

Thermal Oxidation of Mono-Unsaturated Short Chain Fatty Acids: I. Ethyl 3-Hexenoate

CAROL B. WHITLOCK¹ and W.W. NAWAR, Department of Food Science and Nutrition, University of Massachusetts, Amherst, Massachusetts 01002

ABSTRACT

Ethyl 3-hexenoate was oxidized for 6 hr at 150 C. The "more volatile" fraction was swept out of the oxidizing flask and into a cold trap. The "less volatile" products remaining in the oxidizing flask were isolated by direct injection onto a preparative-scale gas chromatographic column followed by trapping in glass capillary tubes. The decomposition products were identified by gas chromatography, mass spectrometry, infrared spectrophotometry, and chemical derivatization. The major products included epoxy esters, unsaturated keto- and hydroxy-esters, and dehydromers. Aldehydes, short chain esters, and ketones were produced less abundantly. No aldehyde esters were detected.

INTRODUCTION

The oxidation of short chain fatty acids has not been extensively studied because they are present in substantial amounts in only a few fats. Most investigators choose to study fatty acids containing more than 10 carbon atoms. Yet short chain, mono-unsaturated fatty acids have been reported in oxidizing fats. For example, 2-octenoic acid was found among the products of autoxidation of methyl linoleate by Horvat and co-workers (1), and hexenoic and octenoic acids are also produced in corn oil during frying (2). Obviously, these fatty acids can undergo further degradation themselves. Furthermore, short chain fatty acids are suitable as model systems for studying the full spectrum of oxidation products from the more volatile degradation products through the dimeric ones.

Seyfarth and Schulz (3) and Rieche et al. (4) studied the oxidation at 65 C of 2- and 3-butenate esters, α -hydroxy butenoate esters, 3,6-heptadienoic acid esters, and the gamma lactones of 4-hydroxy-2-pentenoic and 4-hydroxy-3-pentenoic acids. Analysis of the peroxides formed showed that the position of hydroperoxide formation depends on factors which influence the activation of C-H groups (e.g., double bonds, ester, and hydroxyl groups). Hydroperoxides containing a conjugated structure were highly favored. Thus, the number of hydroperoxide isomers formed was less than that predicted by Farmer's Theory. The formation of dimeric and polymeric compounds was noted, but the structures of these were not identified. Substrates with unsaturation in the 3-position were oxidized at a much faster rate than those with 2-position unsaturation because of the activating influence of both the double bond and carbonyl groups. The introduction of an alpha hydroxyl group increased the rate of oxidation of both esters.

EXPERIMENTAL PROCEDURES

Materials

Ethyl 3-hexenoate was purchased in the highest purity available. Gas chromatographic analysis showed several lower mol wt impurities and a number of higher mol wt compounds. After purification by vacuum Vigreux distillation, the ester became colorless and all impurities as

detected by GC were eliminated with the exception of the ethyl 2-hexenoate isomer, which constituted ca. 17% of the purified ester. To determine the contribution of ethyl 2-hexenoate, this isomer was also obtained, purified, and oxidized under conditions identical to those used for ethyl 3-hexenoate.

Oxidation Treatment

Half-gram samples of each ester were oxidized in a glass tube which was heated in an oil bath at 150 C for 6 hr (occasionally at 130 C for 8 hr). Dry compressed air was bubbled slowly through the ester. The "more volatile" degradation products were swept out of the oxidizing flask into a trap cooled with dry ice-acetone.

Gas Chromatography

An F & M dual column Model 810 gas chromatograph equipped with a flame ionization detector and temperature programming was used.

The "more volatile" compounds were collected by rinsing the cold trap with 5 ml of CS₂. The rinsings were condensed to ca. 100 μ l, and 1 μ l aliquots were analyzed on three different columns: a 12 ft x 1/8 in. Carbowax 20 M (15% on Gas-Chrom P), a 6 ft x 1 1/8 in. diethylene glycol succinate (DEGS) (2% on Gas-Chrom P with 2% H₃PO₄), and a 500 ft x 0.2 in. SF-96 capillary column.

