Photosensitized Oxidation of Methyl Linoleate Monohydroperoxides: Hydroperoxy Cyclic Peroxides, Dihydroperoxides, Keto Esters and Volatile Thermal Decomposition Products[1]

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ABSTRACT

Previous studies of lipid secondary oxidation products have been extended to 6-membered hydroperoxy cyclic peroxides from the singlet oxygenation of a mixture of 9- and 13-hydroperoxides from autoxidized methyl linoleate. The oxidation product was fractionated by silicic acid chromatography with diethyl ether/hexane mixtures, and selected fractions were separated by polar phase high performance liquid chromatography. Products characterized by thin layer chromatography, gas liquid chromatography, ultraviolet, infrared, nuclear magnetic resonance and mass spectrometry included: 6-membered cyclic peroxides (13-hydroperoxy-9,12-epidioxy-10- and 9-hydroperoxy-10,13-epidioxy-11-octadecenoates), dihydroperoxides (8,13- and 9,14-dihydroperoxyoctadecadienoates) and keto dienes (9- and 13-oxooctadecadienoates). The 6-membered hydroperoxy cyclic peroxides are apparently formed by 1,4-addition of singlet oxygen to 9- and 13-hydroperoxides with *trans, trans*-conjugated diene systems. Thermal decomposition of the 6-membered hydroperoxy cyclic peroxides at 200 C produced methyl 9-oxononanoate and hexanal as the major volatiles. Other volatiles included 2-pentylfuran, pentane, 4-oxo-2-nonenal, methyl furanoctanoate and methyl 9,12-dioxo-10-dodecenoate. *Lipids* 18:868-876, 1983.

INTRODUCTION

In early studies of autoxidation of linoleate and linolenate, several investigators postulated the formation of 6-membered hydroperoxy cyclic peroxides as secondary products (1-5). However, in more recent investigations (6,7) of linoleate autoxidation, such 6-membered epidioxides were not identified among the secondary oxidation products. In later studies of lipid secondary oxidation products, 5-membered hydroperoxy epidioxides were identified in photosensitized oxidized methyl linoleate (8,9) and linolenate (10,11), and in autoxidized linolenate (12,13). Hydroperoxy bicyclic endoperoxides were also identified in oxidized linolenate (10,14).

A 6-membered hydroperoxy epidioxide, 2-hydroperoxy-3,6-epidioxy-hexane, was prepared from 1-hydroperoxy-4-hexene by free radical cyclization after abstraction of the hydroperoxy proton with di-*tert*-butylperoxy oxalate (15,16). Six-membered hydroperoxy epidioxides apparently form during the autoxidation of squalene (16,17). Also 6-membered epidioxides can be obtained by 1,4-addition of singlet oxygen ($^1O_2$) to 1,3-diene compounds (18-22). Recently, a 6-membered hydroperoxy cyclic compound formed by 1,4-addition from linoleate hydroperoxides was suggested as a precursor of pentyl furaldehyde and pentyl furan (23).

Recent evidence suggests the importance of preventing photosensitized oxidation even in refined oils (23-25). Five-membered hydroperoxy epidioxides from photosensitized oxidized linoleate and linolenate were shown to be important precursors of volatile products formed by thermal decomposition (9,26). The conjugated 9- and 13-hydroperoxy octadecadienoates from autoxidized linoleate can be expected to form cyclic peroxides by oxidation with $^1O_2$. This paper reports our investigation of the reaction of 9- and 13-linoleate monohydroperoxides with $^1O_2$. Six-membered hydroperoxy epidioxides formed as major products were thermally decomposed to examine their possible role as precursors of volatile oxidation products.

EXPERIMENTAL

Materials and Methods

The methyl linoleate (100% by gas liquid chromatography [GLC]) used and the removal of oxidation products before autoxidation

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were described previously (9). A mixture of 9- and 13-monohydroperoxides was then prepared by silicic acid chromatography of autoxidized methyl linoleate,and the fractions were checked for purity by thin layer chromatography (TLC) (9). Previous procedures were used for preparing derivatives of monohydroperoxy cyclic (13) and dihydroperoxy and keto compounds (10) suitable for gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and mass spectrometry (MS). The mixture of linoleate monohydroperoxides, 9- and 13-OOH (500 mg), was treated with $^1O_2$ generated by gaseous O_2 in the presence of methylene blue (10 mg) as sensitizer in a CH_2Cl_2 (80 ml) solution at 0 C for 16 hr in an open tube in the same photochemical apparatus previously described (9). Under these conditions, there was no evidence that methylene blue was bleached or decomposed. Oxidation under these conditions, monitored by TLC and peroxide value determination, gave ca. 80% conversion of monohydroperoxides to secondary oxidation products.

