Volatile Products from Room Temperature Autoxidation of *cis, cis*-6, 9-Octadecadiene. Analysis by Combined Gas Chromatography-Mass Spectrometry

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Abstract

The volatile products from autoxidation at ambient temperature of *cis,cis*-6, 9-octadecadiene have been analyzed by combined capillary gas chromatography-mass spectrometry (Cap GC-MS). The compounds of interest from a mechanistic viewpoint were pentane, pentanal, hexanal, 1-pentanol, octane, 2-heptenal, octanal, and nonanal. Other compounds which appear to be secondary reaction products were 2-pentylfuran, 3-hexen-1-ol, amyl formate, hexyl formate, and octyl formate.

Introduction

In order to obtain further knowledge about the mechanism of formation of the volatile compounds from autoxidation of linoleate derivatives, *cis,cis*-6,9-octadecadiene (the hydrocarbon analogue of linoleic acid) was autoxidized at room temperature with purified oxygen which had been passed through Linde Type 5A Molecular Sieve. It should be noted that numerous investigators have actively worked on the problem of determining the mechanism of formation of volatiles from linoleate derivatives (1,2).

Some mechanistic interpretation of product formation and the relationship between the oxidative path of the model system and linoleate derivatives are discussed.

Experimental Procedures

Nineteen milliliters of *cis,cis*-6,9-octadecadiene (greater than 99% purity as analyzed by capillary GLC: UV absorption spectrum showed the absence of conjugated diene; and IR spectrum indicated that more than 97% of the carbon-carbon double bonds were *cis*) were oxidized as a film on purified glass wool by exposure to purified oxygen (760–790 mm Hg) at room temperature in laboratory light. *Cis,cis*-6,9-octadecadiene was prepared from lithium aluminum hydride reduction of the tosylate of *cis,cis*-6,9-linoleyl alcohol (3). After four days of oxidation the hydrocarbon had a peroxide number of 1880 mmole/kg. The volatiles were distilled for 6 hr from the autoxidized hydrocarbon at 25 C and 2–7 × 10^{-2} Torr and collected in a U-tube immersed in liquid nitrogen. The condensate (0.4 ml) was separated into two layers. The lower layer, mostly water, was not analyzed in this study; however, the upper layer (approximately 60 μl) was analyzed by combined gas chromatography-mass spectrometry (GC-MS).

Cap GC-MS Analysis

Gas chromatographic separation of the volatile products was achieved with a 200-ft, 0.01-in. capillary column coated with General Electric SF 96-(50) silicone oil containing 1% Carbowax 20 M, programmed from 65 to 180 C in 60 min. The Cap GC-MS technique with the Bendix Time-of-Flight Mass Spectrometer has been described in prior publications (4,5). Although GC-MS is very useful for analysis of small liquid samples (down to 1.0 μl), results from this technique alone can only be used for tentative identification of the compounds present. In this work an unknown compound is considered to be identified when its GLC retention time and mass spectrum have been shown to be identical to those of an authentic sample of the compound.

Results and Discussion

A typical temperature-programmed chromatogram obtained with a hydrogen flame detector is shown in Figure 1. The compounds identified are given in Table I. Relative retention times are given in Table II. The mass spectral data were compared with those of authentic compounds or with our own MS catalog, and in addition, all compounds listed without parentheses in Tables I and II were confirmed by retention times. One or more compounds remain unidentified in peaks 9, 13 and 16. Examination of the mass spectra from peak 15 suggested 3-octen-2-one, however, no authentic sample of this material was available for comparison of GLC retention time and mass spectra. Analysis of the volatiles from autoxidized

Volatiles from Autoxidized cis, cis - 6,9 - Octadecadiene

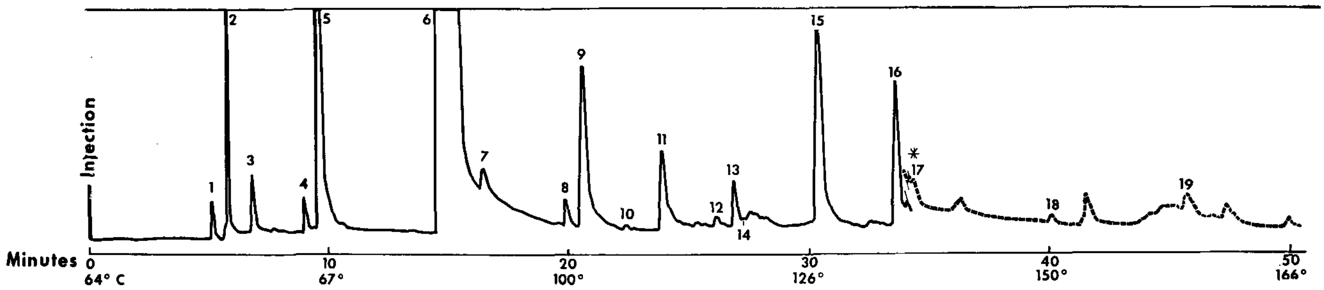

FIG. 1. Gas chromatogram of volatile oxidation products.

