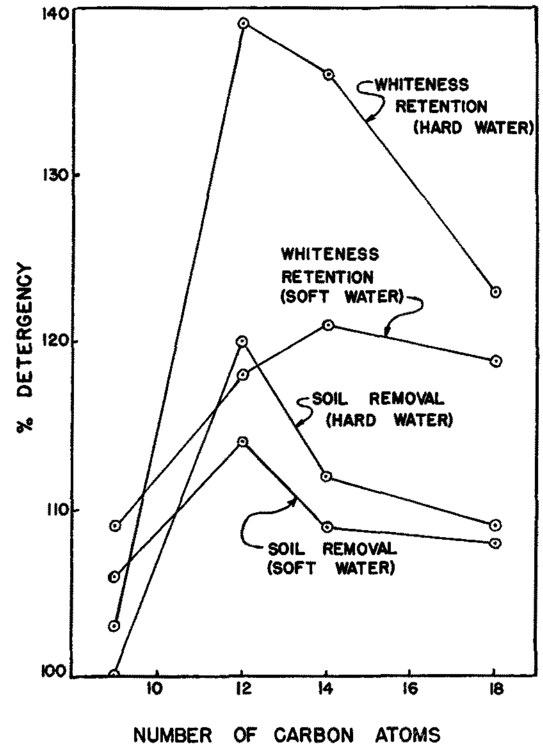
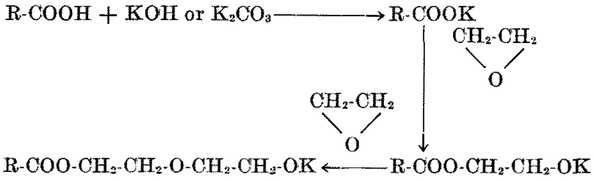


FIG. 5. Variation in detergency with number of carbon atoms in the fatty acid chain.

Remarks on the Mechanism of Ethenoxification

The esterification followed by etherification with ethylene oxide, more conveniently termed herein as "ethenoxification," apparently proceeds on the hydroxyl group of greatest acidity. This statement is based on the inability to etherify the secondary hydroxyl group of 12-hydroxystearic acid in the presence of the carboxyl group or primary alcohol group. It is well known that ethenoxification proceeds only in the presence of an alkaline catalyst. The reaction probably proceeds in the following manner wherein the catalyst actually enters into the reaction.



$$\begin{array}{l} R\text{-}COOH + KOH \text{ or } K_2CO_3 \longrightarrow R\text{-}COOK \\ R\text{-}COOK \xrightarrow{CH_2\text{-}CH_2\ (O)} R\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}OK \\ R\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OK \xleftarrow{CH_2\text{-}CH_2\ (O)} R\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}OK \end{array}$$

Since the primary alcoholic group in monoethenoxy 12-hydroxystearate is more acidic than the secondary hydroxyl group, the ethenoxy groups apparently add directly to the potassium salt of the primary alcohol exclusively. There is also some evidence that the carboxyl group is completely esterified before any primary alcoholic hydrogens are replaced. For example, titratable acidity of a monoethenoxy pelargonate was found to be negligible. It is also interesting that the addition of the first ethenoxy group to the carboxyl group proceeds at a substantially slower rate than subsequent ethenoxification.

Summary

Polyethenoxy alkanoates of varying ethenoxy chain length were prepared, and comparative detergency values were obtained on these substances. It was noted that approximately two-thirds of one ethenoxy group for each carbon atom in the hydrophobic portion of the molecule was essential for optimum detergency values. The nonionic esters prepared from lauric and myristic acids possessed substantially greater detergency than pelgargonic and stearic acids. 12-Hydroxystearic acid was likewise condensed with ethylene oxide, and curiously enough no ethenoxy groups were found attached to the secondary hydroxyl group. A partial explanation for this behavior based on the addition of ethylene oxide to the hydroxyl group of greatest acidity is presented.

