Epoxidation of *Lesquerella* and *Limnanthes* (Meadowfoam) Oils

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Lesquerella gordonii **(Gray) Wats and** ***Limnanthes alba*** **Benth. (Meadowfoam) are species being studied as new and alternative crops. Triglyceride oil from lesquerella contains 55–60% of the uncommon 14-hydroxy-*cis*-11-eicosenoic acid. Meadowfoam oil has 95% uncommon acids, including *ca.* 60% *cis*-5-eicosenoic acid. Both oils are predominantly unsaturated (3% saturated acids), and have similar iodine values (90–91), from which oxirane values of 5.7% are possible for the fully epoxidized oils. Each oil was epoxidized with *m*-chloro-peroxybenzoic acid, and oxirane values were 5.0% (lesquerella) and 5.2% (meadowfoam). The epoxy acid composition of each product was examined by gas chromatography of the methyl esters, which showed that epoxidized *L. gordonii* oil contained 55% 11,12-epoxy-14-hydroxyeicosanoic acid, and epoxidized meadowfoam oil contained 63% 5,6-epoxyeicosanoic acid, as expected for normal complete epoxidation. Mass spectrometry of trimethylsilyloxy derivatives of polyols, prepared from the epoxidized esters, confirmed the identity of the epoxidation products and the straightforward nature of the epoxidation process. Synthesis and characterization of these interesting epoxy oils and derivatives are discussed.**

KEY WORDS: **Epoxidation, epoxidized lesquerella oil, epoxidized meadowfoam oil, fatty di-, tri- and tetraols, GC, GC-MS, *Lesquerella gordonii, Limnanthes alba*, meadowfoam, *m*-Cl-peroxybenzoic acid, methyl (5,6,13,14-diepoxy decosanoate; 5,6-epoxy docosanoate; 13,14-epoxy docosanoate; 5,6-epoxy eicosanoate; 11,12-epoxy-14-hydroxy eicosanoate diastereomers), TMS derivatives.**

Lesquerella and *Limnanthes* (meadowfoam) species are important to the U.S. Department of Agriculture's New Crops Program and are currently targeted as alternative crops for western regions of the United States (1). They provide seed materials, including unique oils, that can be converted to products with industrial uses. Seed oil of *Lesquerella gordonii* contains 55–60% of an uncommon fatty acid, 14-hydroxy-*cis*-11-eicosenoic. Meadowfoam has 95% uncommon acids, including *ca.* 60% *cis*-5-eicosenoic acid. Each oil is predominantly monounsaturated, with an iodine value of 90–91. We were struck by the fact that epoxidation of these oils would potentially yield materials with significant oxirane values (5.7% theoretical) and properties that could be useful in coatings, plasticizer-stabilizers, polymers and lubricants. The longer chainlengths and unusual positions of the oxirane groups in both products, and the proximity of the hydroxyl group to the oxirane ring in the lesquerella product, would make these epoxidized oils different from any currently available. To evaluate the course of epoxidation of these oils, we chose mild epoxidation conditions to prepare these novel products for characterization, and we report the results in this paper.

EXPERIMENTAL PROCEDURES

Materials. Lesquerella gordonii and *Limnanthes alba* oils were obtained by hexane extraction of seed. Technical-grade (85%) *m*-chloroperoxybenzoic acid (CPBA) was obtained from Aldrich Chemical Co. (Milwaukee, WI). Solvents (benzene, hexane, petroleum ether, ethyl ether, methanol) were reagent- or spectroscopic-grade.

Epoxidation. Lesquerella gordonii oil [molecular weight (MW) *ca.* 944] and *L. alba* oil (MW *ca.* 973) (5.00 g in 50 mL benzene) were epoxidized at less than 25°C (ice bath) with CPBA (4.10 g in 75 mL benzene, 10% excess CPBA) in the presence of $NaHCO_3$ (3.75 g) as described previously by Chang (2), except that the CPBA in benzene was added in quarters, each portion over a 20-min interval, and aliquots of the reaction mixture were removed just prior to each addition of CPBA (3). An additional aliquot was taken 20 min after addition of the last quarter of CPBA, and a final aliquot was taken the next morning (reaction mixture remained overnight at room temperature). Progress of epoxidation then was retrospectively examined by thin-layer chromatography (TLC) of the aliquots (3). Initial yields of epoxidized lesquerella oil (MW *ca.* 998) ranged from 40 (run 1) to 79% (run 3). Emulsions formed during alkaline and water washings of the benzene-product layer. Runs 4–8 were proportionately scaled-up to 10 g lesquerella oil, and recovered yields of epoxidized products were significantly improved (83–86%). No emulsions were experienced in the work-up of epoxidized meadowfoam oil (MW *ca.* 1028), where isolated yields were 79–85% (10-g scale, 6 runs).

Transesterification and esterification. Fatty acid methyl esters (FAME) were prepared from 10 mg to 1.0 g of the oils by transesterification with 10 mL of 0.28 M sodium methoxide in methanol (3). The mixtures were gently refluxed (5–15 min) until all oil was dissolved and a clear solution was obtained. After addition of saturated NaCl solution, the FAME were extracted into hexane or diethyl ether. The extracts were dried over Na_2SO_4 and filtered, and the solvent was evaporated under nitrogen. This procedure leaves the epoxy groups intact.

FAME also were prepared by saponification of 200 mg of the oil in 4 mL 0.5M NaOH in methanol, followed by reaction with 4 mL 10% BF_3 in methanol. This procedure saponifies the glycerides and generates methyl esters while opening the epoxy groups to pairs of vicinal methoxy-hydroxy derivatives (3,4).

Di- and polyhydroxy derivatives of the epoxidized oils were prepared as described by Smith *et al.* (5). Epoxidized lesquerella or meadowfoam oil (1.5 g) in glacial acetic acid (15 mL) was refluxed for 3 h under an atmosphere of nitrogen, excess acetic acid was stripped under vacuum, and the hydroxy acetylated oils were treated with 25 mL 0.28 M sodium methoxide in methanol to simultaneously transesterify the acetyl and glyceride groups. After dilution with saturated NaCl solution (50 mL), the polyhydroxy FAME were isolated as white solids by extraction with ethyl ether, drying over anhydrous Na_2SO_4, filtering and evaporation of the ether.

