Acid-Catalyzed Condensation of Oleic Acid into Estolides and Polyestolides

Terry A. Isbell*, **Robert Kleiman** and **Beth A. Plattner**
USDA, ARS, NCAUR, New Crops Research, Peoria, Illinois 61604

Oleic acid, when treated with 1.0 equivalent of perchloric acid at 50°C, produced a 76% yield of polyestolide. The concentration of mineral acid greatly affected the rate of estolide formation, with increased rates under high acid concentrations. Over a range of temperatures from room temperature to 100°C, reaction rates increased at higher temperatures. However, high acid concentrations and temperatures produced undesirable side products, primarily lactones. Other acids catalyze the condensation of oleic acid to form estolide with the following relative rates: $HClO_4$ > H_2SO_4 > *p*-toluenesulfonic > $BF_3 \cdot Et_2O$ > montmorillonite K-10 > HCl > H_3PO_4, HNO_3. Addition of water impedes the formation of estolide.

KEY WORDS: **Estolide, mineral acids, montmorillonite, oleic acid, perchloric acid, polyestolide, stearolactone, sulfuric acid.**

The recently reported synthesis of estolide (1) from unsaturated fatty acids with montmorillonite clay catalysts at high temperature and pressure has provided a process for the development of unique industrial products. This estolide may see uses in lubricants, cosmetics and coatings. The clay-catalyzed process utilizes monoenoic fatty acids, obtainable from a wide variety of seed oils, in contrast to previous estolide syntheses (2) where a hydroxyl functionality, presumably from castor oil fatty acids, was used for their formation. By using unsaturated fatty acids as precursors to estolides, a new class of oxygenated fatty acids has been achieved.

The mechanism of estolide formation over montmorillonite clay appears to depend on the development of carbocation intermediate 2 at the double bond (Scheme 1). Subsequent capture of carbocation 2 with a second fatty acid molecule 1 will provide estolide 3. This mechanism is supported by the wide range of carbocation rearrangement products that appear in the monomer fraction (3) and the scrambling of the estolide linkage position (4).

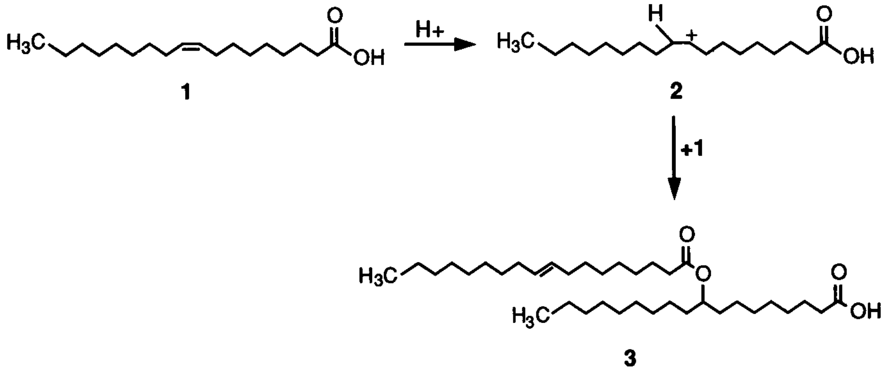
In light of these results, we expected that the conversion of unsaturated fatty acids into estolides could be catalyzed by mineral acids. Evidence to support this assertion could be found in work by Burton and Byrne (5) and Showell *et al.* (6) where oleic acid was treated with mineral acids to form stearolactones and sulfated oils. In addition to lactones, small amounts of estolide were observed. Burton's and Byrne's study (5) involved treatment of oleic acid with concentrated sulfuric acid to make sulfated oils with the formation of estolides and lactones as by-products of the reaction. Similarly, Showell *et al.* (6) treated oleic acid with 70% perchloric acid, and they postulated that estolides served as intermediates in the isomerization of oleic acid to γ-stearolactone.

We set out to optimize the yield of estolide by careful control of the acid concentration, temperature and reaction time in an effort to minimize the extent of double-bond migration, which leads to lactones.

