Autoxidation of the Furan Fatty Acid Ester, Methyl 9,12-Epoxyoctadeca-9,11-dienoate

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ABSTRACT: The objective of this study was to identify autoxidation products of methyl 9,12-epoxyoctadeca-9,11-dienoate ($F_{9,12}$). Previous work has shown that $F_{9,12}$ is a product both of autoxidation and singlet oxygen oxidation of the methyl ester derivative of conjugated linoleic acid (CLA). $F_{9,12}$, 95% pure, was synthesized from methyl ricinoleate. The synthetic $F_{9,12}$ was heated at 50°C in sealed tubes containing air. Each tube contained 6 mg $F_{9,12}$ and 1 mg methyl stearate as an internal standard. Samples were taken at 4.5, 7, 23, 46.5, 69.5, and 93 h. The oxidized $F_{9,12}$ was dissolved in isooctane and analyzed by gas chromatography (GC), GC-direct deposition-Fourier transform infrared spectroscopy, and GC-electron ionization mass spectrometry. CLA methyl ester was oxidized in a similar manner. Under these conditions, the half-lives of CLA and $F_{9,12}$ were 40 and 35 h, respectively. Oxidation products of $F_{9,12}$ that were identified included: 5-hexyl-2-furaldehyde (**I**), methyl 8-oxooctanoate (**II**), methyl 13-oxo-9,12-epoxytrideca-9,11-dienoate (**III**), methyl 8-oxo-9,12-epoxy-9,11-octadecadienoate (**IV**), and methyl 13-oxo-9,12-epoxy-9,11-octadecadienoate (**V**).

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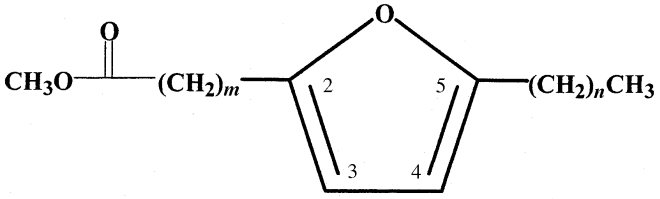
KEY WORDS: Autoxidation of furan fatty acids, conjugated linoleic acid (CLA), furan fatty acids.

Methyl 9,12-epoxyoctadeca-9,11-dienoate ($F_{9,12}$) is one of several secondary autoxidation products of methyl esters of conjugated linoleic acid (CLA) (1). CLA, a mixture of geometric and positional isomers of octadecadienoic acid containing conjugated double bonds, is reported to have a broad range of anticarcinogenic and other physiological properties in animals dosed near the levels that occur naturally in some foods (2,3).

The furan moiety of $F_{9,12}$ was first identified as a component of *Exocarpus* seed oil (4). This was the first report of a naturally occurring 2,5-disubstituted furan fatty acid moiety (F-acid). The general formula for F-acids is shown as the methyl ester in Scheme 1. (For a C_{18} F-acid $m = 7$ and $n = 5$.) Since the first report of $F_{9,12}$, many different C_{18} and C_{20} F-acids have been reported in fish (5,6), latex (7), cattle liver (8), and plants (9). In these F-acids, the 3- and 4-positions of the furanyl moiety may also contain a methyl group.



SCHEME 1

Previous studies of oxidations of the 2,5-disubstituted F-acid moiety showed that it does not have the strong antioxidant properties that are associated with the tri- or tetra-alkyl substituted F-acids (10). Oxidation with lipid hydroperoxides (11,12), *m*-chloroperoxybenzoic acid (13), or ultrasound (14) yields products with a dioxoene functional group (e.g., methyl 9,12-dioxooctadec-10-enoate). Compounds with the dioxoene function are reported to be strong inhibitors of blood platelet aggregation (15). Oxidation of $F_{9,12}$ on silica is reported to produce several products including methyl 9,12-dioxooctadeca-7,10-dienoate and methyl 9,12-dioxooctadeca-10,13-dienoate (16).

The results presented here differ from previous oxidations both in the experimental design (exposure to ambient air) and in the products identified. Data presented here are limited to those compounds that elute in <1.5 h using a CP-Sil 88 capillary column.

MATERIALS AND METHODS

Oxidation. $F_{9,12}$ (60 mg) and methyl stearate (10 mg) were dissolved in 10 mL of petroleum ether (bp 30–60°C). This solution (1 mL) was added to each of seven test tubes (110-mL volume) and the petroleum ether was removed from the tubes by a stream of argon. The tubes, containing air, were capped and placed in an oil bath at 50°C. Individual tubes were removed from the bath at 4.5, 7.0, 23.0, 46.5, 69.5, and 93 h and stored for at least 1 h at −20°C prior to gas chromatography (GC) analysis. The materials were dissolved in 2 mLof isooctane for injection. A similar experiment was performed with the methyl esters of CLA. The solution was injected into the gas chromatograph without any further cleanup.