Hydroxy derivatives (10 mg) were silylated with 1 mL Trisil reagent (Pierce Chemical, Rockford, IL) for analysis by gas chromatography (GC) and GC–mass spectrometry (GC-MS) (6).

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Analyses. Oxirane oxygen was determined by HBr titration in acetic acid at 25°C (7). TLC analyses were performed on commercial precoated plates (0.25-mm silica gel 60 F-254; E. Merck, Cincinnati, OH). Developing solvent was hexane/diethyl ether/acetic acid (60:40:1, vol/vol/vol). Epoxy components were revealed on TLC plates (without fluorescent indicators) by the picric acid technique (8,9). Visualization of all components was by iodine vapor and then by charring at 130°C after spraying the plate with sulfuric-chromic acid solution.

For GC analysis of FAME or epoxidized FAME, a 1-μL sample (10 mg/mL in hexane) of FAME was injected into an HP 5890A GC (Hewlett-Packard Co., San Fernando, CA) equipped with a 15 m × 0.25 mm DB-1 fused-silica capillary column (J&W Scientific, Rancho Cordova, CA), helium carrier gas and flame-ionization detector (FID). Oven temperature was programmed from 180–250°C at 7.5°C/min with an initial hold for 1 min at 180°C and a final hold of 10 min at 250°C. A 30 m × 0.24 mm SP-2340 capillary column (Supelco Inc., Bellefonte, PA) in an SP-7100 GC (Spectra Physics, San Jose, CA) with helium carrier gas and FID was also used to analyze FAME of lesquerella, meadowfoam and epoxidized FAME of meadowfoam (1-μL injection; oven programmed from 180–250°C at 3°C/min).

Epoxidized FAME, their methoxy-trimethylsilyloxy or, preferably, their di- or polytrimethylsilyloxy derivatives, were characterized by GC–MS with a Hewlett-Packard 5890 GC interfaced to a Hewlett-Packard 5970 Mass Selective Detector (70 eV, source pressure *ca.* 10^{-6} torr). The GC was equipped with a 12.5 m × 0.2 mm crosslinked dimethylsilicone-coated fused-silica capillary column and operated with splitless injection (1 μL). The GC oven was temperature-programmed from 150–220°C at 2°C/min.

A reference sample of C_8–C_{24} FAME (Nu-Chek-Prep, Inc., Elysian, MN) was used for systematic identification of esters by equivalent chainlength (ECL) (10,11).

RESULTS AND DISCUSSION

We previously reported (3) that CPBA epoxidation of *Vernonia galamensis* oil, with its high level of vernolic acid (*ca.* 80%, with a 12,13-epoxy group β to a Δ-9 double bond), proceeded cleanly without competitive solvolytic opening of either the natural or the introduced epoxy groups during the reaction. The mild conditions (<25°C) included benzene as solvent and solid $NaHCO_3$, suspended in the reaction mixture, to neutralize acidity as formed. This same procedure now has been shown to work equally well for epoxidizing lesquerella oil, with its significant quantity of lesquerolic acid (*ca.* 57%, with a 14-hydroxyl group β to a Δ-11 double bond); and for epoxidizing meadowfoam oil, with its high level of Δ-5 unsaturation (including *ca.* 62% *cis*-5-eicosenoic acid) located relatively near the carboglyceryloxy end of the fatty acid chain. Oxirane values averaged 4.95% (lesquerella, 86% of theory, range 4.91–4.02%) and 5.22% (meadowfoam, 92% of theory, range 5.17–5.28%). The products were white solids at room temperature.

FAME prepared from the natural oils and their epoxidized products are compared by GC in Figure 1 (lesquerella) and Figure 2 (limnanthes). At first glance, the relative peak sizes and corresponding shifts in GC retention times for the epoxidized esters (Figs. 1B and 2B), compared to those of their olefinic precursor esters (Figs. 1A and 2A), suggested that epoxidation was straightforward. Indeed, ECL values of the epoxidized products affirmed this conclusion, each epoxy group adding *ca.* 1.5 ECL units to the ECL value of the corresponding saturated reference FAME (10,11) on the DB-1 column. FAME from natural and epoxidized *V. galamensis*, and from epoxidized soybean and linseed oils, served as reference epoxy esters (3). Further evidence for straightforward epoxidation is the almost identical GC distributions of FAME, prepared from epoxidized products, and their precursor

