Characterization of Monomers Produced from Thermal High-Pressure Conversion of Meadowfoam and Oleic Acids into Estolides

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The monomers produced from thermal high-pressure conversion of meadowfoam or oleic acids into estolides were characterized as a complex mixture of fatty acids. Mild reaction conditions produced little change in the starting acids. However, vigorous reaction conditions, *e.g.* ≥3 h at 250°C with stirring, significantly altered the starting fatty acids. *Cis/trans* isomerizaton occurred readily, with the proportion of *trans* isomers reaching 57%. In addition, the double bonds migrated throughout all positions of the hydrocarbon chain with concentrations diminishing outward from the starting double bond position. Branching was also observed to a small extent under these conditions and was even more pronounced in the absence of water. Lactones were also identified in the reaction mixture, with contents near 16% in the meadowfoam series. All products can be explained *via* carbocation rearrangement mechanisms that result from protonation of the starting olefins.

KEY WORDS: Branched fatty acids, *cis/trans* isomerization, estolides, lactones, meadowfoam, monomers, montmorillonite, olefin migration, oleic.

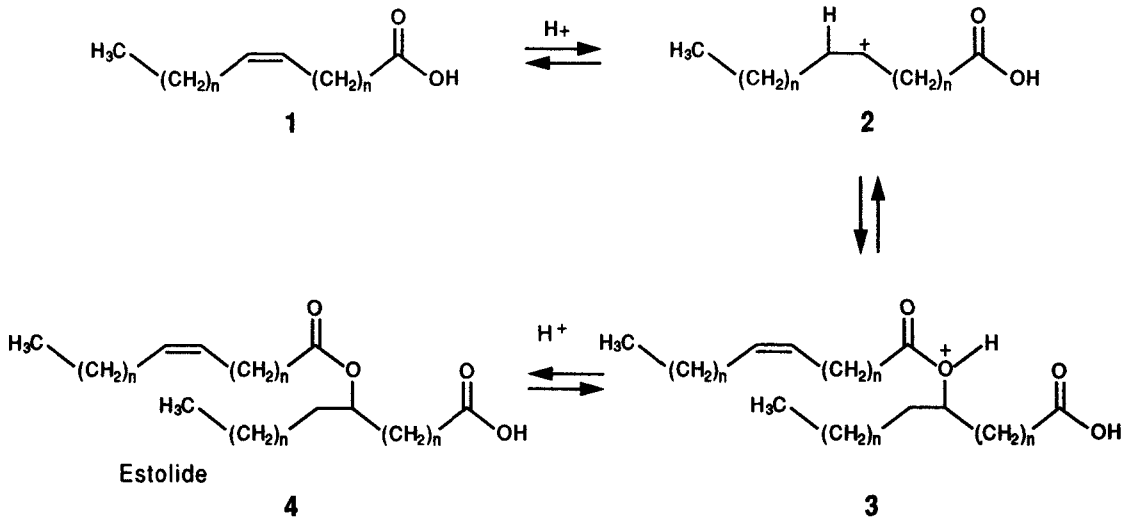
The thermal conversion of unsaturated fatty acids into estolides is a new process (1) that could provide unique industrial products with applications in lubricants, cosmetics and coatings. Formation of estolide proceeds by the reaction is depicted in Scheme 1, where condensation of unsaturated fatty acids occurs over acidic clays.

Currently, estolides are available from the esterification of the hydroxyl group of ricinoleic acid and are used mainly to dehydrate ricinoleic acid in the production of drying oils (2). Ricinoleic estolides are effective drying oils because of the close proximity of the double bond to the ester linkage which promotes elimination of the carboxylic acid to give conjugated dienes.

Estolides produced from the thermal addition of a carboxylic acid to monounsaturated fatty acids give estolides that are more stable than those produced from ricinoleic acid because they do not contain homoallylic double bonds. Furthermore, saponification of the estolide gives novel hydroxy fatty acids that have potential uses in greases and cosmetics.

The bulk of the thermal estolide reaction material (70–90%) remains as a distillable monomer fraction (1). Characterization and evaluation of the monomer fraction for anticipated reuse in the estolide process or for use in other industrial applications should be of value.