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GC and GC–electron ionization mass spectrometry (GC–EIMS). GC was performed by using a Hewlett-Packard (Avondale, PA) 5890A instrument under the following conditions: column, 50 M × 0.25 mm i.d. CP Sil 88 (Chrompack, Raritan, NJ) capillary; helium carrier gas; flame ionization detector (FIO); temperatures (°C): injector 220, detector 280, column 75 for 2 min, raise 20°C/min to 185°C and hold for 33 min, raise at 4°C/min to 225°C. Samples were run in both split and splitless modes.

Low- and high-resolution GC–EIMS analyses were obtained with a Hewlett-Packard 5890 series II gas chromatograph coupled to a Micromass (Manchester, United Kingdom) Autospec Q mass spectrometer and OPUS 4000 data system. The GC–MS system utilized version 2.1 BX software.

The same capillary GC column used to obtain FID data was used to obtain GC–EIMS data. Adjusting the capillary GC column head pressure to 10 psi gave chromatographic results comparable to those used to obtain the GC FID data. The GC–EIMS conditions were: splitless injection with helium sweep restored 1 min after injection; injector and transfer lines 250°C; oven 75°C for 2 min after injection, then raise 20°C/min to 185°C, hold at 185°C 15 min, raise 4°C/min to 225°C, hold at 225°C for 5 min.

The mass spectrometer was tuned to a resolution of 1000 (5% valley) by observing *m/z* 305 in the EI mass spectrum of perfluorokersene (PFK). The mass scale was calibrated with PFK for magnet scans from 440 to 44 daltons at 1 s per decade. Filament emission was 200 μA at 70 eV. Ion source temperature was 250°C. High-resolution MS data were obtained by GC–EIMS with the mass spectrometer operated in voltage scan mode at 11 K resolution.

GC–direct deposition–Fourier transform infrared (GC–DD–FTIR). A Bio-Rad Digilab division (Cambridge, MA) direct deposition Tracer FTS-60A mid-infrared transmission (4000–600 cm^{-1}) system and a Hewlett- Packard model 5890 Series II gas chromatograph were used. This system, which was used with a CP-Sil-88 capillary column, has been described in detail (17). Sixty-four scans were collected at 4 cm^{-1} resolution. The GC effluent was sprayed on a moving 60 × 30 mm ZnSe crystal; the crystal was mounted on a copper block cooled with liquid N_2. The block was mounted on motorized X-Y stage in a vacuum chamber; the IR beam was focused onto the frozen analytes that gave rise to GC peaks. The transmitted IR beam was focused onto a 0.1 mm mercury cadmium telluride detector and the IR measurement took place in real-time and post-GC run modes.

^{1}H nuclear magnetic resonance (NMR) and proton-decoupled ^{13}C NMR spectra. The spectra, described by 32,768 data points (real part), were obtained at 400 and 100 MHz (with broad-band irradiation at 400 MHz for the latter), respectively, by using a Varian NMR Instruments VXR-400S spectrometer equipped with a Nalorac Z-SPEC MD-400-3 microprobe. ^{1}H and ^{13}C pulse widths of 6.7 and 5 μs were employed at transmitter powers of 55 and 53, which correspond to tip angles of 60 and 45°, respectively, with 3-mm sample tubes. ^{1}H and ^{13}C spectral widths of 4 and 20 kHz were used, corresponding to acquisition times of *ca.* 4.1 and 0.82 s, respectively. Both ^{1}H and ^{13}C chemical shifts were referenced to $CDCl_3$ and are reported relative to TMS. Homonuclear 2-dimensional spectra (COSY, NOESY) were recorded with spectral widths of 4164 Hz in each domain while heteronuclear 2-D spectra (HETCOR, HMBC) had spectral widths of 4164 Hz in the ^{1}H domain and 20K Hz in the ^{13}C domain. Both types of spectra were recorded with 1024 data points in the F2 dimension and with 256 incremented spectra of either 16 (COSY, NOESY), 64 (HMBC), or 256 scans (HETCOR) each. Free-induction decays were processed as 2048 × 2048 matrices with appropriate linear prediction, zero-filling, and sine bell (COSY, HETCOR), gaussian (NOESY), or shifted-sine bell (F2)/gaussian (F1) weighting.

Attenuated total reflection (ATR) FTIR spectroscopy. Neat 5-hexyl-2-furaldehyde (50 μL) was examined by using the Bio-Rad FTS-60A system equipped with a ZnSe single bounce horizontal ATR (18) cell (Spectra-Tech, Stamford, CT).

Methyl 9,12-epoxyoctadeca-9,11-dienoate. $F_{9,12}$ was synthesized from methyl ricinoleate and purified by silica chromatography as previously described (16,19).