The "less volatile" compounds which remained in the oxidation flask were analyzed on a 6 ft x 1/8 in. silicone rubber SE 30. For the identification of individual compounds, however, trapping from a 1/2 in. preparatory GC column followed by separation on various 1/8 in. columns was necessary.

Combined Gas Chromatography-Mass Spectrometry

A Varian Aerograph series 1200 gas chromatograph connected to a Hitachi Perkin-Elmer RMU-6A mass spectrometer was used under the conditions outlined previously by LeTellier and Nawar (5).

Infrared Spectroscopy

A Perkin-Elmer 337 grating infrared spectrophotometer with a 4% beam condenser was used. Compounds purified by repeated trappings from GC columns were rinsed into a 0.05 mm path length NaCl cavity cell with spectral grade CCl₄ or CS₂.

Identification

For most of the oxidative decomposition products, identification was accomplished by comparison of their mass spectra and GC retention times (on two or more columns) with those of authentic compounds which were purchased or synthesized in our laboratory. Infrared analysis and/or chemical derivatization were done in certain cases. Hydrogenation of double bonds was carried out according to procedures described by Lustre and Issenberg (6). Ozonolysis was performed according to Beroza and Bierl (7,8) using a dry ice-toluene cold bath and CS₂ solvent. Silylation of hydroxyl groups was done with the aid of Trisil-Z (N-trimethylsilylimidazole, Pierce Chemical Co., Rockford, IL). Ketonic carbonyl groups and oxirane rings were selectively reduced in the presence of ester carbonyls and double bonds by reacting an alcoholic solution of the sample with sodium borohydride.

¹Present address: Rochester Institute of Technology, Rochester, NY 14623

TABLE I
Identified Decomposition Products from the Oxidation of
Ethyl 3-Hexenoate and Ethyl 2-Hexenoate

	From ethyl 3-hexenoate		From ethyl 2-hexenoate
	Peak number	Figure number	
More volatile products			
Acetaldehyde	+	1	+
Propanal	+	2	+
Ethyl formate	-	-	+
Ethyl acetate	+	4	-
Butanal	+	4	+
Ethanol	+	5	+
Ethyl propanoate	+	6	+
2-Pentanone	+	7	+
Ethyl acrylate	+	8	+
Ethyl butanoate	+	9	+
Ethyl pentanoate	+	1	+
Ethyl crotonate	+	1	+
3-Penten-2-one	+	1	-
3-Hexanone	-	-	+
4-Heptanone	-	-	+
Propanoic acid	+	1	-
Butanoic acid	-	-	+
Less volatile products			
Ethyl hexanoate	+	-	+
Ethyl 2-hexenoate	+	-	+
Ethyl 3-hexenoate	-	-	+
Ethyl 3,4-epoxyhexanoate	+	4	+
Ethyl 2,3-epoxyhexanoate	+	5	+
Ethyl 4-oxo-2-hexenoate	+	6	+
Ethyl 4-hydroxy-2-hexenoate	+	8	+
Ethyl 3-ethyl-4-oxo-hexanoate	+	9	+
Dehydrodimers	+	11	+

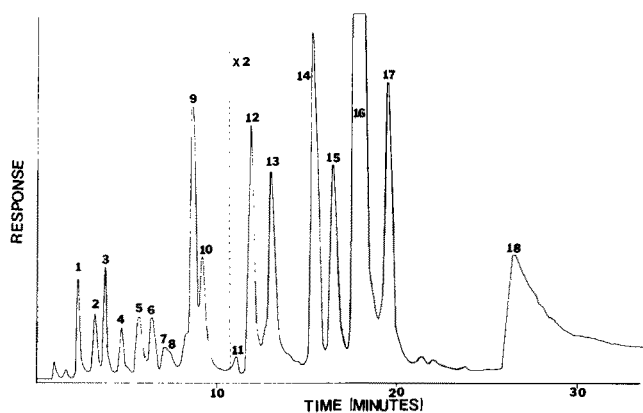


FIG. 1. GC analysis, on Carbowax, of the "more volatile" fraction from oxidized ethyl-3-hexenoate. Peak numbers correspond to identified compounds in Table I.