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Evidence for Hydroperoxide Formation in the Autoxidation of Methyl Linolenate[1, 2]

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THE course and mechanism of the autoxidation of nonconjugated polyene fatty acid esters are considered by some investigators to have the same general pattern (1, 3). Hydroperoxides are considered to be the primary initial reaction products; other reactions that occur such as polymerization, formation of diperoxides and cylic peroxides and scission, are believed to follow to an extent determined by such factors as time, temperature, surface area, etc. The autoxidation of oleates is also believed to follow the same general pattern except that cyclic peroxides as well as hydroperoxides are believed to be produced in the early stages of the reaction, at least under some conditions (12).

Fugger *et al.* (5) in a recent study on the autoxidation of methyl linolenate however proposed that the course of the autoxidation of this ester is significantly different from that of methyl oleate and methyl linole-

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[2] Hormel Institute publication no. 95 and paper no. 157 Journal Series, General Mills Research Laboratories.

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ate. These workers concluded that little, if any monomeric hydroperoxides accumulate in the autoxidation of methyl linolenate, even under mild conditions.

As far as is known, there is no report in the literature of the isolation of hydroperoxides from autoxidized methyl linolenate. Because it has been repeatedly observed that relatively high absorption occurs in the conjugated diene wavelength region of the ultraviolet spectrum of samples of autoxidized methyl linolenate, the objective of this study was to determine to what extent hydroperoxides are produced under mild conditions of autoxidation and, if possible, to isolate them.

Methods

Autoxidation. Highly purified unconjugated methyl octadecatrienoate (approximately 85% of tri-cis, Wijs iodine no. 259.6) prepared by debromination of hexabromostearic acid was autoxidized by keeping approximately 100 g. in the dark at 0 to 2°C. in a loosely stoppered 250-ml. Erlenmeyer flask. The flask was uncovered and shaken at frequent intervals to replenish the supply of oxygen. Under these conditions about 45 days were required to bring the peroxide value to about 600 m.e./kg.

Peroxide determination. Peroxide values on autoxidized ester and peroxide concentrates were determined by an iodometric method in which air was excluded at all critical stages of the determination (10).

Extraction procedure. The countercurrent extraction procedure previously described (10), in which the oxidized fraction was simultaneously separated from unoxidized ester and distributed in the hypophases, was used.

Ultraviolet absorption analyses. The samples were dissolved in redistilled 95% ethyl alcohol and measurements made with a model DU Beckman spectrophotometer.

Infrared absorption spectra. The measurements were made with a Beckman IR-2 instrument equipped with a special slit drive for use with a rock salt prism (13). Generally 10% solutions of the materials in either carbon disulfide or tetrachloroethylene were used, depending on the wave length region under examination. Occasionally measurements were made on thin films when only very small amounts of materials were available.

Hydroxyl values. Hydroxyl content was determined by an acetic anhydride-pyridine method similar to that described by Ogg, Potter, and Willits (7), with slight modifications to increase its sensitivity.

Molecular distillation. Reduced peroxide concentrates in which the free acid was esterified by reaction with diazomethane at 0°C. were subjected to analytical micromolecular distillation by the procedure and in the still described by Paschke and Wheeler (8).

Woburn iodine values. The method of von Mikusch and Frazier (14) was used.

Hydrogenation. Analytical hydrogenations were carried out in 95% alcohol, using a 10% palladium on charcoal catalyst. The apparatus was immersed in a water bath to avoid errors due to temperature fluctuations.

Reduction of peroxides. Peroxide concentrates were reduced with 0.5% stannous chloride solution in ethanol as previously described (11).

Molecular weight. The cryoscopic method of Wilson and Heron (15) with cyclohexanol as the solvent was used for the molecular weight determinations.

Results and Discussion

The first sample of autoxidized methyl linolenate to be examined was autoxidized to a peroxide value of 760 m.e./kg. From 84.17 g. of oxidized ester, a total of 10.28 g. of oxidized fraction (concentrate I) was obtained from the combined hypophase extracts. The analyses (Table I) and the infrared spectra (Figure 1) indicated that this concentrate contained appreciable amounts of hydroperoxides. The strong doublet absorption bands at 10.55 and 10.18 microns in the infrared region showed the presence of a high proportion of cis,trans-conjugated dienes, thus confirming that the absorption of ultraviolet light at 236 mμ was due chiefly to the presence of conjugated diene. On the basis of the specific absorption coefficient at 236 mμ, this concentrate contained about 60% of cis,trans-diene conjugated peroxides (11). Further evidence for the presence of appreciable amounts of monomeric monohydroperoxides in the oxidized fraction was the fact that the reduced product had 1.04 moles of hydroxyl per mole of ester and an iodine value 82% of theory (Table I).