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[1] Agricultural Research Service, USDA.

TABLE I

Volatile Compounds from Autoxidation of *cis,cis*-6,9-Octadecadiene

Peak[a] no.	Compounds[b]	Peak[a] no.	Compounds[b]
1	butane	11	2-heptenal
2	acetone	12	2-octanone
	pentane	13	(unknown ketonic compound)
	1-pentene		
3	butanal		2-pentylfuran
4	2-methyltetrahydrofuran		octanal
5	pentanal	14	1-decene
	heptane	15	(3-octen-2-one)[c] and complex mixture
6	hexanal		
	1-pentanol	16	unknown
	octane		nonanal
7	amyl formate	17	n-octyl formate
8	2-heptanone	18	2-decanone
9	unknown	19	pentyl hexanoate
	3-hexen-1-ol		
10	n-hexyl formate		

[a] Refers to chromatogram of Figure 1. Some small peaks have not been numbered.

[b] Identified by means of comparison of mass spectra and GLC retention time with authentic samples.

[c] Entries in parenthesis were suggested but not confirmed.

TABLE II

Retention Times of Volatile Compounds from Autoxidation of *cis,cis*-6,9-Octadecadiene Relative to n-Hexane[a]

Peak No.	Compounds	Relative Retention Time of Known[b]	Relative Retention Time of Unknown[c]
1	butane	0.65	0.63
2	acetone	0.83	0.78
	pentane		
	1-pentene		
3	butanal	0.97	0.93
4	2-methyltetrahydrofuran	1.18	1.16
5	pentanal	1.26	1.21
	heptane		
6	hexanal	1.87	1.87
	1-pentanol		
	octane		
7	amyl formate	1.97	1.96
8	2-heptanone	2.42	2.38
9	unknown		
	3-hexen-1-ol	2.56	2.52
10	n-hexyl formate	2.70	2.65
11	2-heptenal	2.95	2.96
12	2-octanone	3.25	3.26
13	(unknown ketonic compound)		
	2-pentylfuran	3.38	3.37
	octanal		
14	1-decene	3.42	3.48
15	(3-octen-2-one) and complex mixture	......	3.82
16	(unknown)		
	nonanal	4.23	4.21
17	n-octyl formate	4.43	4.32
18	2-decanone	4.91	5.02
19	pentyl hexanoate	5.68	5.62

[a] GLC retention times were obtained on a 200 ft by 0.01 in. capillary column coated with General Electric SF 96(50) silicone oil plus 1% carbowax 20 M. Column was programmed from 65 to 180 C in 60 min. All retention times were compared to the retention time of purified hexane (6 min).

[b] Retention time of known compound/retention time of hexane.

[c] Retention time of unknown compound/retention time hexane.

6,9-octadecadiene by our GC-MS technique showed many weak ion fragmentation patterns, which indicated the presence of many other components in very low levels. These spectra were not sufficiently strong to permit interpretation of them and thus allow postulation of structures for these compounds. Attempts to increase the concentration of these compounds in the ion chamber of the mass spectrometer by increasing sample size were limited by the capacity of the capillary columns (upper limit, about 2.0 μl; split, 100:1 at input splitter) used. Also, the small quantity of volatiles (60 μl) obtained from autoxidation of the diene prevented separation and trapping of these trace components by preparative GLC for further analytical studies.

Many of the products from autoxidation of *cis,cis*-6,9-octadecadiene appear to form by thermal decomposition of the isomeric 6- and 9-hydroperoxyoctadecadienes (analogues of 9- and 13-hydroperoxides of linoleate). In this research no effort was made to isolate and characterize these two expected intermediates (6).