The monomer fraction obtained from the estolide process is categorized by its two distinct phases, one liquid and the other solid. The liquid monomer may contain branched material which has many established industrial uses (3). In a similar system, the monomers obtained from the dimerization of oleic acid by thermal batch reactors have been thoroughly investigated (4–7) and found to contain branched fatty acids and unreacted monoenes. In light of these findings we set out to characterize the monomer fraction formed in the thermal conversion of fatty acids into estolides.



SCHEME 1

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EXPERIMENTAL PROCEDURES

Materials. Meadowfoam oil was obtained from the Oregon meadowfoam Growers Association (Salem, OR) and was split by Witco Corporation, Humko Chemical Division (Memphis, TN) with high-pressure steam to obtain the fatty acids. Oleic acid was also purchased from Humko Chemical. Boron trifluoride/methanol complex (14% wt/vol) and fatty acid methyl ester (FAME) standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL). Methyl elaidate was purchased from Sigma Chemical Company (St. Louis, MO). Triphenylphosphine was purchased from Eastman Kodak Co. (Rochester, NY) and used without further purification. Palladium (10%) on activated carbon and carbon disulfide (spectrophotometric grade) were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI). Solvents for chromatography or extraction were specified for high-pressure liquid chromatography (HPLC) or an equivalent grade and used without further purification.

Instrumentation. Equivalent chainlength (ECL) determinations were made from gas chromatograms produced from a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a flame ionization detector and an autosampler/injector (Palo Alto, CA). Helium served as the carrier gas in all cases. A saturated methyl ester standard C8-C24 provided a standard curve from which all ECL values were determined.

Nonpolar ECL data were obtained on a SGE-BP1, 25 m × 0.22 mm i.d., column purchased from Scientific Glass Engineering Pty, Ltd. (Austin, TX). Gas chromatographic (GC) analysis was carried out under the following conditions: column flow rate 0.95 mL/min; split ratio 18:1; programmed ramp 170°C to 250°C at 2°C/min with a 5-min hold at 250°C. Injector and detector temperatures were set at 250°C.

Polar ECL data were obtained on a CP SIL-84, 25 m × 0.22 mm i.d., column purchased from Chrompack (Birdgewater, NJ). GC conditions: column flow rate 0.77 mL/min; split ratio 25:1; programmed ramp 120°C to 240°C at 3°C/min with a 5-min hold at 240°C. Injector and detector temperatures were set at 250°C.

Ozonolytic fragments were analyzed on a 25 m × 0.22 mm CP SIL-84 column with the following conditions: column flow rate 0.77 mL/min; split ratio 25:1; programmed ramp from 50°C to 250°C at 5°C/min and hold of 5 min at 250°C. Injector and detector temperatures were set at 250°C.

Gas chromatography-mass spectrometry (GC-MS) analyses were obtained from a Hewlett-Packard 5890A GC with 15 m DB-1 column and a Hewlett-Packard 5970 mass selective detector. Column conditions for FAMEs: programmed ramp 170°C to 250°C at 5°C/min with a 10-min hold at 250°C. Injector temperature 250°C, transfer line set at 280°C. Column conditions for ozonolysis fragments: programmed ramp 50°C to 250°C at 5°C/min and hold of 5 min at 250°C. Injector and transfer line temperatures 250°C and 280°C, respectively.

HPLC separations were performed on a Spectra-Physics 8800/8810 LC pumping system (San Jose, CA) coupled to a Waters 410 Differential Refractometer (Division of Millipore, Milford, MA). A reverse-phase Macro C-18 column, 60Å, 8 μm particle size, 250 mm × 21.4 mm i.d., purchased from Dynamax, a division of Rainin Instrument Company Inc. (Woburn, MA), was used to separate the 20:1 and 22:1 under the following conditions: eluent acetonitrile/acetone 90:10; flow 7 mL/min.

Methods. The monomers were isolated from the crude reaction mixtures by Kugelrohr distillation (180°C at 0.3 torr), with the estolide remaining in the residue. FAMEs were generated by dissolving approximately 200 mg of the monomer in 5 mL of boron trifluoride/methanol complex (14% wt/vol) and heating on a steam bath for 5 min. The reaction mixture was quenched by pouring into 20 mL of hexane and washed 3 × 10 mL with H_2O or saturated brine solution. The resulting solution was dried over $MgSO_4$ filtered and concentrated *in vacuo.* A 2-mg aliquot of the residue was diluted in 2 mL of hexane, and the resulting solution was injected into the GC or GC-MS.

