Methods for Increasing Estolide Yields in a Batch Reactor

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ABSTRACT: Estolides are formed when the carboxylic acid group of one fatty acid forms an ester link at the site of unsaturation of another fatty acid. These compounds have the potential to be used in a variety of applications, such as lubricants, greases, plastics, inks, cosmetics, and surfactants. By manipulating the reaction equilibrium, yields of 20% estolide in clay-catalyzed estolide reactions have been increased to 30%. Reactions conducted at 180°C, where water was vented out of the reactor at specific times, not only gave dimer-free estolides but also yields up to 30%. Steam has also been used instead of water with similar results. Estolides were quite stable at temperatures up to 250°C, even when they were exposed to air.
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KEY WORDS: Dimer acids, estolide, meadowfoam oil fatty acids, montmorillonite, oleic acid.

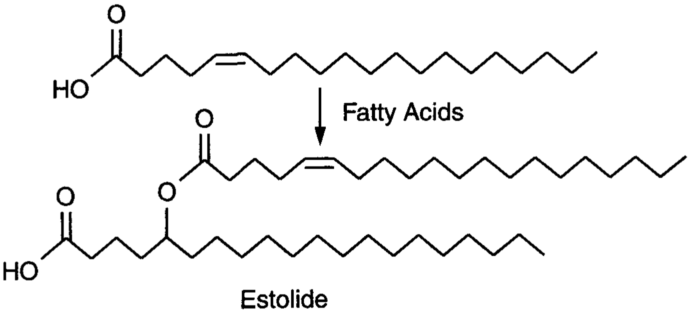

FIG. 1. Estolide formation from fatty acids.

Estolides prepared from monounsaturated fatty acids have potential to be used in lubricants, greases, cosmetics, surfactants, and polymers (1,2). Estolides can be manufactured with little or no modification to the equipment that is currently being used to produce dimer acids (3–5). We expect this esterification reaction to give products in high yields, because even saturated fatty acids can form ester links with the unsaturated chain of another fatty acid. Reactions with mineral acids and fatty acids have produced a mixture of monoestolides with 40% yields and polyestolides with 76% yields (6) (Fig. 1). However, until now, estolide yields in a high-pressure batch reactor, with clay catalyst, had not exceeded 20%. Therefore, studies were continued to increase the yield of estolides. Unlike reactions catalyzed with mineral acids, where the product is formed in the reaction mixture, estolides produced with clay catalysts form on the surface and in the interlamellar spaces of the clay. In the clay catalyst's reaction, only monoestolides form and lactone formation is not seen. The yield is also limited due to steric hindrance and the limited diffusion of estolides from the clay into the reaction mixture.

Estolides were first obtained by reacting meadowfoam oil fatty acids at 250°C with clay catalysts during the preparation of dimer acids (7). At these temperatures, 2% or less water led to the formation of dimer acids, whereas, if the water amount was increased to an optimum amount of 10%, estolide yields increased to 20% without a significant increase in dimer acid formation. If water was present in amounts over 15%, estolide yields started to decline, due to the higher rate of hydrolysis. The formation and decomposition of estolides with the changing amount of water show the important role of water in this equilibrium.

Meanwhile, another set of experiments, in a flow reactor packed with clay catalyst, where no water could be used, led to 27% estolide yields at 180°C, without the formation of dimer acids (Isbell, T., R. Kleiman and S. Erhan, manuscript in preparation). Previously, in the absence of water, in the batch reactor, estolide yields were only 18%, and in the presence of water, no estolide formation was detected at temperatures lower than 250°C (1). At 250°C, the major product was dimer acids. Evidently, in a clay-catalyzed batch reactor, at 180°C, water is necessary to initiate the reaction. However, this water later hydrolyzes the estolides faster than they can form. At 250°C, the high rate of estolide formation offsets the hydrolysis problem, and a steady state is eventually reached. To form estolides at 180°C and to benefit from the advantages of working at lower temperatures, experiments were conducted at different water concentrations. The water in the reaction mixture was later rapidly evaporated by venting the reactor. In this way, water could serve to activate the clay catalyst, and maybe add to the double bonds on the carbon chains of the fatty acids, but would be removed before any significant hydrolysis could start (8–10).

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Estolides, once they are formed, are stable at temperatures up to 250°C (11). This stability indicates that disappearance of estolides in the presence of water is due to hydrolysis, not thermal degradation. Therefore, studies were concentrated on preventing the hydrolysis of estolides and manipulating the esterification equilibrium toward higher yields.