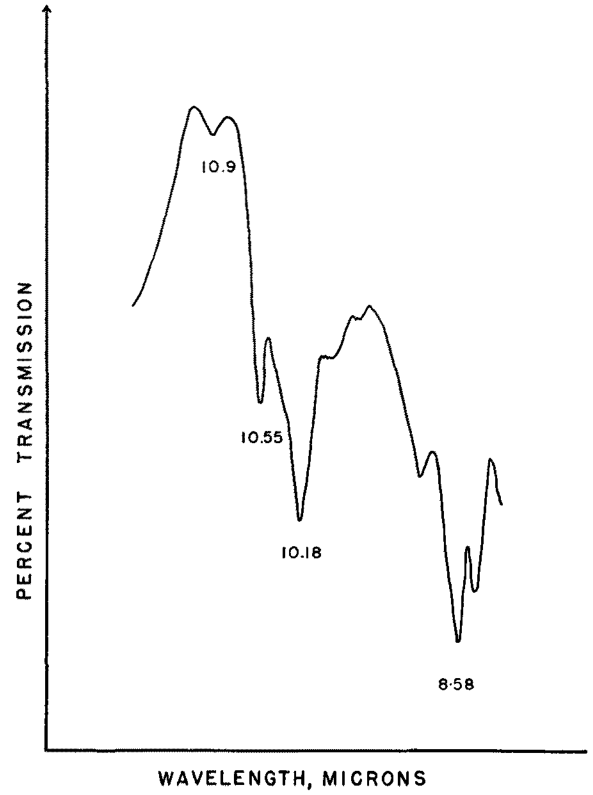

FIG. 1. Infrared spectrum. Concentrate I. (10% solution in CS_2).

The next sample studied was autoxidized to a peroxide value of 645 m.e./kg. and separated into oxidized and unoxidized fractions. The unoxidized fraction had an iodine value of 258.5 (theory 260.4) and a peroxide value of 10 m.e./kg. It showed negligible conjugation (Figure 3 E), and the infrared spectrum was essentially identical to the original unoxidized

TABLE I

Analyses of Concentrate I

	Unreduced	Reduced
Peroxide value (m.e./kg.)	6,000	175
k at 236 mμ	50.8	54.8
k at 270 mμ	6.93	5.8
k at 280 mμ	6.03	7.0
Iodine value (Woburn)	......	204.0
Epoxy oxygen (%)	1.48	0.23
Hydroxy (moles/mole of ester)	......	1.04
Acid value (mg. KOH/g.)	13.5	14.8

linolenate (Figure 4, A and B). The amount of isolated trans-double bond was essentially the same in both samples.

The oxidized fraction, concentrate II (from 98.3 g. of ester), was contained in a series of hypophases as before, but instead of combining all of the oxidized materials, the weight distribution, peroxide values, and ultraviolet absorption at 236 mμ in the individual fraction were determined as shown in Figure 2. Fractions 1-3, 4-7 8-19, and 20-30, which appeared to be of similar composition, were combined for further analyses.

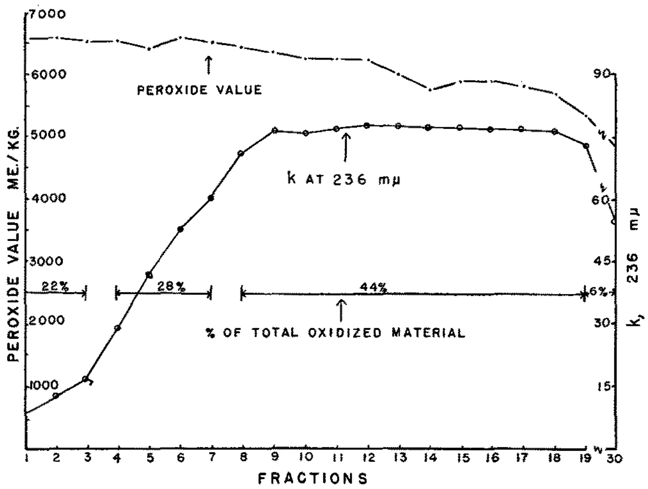

FIG. 2. Distribution analyses. Concentrate II.