The olefinic FAMEs were saturated by dissolving 10 mg of the methyl esters in 3 mL of ethyl acetate over 10 mg of 10% Pd on activated carbon. Hydrogen was bubbled through this solution at room temperature for 20 min, and the catalyst was removed by filtration through a fluted #50 Whatman filter paper (Hillsboro, OR). The filtrate was diluted 1:1 with hexane and injected directly into the GC or GC-MS.

Ozonolytic cleavage (8) of the isolated monomer fractions was accomplished by dissolving 10 mg of monomer in 4 mL of CH_2Cl_2, and the resulting solution was cooled to −78°C in a dry-ice/acetone bath under a stream of O_2. Ozone was passed through the solution until a faint blue color appeared (approximately 3 min). The solution was purged with O_2 until no residual O_3 remained, as indicated by a starch/iodine test strip placed in the effluent from the flask. Triphenylphosphine (15 mg, 2.5 equivalents) was added to the flask, and the reaction was allowed to warm to room temperature. At this point the aldehyde, aldehyde-ester mixture was injected directy into the GC and GC-MS without further manipulation.

The extent of geometrical isomerization for the monomers was determined by infrared (IR) analysis of the *trans* absorption band at 967 cm^{-1} as described in AOCS method Cd 14-61 (9) with the modification published by Lanser (10). Spectra were obtained from a Mattson Cygnus 100 FTIR (Madison, WI) equipped with an EXPERT-IR analytical software program. The monomer (20 mg ± 0.2 mg) was dissolved in 1.0 mL of CS_2, placed in a 1.0-mm KBr cell and scanned 32 times with a CS_2 background. Integration of the *trans* absorption band at 967 cm^{-1} and computation of the percent *trans* isomers with respect to a standard curve developed from methyl elaidate (standards from 5–100% methyl elaidate) provided the percentage of *trans* double bonds for each monomer fraction.

RESULTS AND DISCUSSION

The thermal high-pressure estolide process (1) uses a montmorillonite clay catalyst to initiate condensation of unsaturated fatty acids into estolides. Montmorillonite is a bentonite clay that contains an acidic interlamellar layer (11,12) capable of catalyzing reactions that require acid catalysts (13). Similar clays are used in industry for the bleaching of oils (14–16) or for the production of dimer acids (17). Based on the acidic nature of the clay, a cationic mechanism for the formation of estolides can be considered (Scheme 1). The olefin of fatty acid 1 is protonated

to give carbocation 2 which is subsequently trapped by a second fatty acid molecule to give the protonated estolide 3. The protonated species 3 then loses a proton to give estolide 4. The intermediate species of significance that leads to the formation of monomer is the protonated fatty acid 2. The events that lead to 2 and the subsequent rearrangements associated with this carbocation intermediate dictate the constituency of the monomer fraction.

Table 1 lists the respective reaction conditions used for the formation of estolides, along with the corresponding estolide yields. Two general series of reactions were carried out, those starting with acids derived from meadowfoam oil and those from commercial oleic acid. The reaction mixtures were separated into two fractions by Kugelrohr distillation, the distillate containing the monomers and the residue containing the estolides. The monomers were then converted to their methyl esters and all subsequent analyses were performed on these derivatives.

ECL data provided a rapid insight into the composition of the monomer fractions, with the main fatty acids of the monomer paralleling the starting meadowfoam and oleic fatty acids (Tables 2 and 3). These similarities are

TABLE 1

High-Pressure Thermal Reactions Conditions

#	Mixing	Time	Temp. (°C)	H_2O (%)	Estolide (%)
			Meadowfoam[a]		
A	Rocker	10	250	10	10.4
B	Rocker	6	180	10	1.9
C	Rocker	3	250	10	11.3
D	Rocker	4	300	10	0.5
E	Stirred	6	250	10	6.6
			Oleic[a]		
F	Stirred	3	250	10	10.1
G	Stirred	3	250	12	8.3
H	Stirred	1	250	10	2.1
I	Stirred	6	250	0	0.0
J	Stirred	1	250	0	8.0

[a]Montmorillonite K-10 clay 8% w/w as a catalyst with respect to starting acid was used for all reactions.