EXPERIMENTAL PROCEDURES

Materials. Meadowfoam oil fatty acids were obtained from oil provided by Oregon Meadowfoam Growers Association (Salem, OR) and was split by high-pressure steam by Witco Corporation, Humko Chemical Division (Memphis, TN). Commercial oleic acid and Montmorillonite K-10 were purchased from Aldrich Chemical Company (Milwaukee, WI). Silica gel was purchased from Mallinckrodt Inc. (Paris, KY). The solvents used for chromatography or extractions were of high-performance liquid chromatography (HPLC) or equivalent grade. Boron trifluoride/methanol complex (14% wt/vol) was purchased from Alltech Associates, Inc. (Deerfield, IL).

Methods. All experiments were conducted first with oleic acid and then were repeated with meadowfoam fatty acids (Table 1). Both fatty acids gave similar estolide yields.

In experiments where water was vented out of the reactor, reactions were conducted in 1-L and 4-L high-pressure bombs with mechanical stirrers. These reactors had provisions for venting and ports for collecting samples. The reactors were loaded with fatty acids (100 parts), then clay (8 parts), and finally with distilled water (10 parts). The mixture was stirred thoroughly prior to sealing the reactor under an initial pressure of 60 psi nitrogen. This pressure prevents loss of water from the reaction mixture until the desired removal time. When the time of venting was reached, the vent valve was opened until the pressure dropped to atmospheric. The reactor was then flushed with nitrogen three times before it was again sealed under 60 psi nitrogen.

The reactions at atmospheric pressure were conducted in a glass reactor, fitted with a reactor top with three openings that allowed the use of a mechanical stirrer, a nitrogen inlet tube to keep the reaction under a blanket of nitrogen, and sampling of the reaction mixture and controlling the temperature. The temperature in the glass and steel reactors was maintained with a controller operating in a proportional integral derivative mode that prevented the reaction temperature from going above the set point.

In reactions where the reactor had to be cooled as fast as possible, water was passed through the internal cooling coils of the 4-L high-pressure reactor. Due to the absence of an internal cooling coil in the 1-L high-pressure reactor, the reactor was taken out of the heating jacket and cooled with wet towels under a stream of air. The glass reactor was cooled by taking it out ot the heating mantle. For all reactors, the temperature drop from 250 to 180°C took between five to seven minutes.

Experiments with steam were conducted in the glass reactor. Steam was introduced into the reaction mixture through the nitrogen inlet in thirty-second bursts at desired times.

Upon completion, the reaction mixture was cooled to room temperature, and the contents of the reactor were removed by washing with hexane. The clay was removed by filtration through a Buchner funnel, lined with Whatman #54 filter paper (Maidstone, England). The filtrate was dried over $MgSO_4$ and filtered through a Buchner funnel with a medium-porosity glass frit. Hexane was removed *in vacuo*. The bulk of the monomeric fatty acids (monomers) were removed by distillation at 180°C and 0.3 torr in an Aldrich Kugelrohr distillation apparatus.

Further separation of estolide and monomer was achieved by distillation on a wiped-film molecular distillation apparatus, UIC KD1 (Joliet, IL). Two successive distillations were necessary. The monomer was distilled at 175°C under 1×10^{-1} torr, and then the estolide was distilled at 225°C under 1×10^{-1} torr from higher-boiling fractions. The physical properties of estolides are given in Table 2.

Gas chromatography analyses were done in a Hewlett-Packard 5890 instrument (Palo Alto, CA) with a DB1, 15 M × 0.25 mm column from J&W Scientific Co. (Folsom, CA). The temperature program was from 200 to 390°C at 4°C/min with a 12.5-min hold at 390°C. Methyl esters were prepared with either BF_3 in methanol or diazomethane.

For thin-layer chromatography (TLC) analysis, silica gel-coated plates were used (Whatman, Clifton, NJ) with a solvent system of hexane/diethyl ether/acetic acid (70:29:1).

TABLE 1
Fatty Acid Composition of Meadowfoam Oil Fatty Acids and Oleic Acid

Fatty acids^{a}	Commercial oleic acid	Meadowfoam
14:0	3.2	
16:0	6.2	0.5
16:1^{9}	4.3	
18:0	2.1	
18:1^{9}	61.8	1.4
18:9^{9,12}	7.1	0.5
18:3^{9,12,15}	0.3	
20:0		0.5
20:1^{5}		64
22:1^{5}		3
22:1^{13}		10
22:2^{5,13}		19

[a] Numbers in superscript indicate the position of the double bonds on the carbon chain.