High Performance Liquid Chromatography (HPLC)

A portion of the photosensitized oxidation product (432 mg) was first separated by silicic acid chromatography (9) with diethyl ether/hexane mixtures (given in parentheses) to elute the following fractions: 200 ml (10:90) ketodienes, 100 ml (20:80) + 25 ml (30:70) unreacted monohydroperoxides, 75 ml (30:70) + 75 ml (40:60) 6 membered hydroperoxy cyclic peroxides, 25 ml (40:60) + 100 ml (50:50) + 50 ml (60:40) dihydroperoxides and 50 ml (60/40) + 50 ml (70/30) unidentified polar material + 100 ml diethyl ether/methanol (1:1) residue. The 6-membered hydroperoxy cyclic peroxides and dihydroperoxides were further separated by HPLC, using the same columns and solvent systems to fractionate secondary products in photosensitized oxidized methyl linolenate (10). In the present work, the ultraviolet (UV) detector remained at 215 nm for the entire HPLC separation of dihydroperoxides.

Characterization

The oxidation products were characterized by GC, TLC, UV, infrared (IR), nuclear magnetic resonance (NMR), mass spectrometry (MS) and GC-MS as reported previously (27). In this study for the cyclic peroxides, a Bruker WM-300 WB instrument was used to obtain ^{1}H-NMR spectra at 300 MHz. Analysis of the geometric isomeric composition of linoleate monohydroperoxide was done by HPLC of the hydroxy derivatives obtained after $NaBH_4$ reduction (28). Volatiles were identified by capillary GC-MS using a 0.32 mm x 15 m fused silica column with a polymethylphenyl bonded phase as described previously (26).

RESULTS AND DISCUSSION

Previous work on photosensitized oxidation (methylene blue) of methyl *trans,trans*-8,10-octadecadienoate (29) showed the formation of 6-membered epidioxides by 1,4-addition of $^1O_2$ to a conjugated *trans,trans*-diene. Also, photosensitized oxidation was shown to promote geometric isomerization of conjugated dienoic hydroperoxides from the *cis,trans* to *trans,trans* configuration (30). These studies indicated the possibility that 6-membered hydroperoxy epidioxides may be formed by reaction of $^1O_2$ with conjugated dienoic monohydroperoxides from autoxidized linoleate.

Samples of 9- and 13-linoleate hydroperoxides, photooxidized in the presence of methylene blue, were fractionated by SiO_2 chromatography. Secondary oxidation products were separated and identified functionally by comparison with previously characterized products of photosensitized oxidation (9,10). Quantitative analyses showed the following relative concentrations of secondary products for a sample of 0.4 g linoleate hydroperoxides reacted 16.5 hr with $^1O_2$: 9- and 13-ketodienes (1.2%), unreacted 9- and 13-monohydroperoxides (16.7%), hydroperoxy 6-membered epidioxides (57.9%), dihydroperoxides (17.0%), unidentified polar materials (4.0%) and residue (3.2%). The main products, 6-membered hydroperoxy epidioxides and dihydroperoxides were identified in detail after further purification by HPLC. The ketodienes were identified after silicic acid chromatography.

Six-Membered Hydroperoxy Epidioxides

The silicic acid fraction containing epidioxides was further resolved by polar phase HPLC (Fig. 1) into the pure components, methyl 13-hydroperoxy-9,12-epidioxy-10-octadecenoate (**Ia,b**, Table 1) and methyl 9-hydroperoxy-10,13-epidioxy-11-octadecenoate (**IIa, b**; Table 2), whose structures were established by the spectral and chromatographic studies discussed below. The following relative compositions were estimated by refractive index detection: **Ia**, 21%; **IIa**, 36%; **Ib**, 19.8% and **IIb**, 23.1%.

TLC (silica, diethyl ether/hexane, 60:40) **I, II**; UV inactive and hydroperoxide positive; **Ia**, 0.93; **IIa + Ib**, 0.89 and **IIb**, 0.87 relative to linoleate monohydroperoxides. GC of the

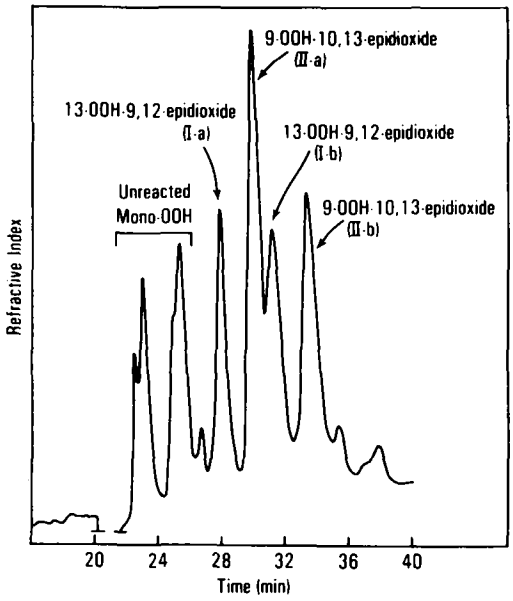


FIG. 1. 10-μm Silica HPLC chromatogram of 6-membered hydroperoxy epidioxides from photosensitized oxidized linoleate monohydroperoxides (flow 4 ml/min; mobile phase, hexane/CH_2Cl_2/ethyl acetate [7:4:1, v/v/v]; refractive index detector, X8; column temperature, 20 C).