Thermal decomposition of 6-hydroperoxy-7,9-octadecadiene would be expected to yield pentyl free radical and 2,4-tridecadienal by cleavage of the 5,6 carbon-carbon bond (Fig. 2). The pentyl free radical could then react by either abstracting a hydrogen atom from substrate and other molecules to form pentane or combine with a hydroxyl free radical to form pentanol. Also pentyl free radicals should react rapidly with oxygen to form pentyl peroxy radicals, which could then abstract hydrogen atoms from other molecules to form pentyl hydroperoxide. Thermal decomposition of the hydroperoxide would yield alkoxide free radical which could react by two pathways. They are: (a) loss of hydrogen to form pentanal, and (b) abstraction of hydrogen atoms from other molecules to form pentanol. Cleavage of the 6,7-bond should yield hexanal and dodecadiene free radical. This vinyl type free radical would be expected to be extremely reactive and could either polymerize or decompose. No volatile compounds were identified in this study which could be readily derived from dodecadiene free radical. Failure to identify these type compounds could be due to the inability of our analytical procedures to remove them from the oxidized diene. Among the predicted products found in this study were pentane, pentanol,

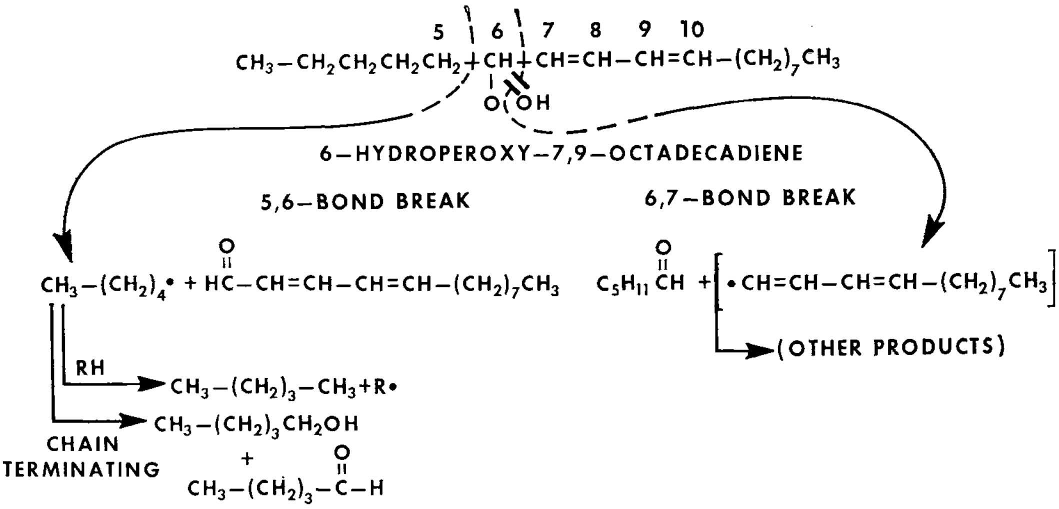

FIG. 2. Mechanism of thermal cleavage of 6-hydroperoxy-7-9-octadecadiene.

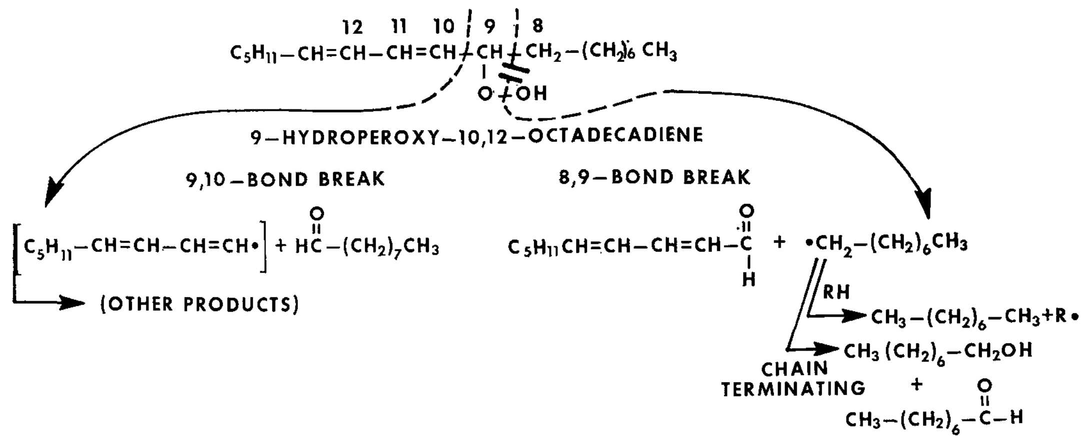

FIG. 3. Mechanism of thermal cleavage of 9-hydroperoxy-10,12-octadecadiene.

pentanal and hexanal. Absence of 2,4-tridecadienal may be due to deficiencies in the analytical and isolation techniques used or to the high reactivity of the dienal towards oxygen. Lillard and Day (7) have shown that a similar dienal, 2,4-heptadienal, rapidly autoxidized at room temperature.