*Methyl 9,12-dioxo-octadeca-*cis*-10-enoate.* Methyl 9,12-dioxo-octadeca-*cis*-10-enoate was synthesized by the reaction of $F_{9,12}$ with *m*-chloroperoxybenzoic acid as reported for methyl 8,11-dioxo-octadeca-*cis*-9-enoate (13).

*5-Hexyl-2-furaldehyde (***I***).* **I** was prepared as previously described (20): 1.2 mL (1.974 g = 0.014 mol) phosphorus oxychloride was added dropwise to 4 mL dimethylformamide at <0°C. The solution was stirred for 1 h at <0°C and then a solution of 1.52 g (0.01 mol) 2-hexylfuran in 4 mL dimethylformamide was added slowly. The reaction mixture was stirred at <0°C for 1 h and maintained at room temperature for an additional 1.5 h. The reaction mixture was then poured into ice water, and solid sodium carbonate (5 g) was added to the aqueous mixture. The mixture was left at room temperature for 16 h. The aqueous mixture was extracted three times with petroleum ether. The petroleum ether was dried with sodium sulfate and then removed, yielding 0.96 g of a dark yellow liquid (53%). Purity was 95.3% as determined by GC. The mass and FTIR and NMR spectra are presented in the Results and Discussion section.

RESULTS AND DISCUSSION

The GC data, based on a neat injection of 0.1 μL, showed a 95+% purity for the synthesized $F_{9,12}$. Figure 1 shows a chromatogram obtained for an open-air oxidation of $F_{9,12}$ for 3 d at 50°C (see the Material and Methods section for parameters used with the CP-Sil 88 column). The numbered peaks were identified from information obtained by using GC-DD-FTIR and high- and low-resolution GC–EIMS.

Peak 1, or (**I**), was confirmed by comparison with a synthetic reference (Material and Methods section). The NMR assignments are given in Scheme 2 (those for ^{13}C are underlined) and the connectivities are indicated in Table 1. The FTIR and GC–EIMS spectra obtained for the synthetic **I** were

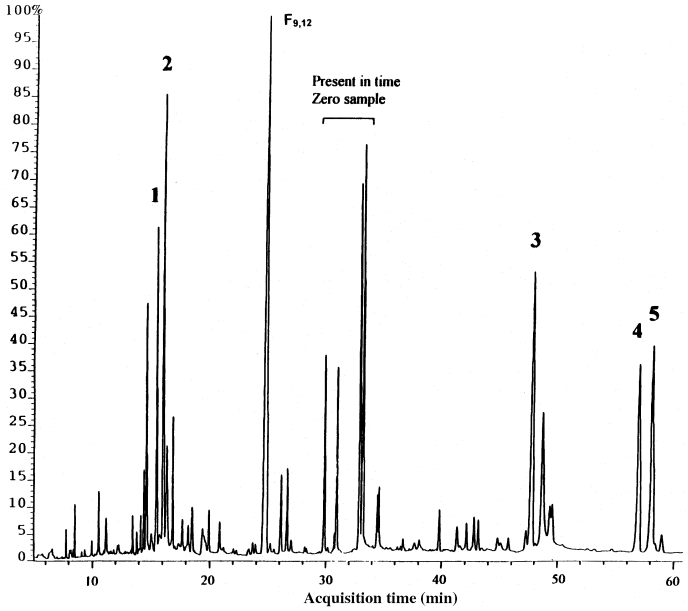
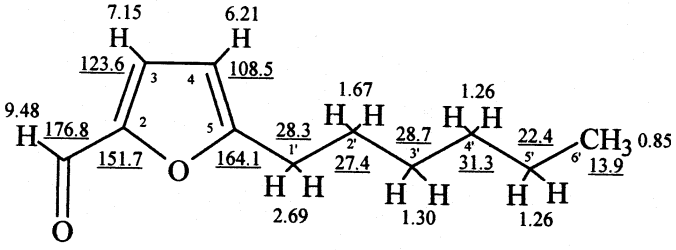


FIG. 1. Gas chromatogram with electron ionization mass spectrometry (GC–EIMS) total ion current detection for $F_{9,12}$, oxidized for 3 d in open air at 50°C. Numbered peaks are identified in the Results and Discussion section. Peaks eluting from 29–34 min were present in the original $F_{9,12}$ reference material.