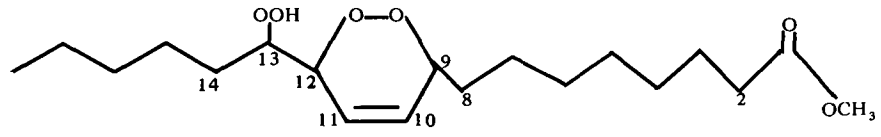
hydrogenated silylated derivatives has the same retentions for **Ia** and **Ib** as 9,12,13-trihydroxystearate, 2.73 and for **IIa** and **IIb** as 9,10,13-trihydroxystearate, 2.67, relative to methyl stearate. IR (CS_2) **I**, **II**: 3,500 (free C-OOH) 3,680-3,220 (bonded C-OOH) and 3,020 (olefinic H) cm^{-1}

MS of the hydrogenated and Ph_3P-reduced derivatives confirmed the general structure of a 6-membered ring with an endocyclic double bond and an exocyclic hydroperoxy group for **I** and **II**. Hydrogenation of **Ia**, **Ib** (Table 1) gave 9,12,13-trihydroxystearate identified by MS (31) after silylation, m/e (rel intensity) **Ia**: M-15, 547 (0.1); M-31, 531 (0.6); M-(90+15), 457 (4); 173 (59); 259 (22); 389 (8); 389-90, 299 (100); and **Ib**: M-15, 547 (0.2); M-31, 531 (1); M-(90+15), 457 (4); 173 (65); 259 (39); 389 (11); 389-90, 299 (100). Hydrogenation of **IIa**, **IIb** (Table 2) gave 9,10,13-trihydroxystearate identified by MS (29) after silylation, m/e (rel intensity) **IIa**: M-15, 547 (0.3); M-31, 531 (1); M-(90+15) 457 (6) ; 173 (45). 259 (83); 303 (55); 213 (100); and **IIb**: M-31, 531 (0.2); M-(90+15), 457 (3); 173 (52); 259 (44); 303 (14); 303-90, 213 (100).

Reduction of **Ia**, **Ib** (Table 1) with Ph_3P produced the unsaturated hydroxyepidioxide derivatives identified by MS after silylation,

TABLE 1

^{1}H-NMR (300 MHz) of 13-Hydroperoxy-9,12-Epidioxy-10-Octadecenoate (I)[a]

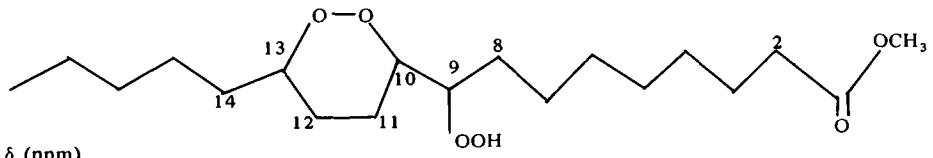


δ (ppm) Ia	δ (ppm) Ib	Multiplicity[b]	Coupling constants Hz[c]	Number of protons	Assignment
8.69	8.75	s		1	OOH
6.01	5.99	s		2	H-10,11
4.61	4.61	m	$J_{12,13}$=4.5	1	H-12
4.54	4.53	m	$J_{9,12}$=2.2	1	H-9
4.14	4.12	m		1	H-13
3.66	3.64	s		3	CH_3O
2.29	2.26	t		2	H-2
1.60	1.56	m		4	H-8,14
1.30	1.32	br		16	H-3-7,15-17
0.89	0.87	t		3	H-18

[a]See Figure 1.
[b]Multiplicity: br=broad, s=singlet, d=doublet, m=multiplet, t=triplet.
[c]Coupling constant for **Ia**.