EXPERIMENTAL PROCEDURES

Materials. Oleic acid (90%), perchloric acid (70%) and montmorillonite K-10 clay were purchased from Aldrich Chemical Co. (Milwaukee, WI). Concentrated sulfuric acid (98%) was obtained from J.T. Baker Chemical Co. (Phillipsburg, NJ). Concentrated nitric acid, monobasic phosphate and dibasic phosphate were obtained from EM Science (Gibbstown, NJ). *o*-Phosphoric acid was purchased from Fisher Scientific (Fair Lawn, NJ). *p*-Toluenesulfonic acid was purchased from Eastman Kodak (Rochester, NY). Boron trifluoride/methanol complex (14% wt/vol) and fatty acid methyl esters (FAMEs) standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL). Solvents for chromatography or extraction were high-pressure liquid chromatography (HPLC) or an equivalent grade and were used without further purification.

Instrumentation. Gas chromatography was performed on a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA) with a flame-ionization detector and an autosampler/injector. Analyses were conducted on two columns: CPSIL-84 25 m × 0.22 mm i.d. (Chrompack,



SCHEME 1

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*To whom correspondence should be addressed at USDA, ARS, NCAUR, New Crops Research, 1815 North University St., Peoria, IL 61604.

Bridgewater, NJ) and an SGE-BP1 25 m × 0.22 mm i.d. (Scientific Glass Engineering Pty. Ltd., Austin, TX). CPSIL-84 analysis conditions were: column flow, 0.95 mL/min; split ratio, 35:1; programmed ramp, 120 to 250°C at 3°C/min and 2 min hold at 250°C. SGE-BP1 analysis conditions were: column flow, 0.87 mL/min; split ratio, 37:1; programmed ramp, 170 to 250°C at 2°C/min with a hold of 5 min at 250°C. Injector and detector temperatures were set at 250°C for all analyses. Saturated C8-C30 FAMEs provided standards for calculating equivalent chainlength values (7).

HPLC analyses were performed on a Spectra-Physics 8100 extended LC system (San Jose, CA) with autosampler/injector coupled to a Varex evaporative light-scattering detector (Burtonsville, MD). A normal-phase silica column (250 mm × 4.6 mm, 60Å, 8 μm), purchased from Dynamax, a division of Rainin Instrument Company Inc. (Woburn, MA), was used to separate the estolide mixture.

Two methods for normal-phase analysis were used to separate the reaction mixtures. Method A (10-min run time) was used as a rapid technique for following the rate of estolide formation in reactions that did not produce lactones. Method B (40-min run time) provided a much more detailed separation of reaction mixtures that included lactones and hydroxy fatty acids.

Parameters for method A were: flow rate, 0.8 mL/min; isocratic solvent system $CH_2Cl_2/CH_3OH/CH_3CO_2H$ (99.0:1.0:0.15). Light-scattering detector conditions were: nitrogen flow, 45 L/min, 10 psi; and drift tube temperature, 35.5°C. Retention times for eluted peaks were: polyestolide, 3.4 min; pentaestolide, 3.6 min; tetraestolide, 4.1 min; triestolide, 4.3 min; diestolide, 4.7 min; monoestolide, 5.2 min; and monomer, 5.8 min.

Parameters for method B were: flow rate, 0.8 mL/min; isocratic solvent system hexane/isopropanol/acetic acid (975:25:0.2). Light-scattering detector conditions were: nitrogen flow, 47 L/min, 15 psi; and drift tube temperature, 50.0°C. Retention times for eluted peaks were: polyestolide, 4.3 min; pentaestolide, 4.5 min; tetraestolide, 4.7 min; triestolide, 5.0 min; diestolide, 5.4 min; monoestolide, 5.9 min; monomer, 6.4 min; 12-hydroxystearic acid, 12.9 min; γ-stearolactone, 16.8 min; and δ-stearolactone, 20.8 min. Other hydroxy acids elute from 10 min to 35 min, depending on the location of the hydroxy position. For example, 4-hydroxystearic acid elutes at 33.3 min and 5-hydroxystearic acid at 35.6 min.