SCHEME 2

TABLE 1
^{1}H and ^{13}C Nuclear Magnetic Resonance Data[a] for 5-Hexyl-2-furaldehyde

Position	^{1}H	^{13}C	Indirect CH connectivities[b]
2	—	151.7	9.48, 7.15, 6.21
3	7.15d (3.5)	123.6	9.48, 6.21
4	6.21d (3.5)	108.5	7.15, 2.69
5	—	164.1	7.15, 6.21, 2.69, 1.67
1′	2.69 t (7.6)	28.3	1.67, 1.30
2′	1.67 qu (7.6)	27.4	2.69, 1.30, 1.26
3′	1.30 m	28.7	2.69, 1.67, 1.26
4′	1.26 m	31.3	1.67, 1.30, 1.26, 0.85
5′	1.26 m	22.4	1.30, 1.26, 0.85
6′	0.85 t (6.7)	13.9	1.26
CHO	9.48	176.8	7.15

[a]Chemical shifts referenced to $CDCl_3$ at 7.26 ppm ^{1}H and 77 ppm ^{13}C; *J*-values in Hz in parentheses.
[b]Proton multiple bond connectivities (HMBC).

useful for the identification of peaks 3–5 (Fig. 1). The FTIR of **I** is illustrated in Figure 2. The band frequencies (cm^{-1}) for the specific functional groups are indicated in the figure. Of special note are bands indicating the conjugation of –C=O

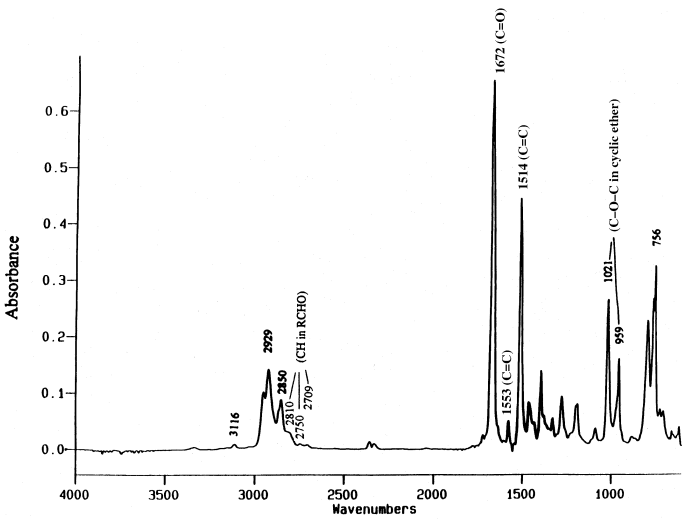


FIG. 2. Attenuated total reflection Fourier transform infrared (FTIR) spectrum of 5-hexyl-2-furaldehyde (**I**). Frequencies are listed for 4 cm^{-1} resolution. The three weak bands at 2709, 2750, and 2810 cm^{-1} are characteristic of the aldehyde C–H stretch, and overtone or combination vibrations (Ref. 24).

(1672 cm^{-1}) with –RC=CH– (1583 and 1514 cm^{-1}). The same three bands, obtained by GC–DD–FTIR (Fig. 3), occurred for peaks 3–5. An additional frequency at 1730 cm^{-1} was also present for these compounds, indicating the presence of an additional ester carbonyl group. Peak 2 was identified as methyl 8-oxooctanoate (**II**) by comparison with its library mass spectrum and the presence of carbonyl IR bands (cm^{-1}) at 1733 (R′COOR) and 1720 (R′CHO) in its IR spectrum.

The GC–EIMS data show molecular weights (*m/z*) of 180 for **I**, 252 for peak 3, and 322 for both peaks 4 and 5. The EI

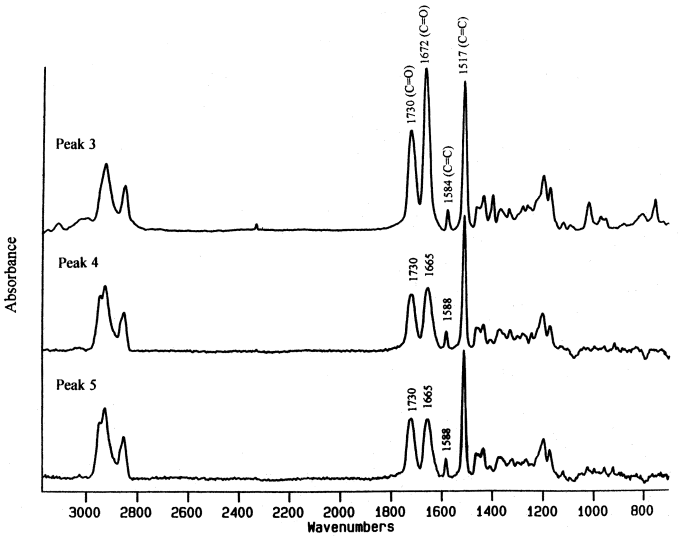


FIG. 3. Gas chromatography–direct deposition–FTIR spectra for peaks 3–5 shown in Figure 1. Wavenumbers (cm^{-1}) are indicated for ester carbonyl (1730) and for α,β-conjugated R_2C=O (1665–1672). The –RC=CH– structure exhibited bands at 1517 and 1584–1588 cm^{-1} (Ref. 24). For abbreviation see Figure 2.

