Estolides from Meadowfoam Oil Fatty Acids and Other Monounsaturated Fatty Acids

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The formation of estolides was detected during the studies on dimerization of meadowfoam oil fatty acids. By adjusting the reaction conditions, it was possible to produce monoestolides with little dimer or trimer formations. Estolides have potential use in lubricant, cosmetic and ink formulations and in plasticizers. This paper reports the conditions for production of estolides from mixed meadowfoam fatty acids, commercial oleic acid, high-oleic sunflower oil fatty acids, *cis*-5,*cis*-13-docosadienoic acid, petroselinic acid and linoleic acid.

KEY WORDS: *cis*-5, *cis*-13-docosadienoic acid, cosmetic, estolide, limnanthes, linoleic acid, lubricant, meadowfoam oil fatty acids, montmorillonite, oleic acid, petroselinic acid, plasticizer.

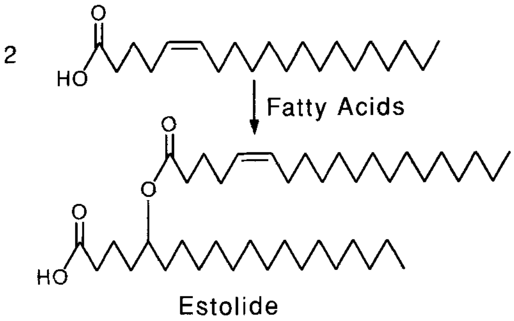

FIG. 1. Formation of estolides from meadowfoam oil fatty acids.

Estolides are defined as fatty acids esterified to the hydroxyl group of a hydroxy fatty acid. Both natural (1–3) and synthetic (4) estolides have been reported. This paper describes a new method in which estolides are prepared directly from monounsaturated fatty acids. The method does not require that a hydroxyl group be present at the onset of the reaction and uses conditions similar to those that produce dimer acids (5). Synthetic estolides previously reported were produced from ricinoleic acid, which already contains the hydroxy group and is derived from imported castor oil. The estolides produced from this reaction were of the multiester variety and were produced for the purpose of subsequent dehydration. This was easily accomplished because of the homoallyllic double bond present in ricinoleic acid. Unlike the polymeric estolides produced from castor fatty acids, this study presents data from reactions that produce monoestolides directly from monounsaturated fatty acids (Fig. 1). The hydroxy fatty acid produced is saturated and, therefore, has greater temperature stability. These estolides have potential for use in lubricants, plasticizers, cosmetics and printing inks. As an additional advantage, production of estolides in existing dimer acid-producing plants should require no major adjustments to equipment between the two processes, making this product more economical.

Estolides were produced from several monounsaturated fatty acids, providing an insight to the reaction mechanism for a variety of estolides. Four different fatty acids were tested in this study. Oleic acid was used because of its low cost, petroselinic acid for the unsaturation it has on the sixth carbon, which will give information on the hinderance effect of the carboxylic acid group, and linoleic acid and *cis*-5, *cis*-13-docosadienoic acid for having two double bonds on the same chain.

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 was purchased from Eastman Kodak Co. (Rochester, NY). Oleic acid was also obtained by the saponification of high-oleic acid sunflower oil and contained 82% oleic acid based on gas chromatographic (GC) analysis. Petroselinic acid (6c-18:1) was isolated from carrot seeds (6), and *cis*-5,*cis*-13-docosadienoic acid ($22{:}2^{5,13}$) was isolated from meadowfoam oil (7). Linoleic acid was purchased from Eastman Kodak Co. The fatty acid compositions of these starting materials are seen in Table 1. Montmorillonite K-10, Montmorillonite KSF, Fuller's Earth and Amberlyst, XN-1010 were purchased from Aldrich Chemical Company (Milwaukee, WI). Dowex 50W-X8 was purchased from J.T. Baker Chemical Company (Phillipsburg, NJ).

Methods. Estolides were produced in either 250-mL or 2-L high-pressure bombs, and placed in rockers or in stirred high-pressure 1-L or 4-L reactors for mixing. The stirred reactors had provisions for sampling during the reactions. The reactors were loaded with fatty acids, then clay and finally with distilled water. Percentages of each are given as parts of reactant per 100 parts of fatty acid. The mixtures were stirred thoroughly and the reactors were sealed under an initial nitrogen pressure of 60 psi. Reaction times are elapsed times after the reaction mixture reached the predetermined reaction temperature. The reaction pressure and the volume of reactants were adjusted so that 88% or more of the added water remained liquid during the reaction. These calculations, from PV = nRT, assumed the reaction pressure was due only to water vapor and nitrogen.