General procedures. Estolide methyl esters were made by dissolving ~100 mg of the free acid estolides in 2 mL tetrahydrofuran (THF) and 2 mL $BF_3 \cdot MeOH$ (14% wt/vol) and held at reflux over a steam bath for 15 min. The crude estolide methyl esters were poured into 10 mL hexane and washed with 3 × 10 mL portions of H_2O, dried over anhydrous Na_2SO_4, gravity-filtered through a Whatman #1 fluted filter paper (Whatman, Maidstone, England) and concentrated *in vacuo.*

Estolide reactions were carried out in constant-temperature reactors of 0.1, 0.5 or 1.0 L, connected to a thermostated circulating bath, which was maintained at ±0.05°C of the desired set point. The reactions were performed by first equilibrating oleic acid at the desired temperature for several minutes, followed by the addition of the appropriate acid. Acids were added and reactions were mixed continuously by an overhead stirrer.

Sulfuric acid reaction. Oleic acid (100 g, 0.35 moles) was equilibrated at 50°C for 10 min, followed by addition of concentrated sulfuric acid (34.3 g, 0.35 moles). The stirred reaction immediately turned black. After 6 h, the reaction was quenched by pouring it into a separatory funnel with 200 mL hexane. The hexane layer was washed twice with 100 mL portions of aqueous 1 M Na_2HPO_4. The second phosphate wash turned the black solution to yellow and formed an emulsion that was broken by THF (up to 100 mL). The estolide solution was then washed (2 × 100 mL) with an aqueous phosphate buffer (pH = 3.7, 129.7 g monobasic phosphate and 0.85 g dibasic phosphate in 1 L H_2O), dried over Na_2SO_4, filtered, concentrated and kugelrohr-distilled (120 to 160°C @ 0.5 torr) to yield 60 g of dark colored estolide.

Perchloric acid reaction. Oleic acid (100 g, 0.35 moles) was placed in a 0.5-L reactor and equilibrated at 50°C for 10 min. Seventy percent $HClO_4$ (50.8 g, 0.35 moles) was added all at once to the stirred oleic acid with an immediate formation of a brown mixture. Vigorous stirring was maintained throughout the course of the reaction to ensure adequate mixing of the two phases. After 2 h, the crude reaction was poured into a 1-L separatory funnel, and the perchloric acid layer was removed. Hexane (200 mL) was added to the separatory funnel, and the mixture was neutralized with 1 M Na_2HPO_4 (2 × 100 mL). THF was added at this point to dissipate the resulting emulsion. The organic layer turned from brown to pale yellow during the 1 M phosphate wash. The pH was then adjusted in the same manner as with the sulfuric acid preparation with a buffered phosphate solution (2 × 100 mL). The hexane layer was separated, dried over Na_2SO_4, filtered and concentrated to give a yellow oil. Kugelrohr distillation (120 to 160°C @ 0.5 torr) provided 69.9 g of yellow-colored estolide (Gardner = 7).

Rate study for the formation of estolide. All rate reactions were conducted as described in the sulfuric acid section with strict control over reaction conditions. Reactions were performed on a 50-g scale in the same 0.5-L reactor with a mechanical overhead stirrer and glass stirring blade. The stirrer settings were identical throughout all studies. Initial rates were determined by removing a small aliquot from the reaction mixture and diluting it immediately in hexane. The aliquots were removed at 1, 3, 5, 15, 30 and 60 min, then hourly. Subsequent analysis was performed on a normal phase HPLC column (by HPLC method A).

95% Concentrated acid, 5% H_2O rate reactions. Rate reactions with 5% H_2O were performed under identical reactor conditions to those rate reactions previously mentioned. Water, 5% by mass of the oleic acid, was either preequilibrated with the oleic acid in the reactor at 50°C or mixed with the mineral acid prior to addition into the reactor.

Estolide hydrolysis reaction "Reaction Equilibrium." Polyestolide (13.2 g, 7.75 mmoles) was equilibrated to 50°C with mechanical stirring. Perchloric acid (70%, 1.1 g, 7.75 mmoles) was added all at once to the stirred reaction, and stirring was maintained throughout the course of the reaction. Aliquots were removed from the reaction at the above-mentioned time intervals and analyzed by HPLC.

Hydrochloric and phosphoric acid reaction. Concentrated HCl (2.95 mL, 35.4 mmoles) was refluxed with oleic acid (10 g, 35.4 mmoles) at 100°C. The stirred reaction was fitted with a Dean-Stark trap to remove water from the reaction. Phosphoric acid (1.0 g) was stirred with oleic acid (10 g) under the same conditions as the HCl reaction.

