glyoxal are present in much higher concentrations in the dicarbonyls isolated from linoleate. This suggests that these compounds are formed in oxidized lipids through favored reactions or possibly through more than one mechanism.

ACKNOWLEDGMENT

This investigation was supported by PHS Research Grant EF-00182 from the National Institutes of Health, Division of Environmental Engineering and Food Protection.

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[Received June 14, 1965—Accepted September 28, 1965]

Volatile Products from Mild Oxidation of Methyl Linoleate. Analysis by Combined Mass Spectrometry-Gas Chromatography

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Abstract

The volatile products from autoxidation of methyl linoleate have been analyzed by combined mass spectrometry-gas chromatography. The principal components were pentanal, hexanal, amyl formate, methyl octanoate, and substituted dioxolanes. Minor components included esters, alcohols, ketones, aldehydes, hydrocarbons, and acetals. Certain unsaturated carbonyl compounds, previously reported, were not detected.

Introduction

IN GENERAL CAPILLARY gas chromatographic analysis of the volatiles from oxidation of lipids indicates complex mixtures. To ascertain fully the nature of such mixtures, the combined technique of fast scan mass spectrometry-capillary gas chromatography (MS-Cap GC) has been applied (1,2). This method of analysis permits identification of many components from as little as 1 μl of a complex mixture (then split 1/100 in the injector of the chromatograph). In favorable cases, a component present in less than 1 part in 10^4 can be identified from this size sample. The method involves no chemical intermediates that might modify the unknowns.

Experimental

Preparation of Methyl Linoleate

Methyl linoleate was prepared from fresh safflower oil, a convenient source of this acid, by the method of Swern and Parker (3). The purity of the ester was estimated to be 97% by GLC analysis using a 75-ft, 0.01-in. capillary column coated with General Electric SF96-50 silicone oil and a 4-ft, 0.25-in. column containing 15% DEGS on firebrick. The peroxide value was negligible.

Oxidation of Methyl Linoleate

Methyl linoleate (19 g), on purified glass wool, was oxidized at room temperature (22C) and in diffuse daylight by purified oxygen passed at a rate of 10 ml/min. The oxygen was purified with Linde Type 5A molecular sieve. After 18 days the ester had a peroxide value of approximately 1000.

Volatile products of the oxidation were swept by the oxygen into a U-tube at –78C. Approximately 0.5 ml of condensate, primarily water, was obtained from the 19 g of the ester. The condensate was extracted with 50 μl of 2,2,4-trimethylpentane by slow rotation (overnight), and the 2,2,4-trimethylpentane extract was analyzed by combined gas chromatography and mass spectrometry.

A control run was performed simultaneously in a parallel apparatus without the ester. The control condensate (20–50 μl) was extracted and analyzed as described. Only solvent and solvent impurities were observed.

MS-Cap GC Analysis

Gas chromatographic separation of the volatile oxidation products was achieved with a 200-ft, 0.01-in. capillary column. The column was coated with General Electric SF96–50 silicone oil containing 1% Carbowax. A typical temperature-programmed chromatogram obtained with a hydrogen flame detector is shown in Figure 1.

For mass spectral analyses the column was removed from the flame detector and the column exit inserted directly into a vacuum manifold leading to the ion chamber of a Bendix Time-of-Flight mass spectrometer (Fig. 2). With the column exit pressure at vacuum, the inlet pressure must be correspondingly reduced in order to obtain the same average linear velocity in the column. This method has the advantages that 1) a greater fraction of the total eluate may enter the mass spectrometer and, 2) possible loss of chromatographic resolution due to eddy currents in corners, etc., is eliminated by the high linear velocities at the vacuum exit (4).

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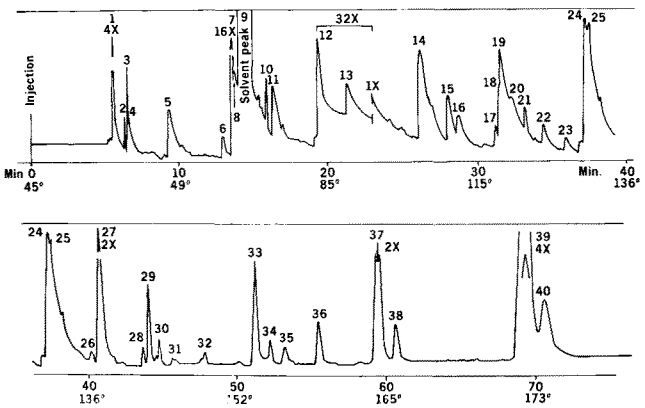


FIG. 1. Gas chromatogram of volatile oxidation products.