TABLE 2

Meadowfoam (MF) Monomers

Monomer	MF	A	B	C	D	E	Equivalent chainlength CPSIL84	BP1
16:0	0.5	1.0	0.5	1.6	1.0	1.1	16.00	16.00
18:0	0.6	0.0	0.0	0.7	0.6	0.0	18.00	18.00
18:1	1.8	4.9	4.9	8.0	1.4	3.4	18.30	17.75
Branched 20:0 and 20:1	0.0	0.0	0.0	0.0	5.2	4.2	19.91	19.36
20:0	1.3	1.1	0.9	1.0	2.9	3.3	20.00	20.00
20:1	60.7	64.9	61.9	69.5	51.6	55.3	20.30	19.75
Branched 22:0 and 22:1	0.0	0.0	0.0	0.0	4.0	0.5	21.17	21.38
22:0	0.0	0.0	0.0	2.6	0.6	0.0	22.00	22.00
22:1	13.6	13.2	18.6	7.4	6.0	15.5	22.31	21.79
22:2	18.2	15.0	13.2	9.2	3.8	0.6	22.57	21.49
γ20:0 Lactone	0.0	0.0	0.0	0.0	12.3	16.1	29.40	21.79

TABLE 3

Oleic Monomers

Monomer	Oleic	F	G	H	I	J	Equivalent chainlength CPSIL84	BP1
14:0	3.6	1.0	2.9	3.7	7.2	7.0	14.00	14.00
14:1	1.3	2.0	1.5	0.7	0.5	0.5	14.30	13.75
Branched 16:0 and 16:1	0.0	0.0	0.0	0.0	10.0	9.5	15.0–15.9	15.2–15.8
16:0	6.6	5.5	5.9	7.1	15.8	13.6	16.00	16.00
16:1	11.9	8.0	9.4	4.7	0.0	0.0	16.34	15.75
17:0	0.0	0.0	0.4	0.0	1.5	1.0	17.00	17.00
17:1	1.3	1.9	1.7	1.7	1.0	0.0	17.28	16.77
Branched 18:0 and 18:1	0.0	1.0	0.9	0.0	48.6	53.2	17.2–17.8	17.1–17.7
18:0	2.0	1.7	1.8	2.4	10.7	0.7	18.00	18.00
18:1	72.6	75.3	72.3	78.6	2.1	11.2	18.30	17.75
Branched 20:0 and 20:1	0.0	0.0	0.0	0.0	2.6	0.5	19.57	19.65
20:0	0.0	0.7	0.6	0.5	0.0	0.7	20.00	20.00
20:1	0.5	0.0	0.0	0.0	0.0	0.0	20.30	19.75
γ18:0 Lactone	0.0	2.2	2.7	0.6	0.0	2.1	27.53	19.60

typified by meadowfoam monomers (A–C) and oleic monomers (F–H).

Meadowfoam monomers D and E proved to be complex mixtures of components in the 20:1 and 22:1 regions that included positional and geometrical isomers of the original monoenes, together with saturated and various positionally unsaturated branched materials. GC data for oleic monomers I and J indicated that little normal unsaturated esters were present and that they contained high levels of both normal and branched saturated esters.

Branching. Hydrogenation of meadowfoam monomers (A–C) (Table 2) gave the expected normal-chain fatty esters. In contrast, hydrogenation of monomers D and E resolved the complex C_{20} and C_{22} regions into normal-chain saturates and branched saturates. ECL assignments for the branched material (ECL nonpolar = 19.4, polar = 19.2 for branched C_{20}) were consistent with methyl-branched esters analyzed on similar columns (18). GC-MS of the 20:0 branch provided a molecular ion of 326, confirming our C_{20} assignment. These data indicate that monomers D and E contained a small amount of branched material (≈5–10%), consisting mainly of monoenoic branched fatty acids.

Hydrogenation of oleic monomer fractions (F–H) (Table 3) gave the expected normal-chain fatty acids. However, monomers I and J had only a small amount of material undergo hydrogenation to the normal fatty acids, with the bulk of the material remaining as a highly complex mixture of unsaturated branched isomers. Eisner reported (5) that highly branched olefins are resistant to hydrogenation and this appears to be the case for monomers I and J.