TABLE 2
Properties of Monoestolides Prepared from Meadowfoam and Oleic Acids

	Meadowfoam	Commercial oleic
Gardner color	10	5.5
Refractive index, N_{25}^{D}	1.4684	1.4711
Surface tension (mN/m)	34.5	35.4
Viscosity @ 38°C (cSt)	133	151
Acid value (mg KOH/g)	90.3	79.3
Iodine value (g I_2/100 g)	63.1	57.7
Unsaponifiable matter (%)	0.97	0.15
Density @ 25°C (g/mL)	0.93	0.915

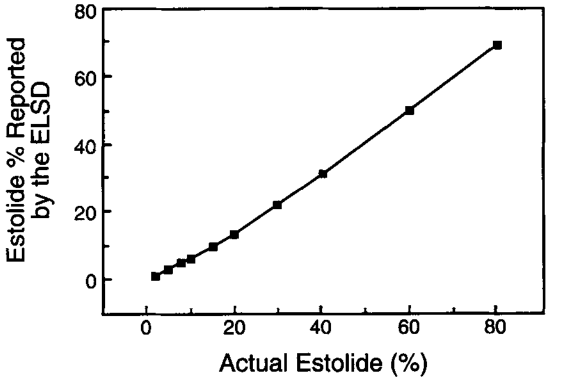

FIG. 2. Calibration curve for the evaporative light-scattering detector (ELSD).

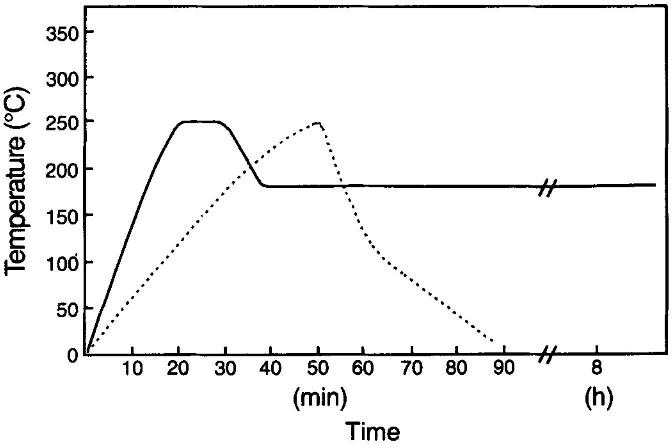

FIG. 3. The effect of venting water on estolide yield.

HPLC analyses were performed on a Spectra-Physics 8100 instrument (San Jose, CA) with a Whatman Partisil PXS 10/25 polar silica column, a column flow rate of 0.8 mL/min and a Varex ELSD II evaporative laser light-scattering detector (ELSD) (Rockville, MD). The detector nebulizing gas was nitrogen, and the drift tube was 75°C with an exhaust temperature of 54°C and had a nitrogen flow rate of 55 mL/min. The mobile phase was 50% dichloromethane, and 50% dichloromethane/methanol/acetic acid (98:2:0.25, vol/vol/vol). The yield of estolide reported in this paper is the concentration of estolide in the final reaction mixture determined by HPLC.

The ELSD response is not necessarily linear with concentration (12,13). Therefore, a calibration curve, seen in Figure 2, was used to equate HPLC results to actual estolide percentage. Pure estolide samples for the calibration curve were prepared by column chromatography performed on a 40 cm × 2.5 cm glass column, packed with silica gel. Monomers were eluted with 100% hexane, and estolides were eluted with a solvent mixture of 70% hexane, 29% ethyl acetate, and 1% acetic acid. The purity of the fractions were determined by TLC with silica gel-coated plates (Whatman) and a solvent system of hexane, diethyl ether, and acetic acid (70:29:1) (Fig. 2).

RESULTS AND DISCUSSION

No estolides were produced with 10% water and 8% montmorillonite clay at 180°C. However, when the same reactions were repeated with the water removed after an initiation time of 1 h, the estolide yield rose to 28%. (Fig. 3). No significant estolide formation was detected until after the removal of water. The experiments, where the initiation period was increased to 2 h or where the initial rate of temperature increase was slowed down from 1 to 2 h, did not change the estolide yields and did not give estolides before the water was removed.

The above yields had been obtained in a 1-L reactor. When the reaction was scaled up in a 4-L reactor, with the same reaction conditons, the estolide yields were identical to the 1-L reaction. The scale-up of estolide reactions did not present problems, and reaction times did not have to be increased to compensate for the increased mass.

When these reactions were repeated with the temperature increased to 250°C, held there for 1 h before the water was removed by venting the reactor, the reaction product was comprised of 5% estolide and 20% dimer acids. This was in agreement with the previous results obtained from experiments conducted at 250°C in the absence of water (1). However, as the rate of estolide formation is higher at 250°C, to take advantage of this effect, reaction mixtures were heated to 250°C and then cooled down to 180°C before the removal of water. Under these conditions, the estolide yields rose to 21% with only 2% dimer acids (Fig. 4). In these reactions, the time of venting did not make a change in the estolide yields. There is a significant drop in temperature as the rapid evaporation of water is taking place. In the reaction where the reactor was vented at 250°C and the venting was used to rapidly bring down the temperature, the dimer acid amount did not increase over 2%; however, the estolide yields did not surpass 21%.