Nonanal and nonadiene free radical would be expected to form from cleavage of the 9,10-bond in 9-hydroperoxy-10, 12-octadecadiene. For the reasons previously discussed nonadiene free radical would be expected to be extremely reactive and thus be consumed or the products derived from it may not be detected by our analytical techniques. Cleavage of the 8,9-bond would be expected to produce octane, octanol, octanal, and 2,4-decadienal. Fig. 3 proposes a mechanistic scheme for their formation. Also, octanol and octanal would be expected to form from octyl free radicals by the same series of reactions postulated for the formation of pentanal and pentanol from pentyl free radicals.

Among the predictable products found in this study were octane, octanol as its formate, octanal, and nonanal. 2,4-decadienal was not found in the volatiles but might be expected to react rapidly with oxygen and thus be consumed or not be identified due to deficiencies in our analytical technique.

In order to obtain further information about the mechanism of autoxidation of the model diene, efforts were made to estimate the levels of major volatile products.

Farmer's theory of oxidation of unsaturated compounds (6) predicts that equivalent quantities of the 6- and 9-hydroperoxides should form. Dismutation of these hydroperoxides according to the mechanism proposed by Bell (8) should yield equivalent quantities of hexanal and nonanal as well as equivalent quantities of octane and pentane. Also, the hypothesis was made that the sole source of the four compounds was thermal cleavage of the two isomeric hydroperoxides. The latter hypothesis is questionable since autoxidation of 2,4-decadienal produces hexanal as the major volatile product (9). The amount of octane found was 15 times that of pentane, and the hexanal concentration was 24-fold that of nonanal. The relative amounts of these compounds were estimated from the peak areas in the GLC chromatograms, plus the relative intensities of certain characteristic mass spectral peaks obtained from Cap GC-MS.

In order to determine the significance of these values an attempt was made to determine the efficiency of the analytical techniques used in this research (vacuum distillation at 2–7 × 10^{-2} Torr, followed by GLC analysis with a 200 ft, 0.01 in. capillary column). Equimolar amounts of pentane, pentanal, hexanal, octane, and nonanal were added to methyl linoleate (PV zero) and distilled from the ester at ambient temperature as previously described. Capillary GLC analysis of the distillate showed that all the higher boiling components (pentanal, hexanal, octane and nonanal) were present in approximately the same relative quantities as in the test solution, but about 80% of the pentane was lost. The loss of pentane could be due to both inefficient trapping and subsequent loss during handling of the sample. Thus the high volatility of pentane could account for the low level of pentane compared to octane (1:15). Nonanal might be less completely removed by distillation from the autoxidized diene than from monomeric methyl linoleate. Methyl linoleate was used as solvent to more closely approximate the oxidized diene. The results of these experiments to determine the precision of the quantitative analytical technique used should be regarded as inconclusive.

Several of the components not predicted by Farmer's hydroperoxide theory which were identified are: 3-hexen-1-ol, 2-heptenal and 2-pentylfuran. Some of these compounds are probably formed by secondary reactions. Also, the identification of formates from the autoxidation of both methyl linoleate and 6,9-octadecadiene suggests that they could form by a rearrangement mechanism during hydroperoxide decomposition.

Methyl esters were identified among the volatiles from autoxidation of methyl linoleate (5) with our analytical technique (GC-MS, plus matching of GLC retention times and MS of unknowns with authentic samples) but were not observed by using the same technique in the volatile fraction from autoxidized *cis,cis*-6,9-octadecadiene. Identification of octane and heptane, the predicted analogues of methyl octanoate and methyl heptanoate, from autoxidation of 6,9-octadecadiene strongly suggests that these two methyl esters previously identified in our research from autoxidation of methyl linoleate (5) originated from the methyl ester end of the linoleate molecule. Octane was one of the major volatile products from autoxidation of *cis,cis*-6,9-octadecadiene and methyl octanoate was among the major volatile products from autoxidation of methyl linoleate. In addition, the identification of nonanal and octyl formate, the predicted analogues of the previously identified 8-formyl methyl octanoate (10,11) and 8-formoxy methyl octanoate (10), further supports this hypothesis.

The identification of hexanal, pentane, nonanal, and octane from autoxidation of the C_{18} diene can be interpreted as further qualitative substantiation of Farmer's theory of oxidation of unsaturated compounds (6) and Bell and coworkers' mechanism of hydroperoxide dismutation (9). However, the identification of compounds not predicted by this theory suggests alternate oxidative pathways and also subsequent reactions of the products formed by hydroperoxide decomposition.

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