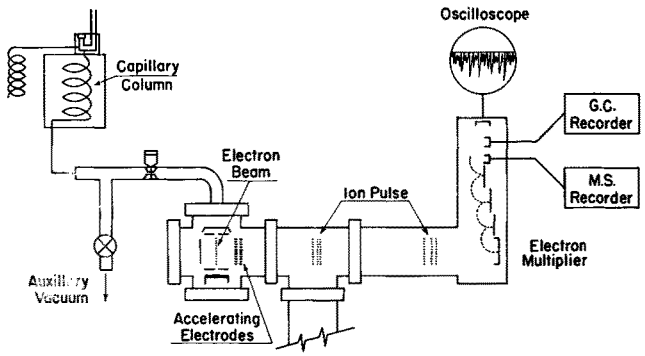


FIG. 2. Schematic diagram of capillary chromatograph and time-of-flight mass spectrometer.

During a mass spectral run, a simultaneous chromatogram was obtained by monitoring the ionization due to mass 29 ($C_2H_5^+$, CHO^+) on a recording potentiometer. Changes in the mass spectrum were observed on an oscilloscope, and as a component was eluted the complete mass spectrum was recorded on a Minneapolis-Honeywell Visicorder. A mass range of 20–200 mass units was scanned in 1 to 3 sec.

High Resolution Mass Spectral Analysis

Certain chromatographic fractions could not be identified from their fast-scan low resolution mass spectra (Figure 1, peaks 29, 30, 33, 34, 37, 38, 39, and 40). Definitive elemental analysis of these compounds was obtained by accurate mass measurement of the appropriate mass peaks on an Associated Electrical Industries MS-9 double-focusing mass spectrometer. To develop these data, the total unfractionated sample was introduced by a batch inlet system and the mass peaks of concern were singled out and accurately measured. Previous data obtained from the MS-cap GC analysis assured that the pertinent mass peaks in the unfractionated sample were not due to other components.

Results and Discussion

The chromatogram of Figure 1 is typical of those from several replicate samples. Minor differences occurred only in the first few peaks. For example, from one oxidation propanal was clearly identified (although not intense); from another oxidation it was barely indicated. In one case, 1-pentene was quite positive, but in most runs it was not detected. No significant differences appeared beyond peak 4 in replicate mass spectral analyses on samples from different oxidations.

The compounds identified are given in Table I. Except where noted, the mass spectral data were compared with those of authentic compounds or with literature data, and, in addition, most compounds were confirmed by satisfactory retention times. The list includes several esters, acetals, alcohols, aldehydes, ketones, and dioxolanes not previously reported.

A number of previously identified alkanals, enals, dienals, and other compounds were not detected in the present study (5–11). Particularly noticeable (by their absence) are ethanal, heptanal, 2-octenal, 2-nonenal, 2,4-nonadienal, and 2,4-decadienal. For example, no peak was observed for 2,4-decadienal at the retention value indicated by an authentic sample (between peaks 35 and 36). Whether the absence of these compounds is due to changes in oxidation method or in sampling has not yet been ascertained. The detection of the various acetals and dioxolanes reported in Table I suggests that some of the aldehydes identified by other workers may be present in the nonvolatile fraction as high molecular weight compounds.

The peaks numbered 18–21 and 24, 25 have not been satisfactorily identified. The retention time of peaks 18 and 19 corresponded to 2-heptenal and 1-octene-3-one (6,12). The mass spectral features expected of a low concentration of this mixture were observed, but the mass spectra could be attributed to similar isomers. In this case, identity was established primarily by gas chromatography and confirmed weakly by the mass spectra.

Identification of peaks 24 and 25 was not made. From the mass spectra, this pair seems to be one major and one minor component. The major component is probably a mono-unsaturated aldehyde or ketone. The logical choice, 2-octenal (7,8), has not been tested.