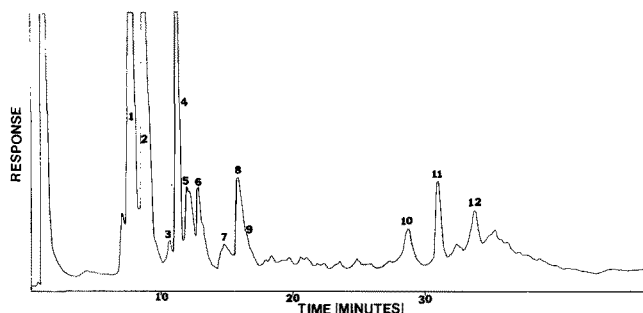


FIG. 2. GC analysis, on SE-30, of the "less volatile" fraction from oxidized ethyl-3-hexenoate. Peak numbers correspond to identified compounds in Table I.

RESULTS

Oxidation of Ethyl 3-Hexenoate

At the end of the oxidation period, the colorless ester had darkened to a clear gold color, and its aroma was characterized as sweet, earthy, and pungent. When periodic determinations of the peroxide value were made, values varied slightly from sample to sample, but the general pattern was the same. The peroxide value increased slightly in the first few hours of the oxidation period, reaching a maximum PV of ca. 350 meq/kg, after which it decreased sharply to ca. 60 after 8 hr, and to 20 after 12 hr.

Typical GC analyses of the "more volatile" and "less volatile" products are shown in Figures 1 and 2, respectively. Table I gives a list of the identified oxidation products. These include aldehydes, ketones, low mol wt simple esters, epoxy-esters, oxo-esters, an unsaturated hydroxy-ester, and three isomeric dehydrodimers. Propanoic acid was a major component of the "more volatile" decomposition products. Ethyl hexanoate remaining in the residual sample contained 20% of the 2-isomer, while that collected in the cold trap had only 12%. Details of the identification of only certain products, which required synthesis or the preparation of chemical derivatives, are discussed below.

Ethyl 3,4-Epoxyhexanoate

The GC retention and the mass and infrared spectra of this component were identical to those of synthesized ethyl 3,4-epoxyhexanoate. The molecular ion (Fig. 3A) is detectable at m/e 158 but extremely small; the loss of H_2O from the molecular ion yields the first clearly visible peak at m/e 140. Ions at m/e 113 and 112 are formed by the losses of the ethoxy group and ethanol, respectively, from the molecular ion. The fragment at m/e 129 represents the loss of an ethyl group from the hydrocarbon end of the molecule; this ion apparently loses ethanol to form the

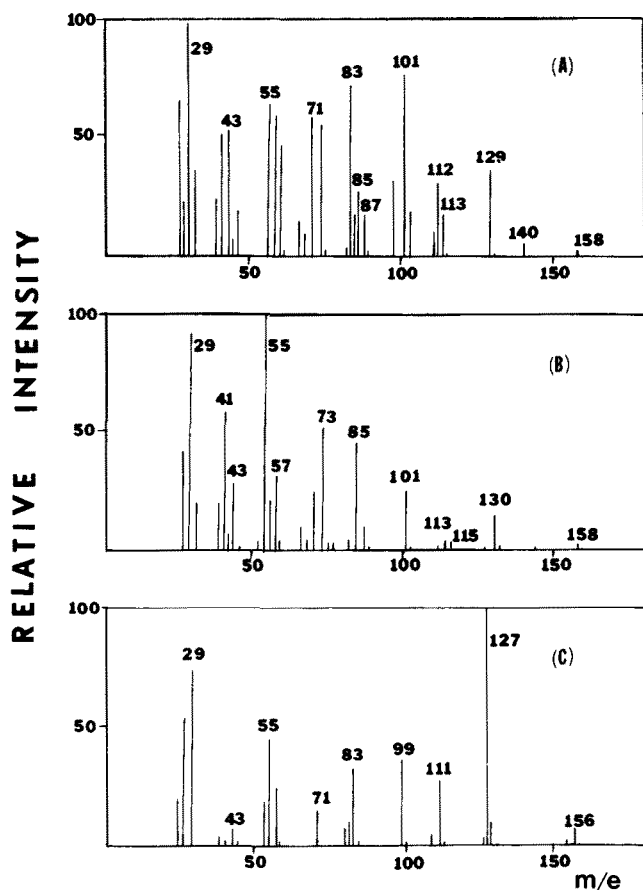


FIG. 3. Mass spectra of compounds identified from thermally oxidized ethyl-3-hexenoate. (A) Ethyl-3,4-epoxy-hexanoate, (B) ethyl-2,3-epoxy-hexanoate, (C) ethyl-4-oxo-2-hexenoate.