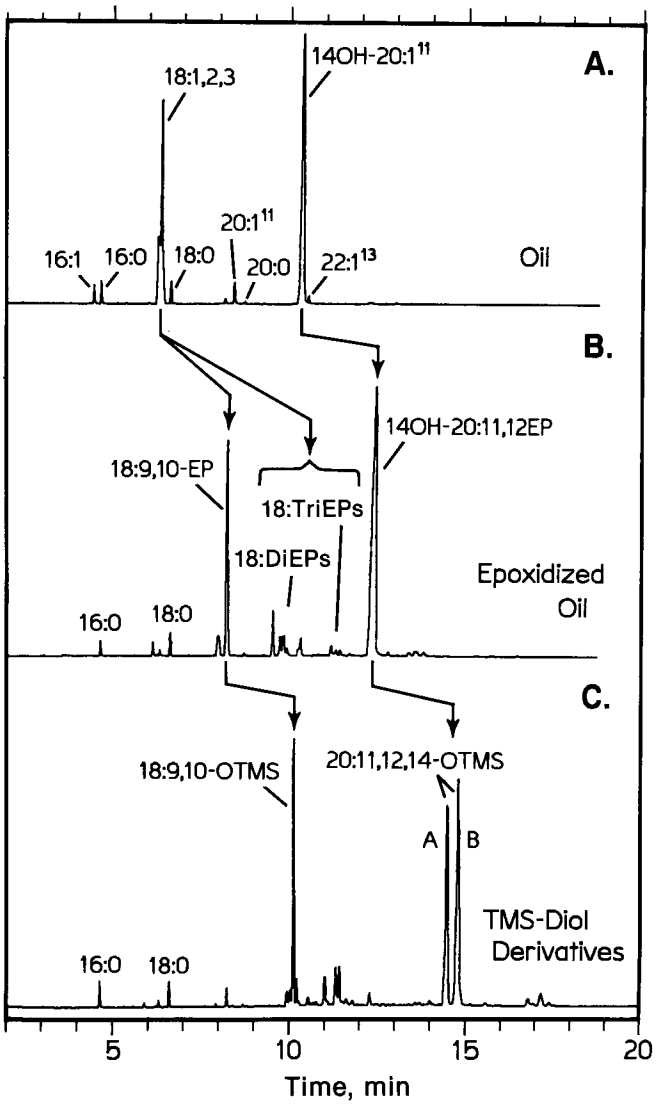


FIG. 1. Gas chromatograms (GC) of fatty acid methyl esters (FAME) of *Lesquerella gordonii* oils. A. FAME of starting oil; esters identified by carbon number:number and location of double bonds, *e.g.*, $20:1^{11}$ = methyl *cis*-11-eicosenoate. B. FAME of epoxidized oil; EP = epoxy group, *e.g.*, 14-OH-20:11,12EP = methyl 11,12-epoxy-14-hydroxy-eicosanoate. C, FAME of silylated dihydroxy derivatives of epoxidized oil; OTMS = trimethylsilyl ether, *e.g.*, 18:9,10-OTMS = methyl 9,10-di(trimethylsilyloxy)-octadecanoate. A and B = diastereomeric methyl 11,12,14-tri(trimethylsilyloxy)-eicosanoates. A 15 m × 0.24 mm i.d. fused-silica capillary column with 0.1 μm DB-1 phase was used; GC oven temperature-programmed from 180 to 250°C at 7.5°C/min; flame-ionization detector. TMS, trimethylsilyl.

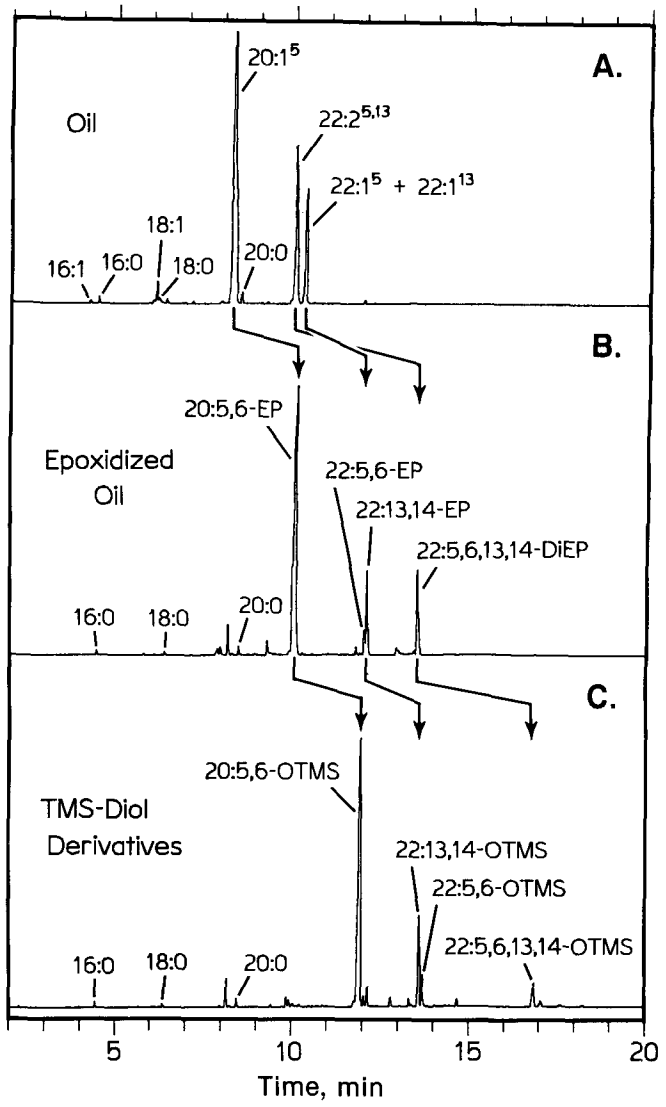


FIG. 2. Gas chromatograms (GC) of fatty acid methyl esters (FAME) of *Limnanthes alba* oils. A. FAME of starting oil; esters identified by carbon number:number and location of double bonds, *e.g.*, $22:2^{5,13}$ = methyl *cis*-5-*cis*-13-docosanoate. B. FAME of epoxidized oil; EP = epoxy group, *e.g.*, 22:5,6-EP = methyl 5,6-epoxy-docosanoate. C. FAME of silylated dihydroxy derivatives of epoxidized oil; OTMS = trimethylsilyl ether, *e.g.*, 22:5,6,13,14-OTMS = methyl 5,6,13,14-tetra (trimethylsilyloxy)-docosanoate. A 15 m × 0.24 mm i.d. fused-silica capillary column with 0.1 μm DB-1 phase was used; GC oven temperature-programmed from 180 to 250°C at 7.5°C/min; flame-ionization detector. TMS, trimethylsilyl.

FAME from the natural oils (Table 1, lesquerella; Table 2, limnanthes). Of the major FAME epoxidation products from the two oils, only the percentages of methyl 13,14-epoxy-docosanoate and methyl 5,6-epoxy-13,14-epoxy-docosanoate from epoxidized meadowfoam oil (Table 2) are lower than the percentages of their respective unsaturated precursors in the natural oil. On-column loss of these higher-MW FAME probably occurs during GC analysis.