Fractions 1-3. This combination of fractions was reduced with stannous chloride and reacted with diazomethane in diethyl ether at 0°C. to esterify the free acid. In spite of the fact that the iodine value was 148 (Table II), the ultraviolet absorption spectrum (Figure 3 C) and the infrared spectrum (Figure 5) both indicated an absence of an appreciable amount of conjugated diene structure. On the other hand, three slight absorption peaks—260, 270, and 280 mμ—were observed in the ultraviolet region of the spectrum. Similar absorption maxima characteristic of conjugated triene were observed in products isolated by Fugger *et al.* (5) from autoxidized methyl linolenate. However in view of the fact that the more highly oxidized material is distributed in these fractions, and there is no evidence in the infrared spectrum (Figure 5) of conjugated structures comparable to those found in alpha or beta eleostearate (9), alkyl conjugated triene, if present, does not appear to be produced in significant amounts under these conditions of autoxidation.

The infrared curve of this material (and of combined fractions 4-7) (Figure 6) also showed a stronger OH band than the combined fractions 8-19 (relatively pure reduced hydroperoxide). This may be due to greater OH concentration or due to greater association of the OH due to the presence of other polar groups. The OH band at 2.96 microns is that of bonded OH and is considerably affected by dilution and polar effects. At 10% in CS_2 this band is much weaker than when solvent is absent, due to dissociation to the free or unbonded OH structure. In spite of the fact that these fractions contained 22-28% polymer as shown by micromolecular distillation analyses, the average molecular weight was only 222. Thus these fractions also appear to contain considerable amounts of low molecular weight compounds, which probably resulted from scission reactions and are therefore a complex mixture of secondary reaction products.

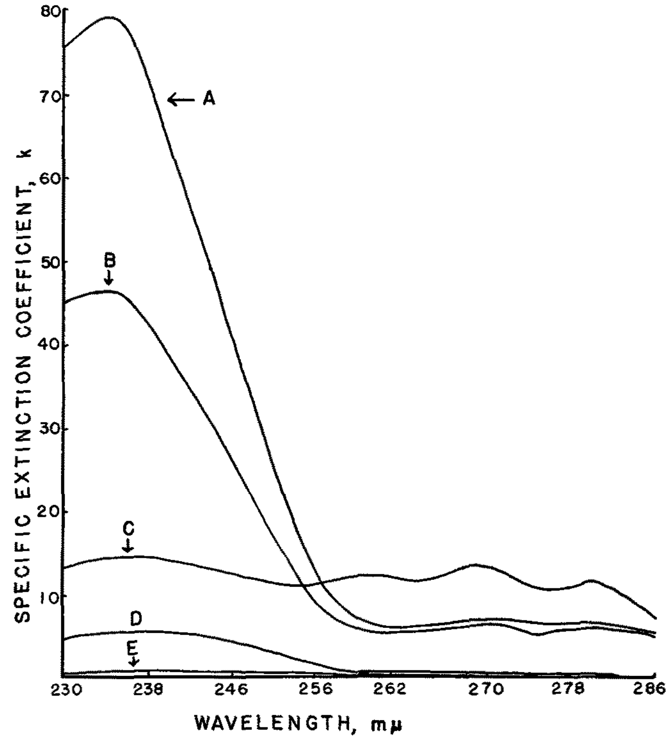

FIG. 3. Ultraviolet spectra
A. Reduced fractions 8-19, concentrate 11.
B. Reduced fractions 4-7, concentrate II.
C. Reduced fractions 1-3, concentrate II.
D. Original autoxidized ester.
E. Recovered unoxidized ester.