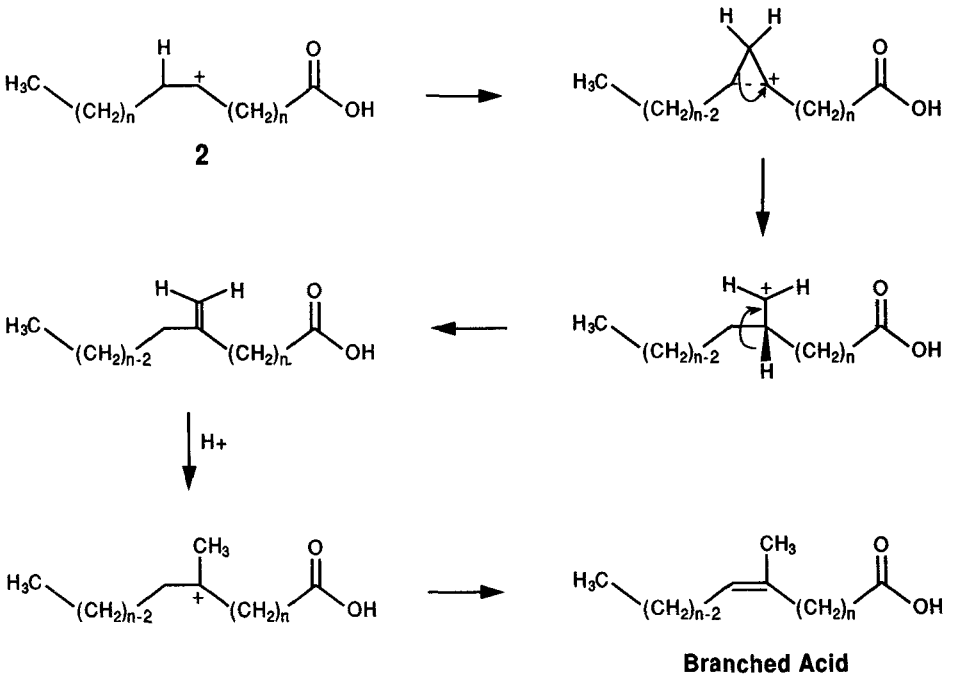
The appearance of branched material is not surprising under these acidic conditions and probably arises from the mechanism depicted in Scheme 2 which has been postulated in similar systems (4,6,7).

A correlation between reaction conditions and the degree of branching can be made. High temperature (reaction D, Table 1) or prolonged contact time with the catalyst at 250°C (reactions E and I, Table 1) provided branched acids (Tables 2, 3). Mixing the solution also plays a role in the extent of branching. Reaction A (Table 1) is in contact with the clay for 10 h in a rocker system with little change in the composition of the starting material (Table 2). In contrast, reaction E is subjected to the same conditions as A, except for the stirring, and gave branched acids under a shorter reaction time.

In the oleic series, all the reactions provided some degree of branching with the exception of monomer fraction H, which had a short reaction time. This indicates that a vigorously stirred solution provided a higher degree of contact of the reactant with the catalyst and thus significant alteration of the starting material.

Water also had a pronounced effect on the proportions of branched acids. In the absence of water, a large degree of branching occurred (reactions I and J, Table 3) probably due to the lack of competitive quenching by water of the cationic intermediates that lead to skeletal rearrangements. It must be noted that the clay inherently contains 7.2% water, which remains as a constant factor in all of the thermal estolide reactions. In the absence of additional water, the conditions of the reactor (250°C) will completely vaporize the water in the clay (Erhan, S.M., R. Kleiman and T.A. Isbell, manuscript in preparation). In contrast, the use of additional water in the reactor will guarantee the presence of water in the reaction mixture by establishing an equilibrium between the gas and liquid phases. The water in the reaction mixture will then compete with cationic intermediates that lead to branched acids.

