Optimization of the Sulfuric Acid-Catalyzed Estolide Synthesis from Oleic Acid

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ABSTRACT: The production of estolide from oleic acid with sulfuric acid as a catalyst was optimized for minimal acid concentration and temperature. Commercial oleic acid forms estolide optimally when reacted at 55°C with 5% vol/vol concentrated sulfuric acid for 24 h under vacuum. The extent of oligomerization was 1.2 estolide units under these reaction conditions. Temperature plays a critical role in the rate of estolide formation as well as in the overall yield, with higher temperatures providing faster rates but lower yields. The ratio of sulfuric acid to oleic acid equivalents also plays a role, where higher acid concentrations gave faster rates and higher yields of estolide. Vacuum had a minor effect on oligomerization and estolide yield.

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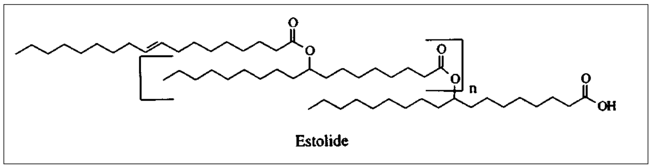
KEY WORDS: Estolide, oleic acid, oleic homopolymer, oligomerization, polyestolide, sulfuric acid.

The development of esters (1) and estolides (2) as biodegradable replacements for many lubricants has progressed rapidly. These types of materials have been shown to be good biodegradable lubricants. Recent work in our laboratory has provided a protocol for the synthesis of oleic estolides (3) (Scheme 1) with mineral acid catalysts (perchloric and sulfuric). The mineral acid-catalyzed process forms unique estolide oligomers (4) from commonly available monounsaturated fatty acids. In addition, the resulting estolides are completely biodegradable (5).

When perchloric acid is used as a catalyst, estolide yields are good (75%) even after short reaction times (2 h), and the extent of oligomerization is greater than two ester units (EN = 2.65). In contrast, a sulfuric acid-catalyzed reaction provided a 60% yield of estolide after 6 h (3). Unfortunately, perchloric acid is a highly corrosive acid and considerably more expensive than sulfuric acid. In light of these limitations, we set out to optimize the production of estolide from oleic acid with a minimal amount of sulfuric acid as catalyst.



SCHEME 1

EXPERIMENTAL PROCEDURES

Materials. Oleic acid (70.5% oleic acid) was provided by Calgene Chemical Co. (Chicago, IL). Oleic acid (90%) and polyphosphoric acid were purchased from Aldrich Chemical Co. (Milwaukee, WI). Concentrated sulfuric acid (98%) and potassium hydroxide were obtained from J.T. Baker Chemical Co. (Phillipsburg, NJ). Methanol, hexane, and acetone (for high-pressure liquid chromatography, HPLC) were obtained from Fisher Scientific Co. (Fair Lawn, NJ). Fatty acid methyl esters (FAME) were obtained from Alltech Associates, Inc. (Deerfield, IL).

Instrumentation. HPLC analyses were performed on a Spectra-Physics 8800 ternary pump (San Jose, CA) with a Spectra System AS3000 auto sampler/injector from Thermo Separation Products (Fremont, CA), coupled to an evaporative light-scattering detector (ELSD III) from Varex (Burtonsville, MD). A Dynamax (250 × 4.6 mm, 60Å, 8 µm) silica column, purchased from Rainin Instrument Co. (Woburn, MA), was used to separate the reaction mixtures. Components were eluted from the column with a 70:30 hexane/acetone mixture at a flow rate of 1 mL/min. The ELSD drift tube was set at 35°C, with the nebulizer set at 10 psi N_2, which provided a flow rate of 1.5 standard liters per minute. Retention times for eluted peaks were: estolide 2.7–3.4 min, and monomer 3.7 min. Data were collected and integrated by a Hewlett-Packard 3365 chem station (Palo Alto, CA). Standard curves for each analyte were derived to correct for the nonlinear response of the ELSD.

Gas chromatography (GC). GC was performed with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame-ionization detector and an auto sampler/injector. Analyses were conducted on two columns: an SP 2380, 30 m

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× 0.25 mm i.d. (Supelco, Bellefonte, PA) and a DB-5, 30 m × 0.25 mm i.d. (J&W Scientific, Folsom, CA). Saturated C_8–C_{30} fatty acid methyl esters (FAME) provided standards for calculating equivalent chainlength (ECL) values.