peak at m/e 83. The large fragment at m/e 101 may correspond to a transannular cleavage with the transfer of one

hydrogen atom (9) to yield the ion $\text{CH}_2\text{-CH}_2\text{-C}(\text{O})\text{-OCH}_2\text{CH}_3^+$. The opposite transannular cleavage with accompanying hydrogen arrangement probably produces the peak at m/e 43 which corresponds to the ion $\text{CH}_3\text{CH}_2\text{CH}_2^+$. Cleavage of the bond between C_2 and C_3 would produce the two fragments at m/e 71 and 87.

The infrared spectrum showed the characteristics of a saturated ester and the bands near 890 cm^{-1} and 1250 cm^{-1} which are characteristic of epoxides. The spectrum was also similar to that published by Horvat et al. (1) for methyl 2,3-epoxyoctanoate. Absorption at 887 cm^{-1} indicates a trans-epoxy ester (10).

Hydrogenation indicated the absence of double bonds, and reduction with sodium borohydride yielded the 2,3-unsaturated-4-hydroxy ester and gamma caprolactone, confirming the presence of the epoxide function in the 3,4-position.

Ethyl 2,3-Epoxyhexanoate

The peak representing this component (peak 5, Fig. 2) was much smaller in size than that of the 3,4-epoxy ester discussed above. Its mass spectrum (Fig. 3B) is considerably different from that of the 3,4-isomer, but identical to that of the synthesized reference compound. As with the 3-isomer, the molecular ion at m/e 158 is extremely small. A simple cleavage of the bond between the carbonyl group and the oxirane ring produces the ions at m/e 85 and 73. A similar cleavage on the other side of the epoxy group yields the fragments at m/e 43 and 115. The ion at m/e 130 represents the loss of 28 mass units from the molecular ion.

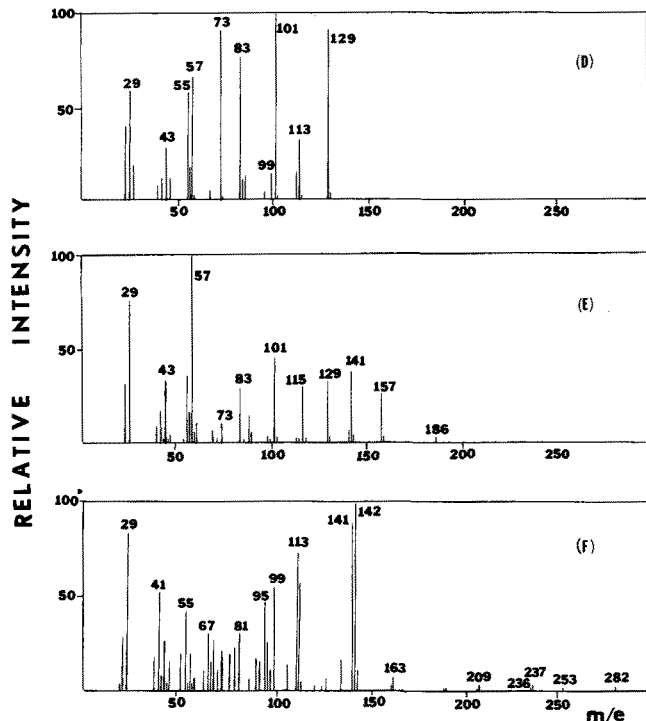


FIG. 4. Mass spectra of compounds from thermally oxidized ethyl-3-hexenoate, (D) ethyl-4-hydroxy-2-hexenoate, (E) ethyl-3-ethyl-4-oxo-hexanoate, (F) dehydromer of ethyl-3-hexenoate.

As with the 3-isomer, the peak at 113 corresponds to the loss from the molecular ion of the ethoxy group.