Boron trifluoride etherate reaction. Oleic acid (20.0 g) was stirred with 2 mL of $BF_3 \cdot O(C_2H_5)_2$ at 50°C with magnetic stirring.

p-Toluenesulfonic acid reaction. *p*-Toluenesulfonic acid (14.0 g, 73.5 mmoles) was added to a magnetically stirred solution of oleic acid (20.0 g, 70.8 mmoles) maintained at 100°C in a heating mantle. After 24 h, the mixture was poured into a separatory funnel with hexane and washed with 2 × 50 mL of 1 M Na_2HPO_4 and with 2 × 50 mL of buffered phosphate solution, previously described. The organic layer was dried over Na_2SO_4, filtered and concentrated.

Clay-catalyzed reactions. Clay-catalyzed reactions were performed by stirring 5.0 g of oleic acid over 1 g of the appropriate clay under a N_2 atmosphere at 150°C. The reaction was quenched by diluting in hexane, followed by filtration to remove the clay catalyst. The filtered hexane was removed *in vacuo* to yield a dark-colored estolide.

Iron (III) clay was made by stirring 345 g clay in 690 mL of 0.25 M $Fe_2(SO_4)_3$ for 2.5 h. The Fe^{+3}-exchanged clay was filtered and washed with deionized water to remove residual iron sulfate solution. Wet Fe^{+3} clay was dried overnight at 70°C in a vacuum oven and stored in a desiccator until use.

RESULTS AND DISCUSSION

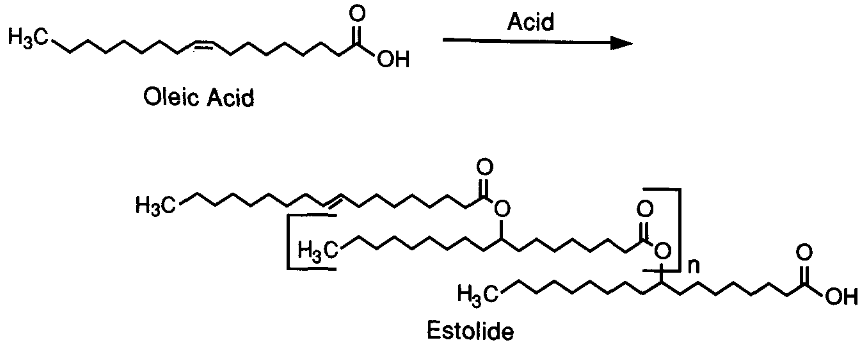
Sulfuric acid reaction. Oleic acid, when reacted with concentrated sulfuric acid at 50°C, provided a 65% yield of estolide **4a** (Scheme 2) after 6 h. A significant amount of polyestolide was formed in **4a** compared to **4d**, which was produced in a high-temperature reaction over montmorillonite clays (1), with monoestolide as the major product.

Examination of the time course plot of the sulfuric acid-catalyzed reaction (Fig. 1) indicates that rapid consumption of the oleic acid occurs in a relatively short time, with the reaction nearing completion at 360 min. Beyond this point, little conversion of oleic acid into estolide is observed. The development of monoestolide appears at the same rate as consumption of oleic acid and reaches a maximum at 250 min. Beyond this time, a small decrease in the monoestolide concentration occurs, and the formation of the higher estolide oligomers (di, tri...) is observed. Consumption of monoestolide is expected because the appearance of higher estolides must come at the expense of the monoestolide.

Diestolide can arise from two independent pathways, which are shown in Scheme 3. Path A requires that monoestolide **3** be protonated to give intermediate cation **5** which captures an oleic acid molecule **1** to give diestolide **6**. In a similar fashion, triestolide could be formed from **6**. Alternatively, **6** could be obtained through path B where oleic cation **2** is captured by monoestolide **3**. A range of other condensations are possible to explain the appearance of higher estolide oligomers either in a step-wise fashion, as in paths A and B, or by a mechanism, such as cation **5** with estolide **3** to yield a triestolide.