TABLE 2

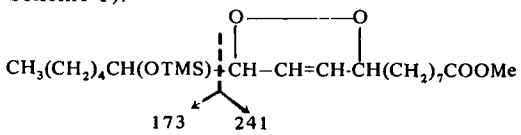
^{1}H-NMR (300 MHz) of 9-Hydroperoxy-10,13-Epidioxy-11-Octadecenoate (**II**)[a]



δ (ppm) IIa	δ (ppm) IIb	Multiplicity[b]	Coupling constants Hz[c]	Number of protons	Assignment
8.76	8.79	s		1	OOH
5.99	6.00	dt	$J_{10,12}=1.3$; $J_{11,12}=10.5$; $J_{12,13}=1.5$	1	H-12
5.90	5.90	ddd	$J_{10,11}=2.7$; $J_{11,13}=1.6$	1	H-11
4.66	4.66	m	$J_{9,10}=7$	1	H-10
4.49	4.48	m	$J_{10,13}=2$	1	H-13
4.17	4.17	m		1	H-9
3.65	3.65	s		3	CH_3O
2.29	2.29	t	J=7.5	2	H-2
1.57	1.57	m		4	H-8,14
1.30	1.31	br		16	H-3-7, 15-17
0.89	0.88	t		3	H-18

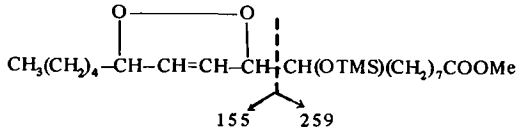
[a]See Figure 1.
[b]Multiplicity: same as Table 1.
[c]Coupling constants for **IIa**.

m/e (rel intensity) **Ia**: M,414 (1); M-16, 398 (2); M-32, 382 (4); 173 (100); 241 (30); and **Ib**: M,414 (0.3); M-16, 398 (1); M-32, 382 (2); M-90, 324 (3); 173 (26) and 241 (2) (see Scheme 1).



SCHEME 1.

Reduction of **IIa**, **IIb** (Table 2) *with* Ph_3P gave the corresponding unsaturated hydroxy epidioxide derivatives identified by MS after silylation, m/e (rel intensity) **IIa**: M,414 (0.7); M-16, 398 (2); M-32, 382 (2); M-90, 324 (2); 259 (56); 155 (58); and **IIb**: M-16, 398 (0.5); M-32, 382 (0.3); M-90, 324 (1); 259 (100); 155 (36) (see Scheme 2).



SCHEME 2.

^{1}H-NMR (300 MHz, $CDCl_3$) for **Ia**, **Ib** (Table 1) and **IIa**, **IIb** (Table 2) provided further evidence for the structures of **I** and **II**. The methine carbon-olefin group-methine carbon structure (-CH-CH=CH-CH-) of the 6-membered epidioxide ring is supported by the long-range coupling constant, 2 Hz, for **Ia** hydrogens 9,12 and **IIa** hydrogens 10, 13. The coupling constant of 4.5 and 7 Hz between the ring methine proton and α hydroperoxy-bearing carbon proton of **Ia** and **IIa**, respectively, serves to distinguish between these positional isomers. Further support for the ring olefin is the *cis* coupling constant, 10.5 Hz, for carbons 11,12 of **IIa**. Other general shifts for the 6-membered hydroperoxy epidioxide structure for **I** and **II** are: 4.17 to 4.12 ppm for the hydroperoxy-bearing carbon methine proton, 4.66-4.61 ppm for the ring methine proton to the α hydroperoxy-bearing carbon, 4.53-4.48 ppm for the other ring methine proton (9), and 6.01-5.90 ppm for the ring olefin protons (29). The small difference in chemical shift between the hydroperoxy-bearing carbons for **Ia** and **Ib** suggested a diastereomeric relationship similar to the shifts found for 5-membered hydroperoxide diastereoisomers (9). However, there was no apparent difference between the same chemical shifts for **IIa,b**. Apparently, **Ia,b** and **IIa,b** are stereoisomers on the basis of their elution order by HPLC relative to the retentions for 5-membered hydroperoxy cyclic peroxides, whose stereochemical structures were established previously (8,9).

These structural studies show that the 6-membered hydroperoxy epidioxides are formed by 1,4-addition of $^1O_2$ to the 1,3-diene system of the linoleate hydroperoxides. The *trans, cis-*

diene hydroperoxides are isomerized in the presence of $^1O_2$ to the *trans,trans* configuration before 1,4-addition (30). Quantitative analyses by HPLC (28) of the dienols produced by $NaBH_4$ reduction of the hydroperoxides before and after cyclization with $^1O_2$ indicated little change in the relative amount of *trans,trans* diene. The *trans,trans* to *cis,trans* ratios of monohydroperoxide mixtures changed by only 2-6% after $^1O_2$ oxidation. These results can be explained according to a scheme in which the photosensitized isomerization (k_1/k_2) from *cis,trans* to *trans,trans* configuration is much faster than the 1,4-cycloaddition (k_3) of $^1O_2$ to the conjugated diene system of linoleate hydroperoxides (Fig. 2).