Confirmation of all major epoxy FAME products was obtained by GC–MS analysis of derivatives. Derivatives were prepared according to the following routes to the hydroxy-methoxy and dihydroxy FAME (Scheme 1). The dihydroxy derivatives were much preferred for locating functional groups, because their trimethylsilyl (TMS) derivatives gave simpler and more readily identifiable

TABLE 1

Gas Chromatographic Analysis of Fatty Acid Methyl Esters (FAME) of *Lesquerella gordonii* Oils (%)[a]

	Composition (%)	
FAME[b]	Oil	Epoxidized oil[c]
16:1	1.0	0.9
16:0	1.4	1.0
18:3	5.3	2.2
18:2	6.0	6.1
18:1	22.4	21.8
18:0	1.5	1.5
20:1	1.0	1.2
20:0	0.2	0.2
$18:1^{9}$-12-OH	0.5	0.9
$20:1^{11}$-14-OH	57.9	57.1
$20:2^{11,17}$-14-OH	1.1	1.2
Others	1.7	5.9[d]

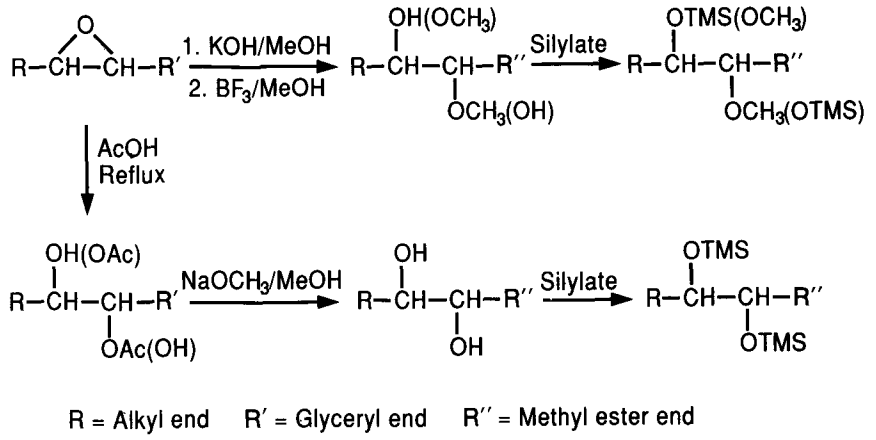
[a]Using a 15 m × 0.24 mm DB-1 nonpolar fused-silica capillary column; see Experimental Procedures section for details. Distribution of 18:1,2,3 in the unepoxidized oil was determined with a 30 m × 0.24 mm SP-2340 polar fused-silica capillary column.
[b]Identified by carbon number:number and location of double bonds and hydroxyl groups.
[c]Mono-, di- or tri-epoxy ester products correspond to the mono-, di- or triene esters listed at the left. Epoxy ester distribution could not be confirmed on the 30-m polar capillary column because methyl 11,12-epoxy-14-hydroxy-eicosanoate and 11,12-epoxy-17,18-epoxy-14-hydroxy-eicosanoate did not elute.
[d]Predominantly three unknown peaks, one (2.1%) preceding the epoxy stearate peak, and two (1.5%, 0.6%) intermingled with the diepoxy stearate peaks, respectively, suggesting that they may be isomers of these compounds.

TABLE 2

Gas Chromatographic Analysis of Fatty Acid Methyl Esters (FAME) of *Limnanthes alba* Oils (%)[a]

	Composition (%)	
FAME[b]	Oil	Epoxidized oil[c]
16:1	0.2	0.1
16:0	0.4	0.6
18:3		0.2
18:2	2.5[d]	0.8
18:1		1.0
18:0	0.3	0.4
$20:1^{5}$	62.7[e]	62.6
$20:1^{11}$		0.7
20:0	0.8	1.0
$22:1^{5}$		3.2
$22:1^{13}$	12.9[f]	10.8
$22:2^{5,13}$	18.7	14.4
22:0	0.1	0.1
Others	1.3	3.0

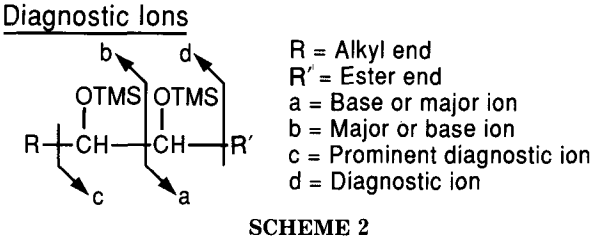
[a]Using a 15 m × 0.24 mm DB-1 nonpolar fused-silica capillary column (see Experimental Procedures section for details). Confirmed on a 30 m × 0.24 mm SP-2340 polar fused capillary column.
[b]Identified by carbon number:number and location of double bonds.
[c]Mono-, di- or tri-epoxy ester products correspond to the mono-, di- or trieneesters listed at the left.
[d]Mostly 18:1 (18:1,2,3 are not resolved on this column).
[e]Predominantly (99%) $20:1^{5}$ ($20:1^{11}$ isomer not resolved on this column).
[f]Predominantly (75%) $22:1^{13}$ ($22:1^{5}$ isomer not resolved on this column).



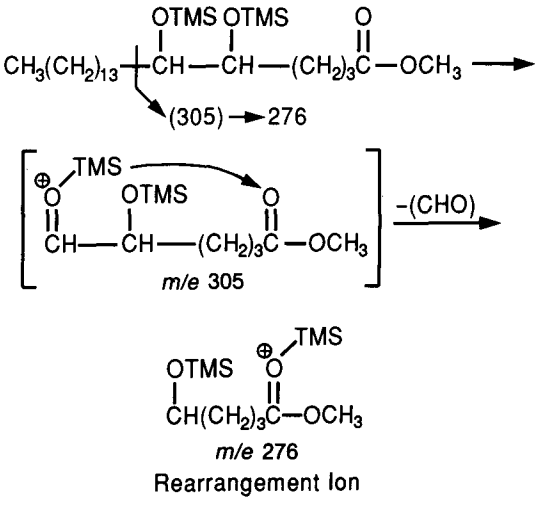
SCHEME 1

fragmentation patterns by MS than did either the silylated hydroxy-methoxy FAME or the underivatized epoxy FAME (12,13). Where di- or triepoxy products were produced (*e.g.*, from linoleic, 5,13-eicosadienoic or linolenic acid), they were converted to tetraol- or hexaol-TMS derivatives, respectively. From lesquerolic acid, a pair of diastereomeric 11,12,14 triol-TMS products were obtained as a result of the asymmetric center at C_{14} in lesquerolic acid. The GC curves for these silylated derivatives are shown in Figures 1C and 2C.