The failure of the reaction to reach completion (as shown by the leveling off of the rate of monomer consumption, Fig. 1) could arise from three possible conditions. An equilibrium could be established between estolide and monomer under the reaction conditions, such that hydrolysis of the estolide proceeds at the same rate as its formation. Secondly, as polyestolide concentration increases in the reaction mixture, the total unsaturation of the reaction mixture decreases. This decrease in unsaturation will statistically impede the reaction due to the unavailability of reactive sites. Lastly, as polyestolide increases, the stearic hindrance by the alkyl groups within the estolide will impede the approach of incoming nucleophiles to the cationic center, thus inhibiting the condensation reaction and promoting other cationic pathways, such as bond migration. The second condition was tested easily by examination of the monomer fraction for total unsaturation, and the first condition by studying the rate of decomposition of polyestolide under the reaction conditions. Discussion of these results is addressed below.

Perchloric acid reaction. Oleic acid, when treated with 1.0 equivalent of 70% perchloric acid in a vigorously stirred reaction at 50°C, provided a 76% isolated yield of polyestolide **4b** in 2 h. Significantly more polyestolide



4a Acid = H_2SO_4 (n = 0–3, 65%)
4b Acid = $HClO_4$ (n = 0–10, 76%)
4c Acid = *p*-Toluenesulfonic (n = 0–3, 45%)
4d Acid = Montmorillonite K-10 (n = 0–1, 10–30%)

SCHEME 2

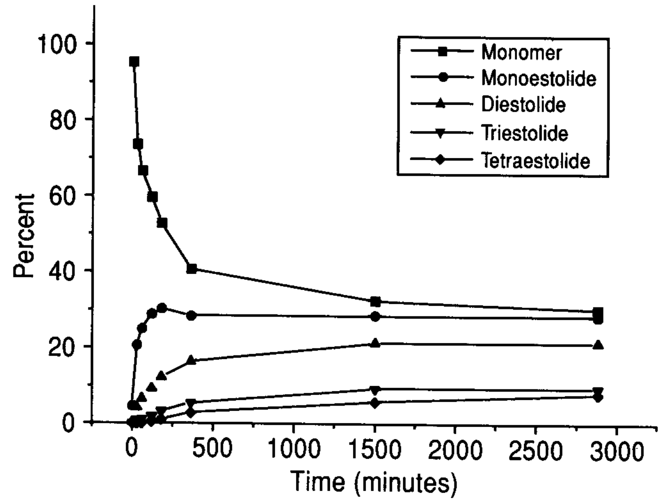


FIG. 1. Time-course plot of products from 1.0 equivalent H_2SO_4 reaction performed at 50°C. Reaction monitored by high-performance liquid chromatography method A.

formed under the perchloric acid conditions than was observed in the sulfuric acid reaction. Perchloric acid also provided a significantly faster rate of estolide formation under similar reaction conditions (Table 1). A time-course plot of the perchloric acid-catalyzed reaction appears in Figure 2. The reaction proceeds at a rapid rate with the entire reaction nearing completion at 120 min. The monoestolide reaches a maximum concentration at 30 min and declines steadily thereafter, in conjunction with the appearance of higher estolide oligomers. The diestolide will eventually surpass the concentration of monoestolide if extended reaction times are allowed. The same arguments for monoestolide consumption as previously stated in the case of the sulfuric acid-catalyzed reaction will also apply here.

The rate of the perchloric acid-catalyzed reaction is strongly influenced by the degree of mixing, due to the heterogeneous nature of the reaction, in contrast to the sulfuric acid reaction, which forms a stable emulsion. Thus, a vigorously mixed reaction provided the most consistent rates by ensuring thorough mixing of the two phases. The observation for the effect of stirring on reaction rate is in accord with Showell's *et al.* (6) observations on the rate of γ-stearolactone formation in the isomerization of oleic acid with perchloric acid.