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 (fast, hardened) (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 products was removed by distillation at 180°C and 0.3 torr in an Aldrich Kugelrohr distillation apparatus. The amount of estolide (wt%) was determined by Fourier transform infrared (FTIR) analysis. FTIR analysis was

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TABLE 1

Fatty Acid Compositions

Fatty acids[a]	Commercial oleic acid	High-oleic acid sunflower oil	Meadowfoam oil	Commercial linoleic acid	Petroselinic acid[b]	22:2 Concentrate from meadowfoam oil
14:0	3.2					
16:0	6.2	3.6	0.5	3.2	6.0	
$16{:}1^{9}$	4.3					
18:0	2.1	4.7		0.9	1.3	0.9
$18{:}1^{6}$					92.0	
$18{:}1^{9}$	61.8	78.5	1.4	22.4	0.6	3.5
$18{:}2^{9,12}$	7.1	10.9	0.5	61.4	0.1	1.8
$18{:}3^{9,12,15}$	0.3			7.6		1.6
20:0			0.5			8.3
$20{:}1^{5}$			64.0			3.9
$22{:}1^{5}$			3.0			0.5
$22{:}1^{13}$			10.0			3.6
$22{:}2^{5,13}$			19.0			72.6

[a] Numbers in superscript indicate the position of the double bonds on the carbon chain.
[b] Obtained from carrot seeds.

done with a 0.0541-mm fixed-pathlength cell with CaF_2 windows in a Mattson CYNGUS instrument (Madison, WI) equipped with an EXPERT-IR analytical software program (8). A detailed paper on these analyses will be published later.

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.

For thin-layer chromatography analysis, silica gel-coated plates were used (Whatman, Clifton, NJ) with a solvent system of hexane/diethyl ether/acetic acid (70:29:1). High-performance liquid chromatography (HPLC) analyses were performed on a Spectra-Physics 8100 instrument (San Jose, CA) with a Whatman Partisil PXX 10/25 polar silica column (Clifton, NJ), a column flow rate of 0.8 mL/min and a Varex ELSD II evaporative laser light scattering detector (Rockville, MD). The detector nebulizing gas was nitrogen, which was heated to 74°C with an exhaust temperature of 54°C and had a flow rate of 55 mL/min. Mobile phase A was dichloromethane, B was dichloromethane/methanol/acetic acid (95:5:0.5, vol/vol/vol) and C was methanol. A pump table is given in Table 2.

GC 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. Injector and detector (flame-ionization detector) temperatures were at 350°C. Methyl esters were prepared with BF_3 in either methanol or diazomethane.

RESULTS AND DISCUSSION

Current processes for dimer acid production use water as a cocatalyst at levels of 2%. Besides preventing the decarboxylation of the fatty acids, water also helps to expand the layers of clay catalyst, increasing its surface area and its efficiency (9,10). We observed in similar reactions that estolide yields increased as the water content increased from 2 to 12%, with 8% clay (5). When this reaction was scaled up from 250 mL to 1 L, without changing the amount of reactants, estolide yields decreased dramatically. Reaction pressures indicated that, with the larger reactor, most of the water stayed in the gas phase during the reaction. When the larger reactor was filled with reactants in proportional amounts to the smaller reactor and the pressure was adjusted so that more than 88% of the added water stayed in the liquid phase, the yields obtained from the smaller reactor could be duplicated. Scaling up of these reactions in reactors from 0.5 L to 4 L (experiment 31) did not present any problems. Estolide yields were comparable when reactors were charged to 76% capacity and pressurized to keep more than 88% of the water liquid at reaction temperatures.

Experiments 1–6 (Table 3) show the effect of water content on estolide yields. There seems to be a need for an optimum amount of water. There is no advantage to water

TABLE 2

Solvent Gradient

Time (min)	Solvent A	Solvent B	Solvent C
0	50	50	0
5	0	50	50
10	0	50	50
15	50	50	0
20	50	50	0

TABLE 3

Effect of Water on Estolide Yield from Meadowfoam Fatty Acids[a]

Experiment number	Water (%)	Clay (%)	Estolide yield (%)
1	8	8	3.0
2	9	8	11.5
3	10	8	11.4
4	12	6	7.0
5	15	8	3.4
6	20	8	3.3

[a] All percentages are for product mixtures obtained from a 3-h reaction at 250°C and 60 psi initial N_2 pressure.

TABLE 4

The Effect of Changing Reaction Conditions on the Yields of Estolides from Meadowfoam Oil Fatty Acids

Experiment number[a]	Temperature (°C)	Time (h)	Pressure (psi)		Estolide yield
			Initial	Final	
7	180	4	20	172	—
8	180	6	20	171	1.9
9	180	6	60	237	1.9
10	200	6	15	245	2.0
11	225	13	80	476	6.3
12	250	3	30	597	10.0
13	250	3	60	640	11.3
14[b]	250	4	60	600	10.3
15[b]	250	5	60	635	9.3
16	250	10	30	620	10.4
17	300	4	100	1000	0.5

[a] All reaction mixtures had 10% water, 8% clay based on fatty acid content and 0.5L stainless-steel rocker reactor.