SP 2380 analysis conditions for standard FAME analysis were: column flow 1.2 mL/min, with a helium head pressure of 15 psi; split ratio 40:1; programmed ramp 150 to 175°C at 2°C/min, 175 to 220°C at 5°C/min, and 220 to 265°C at 20°C/min; injector and detector temperatures set at 250°C. ECL values: *cis* monoene +0.35, *trans* monoene +0.51, hydroxy +8.40, γ-lactone +9.30, and δ-lactone +9.70. Thus, a *cis* 18:1 FAME (methyl oleate) would have an ECL = 18.0 + 0.35 or 18.35.

DB-5 analysis conditions were: column flow 2.8 mL/min, with 25 psi helium head pressure; split ratio 40:1; programmed ramp 150 to 275°C at 5°C/min, hold 2 min at 250°C; injector and detector temperatures set at 250°C. ECL values: *cis* monoenes −0.24, *trans* monoenes −0.17, and hydroxy +1.99. Thus, a *cis* 18:1 FAME (methyl oleate) would have an ECL = 18.0 −0.24 or 17.76.

Methods. Optimization reactions were performed on 37.3 mmoles of commercial oleic acid in a round-bottom flask with the temperature maintained by a temperature controller at ±0.3°C of the set point. Sulfuric acid (% vol/vol as shown in Fig. 1) was added all at once, and mixing was maintained throughout the course of the reaction by magnetic stir bar. Samples were drawn at 5, 15, 30, 60 min and then every hour, diluted in hexane/acetone 50:50, and analyzed by HPLC under the conditions described above.

Large-scale reaction conditions. Oleic acid (250 mL) was placed either in a three-necked glass flask or a 316 stainless-steel (SS316) reactor. This system was then evacuated to 9 mm/Hg for several minutes to degas the oleic acid. The flask was charged with N_2, and then concentrated H_2SO_4 (12.5 mL, 5% vol/vol) was added to the reaction at room temperature with a noted increase in the temperature of the reaction mixture (the initial temperature of 24°C rose to 33°C). For the three-necked flask, mixing was maintained during the addition. In the bomb, mixing was started immediately after the addition of H_2SO_4. Vacuum was reestablished in the system at 9 mm/Hg, and the reaction mixture was warmed to 55°C with stirring set at 300 rpm. Temperature was maintained with a Digi-Sense temperature controller (Cole-Parmer, Niles, IL) for the three-necked flask system and with a robo-temp variac controller (Cole-Parmer) for the SS316 reactor. In the three-necked system, temperature fluctuated ±0.3°C. In the SS316 reactor, temperature ranged ±3°C. After 24 h the reaction was quenched. There was no noticeable corrosion of the SS316 reactor upon removal of the reaction mixture from the vessel.

The reaction mixture was placed in a separatory funnel and allowed to cool to room temperature. Dibasic phosphate (Na_2HPO_4, 0.5 M) was used to neutralize the acid in a ratio of 54 mL of 0.5 M Na_2HPO_4/1.0 mL of H_2SO_4. The resulting water layer had a pH = 5.1. The water layer was removed, and the reaction mixture was concentrated *in vacuo* and then with a vacuum pump at 0.1 torr at 100°C to remove residual water. Pure estolide (95%) was obtained by kugelrohr distillation of the monomer at 140 to 160°C at 0.1 torr pressure. This provided a 70% yield of estolide by mass.

Estolide hydrolysis for oligomerization (EN). Estolide (10 mg) was hydrolyzed at 100°C in a sealed vial with 0.5 M KOH/methanol (0.5 mL). After 1 h, 1.0 mL of a 1.0 M H_2SO_4/methanol solution was added to the vial. The vial was sealed and then heated to 100°C for 10 min. Methyl esters