Ethyl 4-Oxo-2-hexenoate

The mass spectrum of this component (Fig. 3C) supports the proposed structure of an unsaturated oxo-ester. The molecular ion is visible at m/e 156. The base peak at m/e 127 is formed by cleavage of the bond alpha to the carbonyl group and beta to the double bond. A metastable peak at 77.17 corresponds to the loss of $\text{C}=\text{O}$ from the base peak to yield the fragment at m/e 99. The peak at m/e 83 may result from cleavage between the double bond and the ester carbonyl. The loss from the molecular ion of the ethoxy group would produce the fragment at m/e 111.

The infrared spectrum showed absorption at 1740 cm^{-1} and 1715 cm^{-1} , indicating the presence of an ester carbonyl and a ketone carbonyl, respectively, and absorption at 977 cm^{-1} , indicating a trans double bond.

Further confirmation of structure was accomplished by hydrogenation with platinum oxide in ethanol, which yielded ethyl 4-oxohexanoate, γ -caprolactone, and ethyl 4-hydroxy-2-hexanoate. Apparently the hydrogen added to the double bond only, to the oxo-group only, and in some cases to both functions to yield these three products. Synthesis of authentic ethyl 4-oxo-hexanoate confirmed the identity of the major product of hydrogenation, the saturated oxo-ester.

Ethyl 4-Hydroxy-2-hexenoate

Compounds corresponding to peaks 8 and 9 (Fig. 2) were trapped from the preparative scale SE-30 gas chromatographic column and rechromatographed on a 12 ft x 1/8 in. DEGS with 2% H_3PO_4 column which allowed the two components to be collected and examined separately. Peak 8 was about twice as large as peak 9.

Peak 8 was identified as ethyl 4-hydroxy-2-hexenoate. Its mass and infrared spectra as well as its GC retention on DEGS- H_3PO_4 and SE-30 agreed with those of the synthetic reference compound. The molecular ion is not visible (Fig.

4D). The fragment at m/e 129 may result from cleavage alpha to the hydroxyl group and beta to the double bond. This ion further decomposes to give rise to the base peak at m/e 101, as evidenced by a metastable peak at m/e 79.08 ($129^+ \rightarrow 101^+ + 28$). Loss of ethylene from the ester portion could occur via a McLafferty rearrangement. The ion at m/e 129 could lose ethanol to yield the fragment at m/e

83. The peak at m/e 73 may represent the ion $[\overset{\text{O}}{\text{C}}\text{-OCH}_2\text{CH}_3]^+$.

Infrared absorption at 3450 cm^{-1} and the α,β -unsaturated ester carbonyl absorption at 1725 cm^{-1} supported the proposed structure.

Further support for the structure of this compound was obtained by chemical derivatization. Hydrogenation with platinum oxide yielded gamma caprolactone as the sole product. Apparently the saturated gamma hydroxy ester is unstable and immediately forms the lactone. Hydrogenation of the trimethylsilyl derivative resulted in the addition of two mass units to many fragments in the upper mass region of its mass spectrum.

Ethyl 3-Ethyl-4-oxohexanoate

The mass spectrum of the component corresponding to peak 9 had a molecular ion at m/e 186 (Fig. 4E). The fragmentation pattern suggests that the ethyl group is attached to carbon 3. The base peak at m/e 57 may arise from cleavage of the bond between the ketone carbonyl and the tertiary carbon with the ketone fragment retaining the charge. Some of the ester fragment, however, does retain the charge as indicated by the peak at m/e 129. The prominent ion at m/e 157 could result from the loss of an ethyl group. The peak at m/e 141 is due to the loss of the ethoxy group. Three metastable peaks were observed at m/e 105.99, 79.08, and 68.21, corresponding to the loss 28 mass units from the fragments at m/e 157, 129, and 101, respectively.

The infrared spectrum contained a saturated ester carbonyl and a saturated ketone absorption maxima.

Dehydrodimers of Ethyl 3-Hexenoate

Three isomeric structures (I, II, and III, as shown below) are proposed. Peak 11, Figure 2, represents an important part of the "less volatile" decomposition products of oxidized ethyl 3-hexenoate. After elution from the SE-30 preparative scale GC column, further fractionation was possible only on a 500 ft x 0.2 in. Carbowax 20M capillary column held at 205 C. Three peaks of relatively long retention time could be partially separated.