[b] 2-L stainless-steel rocker reactor.

content over 10% by weight of the fatty acid or below 9%. There is a significant decrease in the estolide yield and a substantial increase in dimer acid yields below 9% water content.

Results in Table 4 illustrate the effect of changing reaction temperature, time and pressure on the yield of estolide. Yield increased with increasing temperature up to 250°C. Temperatures over 250°C and pressures over 60 psi, as in experiment 17, gave lower yields. There was no advantage in reaction times over 3 h (Fig. 2). Therefore, the following studies were based upon estolide production conditions of 3 h, 250°C and 60 psi initial nitrogen pressure.

In experiments 14 and 15 (Table 4), a 2-L reactor was used and the reactor charge was proportionate to the 0.5-L reactor. Only the reaction times were increased to 4 and 5 h, respectively, to compensate for the time for heat transfer. The yields became lower as reaction time increased. The decrease in yield is proportionate to the increase in reaction time. It is evident that short reaction times are desirable, and have significant economic advantages as well.

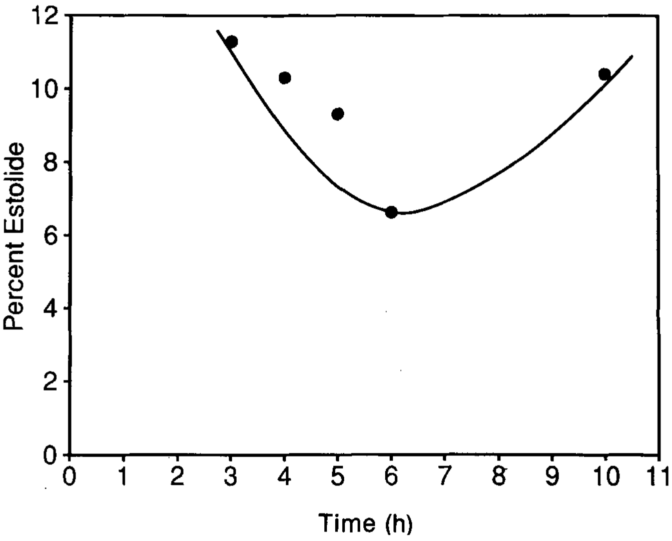

FIG. 2. Change of estolide yield with reaction times.

Commercial production of dimer acids utilize mineral clays as catalysts. These clays are less costly than other catalysts, such as ion exchange resins and zeolites, and are easy to separate from reaction mixtures. They are treated by suppliers to perform at maximum capacity as acid clay catalysts (11). Two types of montmorillonite clays were used in a 0.5-L rocker reactor. Montmorillonite K-10, although less acidic than montmorillonite KSF, had smaller particles and was a better catalyst. Smaller particles with larger surface areas have higher catalytic activity (Table 5). Although there can be severe filtration problems if particles are too small, montmorillonite K-10 did not present this problem. Two sulfonic acid ion exchange resins, comprising a copolymer of styrene and divinylbenzene under Dowex and Amberlyst trademarks, were also tested as catalysts. Amberlyst XN-1010 cannot

TABLE 5

Catalysts Used in Estolide Production from Meadowfoam Fatty Acids

Experiment number[a]	Catalysts	pH	Time (h)	Temperature (°C)	Pressure (psi)		Estolide yield (%)
					Initial	Final	
18	Montmorillonite K-10	3.51	3	250	60	620	11.3
19	Montmorillonite KSF	2.06	3	250	60	450	3.2
20	Dowex 50 × 8-100	2.52	3	250	60	650	8.4
21	Amberlyst XN-1010	1.88	6	100	60	86	1.5

[a] Reactions were made in a 0.5-L stainless-steel reactor mixed with a rocking motion.

TABLE 6

Estolide Yields of Various Fatty Acids

Experiment number	Fatty acid	Estolide yield %[a]
23	Commercial oleic	7.2
24	High-oleic sunflower oil oleic	14.3
25	Linoleic	8.3
26	Petroselinic	5.9
27	*cis*-5, *cis*-13-docosadienoic	11.4

[a] All percentages are for product mixtures obtained from a 3-h reaction at 250°C and 60 psi initial N_2 pressure.