TABLE I

Volatile Compounds from Autoxidation of Methyl Linoleate

Peak[a] no.	Mass spec. and G. C. Confirm	Mass spec. identification
1	methyl formate	
2		(1-pentene)[b]
3	n-pentane	
4	propanal	
5	n-butanal	
6		(2-pentanone)[c]
7	n-pentanal	
8		no identification
9	isooctane-solvent	
10	solvent impurity	
11	n-butanol	
12	n-hexanal	
13	n-amyl formate	
14	2-heptanone	
15	methyl hexanoate	
16	n-hexanol	
17	1,1-dimethoxy-n-hexane	
18	(2-heptenal)	
19	(1-octene-3-one)	
20		no identification
21		〃 〃
22	methyl heptanoate	
23		no identification
24		〃 〃
25		〃 〃
26		〃 〃
27	methyl octanoate	
28		no identification
29		2-ethyl-4-pentyldioxolane
30		isomer of 29
31		no identification
32		〃 〃
33		2-propyl-4-pentyldioxolane
34		isomer of 33
35	n-pentyl-n-hexanoate	
36	1-methoxy-1-n-pentoxy-n-hexane	
37		2-butyl-4-pentyldioxolane
38		isomer of 37
39	2,4-dipentyldioxolane	
40	isomer of 39	

[a] Refer to chromatogram of Fig. 1. Some small peaks have not been numbered.
[b] Entries in parenthesis were suggested but not confirmed.
[c] Good mass spectral evidence. Retention time off by 15 sec.

TABLE II

Accurate Mass of Selected Mass Spectral Peaks From Total Volatile Sample

Elemental composition	Calculated mass	Measured mass
C_6H_9O (trace)	97.06534	97.06524
C_7H_{13}	97.10172	97.10169
$C_7H_{14}O$	114.10446	114.10429
$C_6H_{11}O_2$	115.07590	115.07589
$C_7H_{15}O$ (trace)	115.11228	115.11145
$C_8H_{15}O_2$	143.10720	143.10698
$C_{13}H_{25}O$	213.1854	213.1859

The four pairs of peaks numbered 29–30, 33–34, 37–38, and 39–40 are dialkyl substituted dioxolanes. The mass spectra obtained for peaks 29, 33, 37, and 39 are shown in Figure 3. In all cases the spectra of the smaller satellite peak (spectra not shown in Figure 3) were identical to the more abundant member of the pair indicating that the second peak is a geometric isomer. From Figure 3, it is apparent that these compounds are members of a similar series. Characteristic peaks are noted in all four spectra at masses 143 and 97. Series peaks are noted at 101, 115, 129, 143 (the latter is masked by the characteristic 143 peak), at 171, 185, 199 (masked by Hg^+ background), 213, and at 72, 86, 100, 114.

Precision mass measurement on several of these peaks unequivocally established the elemental composition (Table II). The characteristic peak 143 contains two oxygens ($C_8H_{15}O_2$); peaks with one or three oxygens were not observed at this mass. The characteristic peak 97 was shown to be C_7H_{13}; a low intensity peak, C_6H_9O, was attributed to other components. The series peaks at 115 and 213 both contained 2 oxygens. (A minor peak at 115 due to $C_7H_{15}O^+$ is attributed to the other acetals.) The series peak 114 contains one oxygen.

A small fraction of chromatographic peaks 39 and 40 was collected from a preparatory gas chromatograph equipped with a 4-ft × ¼-in. column containing 20% Apiezon M on Chromosorb P. Examination by IR, NMR, and UV spectroscopy indicated no double bonds, no carbonyl oxygen, and no hydroxyl oxygen. Another sample hydrolyzed in aqueous methanolic hydrochloric acid yielded hexanal (determined as the 2,4-DNPH derivative) and 1,2-heptanediol (determined by mass spectrometry).