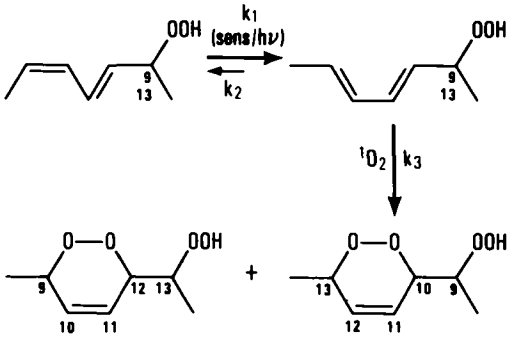


FIG. 2. Scheme for the formation of 6-membered hydroperoxy epidioxides from linoleate monohydroperoxides (sens = sensitizer).

Dihydroperoxides

The appropriate SiO_2 chromatographic fraction was further resolved by polar phase HPLC into positional isomers (Figs. 3 and 4) as described previously for photosensitized oxidized linolenate (10). The HPLC chromatogram (Fig. 3) shows the resolution of dihydroperoxides **III** and **IV** with the following weight percent: **IIIa**, 61.0%; **IIIb**, 9.3%; **IIIc + IVa**, 13.6% and **IVb**, 16.1%.

TLC, all spots peroxide positive and UV active, absolute R_f **IIIa,b**, 0.29; **IIIc, IVa**, 0.24 and **IVb**, 0.11. GC of hydrogenated-silylated derivatives gave retentions relative to methyl stearate: **IIIa,b**, 1.70; **IIIc**, 1.70, **IVa**, 1.78 and **IVb**, 1.78. UV (methanol) **IIIa**: 230 (Em 20,300), **IIIb**: 234 (Em 22,700), **IIIc + IVa**: 230 (Em 22,800), **IVb**, 232 nm (EM 23,300), which indicate conjugated diene functionality. IR (CS_2) **III, IV**: 3,500 (free C-OOH), 3,610-3,200 (bonded C-OOH), 3,010-3,002 (olefinic H), 988-972 (conjugated *trans,trans* unsaturation) cm^{-1}. The UV and IR data show the dihydroperoxides to have *trans,trans* conjugated dienes. Hydrogenation of **III** and **IV** gave 8,13- and 9,14-dihydroxystearates which were identified by MS (31) after silylation, m/e (rel intensity) **IIIa**: M-71, 403 (2); 173 (40); 245 (28) for 8,13-dihydroxystearate; **IIIb**: M-71, 403 (8); 173 (71); 245 (52) for 8,13-dihydroxystearate; **IIIc + IVa** (a di-OOH mixture): M-15, 459 (3); M-57, 417 (17); 159 (75), 259 (74) for 9,14-dihydroxystearate

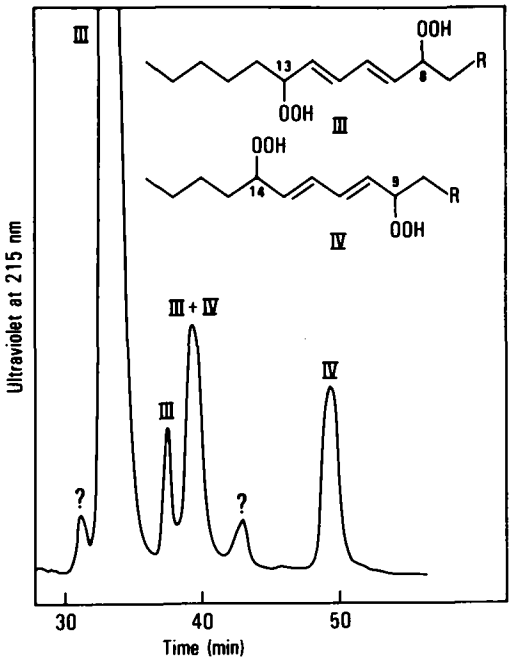


FIG. 3. 6-μm Silica HPLC chromatogram of dihydroperoxides from photosensitized oxidized linoleate monohydroperoxides (flow 20 ml/min: mobile phase, 3% ethanol/hexane [v/v]; UV detector, 0.64 ASU at 215 nm; column temperature, 20 C).

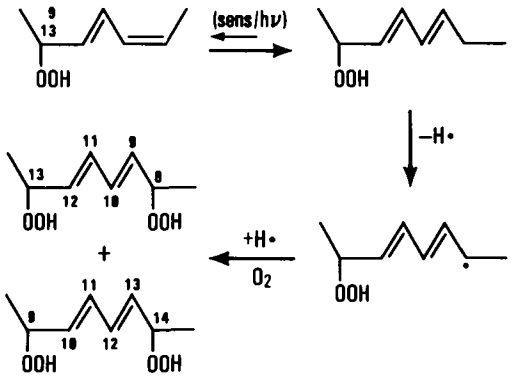


FIG. 4. Scheme for the formation of 8,13- and 9,14-dihydroperoxides from linoleate monohydroperoxides (sens = sensitizer).