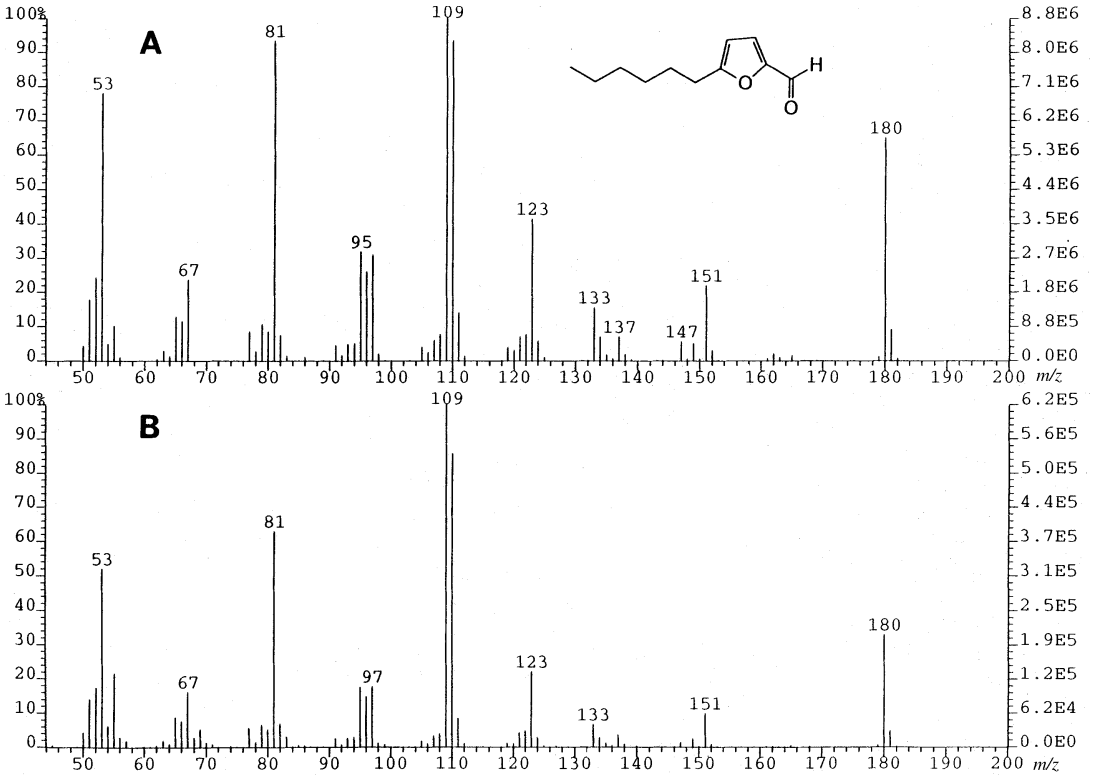


FIG. 4. EI mass spectra of (A) synthetic 5-hexyl-2-furaldehyde (**I**) and (B) gas chromatographic peak 1 in Figure 1. For abbreviations see Figures 1 and 2.