In previous studies, a reaction without water had yielded 27% estolide for a few minutes before disappearing, giving a product of mainly dimer acids. At that time, these results could not be duplicated at 250°C. The same experiment was tried where a reaction mixture with no water was heated to 250°C, held for 10 min, then cooled down to 180°C and held

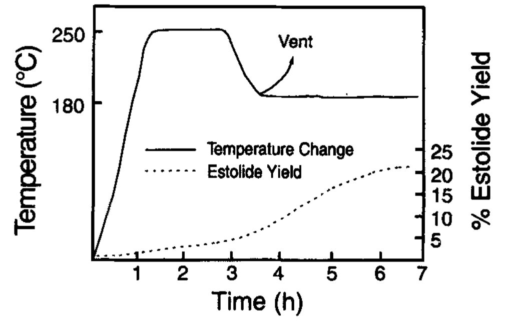

FIG. 4. The effect of temperature variance on estolide yield.

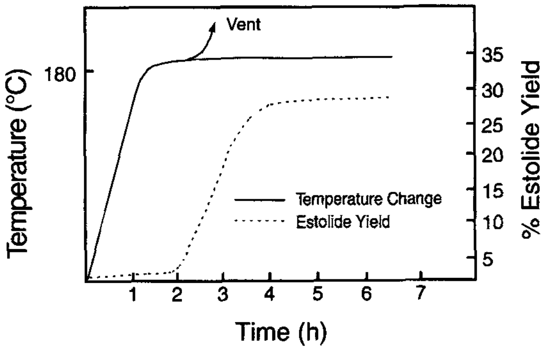

FIG. 5. Time vs. temperature curves in reactions at 250°C, containing no water.

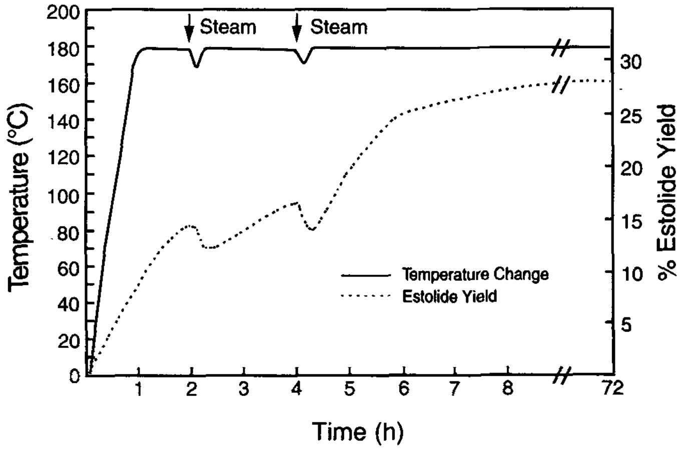

FIG. 6. The effect of water introduced in bursts of steam.

at this temperature for 7 h. Although there was no significant dimer acid, the estolide yields did not exceed 8%. A similar reaction, where the reactor was immediately cooled to 30°C from 250°C, also gave about 8% estolide (Fig. 5).

A glass reactor was used for additional experiments in which water was introduced into the reaction mixture as steam. In this way, water can be introduced at a high temperature and will only stay in the mixture a short time before it evaporates. With this method, it is also possible to introduce steam as many times as desired. The estolide yields of these reactions were 28%, similar to the experiments conducted in the high-pressure reactors, where water was vented. However, there was a difference in the rate of formation of estolides (Fig. 6). After each burst of steam, the estolide yield decreased for awhile and then increased. If these reactions were continued beyond 3 h, unlike the venting experiments where the yield of estolide did not change with prolonged reaction times, the yield of estolides kept increasing. At 6 h, the yields were 25%, and after three days, over 28%. However, due to such long reaction times being economically unattractive, the reactions were not continued past three days (Fig. 6).

In both reaction types where water is removed, the estolide yields were better than in reactions where water is either absent from the beginning or is kept in the reaction mixture throughout the reaction. It will not be necessary to make changes in existing reactor designs to take advantage of these methods to produce estolides.

Estolides are stable at high temperatures (11), and even in the presence of air. Estolide yields did not decrease when reactions were conducted without a nitrogen blanket. However, the color of the reaction mixture was darker. Purification and bleaching provided estolides of similar quality. There is no difference between estolides produced under nitrogen cover or exposed to air. Studies are continuing on the stability of estolides at high temperatures.

The stability of estolides under these conditions indicate that any accidental exposure of estolides to air at temperatures up to 250°C will not have a degrading effect on the product and that estolides will be suitable for use in formulations designed to function at high temperatures.

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