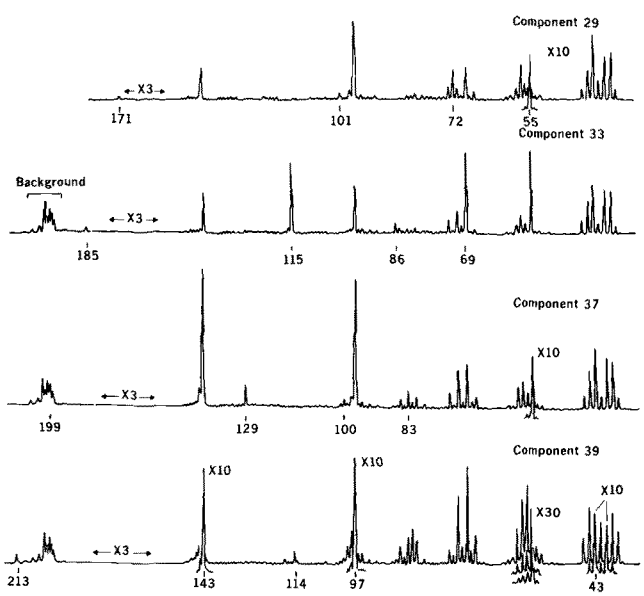
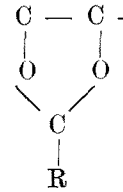


FIG. 3. Mass spectra of substituted dioxolanes.

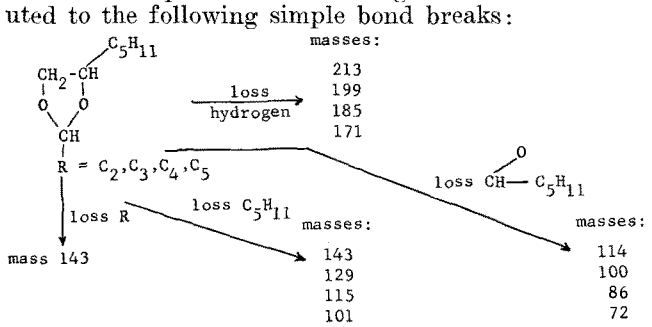
These data suggested that the compounds are dioxolanes of the general formula



where R = C_2,C_3,C_4,C_5.

An authentic sample of 2,4-dipentyldioxolane was prepared by condensation of hexanal and 1,2-heptanediol by a general technique (13). Analysis of synthetic 2,4-dipentyldioxolane on a GLC capillary column showed the presence of two peaks with the same retention times as peaks 39 and 40. These components were separated on two different GLC preparative columns and shown to be isomers by infrared and mass spectroscopy. These isomeric compounds are presumably *cis*-2,4-dipentyldioxolane and *trans*-2,4-dipentyldioxolane. The NMR spectrum further confirmed the identity of the original compound corresponding to peak 39 with one of the isomers of synthetic 2,4-dipentyldioxolane. The same method established that the compound corresponding to peak 40 was the same as the second component of the synthetic 2,4-dipentyldioxolane.

The principal differences in the infrared spectra of the *cis* and *trans* isomers of 2,4-dipentyldioxolane are at frequencies below 2000 cm^{-1} and are shown in Table III. Another model compound, 2,4-dimethyldioxolane. was synthesized (14). The compound was partially separated into its *cis* and *trans* isomers by distillation through a Todd Spiral Column, and then further purified using a Carbowax 20 M GLC preparative column. NMR spectra were taken on the *cis* and *trans* isomers of 2,4-dimethyldioxolane. On the basis of the chemical shift of the C 2 ring proton the compound corresponding to peak 39 is *cis* 2,4-dipentyldioxolane by comparison with *cis* 2,4-dimethyldioxolane. This configuration was established only by analogy to the configurations previously assigned to the two forms of 2,4-dimethyldioxolane (15,16). The mass spectrum of the synthetic 2,4-dipentyldioxolane confirmed the identification. Thus, except for the important mass peak at 97, the features of the mass spectra shown in Figure 3 can be attributed to the following simple bond breaks:



The ion at mass 97 is $C_7H_{13}^+$. Presumably, this ion forms by transfer of a hydrogen to one of the oxygens in the parent ion and subsequent loss of RCHOOH to form $C_7H_{13}^+$. Methyl and pentyl formate presumably formed by cleavage at carbon 1. The abundance of pentyl formate is interesting and may result from reaction of an intermediate $C_5H_{11}\cdot$ or $C_5H_{11}O\cdot$ radical. Other formates were not observed. Formic acid has been reported from oxidation of oleic acid (17).