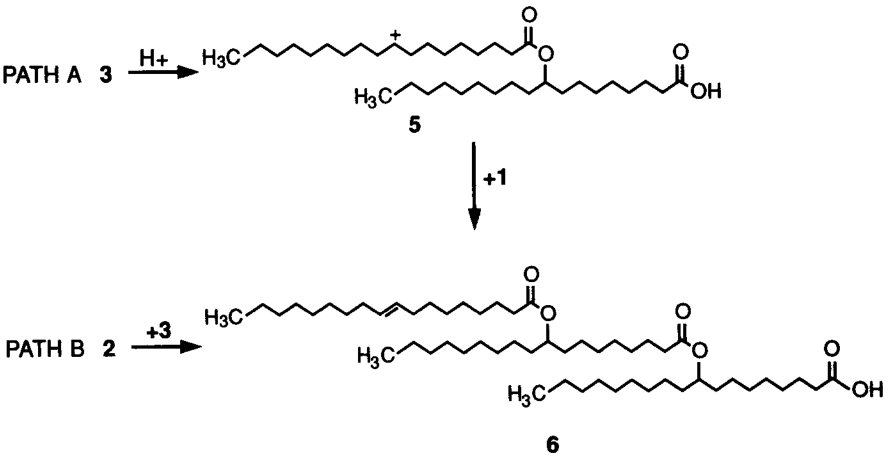
Effect of acid concentration on reaction rate. A series of reactions was performed to monitor the rate of estolide formation with respect to the concentration of perchloric and sulfuric acid (Table 1). Perchloric acid provided faster rates ($\sim$5.8 times faster) for estolide formation than sulfuric acid under similar reaction conditions (Entry B and F, Table 1). In addition, estolides produced by perchloric acid were light yellow in color, compared to a black material from the sulfuric acid reaction.

Because the rate of reaction is dependent on acid concentration, a mechanism that entails the formation of a distinct carbocation intermediate is likely. In addition, the dependence of rate on acid concentration indicates a general acid-catalyzed process (8), which is similar to that reported in the literature for the addition of carboxylic groups to alkenes (9).

The unexpected rate difference between sulfuric and perchloric acids probably arises from the formation of an intermediate during the sulfuric acid reaction. A plausible explanation, based on sulfonation literature (5), indicates that the addition of sulfuric acid to unsaturated fatty acids will produce sulfated oils. The sulfated oil is stable at low temperatures ($\leq$20°C) in the presence of acid, but at elevated temperatures (50°C) the sulfate ester quickly decomposes, and estolides and lactones are observed (5).

The formation of a sulfated intermediate would impede the rate of formation of estolide by requiring a second hydrolysis step of the sulfate to produce the carbocation. The carbocation will ultimately be captured by a second fatty acid to give estolide.

Effect of H_2O on estolide formation. Differences in the rate of estolide formation and degree of color for the sulfuric acid reaction, compared to the perchloric acid reaction, might be due to the presence of water in the reaction mixture. Perchloric acid is a 70% solution of perchloric acid in water, whereas concentrated sulfuric acid is 98% sulfuric. To examine the effects of water on the rate of estolide formation, sulfuric acid was diluted to a 70% solution. The acid solution was reacted in the



SCHEME 3

TABLE 1

Relative Rate of Estolide Formation with Respect to Acid Concentration[a]

Acid	Entry	Temperature (°C)	$\%H_2O^b$ Oleic acid	$\%H_2O^c$ Acid	Concentration[d]	Relative rate
H_2SO_4 (98%)	A	50	0	0	0.5	0.14
	B	50	0	0	1.0	1.00
	C	50	0	0	2.0	2.88
	D	50	5	0	1.0	0.04
$HClO_4$ (70%)	E	50	0	0	0.5	1.30
	F	50	0	0	1.0	5.78
	G	50	0	0	2.0	15.79
	H	75	0	0	0.1	1.65
	I	20	0	0	1.0	0.20
	J	50	5	0	1.0	0.03
	K	50	0	5	1.0	0.003

[a] All reactions were performed with mechanical stirring.

[b] Denotes the $\%H_2O$ by mass with respect to the mass of oleic acid (premixed with the oleic acid prior to addition of mineral acid).

[c] Denotes the $\%H_2O$ by mass with respect to the mass of oleic acid (premixed in the mineral acid).

[d] Concentration denotes the number of equivalents of acid used with respect to the oleic acid concentration.

same fashion as the 1.0 equivalent perchloric acid reaction, by maintaining the correct H^+ concentration. The diluted sulfuric reaction developed two distinct phases and no estolide formed even after 24 h.

