcohol[a]

Estolide ester[b]	GC EN	GC IV	Capped (%)[c]	Gardner color	AV (mg/g)	Pour point (°C)	Cloud point (°C)	Viscosity @ 40°C (cSt)	Viscosity @100°C (cSt)	Viscosity index
A-2EH	1.50	6.1	62	18	1.60	−9	−7	89.8	14.3	165
B-2EH	1.46	11.3	60	18−	1.32	−12	−10	88.8	14.9	176
C-2EH	1.31	16.5	54	15−	0.87	−21	−20	55.3	10.4	181
D-2EH	1.26	16.2	48	14	0.99	−33	−34	65.3	11.7	177
E-2EH	1.00	25.0	33	17+	1.15	−42	−36	34.9	7.2	178

[a] Esterification reactions were run with magnetic stirring and 0.5 M BF_3 at 60°C. IV, iodine value; AV, acid value; for other abbreviation see Table 2.
[b] Estolide 2-ethylhexyl (EH) ester.
[c] Ratio of estolide capped with saturated FA determined by GC (SP-2380 column, 30 m × 0.25 mm i.d.; Supelco, Bellefonte, PA).

NMR: δ 179.7 (*s*, HO–*C*=O), 173.6 (*s*, –CH–O–(*C*=O)–CH$_2$–), 130.5 (*d*, –*C*H=*C*H–, very small signal, only a small amount of alkene present), 74.0 (*d*, –*C*H–O–C=O), 34.6 (*t*), 34.0 (*t*), 33.9 (*t*), 32.5 (*t*), 31.8 (*t*), 31.8 (*t*), 29.6 (*t*), 29.5 (*t*), 29.5 (*t*), 29.5 (*t*), 29.4 (*t*), 29.4 (*t*), 29.4 (*t*), 29.3 (*t*), 29.2 (*t*), 29.2 (*t*), 29.1 (*t*), 29.1 (*t*), 29.0 (*t*), 25.2 (*t*), 25.2 (*t*), 22.6 (*t*), and 14.0 ppm (*q,* –*C*H$_3$).

^{1}H and ^{13}C NMR of estolide 2-ethylhexyl ester A-2EH (Table 3). ^{1}H NMR: δ 5.38–5.34 (*m*, 0.4H, –C*H*=C*H*–), 4.88–4.82 (*m*, 1.71H, –C*H*–OC=O–), 3.97 (*d*, *J* = 5.7 Hz, 2.0 H, –OC*H*$_2$–CH(CH$_2$–)CH$_2$–), 2.31–2.24 (*m*, 5.6H, –C*H*$_2$–(C=O)–O–CH$_2$–, –C*H*$_2$(C=O)–O–CH–), 1.96–1.19 (*m*, 81.8H), and 0.90–0.83 ppm (*m*, 14.4H, –C*H*$_3$). ^{13}C NMR: δ 174.0 (*s*, *C*=O), 173.5 (*s*, *C*=O), 130.0 (*d*, –*C*H=*C*H–, very small signals, only a small amount of alkene present), 73.9 (*d*, –*C*H–O–C=O), 66.5 (*t*, –O–*C*H$_2$–CH–), 38.6 (*d*, –CH$_2$–*C*H–(CH$_2$–)–CH$_2$–), 34.6 (*t*), 34.0 (*t*), 31.8 (*t*), 31.8 (*t*), 30.3 (*t*), 29.5 (*t*), 29.4 (*t*), 29.2 (*t*), 29.2 (*t*), 29.1 (*t*), 28.8 (*t*), 25.2 (*t*), 25.0 (*t*), 23.7 (*t*), 22.9 (*t*), 22.6 (*t*), 14.0 (*q,* –*C*H$_3$), 13.9 (*q,* –*C*H$_3$), and 10.9 ppm (*q,* –*C*H$_3$).

RESULTS AND DISCUSSION

Table 2 outlines a series of reactions (see Fig. 1) that explore the formation of new, saturated/capped estolides as the amount of $HClO_4$ was varied and all other reaction parameters were held constant. Vacuum distillation removed any excess FA and by-products, providing neat estolide samples. The equivalents of $HClO_4$, percent yields, EN, 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 FA. Estolides are formed from the cationic homo-oligomerization of unsaturated FA resulting from the addition of an FA carboxyl adding across the olefin (16). This condensation can continue, resulting in oligomeric compounds in which the average extent of oligomerization is defined as the EN (EN = n + 1; Fig. 1) (17). When saturated FA are added to the reaction mixture, the oligomerization terminates upon addition of the saturated FA to the olefin since the saturate provides no additional reaction site to further the oligomerization. Because the estolide is stopped from further growth at this point, we term the estolide as being "capped" (4).