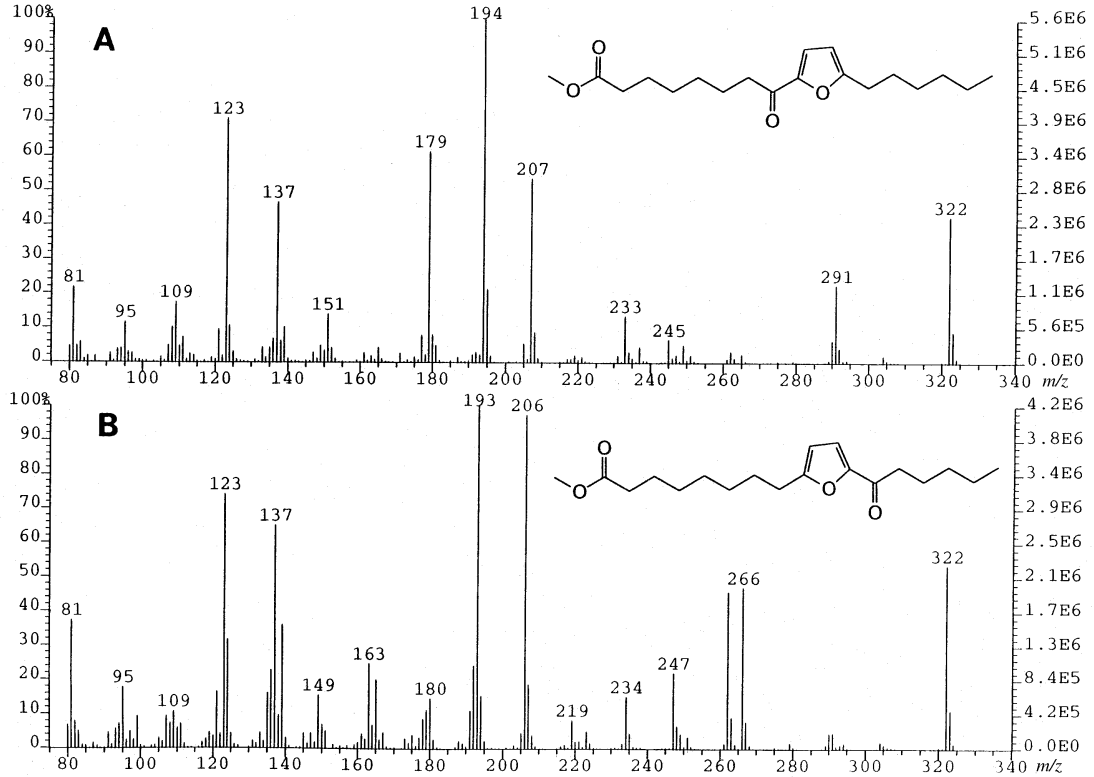


FIG. 5. EI mass spectra of peak 4 identified as methyl 8-oxo-9,12-epoxy-9,11-octadecadienoate (**IV**) in Figure 5A and peak 5 identified as methyl 13-oxo-9,12-epoxy-9,11-octadecadienoate (**V**) in Figure 5B. For abbreviation see Figure 1.

mass spectrum of **I** is shown in Figure 4A. Their mass spectra are characterized by successive losses from the alkyl chain (*m/z* 165, 151, 137, 123, 109) and a hydrogen rearrangement with cleavage of the chain β to the furan ring (*m/z* 110). The low-mass ion series (*m/z* 81, 95, 109) attributed to furylalkyl compounds (21) is present in the mass spectrum of **I** and in the mass spectra of peaks 1 and 3–5. The IR spectrum of peak 3, which is consistent with an α,β-conjugated carbonyl and an additional ester carbonyl, was identified as methyl 13-oxo-9,12-epoxytrideca-9,11-dienoate (**III**).

The components eluting at retention times between 29 and 34 min are impurities in the synthesized $F_{9,12}$ such as dihydrofuran fatty acid methyl esters (16).

GC–FTIR data provided evidence (above) of the presence of a conjugated carbonyl in both peaks 4 and 5. The GC–EIMS data for peaks 4 and 5 are shown in Figure 5. Loss of the elements of water (*m/z* 304) from the molecular ion (*m/z* 322) and the presence of the acylium ion (*m/z* 291) are consistent with a methyl ester structure. The abundant ions in the EI mass spectra of methyl 8-oxo-9,12-epoxy-9,11-octadecadienoate (**IV**) and methyl 13-oxo-9,12-epoxy-9,11-octadecadienoate (**V**) arise from fragmentation directed by the keto and furan functions. The most readily understood processes that may occur are (i) cleavage α to the carbonyl, (ii) cleavage β to the furan ring, (iii) γ hydrogen rearrangements with cleavage β to the carbonyl, and (iv) cleavage γ to the carbonyl corresponding to allylic bond rupture of the enol form or formation of a cyclic oxonium ion (22). The structures of **IV** and **V** are such that some of the postulated fragmentation pathways may produce isobaric products. For example, cleavage of the carbon chain of the 8-oxo isomer (**IV**) α to the carbonyl (i) and cleavage β to the furan ring (ii) of the 13-oxo isomer (**V**) would give rise to *m/z* 179 (Scheme 3). Cleavage of the carbon chain α to the carbonyl (i) would give rise to *m/z* 251 for compound **V**, but cleavage β to the ring (ii) of **IV** would also give rise to *m/z* 251. Thus, the task of distinguishing between the two molecules requires rationalizing fragmentations that are unique for each structure. This task is aided by elemental composition data for the ions of interest.

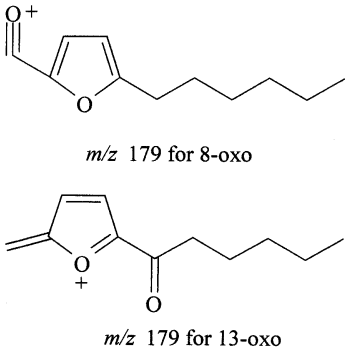
An elemental composition of $C_{12}H_{17}O_2$ for *m/z* 193 in Figure 4B is consistent with cleavage γ to the furan ring for compound **V**. γ-Hydrogen rearrangement to the furan oxygen would result in radical-directed cleavage γ to the furan ring (Scheme 4).

γ-Hydrogen rearrangement to a carbonyl oxygen with cleavage β to the carbonyl (category iii, above) can occur at the ester or keto function. This process is the origin of *m/z* 74 in the EI mass spectra of saturated fatty acids. γ-Hydrogen rearrangement at the keto function with cleavage β to the carbonyl will give rise to *m/z* 194 if the keto is at C_8 (compound **IV**), and *m/z* 266 if the keto is at C_{13} (compound **V**) (Scheme 5).