In general, mass spectra of silylated hydroxy FAME contain M−15 (methyl), M−31 (methoxyl), M−47 (methyl + methanol), M−90 [$(CH_3)_3SiOH$] and prominent *m/z* 73 ions [$(CH_3)_3Si^+$]. A generalized MS fragmentation pattern, such as the following, is appropriate for most of the derivatives prepared in this work (Scheme 2). Base or major ion fragments result from ionization and subsequent cleavage between OTMS groups, frequently with the charge carried by the carbomethoxy end of the molecule (Path a, Scheme 2). Major ions (or base ions) arise from this fragmentation when charge is carried by the hydrocarbon end of the molecule (Path b, Scheme 2). Prominent diagnostic ions arise when cleavage occurs on either side of the OTMS groups, with charge carried by the carbomethoxy end (Path c, Scheme 2) or hydrocarbon end (Path d, Scheme 2). The complexity of the mass spectrum increases as the number of TMS groups increases to three, four or more.



SCHEME 2



SCHEME 3

Frequently, rearrangement ions (12,14) result from Path c (Scheme 2) cleavage when the TMS group migrates to the acyl oxygen of the carbomethoxy group, during which 29 mass units (CHO) are lost, as in the following example (Scheme 3). These rearrangement ions are readily recognized by their even number masses.

Structural confirmation for the major FAME product of epoxidized lesquerella oil (Fig. 1B), methyl 11,12-epoxy-14-hydroxy-eicosanoate (*ca.* 57%, Table 1), is provided by the mass spectrum shown in Figure 3 for the silylated diastereomeric triol-A derivative (MW 590, Fig. 1C), methyl 11,12,14-tri(trimethylsilyloxy)-eicosanoate. The base peak at *m/z* 187 (100%) and small peak at *m/z* 415 (4%) locate the original hydroxyl group of lesquerolic acid, fragmentation occurring on the carbomethoxy- and on hydrocarbon-sides of the OTMS group at C_{14}, respectively. The major diagnostic ion at *m/z* 287 (45%) results from Path a (Scheme 2) cleavage between C_{11} and C_{12} OTMS groups, and, along with the rearrangement ion at *m/z* 360 (11%) and diagnostic ions at *m/z* 299 (2%) and 389 (<1%), locate the precursor epoxy group at the original 11,12 double bond of lesquerolic acid (Fig. 3).

Justification for labeling peak B in Figure 1C as the diastereomeric methyl 11,12,14-tri(trimethylsilyloxy)-eicosanoate is warranted by the exact identity of triol-B's mass spectrum (not shown) to that of the silylated triol-A (Fig. 3). Interestingly, the asymmetric center at C_{14} in

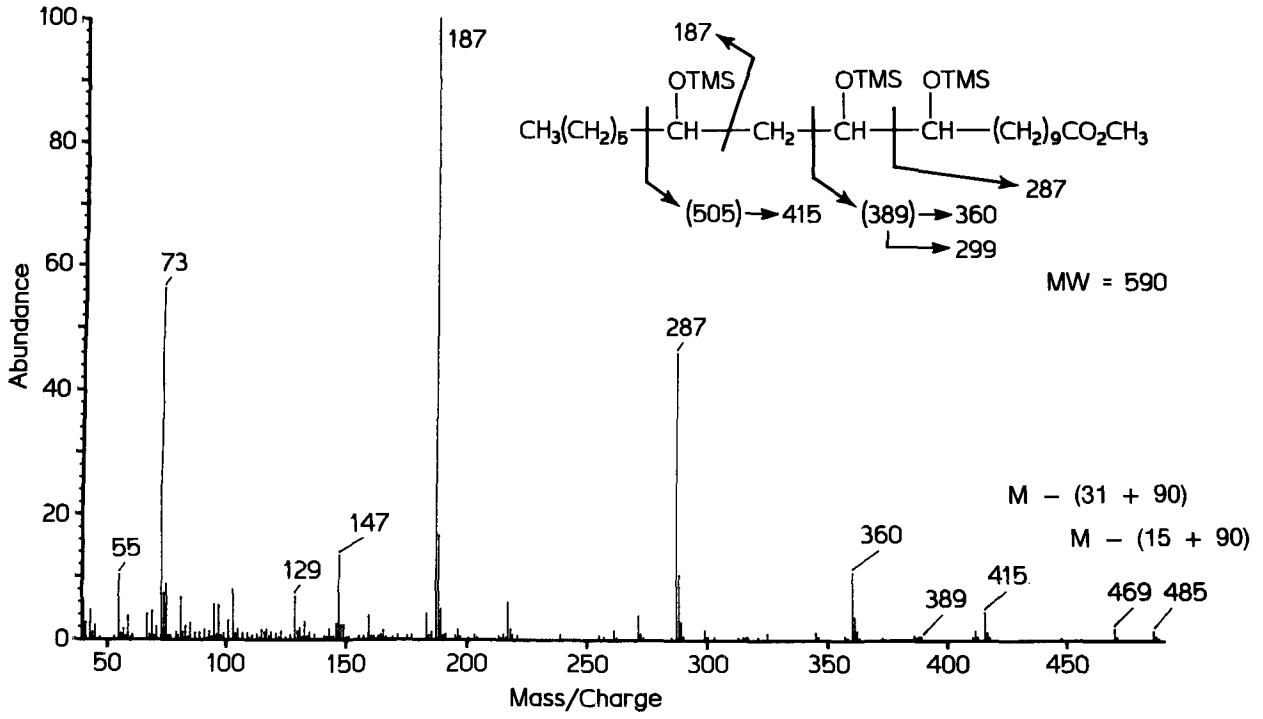


FIG. 3. Electron impact (70 eV) mass spectrum of methyl 11,12,14-tri-(trimethylsilyloxy)-eicosanoate (MW 590), a triol derivative (A, Fig. 1C) of the major product (57%, methyl 11,12-epoxy-14-hydroxy-eicosanoate, Fig. 1B) from epoxidized *Lesquerella gordonii* oil. MW, molecular weight. OTMS, trimethylsilyl ether.

lesqueroloyl groups in lesquerella oil must result in the production of diastereomeric hydroxy epoxides in the epoxidized oil, yet their FAME give a single GC peak on the nonpolar capillary column (Fig. 1B). In contrast, the presence of two asymmetric centers (C_{12}, C_{13}) in the vernoloyl groups in vernonia oil previously resulted in the production of diastereomeric methyl 9,10-epoxy-12,13-epoxy-octadecanoates, which were separable by GC, even on a short nonpolar capillary column (3).