Fractions 8-19. Fractions 8-19 likewise were reduced with stannous chloride and free acid esterified with diazomethane at 0°C. in ethyl ether. Fractions 4 to 7 are not further considered since they obviously

TABLE II

Analyses of Combined Fractions of Reduced Linolenate Peroxide in Concentrate II
(Original PV 645)

	Fractions			
	1-3	4-7	8-19	20-30
Peroxide value ((m.e./kg.)	600.	153	100	110
k at 234 mμ	14.6	46.1	78.7	50.7
Molecular weight	222	286	310	298
Hydroxy (moles/mole ester)	1.07	0.91	1.08	0.82
Iodine (Woburn)	148	172	207	208
% Monomer	72.2	77.6	92.8	......
% Dimer	17.8	15.7	4.5	......
% Higher polymer	10.0	6.7	2.7	......
% of total oxidized fraction	21.7	28.1	44.0	6.2

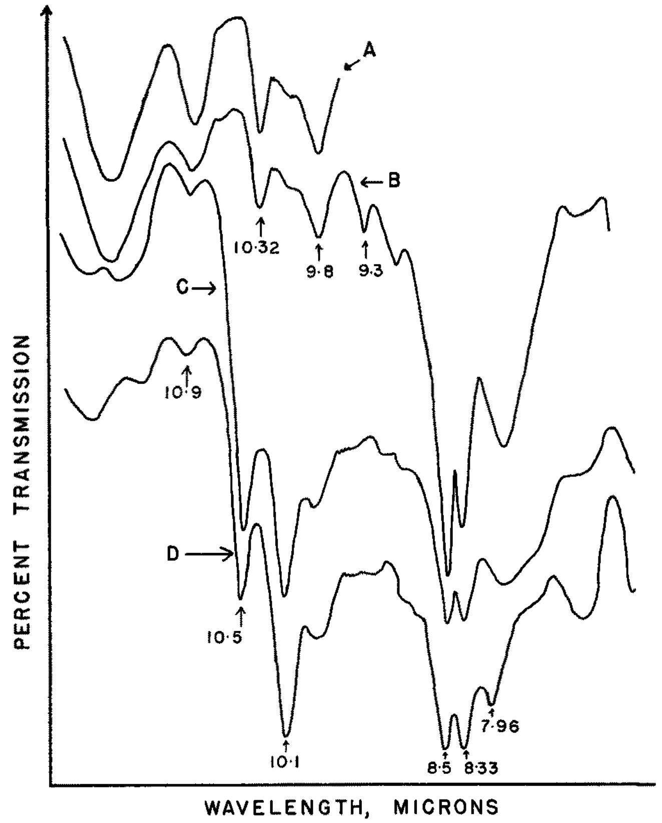

FIG. 4. Infrared spectra.

A. Original unoxidized methyl linolenate (10% solution CS_2).
B. Recovered unoxidized methyl linolenate (10% solution CS_2).
C. Distilled monomer of reduced fractions 8-19, concentrate II (thin film).
D. Distilled monomer of a reduced linoleate peroxide concentrate (original PV 1020 m.e./kg., autoxidation at 0°C.) (thin film).

consisted of mixtures of products, some similar to those in the first three fractions and others similar to materials distributed in fractions 8-19.

The specific absorption coefficient at 234 mμ of combined fractions 8-19 (Table II) was about 86% of the theoretical for a cis,trans-conjugated diene methyl hydroxyoctadecatrienoate. The infrared absorption spectrum (Figure 5) showed sharp, strong doublet bands for cis,trans-conjugated diene in accord with the ultraviolet absorption characteristics. Further evidence that these fractions consisted primarily of cis,trans-conjugated diene methyl monohydroxyoctadecatrienoate was given by the analyses in Table II. According to the Woburn iodine value, approximately 84% of the original unsaturation, or 2.5 double bonds per mole of ester, was present in these fractions, but this value may be low due to stearic factors or other errors in applying the method to these materials. The hydroxy content was equivalent to 1 mole per mole of ester. The average molecular weight was in close agreement with the theory for a monomer produced by the reduction of an octadecatrienoic hydroperoxide, and the distillation analyses showed the presence of only 7.2% polymer. The value for monomer by distillation analyses in this series of fractions as well as the others must be considered a minimum because of the presence of a small amount of unreduced peroxide, which probably would polymerize under the conditions of distillation. Nevertheless it was of interest to note that the average molecular weight increased in the fractions having less polymeric material, indicating less contamination with low molecular weight impurities.