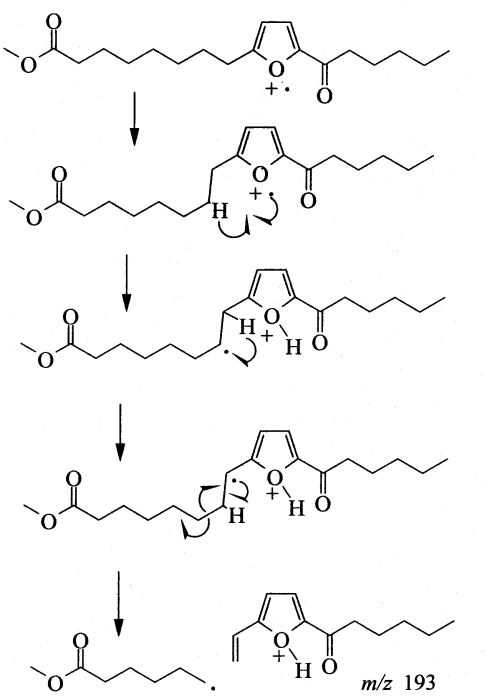
γ-Hydrogen rearrangement in the molecular ion and neutral losses of the elements of methanol and carbon monoxide may account for the presence of *m/z* 290 and 262 in the spectra. Corresponding losses from the ion at *m/z* 266 for compound **V** would result in *m/z* 234 and 206 in Figure 4B. Cleavage γ to the ketone (category iv, above) would give rise to three possible ion structures corresponding to *m/z* 207 for compound **IV** and *m/z* 279 for compound **V** (Scheme 6).

On the basis of the MS and IR data, the mass spectrum in Figure 4A is identified as that of the 8-oxo isomer (**IV**) and the mass spectrum in Figure 4B is identified as that of the 13-oxo isomer (**V**). Thus, GC peak 4 is assigned the structure of compound **IV** and GC peak 5 that of compound **V**.

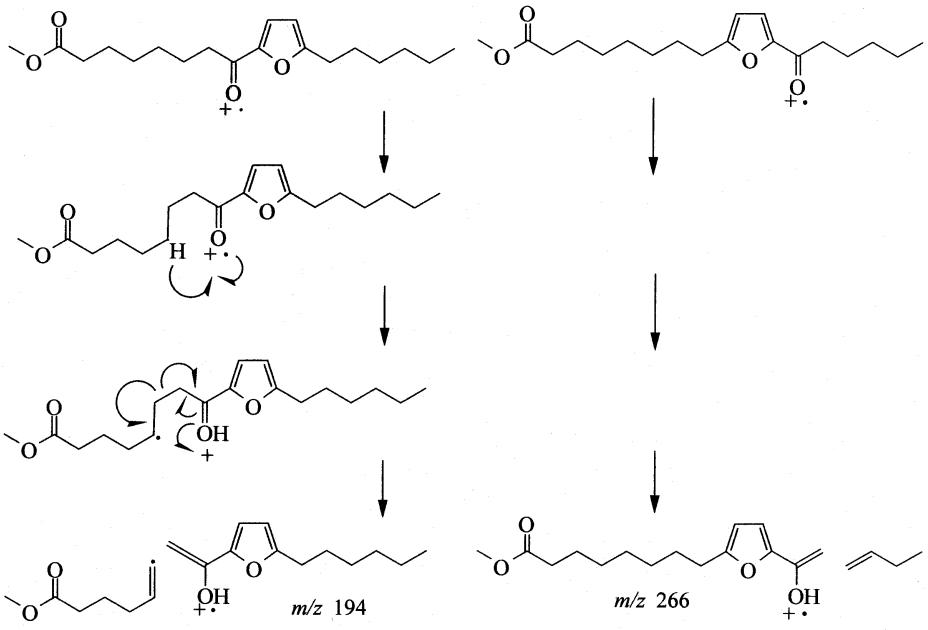
The rate of oxidation for $F_{9,12}$ was determined in sealed tubes containing 110 cm^3 air in order to avoid ambient singlet oxygen, which is known to react with conjugated dienes (23). The appearance (mg × 50) of oxidation products **I**, **II**, and **IV** is shown in Figure 6. The appearance of **V** is quantitatively equivalent to **IV** and is therefore not shown. The time at which [**I**] and [**III**] maximize is *ca.* 28 h, whereas concentrations of **IV** and **V** (not shown) continue to increase at 93 h. These data are consistent with these sets of products arising