As the amount of $HClO_4$ was decreased from 0.4 to 0.01 equiv, there was a decrease in the percent yield (64 to 31%). As expected, when the amount of $HClO_4$ decreased, the EN decreased, a result that has been observed previously by Cermak and Isbell (4,6). Also, as the EN decreased, there was an improvement in the low-temperature properties as evidenced by a decrease in the pour and cloud points, i.e., the estolide became a better low-temperature lubricant. The remaining physical properties listed in Table 2 are similar to each other.

The alcohol portion of the ester functionality was shown by Isbell *et al.* (18) to play a significant role in pour-point reductions, since branched-chain alcohols dramatically lower the pour point. Thus, these estolides were converted to their corresponding 2-ethylhexyl estolide esters by the addition of 0.5 M 2-ethylhexanol/BF_3 at 60°C for 2–4 h for enhanced pour-point capability and because of economic considerations. Samples were vacuum-distilled to remove any excess 2-ethylhexanol, providing pure estolide 2-ethylhexyl ester samples. The lower EN values for the products of the esterification reaction, conversion to the corresponding 2-ethylhexyl ester, are reported in Table 3. We concluded that a small amount of the estolides undergoes transesterification, thus giving a lower EN value. Regarding the physical properties of the estolide 2-ethylhexyl esters (Table 3), there was the expected increase in Gardner color caused by the estolide undergoing an additional treatment with acid. As with the free-acid estolides in (Table 2), when EN decreased, the pour and cloud points also decreased. The best-case estolide, E-2EH, had excellent low-temperature properties (Table 3; pour point −42°C and cloud point −36°C). For the estolide synthesized with the lowest equivalent acid to be economically feasible, however, there must be an improvement in yield. Without an improved yield, the standard for comparison would be estolide D-2EH, which also had excellent low-temperature properties (Table 3; pour point −33°C and cloud point −34°C).

EN and IV play a critical role in the physical properties of the estolide. We previously reported (10) that saturated/capped estolides of oleic acid gave pour points superior to those of homo-oleic estolides when medium-chain saturated FA were used. By lowering the IV of the estolides, we observed dramatically improved oxidative stability (19). Estolides synthesized under lower perchloric acid equivalents gave lower EN values and decreased saturate capping (Table 3).

Saturated and hydroxy FA values were obtained from GC analysis of the estolides, which were saponified and esterified. The hydroxy FA were all combined but are known to give a Gaussian distribution of hydroxy positions derived from the estolide (4). The percentage of saturated/capped estolides was calculated from Equation 1:

$$[(\text{saturated FA})/(100 - \text{hydroxy FA})]\cdot 100 = \%\ \text{saturated capped} \qquad [1]$$

As a result, the IV were higher. At the lowest perchloric acid equivalent (0.01 mol equiv), cuphea provided an estolide of EN = 1.0 when converted to its 2-ethylhexyl ester. This material had a good pour point (−42°C) and excellent rotating bomb test times with small amounts of antioxidant (<2%) added.

The results given below demonstrate the advantages of using a one-pot process (Fig. 1) to synthesize cuphea–oleic estolide esters. The source of the saturated FA was limited, owing to a very small quantity of cuphea seed; most of the seed harvest was labeled as plantable seed for the next growing season. Previous data showed that other saturated/capped estolides had excellent low-temperature properties with low equivalents (0.05 equiv) of $HClO_4$ (4–6). This process converted the FA 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 FA, by-products, and 2-ethylhexyl alcohol, providing neat estolide ester samples. This *in situ* reaction produced a new cuphea–oleic estolide ester that had excellent properties (EN 1.32; IV 14.5; 67.7% capped; Gardner color 12). The low-temperature properties (pour point –42°C and cloud point –41°C) and viscosities compared favorably to commercially available lubricants (viscosity at 40°C, 73.6 cSt, and at 100°C, 12.5 cSt; viscosity index, 170). This estolide was about 68% capped with saturated FA, which made this material much more oxidatively stable than the simple oleic estolides (19), i.e., as the amount of unsaturation decreased, there was a dramatic improvement in oxidative stability.