To further examine the effects of water, small amounts of water were premixed with the oleic acid or the mineral acid prior to the mixing of the reactants. When oleic acid was emulsified with 5% water by mass, prior to the addition of 1.0 equivalent of perchloric acid, the reaction provided estolide at a rate ~200 times slower than the $HClO_4$ reaction without additional water (Entry J, Table 1). Sulfuric acid, when reacted with oleic acid emulsified with 5% H_2O, also provided estolide at nearly the same rate as the $HClO_4$/5% H_2O reaction (Entry D, Table 1). When 5% water with respect to oleic acid was premixed with $HClO_4$ prior to reaction, a further 10-fold decrease in the rate of estolide formation was found (Entry K, Table 1). At these slow rates, small variations in stirring within a given reaction provided ~20% fluctuation in the rate.

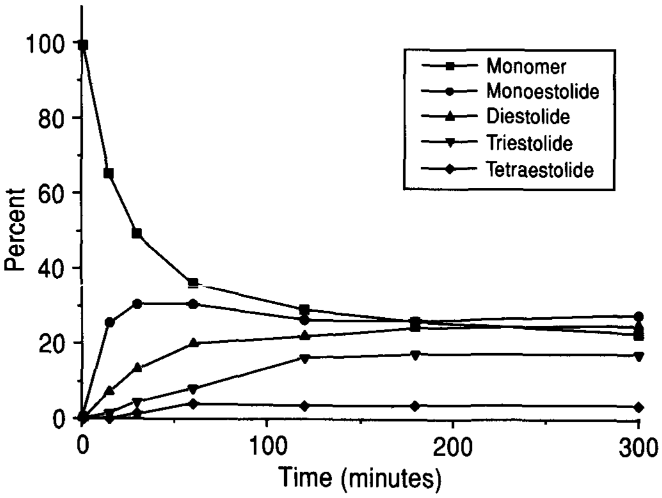


FIG. 2. Time-course plot of products from 1.0 equivalent $HClO_4$ reaction performed at 50°C. Reaction monitored by high-performance liquid chromatography method A.

The values in Table 1 (Entries D, J and K) represent the most consistent data set obtained under these conditions.

Acid decomposition of estolide "Reaction Equilibrium". Isolated polyestolide **4b** was subjected to the 1.0 equivalent perchloric acid repetition conditions (50°C with mechanical stirring) to test for decomposition of estolide into hydroxy fatty acids or monomer. After 24 h, 10% conversion of estolide into monomer had occurred, and after 71 h, 27% monomer was observed. The slow rate of conversion of estolide to monomer under the reaction conditions indicates that the rate of the reverse reaction (estolide to monomer) under the time frame of the forward reaction (2–6 h) is negligible. Thus, the establishment of an equilibrium is not the limiting factor for the failure of the forward reaction to reach completion.

Composition of residual monomer. Perchloric acid monomer was analyzed (3), and a summary of these results is shown in Table 2. The main component of the monomer fraction is the original 18:1 fraction, which has been isomerized both positionally and geometrically as previously reported (3) for a similar process. Other main components include hydroxy fatty acids and γ and δ-stearolactones, with the δ-lactone as the major isomer.

TABLE 2

Characterization of Monomer Fraction[a]

Assignment	Oleic[b] acid	Monomer[b]
C16:0	0.78	2.61
C17:0	0.27	0.00
C18:0	3.88	0.00
C18:1	88.84	58.88
C18:2	5.60	0.00
C18:0 Hydroxy	0.00	21.88
γ-Stearolactone	0.00	2.09
δ-Stearolactone	0.00	3.71
C20:1	0.32	0.00
C20:2	0.31	0.00

[a] Gas chromatography analysis performed by the techniques outlined in Reference 3.

[b] Values reported as percentages.

The composition of the monomer fraction provided an insight into the slow rate of estolide formation beyond 80% conversion. Of the remaining monomer only 59% is monoenoic fatty acid (12% of the total reaction mixture, Table 2) that is capable of reacting by the path depicted in Scheme 1 to produce estolide. The lack of unsaturated fatty acid provides a statistical challenge for a second-order condensation reaction to proceed, thus, an obvious reduction in the rate of reaction would be observed, as is seen in Figures 1 and 2. Of course, the estolide contains one unsaturation on its backbone, which could undergo protonation and further condensation reactions to produce polyestolide. However, the stearic hindrance of the alkyl groups will hinder the approach of an incoming fatty acid, which is already at a reduced concentration (12%) in the reaction mixture. Furthermore, a reaction between two estolides, which are in high concentration (75%) in the reaction mixture, would be even more stearically hindered, due to additional alkyl groups located on the incoming acid functionality. These alkyl groups would have severe interactions with the alkyl groups present on the estolide bearing the cation. Consequently, the reaction rate tails off over time as the monoenoic fatty acid concentration wanes, and other possible condensation reactions become restricted due to stearic hindrance by the alkyl bulk of the estolide.