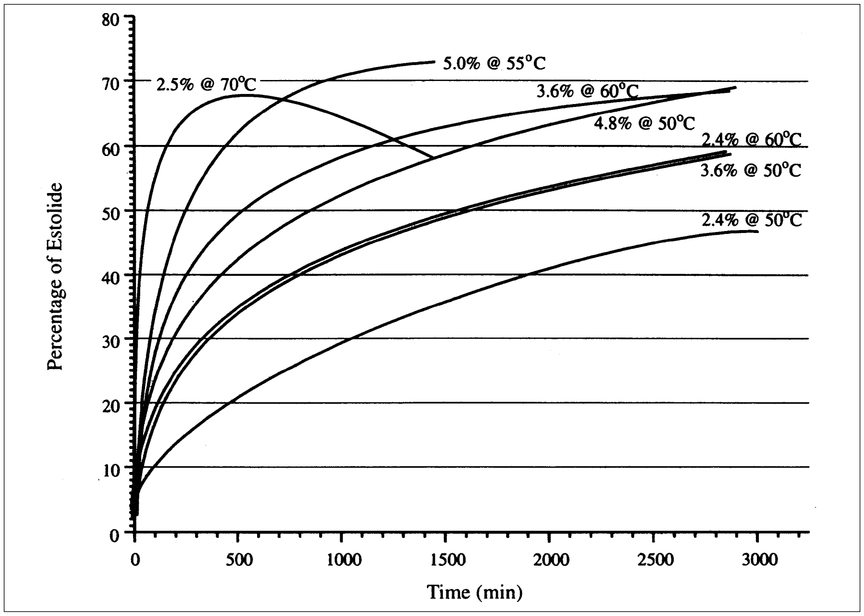

FIG. 1. Time-course plot of estolide formation with respect to sulfuric acid concentration and temperature.

were extracted into a 2-mL mixture of hexane/ethyl acetate (1:1) with a 2-mL water wash. The resulting organic layer was dried over Na_2SO_4 and injected into the GC under the conditions described above.

RESULTS AND DISCUSSION

A series of reactions were performed with a commercial grade of oleic acid (70.5% oleic) and concentrated sulfuric acid. Reactions were followed by normal-phase silica HPLC, coupled to an ELSD. Standard curves for monomer, oleic acid, and estolide were established to account for the nonlinear detector response.

Both acid concentration and temperature were optimized to find a maximum yield of estolide at low sulfuric acid concentrations (Fig. 1). We found that, as sulfuric acid concentration increased, the rate of estolide formation also increased. Figure 1 shows that the optimal reaction conditions occur with 5% catalyst at 55°C and a reaction time near 1500 min (yield 75%). Higher temperatures (>55°C) result in lower amounts of estolide due to the formation of lactone, even at reduced acid concentrations. In contrast, lower temperatures and catalyst concentrations result in slower rates of estolide formation, even with an equilibrium that favors estolide formation. In addition to the data shown in Figure 1, several reactions were run at temperatures >75°C with reduced catalyst concentrations and were found to contain a significant amount of an insoluble dark-colored material (sludge). Larger amounts of sludge form at temperatures >60°C, and sludge formation increases progressively at higher temperatures.

Extent of oligomerization. Several factors influence the extent of estolide formation as well as the overall yield of estolide. To determine the extent of oligomerization of a reaction sequence, the isolated estolides were hydrolyzed by alkali. The resultant esters were examined by GC (Fig. 2) to determine the extent of estolide formation by the ratio of hydroxylated to unhydroxylated fatty esters, and those results are reported in Table 1.

The composition of fatty acids, particularly the amount of oleic acid in the starting fatty acids, plays a significant role in the oligomerization. Higher percentages of oleic acid give larger EN values and yields (entry 2 vs. entry 8, Table 1). Furthermore, perchloric acid is a better catalyst than sulfuric (entry 4 vs. entry 5, Table 1), with 1.7 times more oligomerization and increased yield.

The role of water on the extent of oligomerization was explored because water could hydrolyze the estolide under the acidic reaction conditions. Polyphosphoric acid (0.1% vol/vol) was added to several reactions to see if this hygroscopic material might scavenge excess water present in the reaction. However, polyphosphoric acid had no effect on the oligomerization or the yield of estolide, as noted by entry 12 and entry 13 (Table 1). Similarly, vacuum would serve as a means to remove water from the reaction mixture. Vacuum improved the oligomerization slightly (entry 5 vs. entry 12, Table 1) from 1.02 to 1.25.