TABLE 7

Estolide Yields of Various Fatty Acids

Experiment number	Reactor type	H_2O[a]	Clay[a]	Estolide yield %[b]
28	0.5 L rocked	10	8	7.2
29	1.0 L stirred	10	8	10.1
30	1.0 L stirred	12	8	8.3
31	4.0 L stirred	10	8	9.5

[a] Parts per 100 parts of oleic acid.
[b] Yield is the percent of estolides in the product mixture by weight from the reaction of oleic acid for 3 h at 250°C and 60 psi initial N_2 pressure.

be used above 120°C due to the nature of its polymer backbone. Although the reaction was conducted for an extended time at 100°C, yields of estolide were low. On the other hand, Dowex resin can be heated to 300°C, and at 250°C it functioned effectively as a catalyst to give comparable yields of estolides as obtained with montmorillonite K-10. The added cost of the ion exchange resin might be justified on the basis of the reversibility (12) of these resins, whereas clays cannot be readily regenerated. Also, reaction products are not adsorbed as extensively on these resins as they are on clays, and therefore provide higher yields.

The reactions conditions outlined above were used to produce estolides from other unsaturated fatty acids with clay catalysts. Reactions were run with the same stainless-steel reactor mixed with a rocking motion. These results can be seen in Table 6. In these reactions, oleic acid proved to be a highly suitable starting material for the production of estolides. The yield increased with an increasing amount of oleic acid in the feedstock, as seen in the high-oleic acid sunflower oil fatty acids. Linoleic acid, as expected, also gave comparable yields. Petroselinic acid, having an unsaturation at the sixth carbon, also gave good results, showing that double bonds close to carboxylic acid groups will not hinder the formation of estolides.

The next experiment was conducted with *cis*-5,*cis*-13-docosadienoic acid isolated from meadowfoam oil. The presence of two widely separated double bonds gave expectations of higher yields and the probable formation of diestolides. However, the resulting product consisted of only monoestolides, and yields were not much different from when mixed meadowfoam oil fatty acids were used (Table 4). This experiment supports the finding that the Δ5 double bond is not hindered by the carboxylic acid group to significantly affect the estolide yields.

The formation of estolides is an esterification reaction, which presumably at some point reaches an equilibrium. To test this postulation, a stirred reactor was used from which samples could be withdrawn and quickly analyzed by injecting a diluted aliquot into an HPLC (6). The estolide yields reached a maximum in 1 h in all the reactions. There was no significant increase in estolide yield with reaction times up to 6 h. Thus, it is advantageous to stop the reaction soon after estolide content reaches a maximum level. Stirred reactors also gave higher yields than reactors placed in rockers. Under the same conditions, a stirred reactor (experiment 29, Table 7) produced 30% more estolide than a rocked reactor (experiment 28).

Small amounts of estolides did form in reactions without water (Table 8). When the different fractions were collected during these reactions, it was shown that estolide yields increased for a short time and then decreased dramatically (Fig. 3). Reaction mixtures with water produced estolides whose amounts increased with time, to a certain point, and then remained constant. It is evident that with the reaction mixtures without water, the equilibrium between reactants and products is upset quickly, leading to a rapid disintegration of the estolide. Further research will continue to concentrate on efforts to shift the equilibrium in favor of the products. In estolide reactions, unlike dimerization reactions, saturated and unsaturated fatty acids both enter the estolide reaction through esterification of their carboxylic acid groups. Therefore, in theory, estolide yields of close to 100% can be achieved.

TABLE 8

Estolide Production at 250°C with No Water

Experiment number	Clay (parts)[a]	Time (h)	Pressure (psi) Initial	Pressure (psi) Final	Estolide yield %[b]
32	4	4	60	180	4.3
33	8	6	60	180	2.1
34	8	1	60	180	—

[a] Parts per 100 parts of oleic acid.
[b] Percent of product mixture by weight.

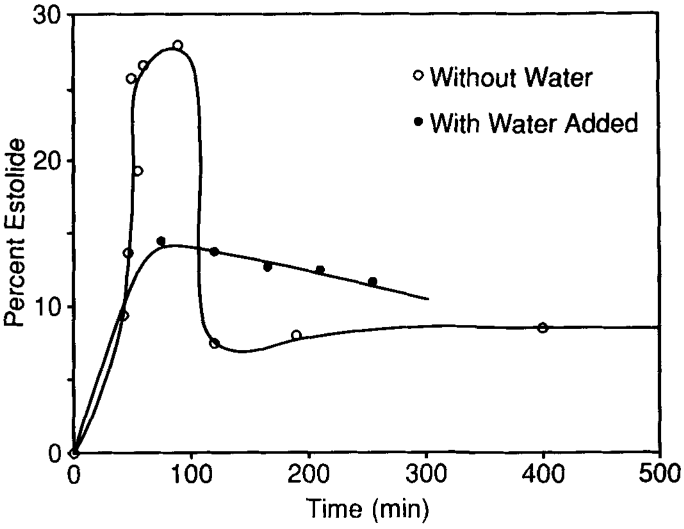

FIG. 3. The role of water in estolide reactions in a batch reactor.

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