The other major epoxy FAME obtained from epoxidized lesquerella oil (Fig. 1B), 9,10 epoxy-stearate (*ca.* 22%, Table 1), arises from epoxidation of oleoyl groups in the oil. The mass spectrum (not shown) of its silylated diol derivative (MW 474) provided confirmation of its structure. The base peak was *m/z* 73. Major ions at *m/z* 259 (90%) and 215 (64%) arise from Paths a and b cleavages, respectively (see generalized fragmentation, Scheme 2), whereas *m/z* 332 (16%) is the expected rearrangement ion resulting from Path c cleavage and TMS migration with loss of CHO (*m/z* 361-29). The small diagnostic ion at *m/z* 317 confirms Path d cleavage. Mass spectra of the epoxy FAME and its hydroxy-methoxy derivatives provided additional confirming evidence (6,12,13).

Assignment of peaks in Figure 1B to di- and triepoxy stearates, generated from linoleic and linolenic acid, respectively, in lequerella oil, were made on the basis of their ECL values as compared to those of authentic epoxy FAME from epoxidized soybean and epoxidized linseed oils. No mass spectral confirmation of these assignments were made.

Structural confirmation for the major FAME product of epoxidized limnanthes oil (Fig. 2B), methyl 5,6-epoxy-eicosanoate (*ca.* 63%, Table 2), is provided by the mass spectrum shown in Figure 4 for the silylated diol derivative (MW 502, Fig. 2C). The base peak at *m/z* 203 (100%) and the major diagnostic ion at *m/z* 299 (55%) result from Paths a and b cleavages (Scheme 2), respectively, between the two OTMS groups at C_5 and C_6. The rearrangement ion at *m/z* 276 (12%) and diagnostic ion at *m/z* 401 (1%) identify cleavages on the hydrocarbon- and carbomethoxy-sides, respectively, of the OTMS groups (Paths c and d, Scheme 2). Additional ions at *m/z* 471 (4%, M−31) and *m/z* 397 (2%, M−[15 + 90]) provide evidence of the derivatives MW of 502. These MS data provide conclusive evidence for locating the epoxy group at the original 5,6 double bond of *cis*-5,6-eicosenoic acid in limnanthes oil.

MS confirmations of silylated diol derivatives of two other limnanthes monoepoxy FAME, 5,6-epoxy-docosanoate (3%) and 13,14-epoxy-docosanoate (11%, Table 2 and Fig. 2B and C) are equally straightforward. Thus, the base peak at *m/z* 203 (100%) and the major diagnostic ion at *m/z* 327 (54%) for methyl 5,6-di(trimethylsilyloxy)docosanoate (Fig. 5) represent Paths a and b cleavages (Scheme 2), respectively, between the OTMS groups. Hydrocarbon-side cleavage (Path c, with loss of 29 mass units) is again illustrated by the rearrangement ion at *m/z* 276 (14%).

For methyl 13,14-di(trimethylsilyloxy)-docosanoate (Fig. 6), the base peak at *m/z* 315 (100%, Path a cleavage, Scheme 2) and major ion at *m/z* 215 (69%, Path b cleavage, Scheme 2) are the results of expected cleavage between

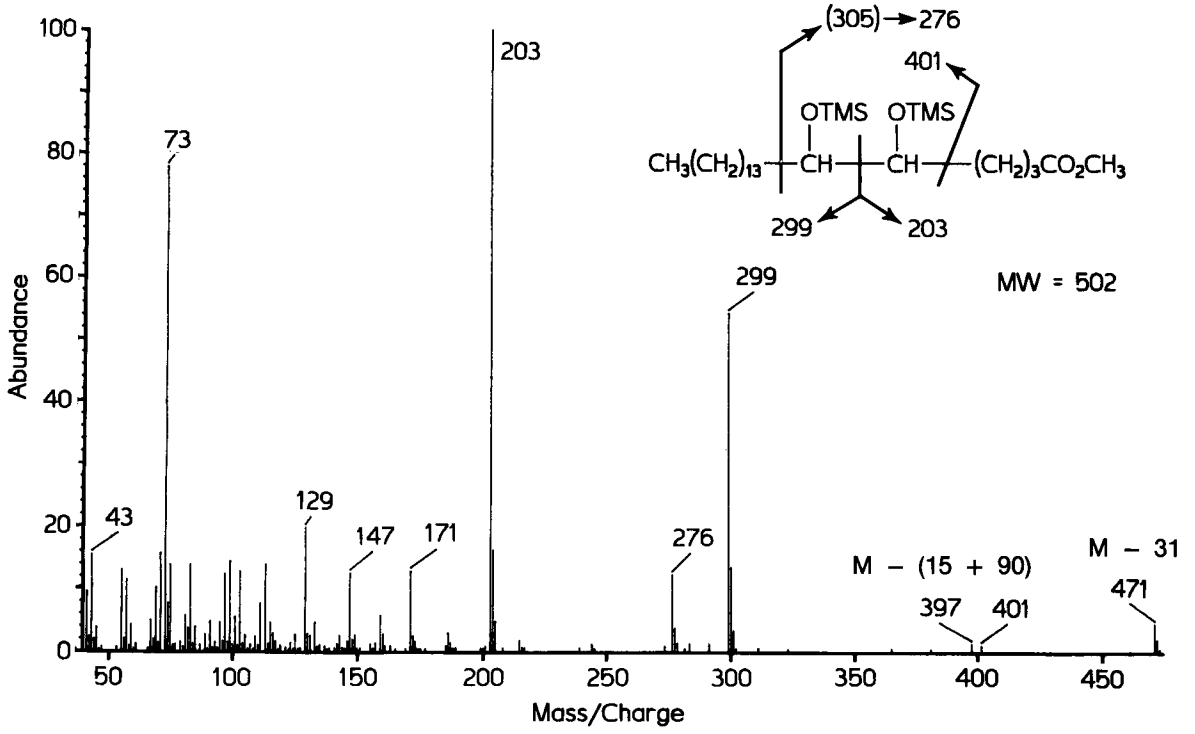


FIG. 4. Electron impact (70 eV) mass spectrum of methyl 5,6-di(trimethylsilyloxy)-eicosanoate (MW 502), a derivative (Fig. 2C) of the major product (63%, methyl 5,6-epoxy-eicosanoate, Fig. 2B) from epoxidized *Limnanthes alba* oil. Abbreviations as in Figure 3.