The cuphea–oleic estolide ester J-2EH had physical properties that were superior to those previously described for coco–oleic estolide esters (Table 4; Ref. 6). As Cermak and Isbell (4) showed, the complex estolides that had the best low-temperature properties were capped with very short chain, saturated FA. Decanoic acid had the best cold-temperature properties, with a pour point of −39°C, followed by octanoic and lauric acids. Table 1 displays the FA profile of the cuphea and coconut FA. Previous data suggest that the cuphea–oleic estolide esters should have pour points around −39°C. However, cuphea contains a mixture of FA and, when used to cap an estolide, has an even greater effect on the cold-temperature properties owing to the increased disruption of the crystal lattice structure (4). Thus, the observed pour point decreased by 2°C, yielding the best low-temperature properties of an estolide to date.

The physical properties of various commercial materials and a coco–oleic estolide 2-ethylhexyl ester were compared with the best-performing cuphea–oleic estolide 2-ethylhexyl ester (Table 4). Estolide J-2EH was picked for comparison based on its estimated production cost. Both of the estolide esters were completely unformulated, unlike the commercial products, which contained up to 40% additives designed to improve cold-temperature properties. All the commercial products shown in Table 4 had cold-weather-functional pour points except the soy-based oil. Soy-based products have previously demonstrated pour points too high for cold-weather climates (8). All of the commercial products listed had higher cloud points than the cuphea–oleic estolide 2-ethylhexyl ester J-2EH. 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-performing cold-weather oil. Both of the estolide esters had physical properties that outperformed the materials currently in the marketplace, even though the estolides remained unformulated. The cuphea–oleic estolide ester had low-temperature properties that should provide a speciality niche for this potential lubricant.

The proton NMR for the free-acid estolides, specifically estolide ester D (Table 2), 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 α-methylene proton shift (2.33 ppm) adjacent to the acid and the α-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 α-ester/α-acid can be used as another means to determine the EN complementary to the GC method. The NMR indicates some presence of alkene in the estolide by the appearance of an alkene signal at 5.38–5.33 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 (acid) and 173.6 ppm (estolide ester). The other distinctive signal is the methine carbon at 74.0 ppm, which is common to estolides. These major peaks in the carbon NMR were also confirmed by a distortionless enhancement by polarization transfer (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 3, specifically, estolide ester A-2EH, gives some predictable signal changes compared with the proton NMR of the free-acid estolides. The α-carbonyl methylene protons have similar shifts, resulting in a multiplet from 2.31–2.24 ppm. As before, the alkene signal is noticeable at 5.38–5.34 ppm, confirming the IV determined by GC. The carbon NMR signals are indicative of the estolide 2-ethylhexyl ester and were confirmed by a DEPT experiment.

Estolides D and D-2EH (Tables 2 and 3) were saponified in 0.5 M KOH/MeOH, then esterified with 1 M H_2SO_4/MeOH to give the corresponding hydroxy and nonhydroxylated fatty esters. The isolated mixture of FA esters was then silylated and analyzed by GC–MS (20). The main mass spectral features were *m/z* 371 (M^+ – 15, 1.2%), 73 (TMS^+, 100%), and a Gaussian

TABLE 4
Comparison of Low-Temperature Properties and Viscosity Index of Cuphea–Oleic Estolide 2-EH Esters to Those of Commercial Lubricants

Lubricant	Pour point (°C)	Cloud point (°C)	Viscosity @ 40°C (cSt)	Viscosity index
Commercial petroleum oil[a]	–27	2	66.0	152
Commercial synthetic oil[a]	–21	–10	60.5	174
Commercial soy-based oil[a]	–18	1	49.6	220
Commercial hydraulic fluid[a]	–33	1	56.6	146
Coco-oleic 2-EH estolide ester[b]	–33	–33	92.8	170
J-2EH[b]	–42	–41	73.6	170

[a] Commercial, fully formulated material from local vendors.
[b] Unformulated (see text). For abbreviation see Table 3.

fragment representing cleavage at the C–C bond adjacent to the silyloxy positions (masses 173 to 315). The fragments and abundances were very similar to complex estolide data reported previously (4,6). 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 the complex estolide data reported previously (4,6). This method demonstrated that, during the estolide reaction, there is migration of the double bond.

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