Analyses of the distilled monomer from fractions 8-19 (Table III) showed that it had 90% of the theoretical conjugation for a cis,trans-diene conjugated methyl monohydroxyoctadecatrienoate. The infrared spectrum on a thin film of the distilled monomer (Figure 4 C) showed, in accordance with chemical and ultraviolet analyses, that no alteration of existing structures occurred during the distillation.

Also shown in Table III are the analyses on the reduced and unreduced hydroperoxide fractions (concentrate III), isolated from another sample of methyl linolenate autoxidized to a peroxide value of 602 m.e./kg. of ester. The analyses of this concentrate followed the same general pattern as that of concentrate II. Fractions 9-22 consisted mostly of hydroperoxides, as shown by the high diene conjugation and little loss of unsaturation (Table III). In this case hydrogen values were obtained, and it should be noted that the hydrogen uptake corresponded more nearly with the theoretical for a triene than did the iodine value determined on the reduced fractions 8-19 of concentrate II. The hydrogen value on unreduced fractions 9-22, concentrate III, appeared to be low from a consideration of the value on the reduced concentrate. However since linolenate hydroperoxides are labile, the catalyst may have caused decomposition, or reduction by dehydrogenation of the ethanol solvent may have occurred.

Thus on the basis of the analyses on the reduced peroxides of these materials and their distilled monomers, it is concluded that the major portion of the original material in fractions 8-19 of concentrate II

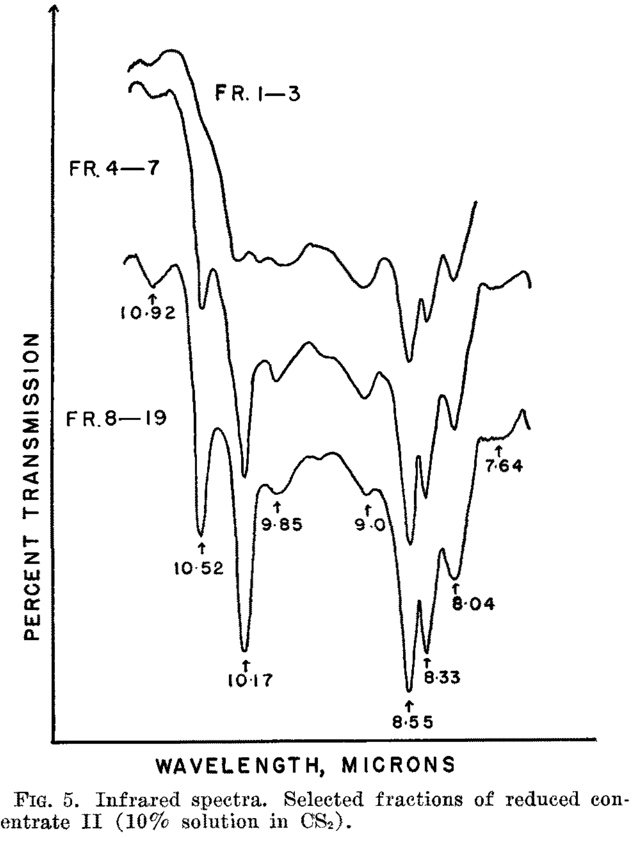

FIG. 5. Infrared spectra. Selected fractions of reduced concentrate II (10% solution in CS_2).