and M-71, 403 (9); 173 (51); 245 (40) for 8,13-dihydroxystearate; and **IVb**: M-15, 459 (2); M-57, 417 (20); 159 (66); 259 (55) for 9,14-dihydroxystearate. Reduction of **IIIa** and **IVb** with $NaBH_4$ gave dihydroxy-octadecadienoates identified by MS (8) of the silylated derivatives, m/e (rel intensity) **IIIa**: M-15, 455 (0.4); M-31, 429 (3); M-71, 399 (6); 327 (2); 237 (27); 399 (3); 309 (35) for 8,13-dihydroxyoctadecadienoate (see Scheme 3) and **IVb**: M-15, 455 (1); M-31, 429 (5); M-57, 403 (8); 323 (5); 233 (18); 413 (7); 323 (22) for 9,14-dihydroxyoctadecadienoate (see Scheme 4).

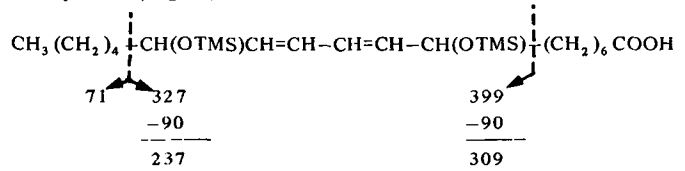
The ^{1}H-NMR data support the UV and IR evidence for olefinic conjugation (6.98-5.25 ppm) and TLC evidence for hydroperoxy functionality (8.25-7.82 ppm, C-OOH; 4.87-4.30 ppm CH-OOH). Based on the MS of the reduced derivatives of **III**, **IV**, the following ^{1}H-NMR assignments are made (^{1}H-NMR, 90 MHz, $CDCl_3$) **IIIa**: 8.22 (br s, 2, OOH), 6.97-5.25 (m, 4, H-9-12), 4.57 (m, 2, H-8,13), 3.67 (s, 3, CO_2CH_3), 2.31 (t, 2, H-2), 2.00-1.50 (m, 4, H-7,14) and 0.93 (t, 3, H-18); **IIIb**: 8.25 (br s, 2, OOH), 6.75-5.25 (m, 4, H-9-12), 4.30 (m, 2, H-8,13), 3.67 (s, 3, CO_2CH_3), 2.31 (t, 2, $CH_2CO_2CH_3$), 1.50-1.80 (m, 4, H-7,14) and 0.92 (t, 3, H-18); **IIIc + IVa**: 8.12 (s, OOH) 6.98-5.25 (m, CH=CH-CH=CH), 4,87 (m, CHOOH), 4.40 (m, CHOOH), 3.67 (s, CO_2CH_3), 2.31 (t, $CH_2CO_2CH_3$), 0.92 (t, CH_3-C); **IVb**: 7.82 (br s, 2, OOH), 6.50-5.25 (m, 4, H-10-13), 4.36 (m, 2, H-9,14), 3.67 (s, 3, CO_2CH_3), 2.32 (t, 2, H-2), 1.83-1.50 (m, 4, H-8-15) and 0.92 (t, 3, H-18).

The 8,13-dihydroperoxy-*trans*-9, *trans*-11- and 9,14-dihydroperoxy-*trans*-10, *trans*-12-octadecadienoates identified here may be free radical side products of the $^1O_2$ reaction formed by H-abstraction on C-8 and C-14 α to the conjugated diene system (Fig. 4). The free radical intermediate apparently is localized on C-8 or C-14 before reacting with O_2. If a delocalized pentadiene radical was formed between C-8 and C-12 or between C-10 and C-14, then 12,13- and 9,10-dihydroperoxides would be expected, but these dihydroperoxides were not detected. In a recent report (32), nonconjugated diene 8- and 14-monohydroperoxides were identified in minor amounts in oxidized methyl linoleate. The products may be rationalized as side products formed by free radical abstraction on α C-8 and C-14 positions of linoleate without delocalization. The expected dihydroperoxides, however, have not been reported in autoxidized linoleate. An alternative mechanism to explain the formation of 8,13- and 9-14-dihydroperoxides in the presence of $^1O_2$ may involve the 6-membered epidioxides undergoing H-abstraction on C-8 or C-14, loss of O_2 and rearrangement of double bonds. Further work is needed to clarify these mechanisms.