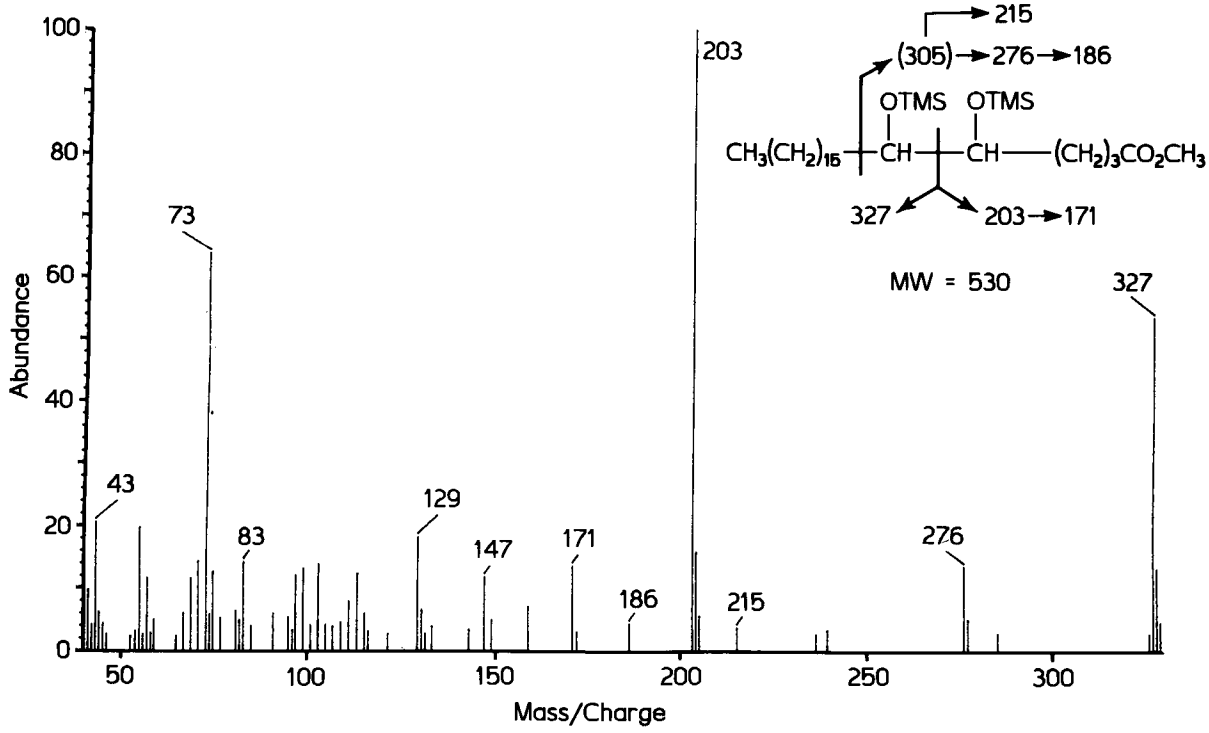


FIG. 5. Electron impact (70 eV) mass spectrum of methyl 5,6-di(trimethylsilyloxy)-docosanoate (MW 530, a derivative (Fig. 2C) of a minor product (3%, methyl 5,6-epoxy-docosanoate, Fig. 2B) from epoxidized *Limnanthes alba* oil. Abbreviations as in Figure 3.