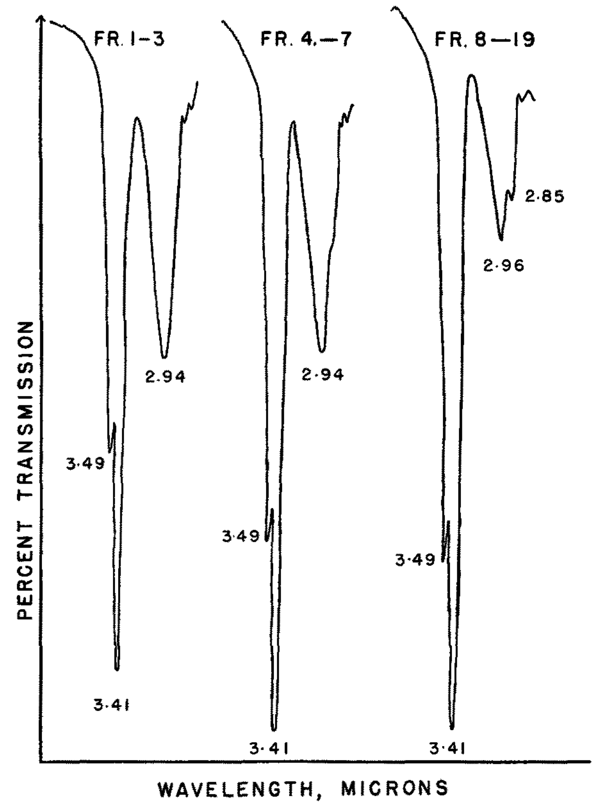

FIG. 6. Infrared spectra. Selected fractions of reduced concentrate II (10% solution in CS_2).

and 9-22 of concentrate III consisted of monomeric conjugated diene octadecatrienoate hydroperoxides. Further it appeared that most of the diene conjugation in the oxidized fractions was associated with the hydroperoxides. The evidence for this was a) an increase in diene conjugation, associated with fractions having higher unsaturation and less polymer formation, and b) diene conjugation was highest in the isolated hydroperoxide fractions.

On the assumption that a measure of diene conjugation gives a measure of trienoic monohydroperoxide content, combined fractions 1-3, concentrate II, in accord with the chemical analyses, was considered to be essentially devoid of this type of hydroperoxides. Combined fractions 4-7, although having some characteristics similar to fractions 1-3, that is, relatively high polymer content and strong absorption band at 2.9 microns, was calculated on the basis of its specific extinction coefficient at 234 mμ (Table II) to contain about 50% of such hydroperoxides. The infrared spectrum (Figure 5) of the material in these fractions showed some cis,trans-diene conjugation in agreement with the ultraviolet absorption coefficient at 234 mμ. From the yields and analyses of the various fractions of concentrate II, it is estimated that under these conditions the autoxidation products of methyl linolenate are about 60% monomeric conjugated diene hydroperoxides of octadecatrienoate and about 15% polymeric material.

TABLE III

Analyses of Selected Fractions from Concentrate II and Concentrate III

	Concentrate II		Concentrate III	
	Reduced fractions 8-19	Distilled monomer from reduced fractions 8-19	Reduced fractions 9-22	Unreduced fractions 9-22
Peroxide value (m.e./kg.)	100	......	159	6,100
k at 234 mμ	78.7	83.0	78.1	72.3
Molecular weight	310	......	314	292
Hydrogenation (moles/mole of ester)	......	......	2.8	3.45
Hydroxyl (moles/mole of ester)	1.09	1.0	0.97	......
Iodine value (Woburn)	207	229	......	......
% of total oxidized fraction	44.0	40.5	39.7	39.7

Although both conjugated and nonconjugated hydroperoxides presumably can form in the autoxidation of methyl linolenate, no direct evidence was obtained for the presence of any nonconjugated hydroperoxides in this study. This is analogous to the autoxidation of methyl linoleate (2, 11), in which it was shown that at least 90% of the peroxides were conjugated. This analogy is also evident in Figure 4, where the infrared spectrum of a typical reduced linoleate hydroperoxide (D) is seen to be virtually identical with that of a reduced linolenate hydroperoxide (C).

Summary

1. The results of chemical, spectral, and distillation analyses on the isolated oxidized fractions of three samples of methyl linolenate autoxidized at 0°C. to peroxide values from 600 to 760 m.e./kg. indicated that about 60% of the products consisted of cis,trans-conjugated diene methyl octadecatrienoate-monohydroperoxide.

2. A product was isolated from the reduced peroxide concentrates which consisted of about 90% cis,trans-conjugated diene methyl monohydroxyoctadecatrienoate.

3. Analytical micromolecular distillation analyses showed that the total oxidized material isolated from samples of autoxidized methyl linolenate contained only about 15% polymeric material under the conditions of autoxidation employed in this study.

4. Linolenate was shown to be similar to linoleate in forming a cis,trans-conjugated monomeric monohydroperoxide as a major initial product of autoxidation at 0°C.

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