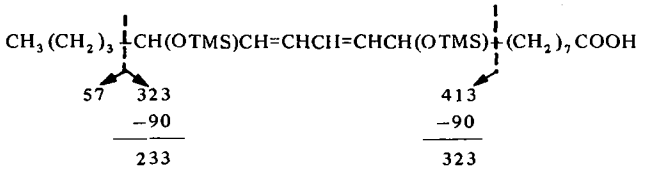
Ketodienes

Another SiO_2 chromatographic fraction was shown to consist of a mixture of methyl 9-oxo-*trans,trans*-10,12- and 13-oxo-*trans,trans*-9-11-octadecadienoates. TLC: absolute R_f, 0.80, UV positive and peroxide negative. UV (methanol) 277 nm (Em 20, 962) is similar to the spectrum previously reported for conjugated ketodiene (33). IR (CS_2) 3,002 (olefinic H), 1,732 (ester carbonyl), 1,681, 1,668, 1,632 (keto carbonyl) 988 (conjugated *trans,trans* unsturation) cm^{-1}. ^{1}H-NMR (90 MHz, $CDCl_3$): 7.50 (m, 1; CH=C-C=O), 6.30-5.62 (m, 3, CH=CH-C=CH-C=O) 3.67 (s, 3, CO_2CH_3), 2.55 (t, 2, C=C-C=OCH_2), 2.36 (t, 2, CH_2CO_2C) 2.15 (m, 2, CH_2C=C) and 0.90 (t, 3, CH_3C). IR and ^{1}H-NMR data are consistent with that reported for *trans,trans* ketodiene (33).

MS gave the the following characteristic



SCHEME 3.



SCHEME 4.

fragments, m/e (rel intensity): M, 308 (32); M-31, 277 (13); 237 (37); 151 (100) for methyl 13-oxo-9,11- and/or 9-oxo-10,12-octadecadienoate. The location of the keto groups and the confirmation of a mixture of 9- and 13-keto compounds is based on MS of hydrogenated derivatives after silylation, m/e (rel intensity): M-31,355 (3); 173 (100); 315 (56) for 13-OTMS-stearate and 259 (48); 229 (43) for 9-OTMS-stearate. These keto dienes may be dehydration side products (6) of monohydroperoxides after their isomerization, catalyzed by $^1O_2$, to the *trans,trans*-configuration.

Volatile Decomposition Products

Methyl 13-hydroperoxy-9,12-epidioxy-10- and 9-hydroperoxy-10,13-epidioxy-11-octadecenoates were each decomposed on a GC injection port at 200 C in a capillary GC-MS system, and the volatiles produced were identified as described previously (26). The fragmentation schemes in Figure 5 account for ca. 94% of the volatiles identified in Table 3. The most important cleavage, A, between the hydroperoxide-bearing carbon and the peroxide ring gave 47% hexanal, 5% methyl 9,12-dioxo-10-dodecenoate and, after dehydration of the ring fragment, 4.7% methyl 8-(2-furyl)octanoate from the 13-hydroperoxy epidioxide (I). The same cleavage gave 55.6% methyl 9-oxononanoate, 5% 2-pentylfuran and 6.5% 4-oxo-2-nonenal from the 9-hydroperoxy epidioxide (II). The second most important cleavage, B, between the ring alkene and the ring oxygen, on the side opposite the hydroperoxide, produced 23% methyl 9-oxononanoate from I. The same cleavage gave 11.4% hexanal, 3.7% methyl

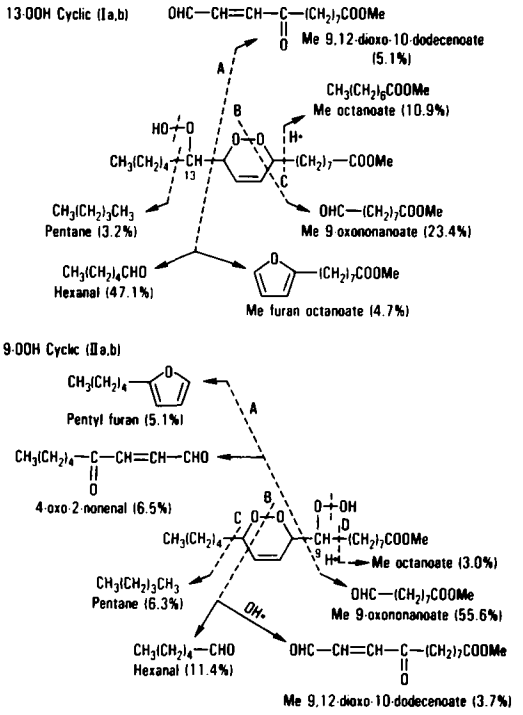


FIG. 5. Scheme for the formation of volatiles by thermal decomposition of 6-membered hydroperoxy epidioxides.