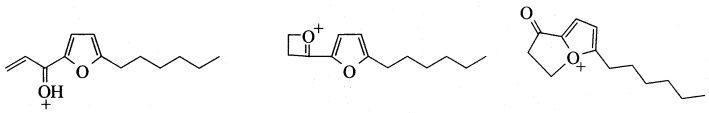
SCHEME 3



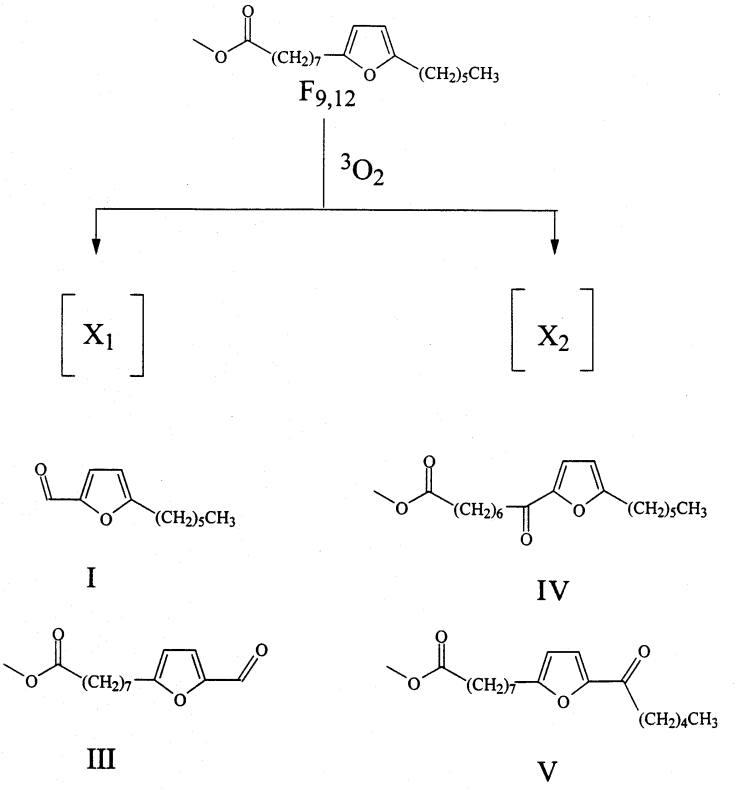
SCHEME 4



SCHEME 5



SCHEME 6



SCHEME 7

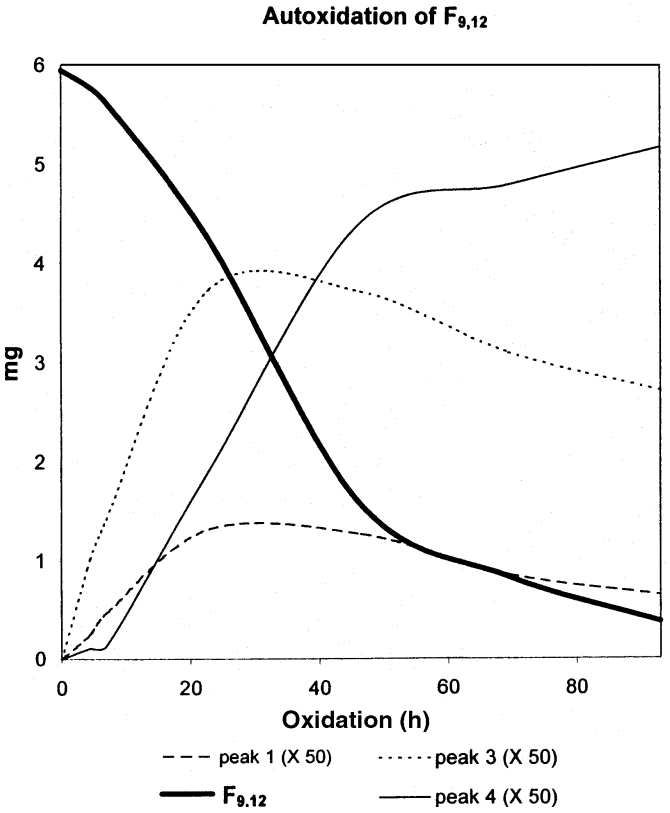


FIG. 6. The disappearance of $F_{9,12}$ and the amounts (mg × 50) of peaks 1, 3, and 5 vs. oxidation time (sealed tubes at 50°C).

from different intermediates (Scheme 7). One-half of the $F_{9,12}$ is oxidized at *ca.* 35 h. Methyl esters of CLA are 50% oxidized at *ca.* 40 h under similar conditions. The quantities of oxidation products detected by GC is low compared to the [$F_{9,12}$] at time zero (e.g., the sum of **IV** and **V** present at 93 h of oxidation amounts to 5% of the total mass balance). Of the six compounds indicated in Figure 1, only $F_{9,12}$ and **II** were detected in the oxidation of methyl CLA. This work is limited to the identification of compounds eluting <1.5 h on the CP-Sil 88 column. The compound methyl 9,12-dioxooctadecadec-10-enoate did not give a response either for the compound itself or for any artifact or breakdown products using the parameters described here.

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