The mass spectra of the three peaks were similar. A small molecular ion is visible at m/e 282 (Fig. 4F). The strong $\frac{M^+}{2}$ and $\frac{M^+}{2} + 1$ are typical of dehydrodimers, as discussed by Wheeler and White (11). In the upper mass range, fragments at 236, 237, and 253 are due to losses of ethanol, ethoxy,

and ethyl groups, respectively. The loss of $[\overset{\text{O}}{\text{C}}\text{-OCH}_2\text{CH}_3]$ from the molecular ion gives rise to the fragment at m/e 209. The peak at m/e 163 may result from the loss of one ethyl and two ethoxy groups. The loss of an ethyl group from the base peak yields a large peak at m/e 113. The fragment at m/e 99 probably corresponds to the ion

$[\text{CH}=\text{CH}-\overset{\text{O}}{\text{C}}\text{-OCH}_2\text{CH}_3]^+$.

Further analysis could be done only on the combined isomers. In the infrared spectrum, two ester carbonyl absorptions were observed at 1740 cm^{-1} and 1730 cm^{-1} , indicating the presence of saturated and α,β -unsaturated ester groups. Doublets near 1240 cm^{-1} and 1160 cm^{-1} indicated C-O-C asymmetric and symmetric stretching of two ester groups, one conjugated with a double bond and one not (12). Similarly, a doublet near 970 cm^{-1} indicated

two isolated trans double bonds, one conjugated with the ester carbonyl and one not.

The mixture of the three components was hydrogenated with platinum oxide and the resultant material subjected to GC-MS analysis. The mass spectrum of the hydrogenated mixture is similar to that of the nonhydrogenated dehydrodimer in its general pattern. The molecular ion has shifted to m/e 286, an increase of four mass units, indicating the presence of two double bonds in the original structure.

Ozonolysis yielded propanal, and two compounds with M^+ 228 and M^+ 184. As shown below, the products expected from structures I and II are propanal and two compounds with M^+ 230 and M^+ 186. Perhaps two protons are lost upon electron impact in the mass spectrometer.

The other two products predicted from ozonolysis of structure III (i.e., M^+ 142 and M^+ 102) may have been formed but not detected by GC. Dialdehydes and many tri- and polyfunctional compounds produced by ozonolysis have been reported to be unstable under conditions of GC analysis (13). Dialdehydes with at least one active methylene group are so reactive that they disappear soon after liberation from the ozonide. Upon ozonolysis, structure III would give rise to such unstable products.

As did the components of peak 11, the synthetic dehydrodimers separated into three peaks only on the capillary Carbowax 20 M column. Mass and infrared spectra as well as GC retention data on three different columns were similar for both the synthetic and the isolated compounds.

Oxidation of Ethyl 2-Hexenoate

The decomposition products identified from the thermal oxidation of ethyl 2-hexenoate are shown in Table I. As in the oxidation of ethyl 3-hexenoate, aldehydes, ketones, simple esters, and ethanol were produced. Butyric acid constituted a major product. Ethyl crotonate, the epoxy-ester, and ethyl-substituted oxo-ester were also products of oxidation of ethyl 3-hexenoate, as shown above.

The dehydrodimer peak from ethyl 2-hexenoate is smaller in proportion to the other "less volatile" products than in the case of ethyl 3-hexenoate. Its mass spectrum is identical to that of the dehydrodimer from ethyl 3-hexenoate.