Geometrical isomerization. Because the bulk of the monomer fraction remained unsaturated, the extent of elaidinization was obtained by measurement of the *trans*



SCHEME 2

adsorption band at 967 cm^{-1} in the IR spectra (9,10). These results are reported in Table 4. Meadowfoam monomers (A–C) contained small amounts of *trans* isomers, whereas samples D and E showed significant amounts of geometrical isomerization, with monomer E containing 43.7% *trans* isomers. Significant elaidinization also occurred in the oleic monomers, as evidenced by the *trans* IR absorbance data shown in Table 4. As the amount of *trans* isomers increased, the probability of the monomer becoming a solid increased. This correlation is in accord with the observed increase in the melting point of elaidic acid (45°C) with respect to oleic (16°C). The relationship between solid monomers and *trans* olefins is consistent in the oleic monomer series, with the exception of I where a minor amount of *trans* isomers was produced. However, reaction I contained a large amount of saturates (33%), which would yield a liquid/solid mixture.

Geometrical isomerization is a facile process, with an equilibrium value of 57% for oleic acid over bentonite clays (19). The oleic monomers (F and G) listed in Table 4 parallel this equilibrium value. Mechanistically, *cis/trans* isomerization would occur under acid catalysis by protonation of 1 to give the cation 2 which then undergoes C–C bond rotation, followed by loss of the proton to give *trans* isomers of 1 (Scheme 1).

Positional isomerization. Because the conditions for the formation of estolides is similar to that used in the dimerization of fatty acids, we expected to find a significant amount of double-bond migration as previously reported in the dimerization of oleic acid (13–14). The extent of double bond migration was determined by ozonolytic cleavage (8), and the results of this study are shown in Table 5.

Monomers D and E were separated into monoene fractions 20:1 and 22:1 by preparative reverse-phase HPLC. Each monoene fraction (10 mg) was subjected to reductive ozonolysis. Quantitation of the resultant aldehyde and aldehyde-ester fragments was performed with regard to the differing flame-ionization detector (FID) responses (8) for chainlength and carbonyl carbons present in each fragment. Comparison of both components resulting from each positional isomer agreed within ±2 mole% and allowed us to locate and quantitate the position of each double bond in the monomer fraction. ECL data for the ozonolysis fragments are listed in Table 6. The assignments were confirmed by GC-MS. Aldehydes were identified by molecular ion and/or McLafferty rearrangement (20) ion 43 and the γ-scission ion 57. Aldehyde-esters were confirmed by molecular ion and/or the previously mentioned

TABLE 4

Geometrical Isomerization

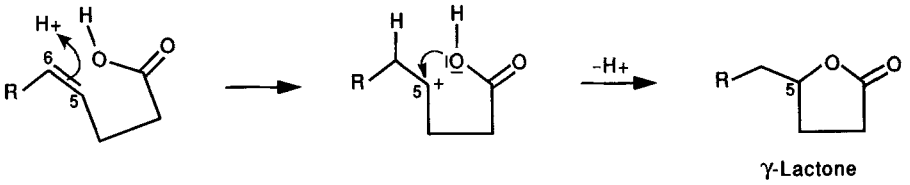
Monomer	Phase	% *trans* (967 cm^{-1} infrared absorbance)
Meadowfoam		
A	Liquid	2.3
B	Liquid	1.2
C	Liquid	8.3
D	Solid	18.7
E	Solid	43.7
Oleic		
F	Liquid/Solid	56.3
G	Liquid/Solid	56.5
H	Liquid	14.1
I	Liquid/Solid	3.1
J	Liquid	9.7

TABLE 5

Double-Bond Location by Ozonolysis

	Meadowfoam monomers						Oleic monomers	
Olefin position	MF[a]	B	C	D (20:1)	D (22:1,2)	Oleic	F	H
2				0.2				
3				0.6			0.2	
4			2.2	10.0	2.2		1.0	
5	85.9	86.2	78.2	32.1	9.9		1.7	0.5
6			3.0	8.7	5.7		3.9	0.9
7			0.7	7.7	6.1		7.2	1.9
8			2.8	6.7	5.7		18.6	6.6
9	3.9	5.3	2.6	5.9	6.3	92.9	24.6	67.2
10			1.1	6.9	6.1		21.5	13.8
11	1.2	0.9	0.9	4.3	5.2	7.1	9.9	6.2
12			0.6	3.6	5.8		5.6	1.2
13	8.2	7.6	7.6	3.1	16.4		2.9	0.9
14			0.4	2.6	5.4		1.8	0.3
15				2.2	5.0		0.7	
16				1.9	4.8		0.5	
17				1.8	4.5			
18				1.4	4.2			
19				0.2	3.2			
20					3.1			
21					0.4			

[a]MF denotes meadowfoam fatty acids. All data are normalized with respect to the total unsaturation present in each monomer fraction.