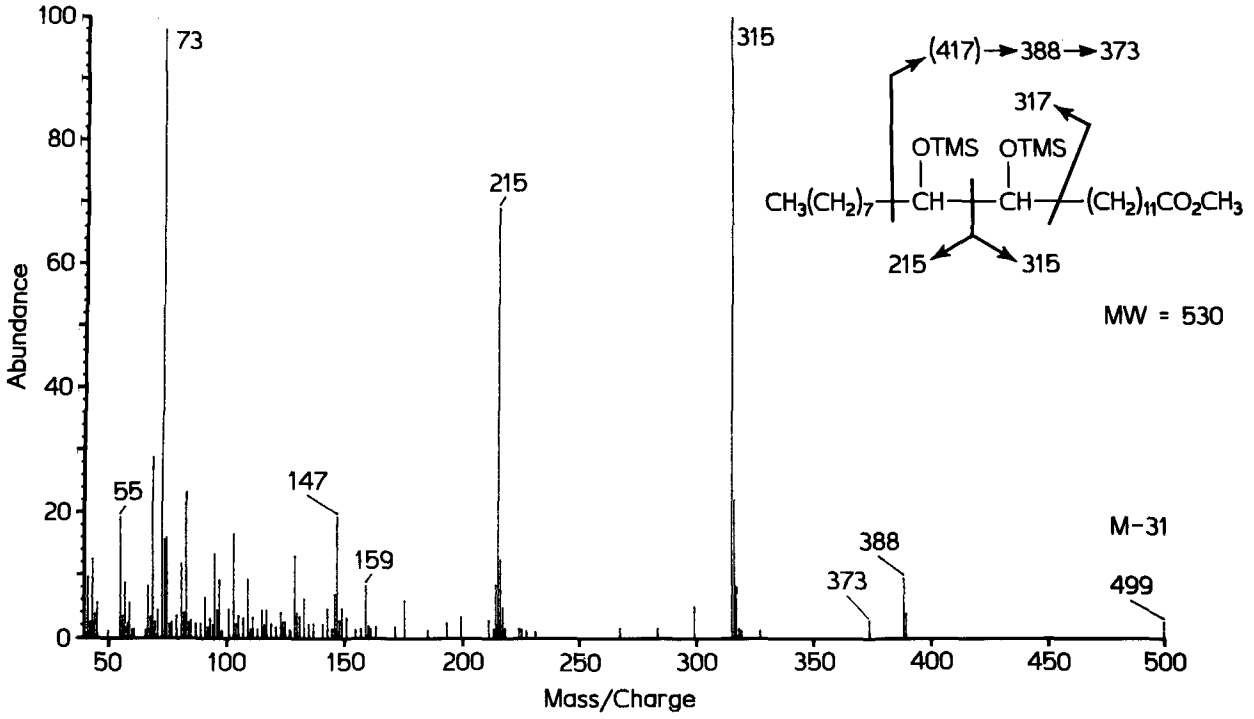


FIG. 6. Electron impact (70 eV) mass spectrum of methyl 13,14-di-(trimethylsilyloxy)-docosanoate (MW 530), a derivative (Fig. 2C) of a significant product (11%, methyl 13,14-epoxy-docosanoate, Fig. 2B) from epoxidized *Limnanthes alba* oil. Abbreviations as in Figure 3.

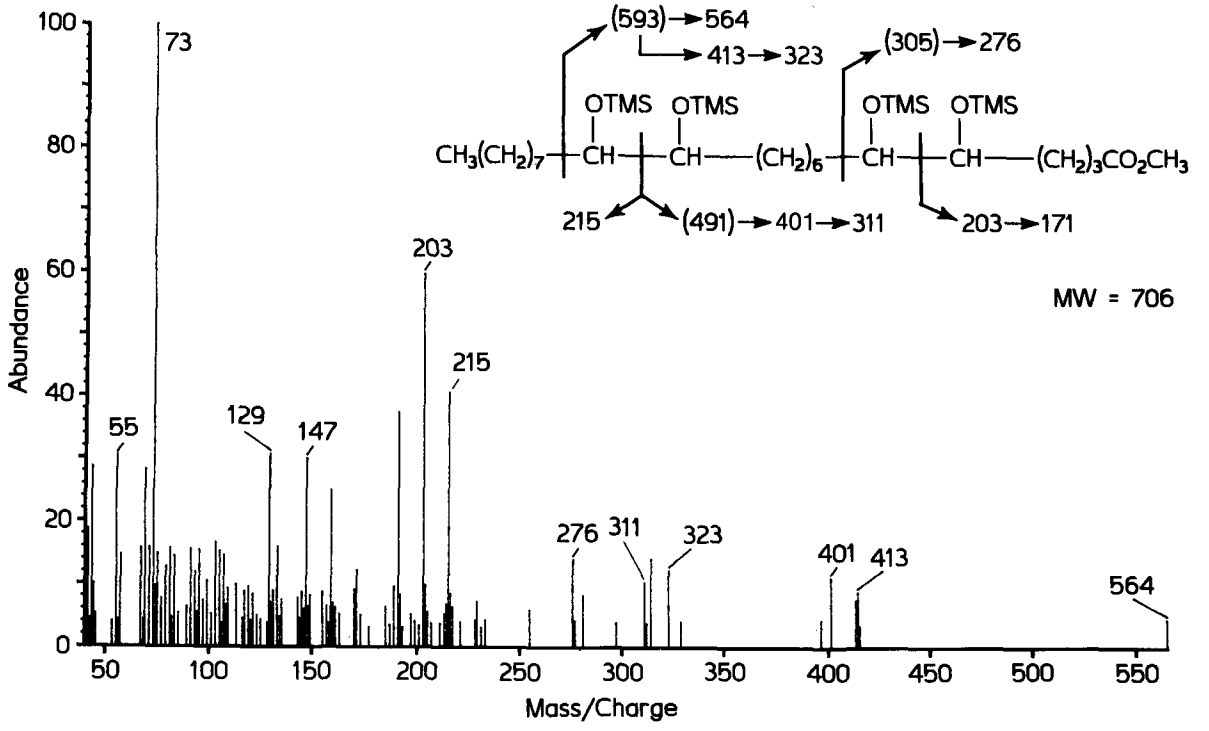


FIG. 7. Electron impact (70 eV) mass spectrum of methyl 5,6,13,14-tetra-(trimethylsilyloxy)-docosanoate (MW 706), a derivative (Fig. 2C) of a significant product (14%, methyl 5,6-epoxy-13,14-epoxy-docosanoate, Fig. 2B) from epoxidized *Limnanthes alba* oil. Abbreviations as in Figure 3.

the OTMS groups at C_{13} and C_{14}. Cleavage on either side of the OTMS groups accounts for the rearrangement ion at *m/z* 388 (10%, Path c, with loss of CHO, Scheme 2) and diagnostic ion at *m/z* 317 (8%, Path d, Scheme 2). The MW 530 is implied by the ion at *m/z* 499 (3%, M−31).

The last significant FAME product from epoxidized limnanthes oil is methyl 5,6-epoxy-13,14-epoxy-docosanoate (14%, Table 2 and Fig. 2B and C). MS of the silylated tetraol derivative, methyl 5,6,13,14-tetra(trimethylsilyloxy)-docosanoate (Fig. 7), gave major ions at *m/z* 203 (60%, cleavage Path a between the C_5 and C_6 OTMS groups) and *m/z* 215 (41%, Path b cleavage between the C_{13} and C_{14} OTMS groups). Also observed are the expected rearrangement ions at *m/z* 276 (14%, Path c cleavage between C_6 and C_7, with loss of CHO) (Scheme 2). Multiple losses of 90 mass units [$(CH_3)_3SiOH$] from intermediate primary ions (*m/z* 593 and 491) are apparent from ions at *m/z* 413 (9%), 401 (11%), 323 (12%) and 311 (10%). The base peak is *m/z* 73 [$(CH_3)_3Si^+$].

The MS data presented above support the structures of all major epoxidation products. The results of this study clearly show that epoxidation of lesquerella and limnanthes oils with *m*-Cl-peroxybenzoic acid proceeded in a straightforward manner. Neither the location of the double bond (Δ-5, -9 or -13), nor the proximity of a reactive β-hydroxyl group influenced the addition of active oxygen to points of unsaturation, except that the asymmetric center at C_{14} in lesquerolic acid resulted in the formation of hydroxy-epoxides that yielded diastereomeric triol derivatives.

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