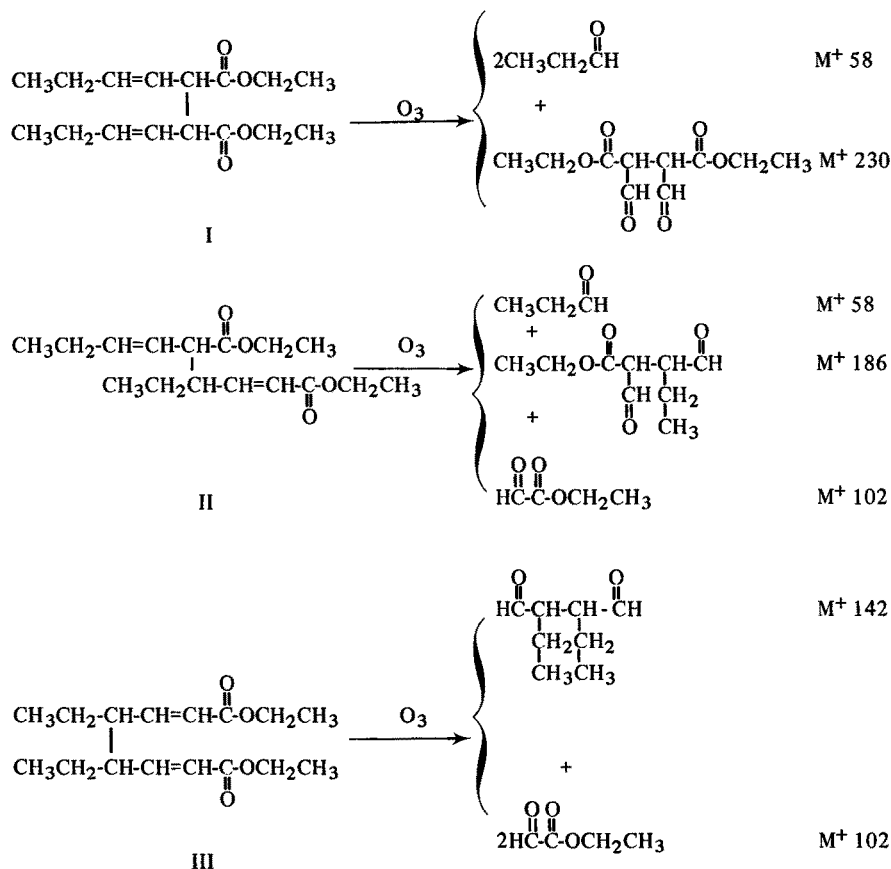
As with the ethyl 3-hexenoate, the largest peak in the "less volatile" fraction corresponds to the epoxy ester; however, the oxirane ring in this structure is located in the 2,3-position.

The qualitative composition of the "more volatile" portion of the oxidation products of ethyl 2-hexenoate is very similar to that of ethyl 3-hexenoate. The unsaturated ketone 3-penten-2-one, prominent in the "more volatile" fraction of the 3-isomer, is absent. Ethyl formate was not detected in the oxidation products of the 3-isomer.

Although many of the same compounds were present in both esters, important differences in quantity are obvious. Ethyl butanoate, ethyl pentanoate, ethyl crotonate, and ethyl hexanoate correspond to large peaks in the case of ethyl 3-hexenoate, but they are present only at extremely low levels in the case of the 2-isomer. The very small amount of ethyl 3-hexenoate produced during the oxidation of the 2-isomer contrasts with the large increase in proportion of ethyl 2-hexenoate during the oxidation of the 3-isomer. A small amount of methyl 2-hexenoate was also found among the "more volatile" components from the oxidation of ethyl 2-hexenoate.

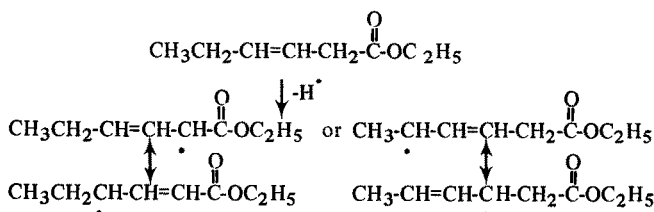
DISCUSSION

From the results of this study it appears that most of the oxidation products of short chain, mono-unsaturated fatty acids arise from the decomposition of both hydroperoxide



and epoxy intermediates. The position of the double bond is important since the predominance of specific hydroperoxide isomers varies according to whether or not conjugation of the double bond with the carbonyl function of the carboxyl group was produced. This observation was also reported by Rieche et al. (4).

In case of ethyl 3-hexenoate, alpha hydrogen abstraction may occur at position 2 or 5.