The most significant effect on the oligomerization is attributable to the acid concentration, with higher acid concentrations giving higher degrees of oligomerization (entries 6 through 9, Table 1). In addition, the reaction temperature had some effect on oligomerization, where higher temperature gave a slight increase in EN (entry 8, entry 10, entry 11 and entry 12, Table 1). In summation, the ability to dictate the oligomer distribution by the amount of catalyst, reaction tem-

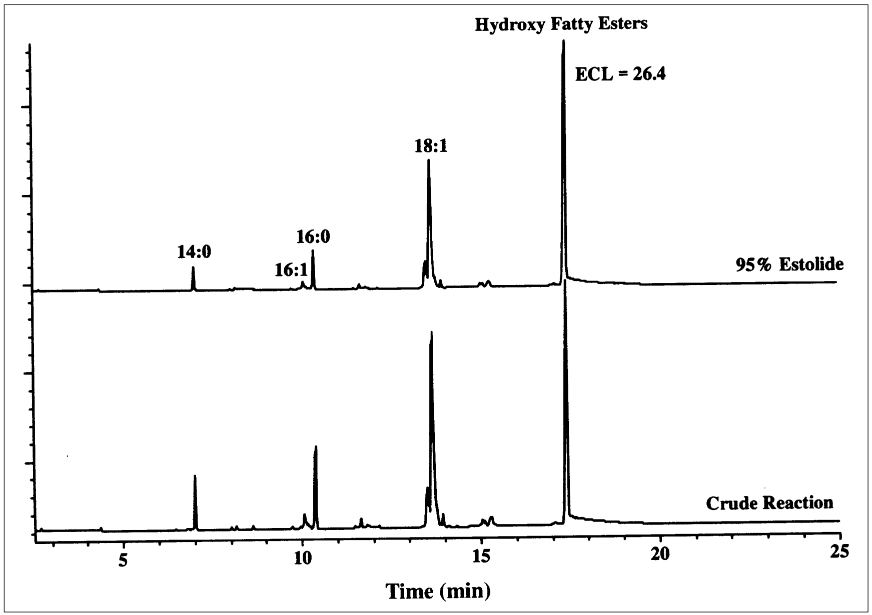

FIG. 2. Gas chromatographic traces of hydrolyzed estolides as their fatty methyl esters on an SP 2380 column; ECL, equivalent chainlength.

TABLE 1
Effect of Acid Concentration on Oligomerization

Entry	Oleic source[a]	Acid	Percentage catalyst[b]	Temperature (°C)	Vacuum	H_3PO_4[c]	EN[d]	Percentage estolide[e]
1	A	$HClO_4$	13.5	50	N	N	2.83	77
2	A	H_2SO_4	5.0	55	Y	N	2.02	80
3	A	H_2SO_4	5.0	55	N	Y	1.01	70
4	B	$HClO_4$	5.0	55	N	N	1.75	72
5	B	H_2SO_4	5.0	55	N	N	1.02	57
6	B	H_2SO_4	16.8	50	N	N	2.42	63
7	B	H_2SO_4	10.0	55	Y	N	1.94	76
8	B	H_2SO_4	5.0	55	Y	N	1.29	71
9	B	H_2SO_4	2.5	55	Y	N	1.33	55
10	B	H_2SO_4	5.0	65	Y	N	1.95	74
11	B	H_2SO_4	5.0	45	Y	N	1.73	47
12	B	H_2SO_4	5.0	35	Y	N	1.25	62
13	B	H_2SO_4	5.0	55	Y	Y	1.29	74

[a] A = 90% oleic acid purchased from Aldrich Chemical Co. (Milwaukee, WI); B = 70% oleic acid supplied by Calgene Chemical Co. (Chicago, IL).

[b] Percentage catalyst as 100 × vol/vol.

[c] Polyphosphoric acid at 0.1% (vol/vol) with respect to oleic acid.

[d] Estolide number calculated from gas chromatography (GC) percentage hydroxy by hydrolysis of the estolide and GC analysis of the resulting hydroxy methyl esters (FAME) with respect to saturated and unsaturated FAME.

[e] Determined by high-pressure liquid chromatography on a Dynamax silica column (Rainin Instrument Co., Woburn, MA) 250 × 4.6 mm i.d., eluted with hexane/acetone 70:30 at 1mL/min.

perature, and pressure is an important feature of this reaction with consequences on pour point and viscosity of the estolide product.

ACKNOWLEDGMENT

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