Effects of other acids on the formation of estolides. A small survey was conducted to identify those acids that may promote the formation of estolides. In addition to perchloric and sulfuric, three other mineral acids were examined (hydrochloric, phosphoric and nitric acid) but proved to be of little value for the production of estolides. Both hydrochloric and phosphoric acid reactions were run at 100°C and fitted with a Dean-Stark trap to remove excess water that is present in these concentrated acids. Hydrochloric acid provided only 0.5% yield of estolide after 24 h; phosphoric acid provided a 14% yield of estolide after seven days; and nitric acid failed to produce any estolide after 48 h at 50°C. The large quantity of water in these acids could be responsible for the lack of estolide formation, as was predicted by the reduced rates when water was added to the perchloric and sulfuric acid reactions.

Boron trifluoride etherate, a Lewis acid, provided a 71% yield of estolide after 7 d at 50°C. *p*-Toluenesulfonic acid gave a 45% yield of estolide after 24 h at 100°C but failed to produce any estolide at 50°C, where the *p*-toluenesulfonic acid appeared to be insoluble. The melting point of *p*-toluenesulfonic acid is 103–105°C. Consequently, the 100°C reaction temperature caused the acid to melt, providing an emulsion which allowed a greater contact of oleic acid with the catalyst.

The last catalyst examined was montmorillonite K-10 clay, which was used as a comparison to the high temperature batch process (1). Reaction conditions similar to those by Ballantine *et al.* (10–12) were employed with 20% clay by mass with oleic acid under nitrogen at 150°C. The reaction yielded 32.6% yield of estolide after 118 h. Similarly, an Fe^{+3} cation-exchanged montmorillonite clay under the same reaction conditions gave 41.4% yield of estolide after 118 h. These reactions produced mainly monoestolide with a small amount of diestolide. Polyestolide was not observed under these reaction conditions, probably due to the spacial restrictions of the interlamellar layer of the clay (13). The slow rate of estolide formation over montmorillonite clays is probably due to the small H^+ concentration within the clay (0.04–0.08 mmoles of H^+/g clay).

Effect of temperature on estolide formation. The rate of estolide formation is highly dependent on the temperature. At room temperature, perchloric acid (1.0 equivalent)-catalyzed estolide formation proceeds at a slow rate (Entry I, Table 1) with little formation of side products. However, at a higher temperature (75°C), even with reduced concentrations of perchloric acid (0.1 equivalent), the rate of estolide formation is accelerated (Entry H, Table 1), but side reactions begin to predominate, chiefly the formation of lactones as previously shown by Showell *et al.* (6).

Work-up. The work-up of the crude estolide reactions proved to be difficult, due to the formation of emulsions during the quenching of excess mineral acid. Initially, a system of diluting the crude reaction mixture in hexane (2 mL hexane/gram of reaction), followed by addition of a stoichiometric amount of solid $NaHCO_3$ (determined by KOH titration), was used to adjust the acid value of the reaction mixture to 90 mg KOH/g of reaction mixture. This technique allowed the mixture to be distilled, but usually provided a severe emulsion, which often could not be dissipated, accompanied by a violent evolution of gas during the bicarbonate addition. In addition, the estolide was often converted to its sodium salt, and filtration of the dried solution was difficult. To overcome these problems, a two-step buffer work-up was devised, where the excess acid was neutralized with aqueous 1 M dibasic phosphate solution, followed by a wash with a pH ∼ 4.0 buffer to minimize the salting of the estolide. An emulsion still formed in the 1 M dibasic phosphate wash but was eliminated by the addition of THF. Other solvents and co-solvents were tried, including ether, but failed to aid in ridding the emulsion. THF proved to be far superior, due to its hydrogen-bonding capabilities. Interestingly, during the basic 1 M phosphate wash, the color of the hexane layer changed from black to pale yellow. This color change was not observed in the $NaHCO_3$ work-up.

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