TABLE 3

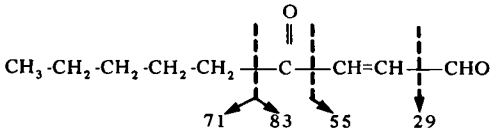
GC-MS Analysis[a] of Volatiles from Thermally Decomposed Hydroperoxy 6-Membered Cyclic Peroxides

Volatile compounds	Relative retention[b]	Relative percent (cleavage, type[c])	
		13-OOH cyclic (I)	9-OOH cyclic (II)
Acetaldehyde	0.05	0.9	0.7
Pentane	0.06	3.2 (D)	6.3 (C)
Hexanal	0.24	47.1 (A)	11.4 (B)
2-Pentylfuran	0.74	0.6	5.1 (A)
Me Octenoate	0.98	0.6	0.1
Me Octanoate	1.00	10.9 (C)	3.0 (D)
Me 8-oxooctanoate	1.31	0.2	–
4-Oxo-2-nonenal[d]	1.32	0.7	6.5 (A)
4-Oxononanal	1.34	–	0.2
9-Oxononanoate	1.47	23.4 (B)	55.6 (A)
Me 8-(2-furyl)octanoate[e]	1.69	4.7 (A)	0.8
Me 10-oxo-8-decenoate	1.72	–	3.3
Me 9,12-dioxo-10-dodecenoate[d]	2.09	5.1 (A)	3.7 (B)
Unidentified	–	2.6	3.3

[a]Quantitation based on flame ionization detection.
[b]Retention relative to methyl octanoate at 10.05 min.
[c]Based on schemes in Figure 5.
[d]Tentative identification.
[e]MS reported by Tressel et al. (34).

9,12-dioxo-10-dodecenoate from **II**. The third important fragmentation, C, between the peroxide ring and the other substituent produced 11% methyl octanoate from **I** and 6% pentane from **II**. Cleavage, D, on the side of the hydroperoxy carbon away from the ring, gave 3% pentane from **I** and 3% methyl octanoate from **II**.

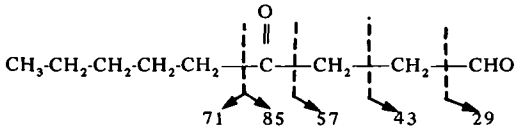
The 1,4-dicarbonyl compounds (Fig. 5, Table 3) detected among the volatiles from cyclic peroxides **I** and **II** apparently have not been identified before. The 4-oxo aldehydes were identified by the following characteristic mass ions: M, 154 (2); M-29, 125 (34); m-55, 99 (14); 83 (85); 71 (13); 55 (69); 29 (29); according to fragmentation in Scheme 5.



4-oxo-2-nonenal

SCHEME 5.

and M-29, 127 (6); 127-H_2O, 109 (16); M-57, 99 (24); 85 (30); 71 (27); 57 (100); 43 (76); and 29 (34); according to fragmentation in Scheme 6.



4-oxononanal

SCHEME 6.

The 4-oxononanal (0.2%) is apparently formed from hydrogen radical abstraction by the nonenal compound. Methyl 9,12-dioxo-10-dodecenoate was identified from the characteristic ion M-31, 209 (31); 197 (7); 153 (2); 139 (2); 125 (11); 111 (15); 97 (30); 83 (30); 55 (100); and 29 (12); according to the fragmentation in Scheme 7.

Substituted furans have been detected in soybean and cottonseed oils (35-38). At least three mechanisms have been postulated for the formation of 2-pentylfuran. Chang et al. (37) postulated but did not identify 4-oxononanal as a precursor which could give 2-pentylfuran by cyclization. Parsons (38) suggested decomposition of linoleate 9-hydroperoxy octadecadienoate and reaction with oxygen to form a vinyl hydroperoxide that can cyclize to form a furan. Frankel (23) suggested that 2-pentylfuran could be formed from decomposition of a 6-membered hydroperoxy epidioxide such as **II** via pentyl furaldehyde. We have identified and proven in this study that **II** is a 2-pentylfuran precursor (Table 3, Fig. 5). Since 4-oxo-2-nonenal is formed from **II**, it also may be a precursor of 2-pentylfuran (37). The 8(2-furyl) octanoate previously identified by Tressel et al. (34) can be formed by decomposition of the 6-membered hydroperoxy epidioxide **I** (Table 3, Fig. 5). Thus, the 6-membered hydroperoxy epidioxides are potential precursors of volatiles including substituted furans, 1,4-dicarbonyl compounds, aldehydes and esters that are known to have an impact on flavor of fats. The thermal fragmentation between the epidioxide and hydroperoxide group agrees with our previous studies of related cyclic peroxides (9,26) and is sufficiently predictable that it could be used as a structural tool for these types of compounds.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the US Department of Agriculture over other firms or similar products not mentioned.

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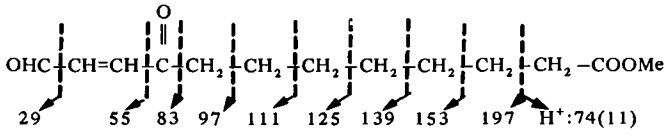

Me 9,12-dioxo-10-dodecenoate

SCHEME 7.

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