γ-Lactone

SCHEME 3

TABLE 6

Equivalent Chainlength (ECL) Table of Ozonolysis Fragments on a Polar CPSIL 84 Column

Aldehydes	ECL	Aldehyde-esters	ECL
3[a]	5.08		
4[a]	5.20	4	10.37
5	5.45	5	11.85
6	5.87	6	13.40
7	6.49	7	14.56
8	7.33	8	15.63
9	8.35	9	16.64
10	9.45	10[b]	17.99
11	10.57	11	19.24
12	11.67	12	20.43
13	12.74	13	21.57
14	13.77	14	22.65
15	14.74	15	23.69
16	15.67	16	24.69
17	16.56	17	25.67
18	17.76	18	26.55
		19	27.44
		20	28.28
		21	29.10

[a] Aldehydes 3 and 4 appear in the shoulder of the solvent peak and can be assigned but do not provide any additional information in terms of quantitation.

[b] The C10 aldehyde-ester had the same retention time as 18:0, thus confirmation of its assignment must be made with the corresponding aldehyde.

aldehyde fragments plus the McLafferty fragment 74 and the γ-scission fragment 87 from the ester (21). Ozonolytic cleavage of meadowfoam and oleic acids provided additional standards for the ozonolysis fragments.

Solids D and E produced nearly identical monoene distribution patterns. The C_{20} monoene fraction of reaction D shown in Table 5 shows diminishing amounts of olefin as the unsaturation migrates away from the original Δ5 position. The increased percentage of olefin that is observed in the Δ10 position arises from small amounts of Δ9 and Δ11 monoenes that are present in meadowfoam. The C_{22} monoene fraction of D (Table 5) indicates a more equal distribution among the double-bond positions due to the presence of two different monoenes in the starting material (Δ5, 3.3% and Δ13, 10.3% for the C_{22} of meadowfoam).

Meadowfoam monomers (A–C) were subjected to ozonolysis without chromatographic separation because of their similarity to the original meadowfoam fatty acid mixture, as shown in Table 2. Monomers A and B were identical in positional isomerization and only differed slightly from the original meadowfoam fatty acids (Table 5). Monomer C, however, had an increased amount of olefin migration, as shown in Table 5. Analyses for positional isomerization in the oleic series were performed on the unfractionated monomers, and double-bond migration occurred throughout all positions of the chain. Monomers F and G have olefin distributions centered around the original Δ9 position, as represented by monomer F shown in Table 5. Monomer H had only a small amount of olefin migration, with the unsaturation residing mainly at the Δ9 position. The two highly branched monomers J and K were not analyzed for positional isomerization because of the high content of branched isomers in these samples.

Olefin scrambling occurred to the greatest extent in the stirred reactions and in those reactions that had long reacton times. Reaction A had little olefin migration in comparison to the stirred reaction E, where significant migration occurred. Higher temperatures, as in D, produced extensive double-bond migration in comparison to B (essentially no migration). Contact time of the fatty acids with the catalyst (H *vs.* F) also played a role in positional isomerization because little change occurred in the 1-h reaction (H, Table 5).

Lactones. Lactones are also present in the meadowfoam monomer samples. The Δ5 olefin of meadowfoam, the predominate unsaturation present, lies in close proximity to the acid functionality. Protonation of the Δ5 position followed by capture with the carboxylic acid leads directly to the lactone, Scheme 3. The γ-eicosanolactone was the predominate lactone formed (13.9%), together with a small amount of the δ-eicosanolactone (1.6%), which is in accord with the literature (17,22). Both MS and ^{1}H-nuclear magnetic resonance (NMR) of the isolated lactones were identical with published spectra (17). Only small amounts of lactone are present in the oleic monomers because the original unsaturation is located at the Δ9 position, and migration of the unsaturation down the chain must occur to a significant extent before lactone will be formed. However, γ-stearolactones have been reported from oleic acid by acid catalysis with perchloric acid (23–25).

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