The 2,4-dialkyldioxolanes and acyclic acetals, 1,1-dimethoxyhexane and 1-methoxy-1-pentoxyhexane,

TABLE III

Infrared Bands[a] of Cis and Trans Dipentyldioxolane Below 2000 cm^{-1} [b]

Trans cm^{-1}	*Cis* cm^{-1}	*Trans* cm^{-1}	*Cis* cm^{-1}
1736 w	1738 vw	1048 s	1044 s } br
1466 s	1466 s	1030 sh	1020 sh }
1461 sh	1462 sh	990 m	992 sh
1457 sh	1458 sh	947 m	944 m
1433 m	1435 m	913 m, sh	921 m
1410 m	1415 m	905 m	899 m
1378 m	1378 s	820 w	819 w
1341 m	1352 sh	786 vw	788 w
1302 vw	1340	768 w	767 w
1280 vw	1307 w	726 m	726 m
1267 vw	1280 w	710 sh	710 w
1233 w	1268 w	545 w, br	648 vw, br
1218 w	1236 w	535 w	538 w
1190 vw	1195 w		
1140 vs, br	1141 vw } br		
1112 vs	1115 vs }		
1075 m	1072 m		

[a] Key: br, broad; m, medium; s, strong; sh, shoulder; vs, very strong; vw, very weak; w, weak.
[b] All bands have precision of ± 2 cm^{-1}.

may form in the mixture on standing. However, acetals are known to form under anhydrous conditions, and, because of the absence of 1,2-heptandiol, methanol, and pentanol, our acetals must have formed by another mechanism. It is uncertain that our analytical procedures are capable of detecting 1,2-heptanediol in the condensate.

Pentyl hexanoate is also somewhat anomalous, in that the abundance of methyl octanoate (compare peak 27 and peak 15) would lead one to expect a relatively large amount of pentyl octanoate. No pentyl octanoate was observed. Butanol and hexanol are observed as the free alcohols but are not observed in any combination (ester, acetal, etc.). Pentanol is not observed as the free alcohol but is detected in significant abundance combined as an ester or as the mixed acetal (peak 36). Pentane was observed as has been previously noted (18).

ACKNOWLEDGMENTS

Dr. T. H. Applewhite gave valuable discussion and guidance in interpretation of some data; Dr. R. G. Buttery aided in the collection of GLC fractions; Dr. R. E. Lundin performed the NMR analysis, and Dr. J. R. Scherer performed the IR analysis.

Research was supported in part by funds from the Office of Civil Defense, Department of Defense.

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[Received June 14, 1965—Accepted September 3, 1965]

Production of Cyclic Fatty Acids: Water as the Reaction Solvent[1]

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Abstract

In an attempt to lower processing costs of producing cyclic fatty acids by a high-temperature alkali treatment, water was tested as the reaction solvent instead of ethylene glycol, previously used. Based on extensive tests in a high-pressure autoclave, saturated cyclic (cyclohexanoic) fatty acids were produced under economic reaction conditions, including a temperature of about 300C; a 4:1 solvent ratio and 50% excess sodium hydroxide catalyst. The lower yield of saturated cyclic fatty acids by the water process is more than offset by the fewer steps and reduced evaporation costs.

Introduction

CYCLIC FATTY ACIDS (CFA) derived from linolenic acid offer a unique new chemical to increase the use of linseed oil. They have valuable properties for coatings, cosmetics, plasticizers and lubricants and should find a sizable industrial market (2,4,7,8). Previously data have been given on product yields obtained with various reaction temperatures, catalyst concentrations and either solvent-to-oil or solvent-to-fatty acid ratios (5,6). Results with ethylene glycol, diethylene glycol and t-butanol as solvents and with sodium hydroxide, potassium hydroxide, potassium t-butoxide and the monosodium salt of ethylene glycol as catalysts, have been described. On the basis of limited data, water was not originally considered to be a suitable solvent. Because of certain disadvantages with using glycols, water has been reevaluated as a reaction solvent and found to offer a distinct economic advantage when used under optimum operating conditions.

Under the conditions of reaction used to prepare CFA, ethylene glycol undergoes partial condensation to form diethylene glycol as shown by gas chromatographic analysis of the recovered reaction solvent. Apparently higher glycols are also formed. Secondly, distillation of the used glycol solvent, necessary to purify it for reuse in subsequent reactions, increases the cost of the process, and the presence of high-boiling polyglycols increases solvent losses. Thirdly, a small but appreciable amount of ester is formed between the glycol and the fatty acids following the reaction and neutralization of the catalyst, despite careful use of the stoichiometric amount of dilute sulfuric acid. This fatty acid-glycol ester is recovered in the polymer because it does not distill under the

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