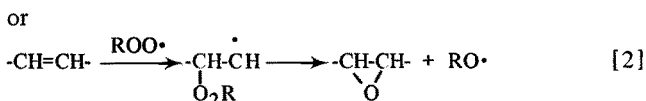
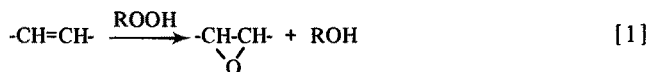
Position 2 is likely to be the preferred site since the free electron would be in conjunction with both the double bond and the carbonyl group. Isomerization of the double bond places the free radical in positions 4 and 3. Of all four sites, position 4 seems the most likely to predominate, since the double bond and the carbonyl would be in conjugation. In accordance with this, the oxo- and hydroxy-esters identified among the "less volatile" products were substituted in the 4-position.

In the case of ethyl 2-hexenoate, alpha hydrogen abstraction can occur only at position 4. The resulting free radical can theoretically isomerize to position 2, but that is unlikely since the double bond would no longer be in conjugation with the ester carbonyl. Thus, both the 2-hexenoates and the 3-hexenoates favor hydroperoxide formation on carbon 4. This explains why many products, particularly the oxo- and hydroxy-esters in the 4-position, are identical for both the 3- and 2-isomers.

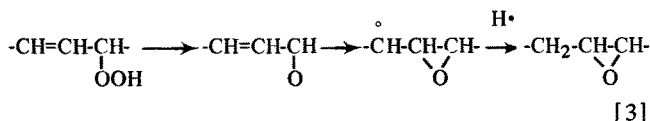
Along with the epoxy-ester and 4-oxo-ester, the dehydrodimers were major compounds produced early in the

oxidation of the hexenoates. Dehydrodimers have been produced from unsaturated esters by the action of heat alone (14), of heat plus oxygen (15), and of gamma irradiation (16). They form from the union of two free radicals with or without isomerization of the double bond. Theoretically, 10 dehydrodimers could form from the 3-hexenoates. However, Howton (16) reported that dehydrodimers from irradiated oleate do not form in proportions equal to those of chance combinations; the isomers containing the cross-linkage closer to the carboxyl group predominated. In the present study, only the I-I and I-II dimers were produced in quantities sufficient for detection. The amount of dehydrodimers produced from the 2-hexenoates was less than that produced from the 3-isomers. This may reflect the reduced number of free radicals available for dimerization of the 2-hexenoates.

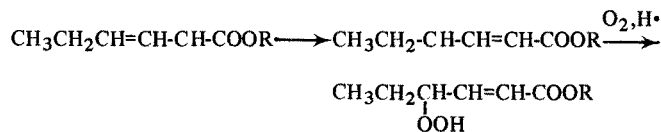
Epoxy esters with the oxirane group at the site of the double bond were major products of the oxidation of the 3- and 2-hexenoates in this study. Controversy exists regarding the mechanism of epoxide formation (17-19). Epoxides may form by direct attack of hydroperoxides or peroxy radicals on the carbon-carbon double bond (20).



Epoxides may also form intramolecularly by decomposition of hydroperoxides.



From the 3-isomers, the 3,4-epoxyhexanoates could be formed intramolecularly as proposed by Swern (18). A free radical would abstract an alpha hydrogen from C₂, the double bond would isomerize to the 2-position to become conjugated with the ester carbonyl, and the hydroperoxide would form at C₄.



Degradation of the hydroperoxide according to reaction 3 would lead to the 3,4-epoxyhexanoates. However, this mechanism is not likely to be responsible for the production of 2,3-epoxyhexanoate from the 2-isomer. Abstraction of an alpha hydrogen from C₄ would occur as the initial step in hydroperoxide formation, but isomerization of the double bond to the 3-position is unlikely because this would result in the loss of conjugation stabilization. Thus, the hydroperoxide group most probably forms at C₄, and the epoxy group produced according to reaction 3 would again be in the 3,4-position. Since 2,3-epoxy esters were produced during the oxidation of the 2-hexenoates, the most plausible mechanism involves direct attack on the double bond according to reactions 1 or 2.

To confirm the mechanisms proposed here, the thermal oxidation of some 6-carbon and 8-carbon mono-unsaturated free acids as well as their methyl esters was examined. The results are reported in a subsequent paper.

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