

oxide radicals which could add olefin, thus building up a polymeric chain in which the repeating unit is $-\text{CHR}'-\text{CHROO}-$.

Although molecular weight measurement indicated only dimer formation, the solvent used possibly partially decomposed the polymers to the more stable peroxide structure.

Treibs in a recent report (13) stated that only a 1,4 reaction occurred and produced polymers through peroxide bridges. The data presented here support this view but add the possibility of both 1,2 and 1,6 addition to the conjugated triene system.

Summary

The autoxidation of methyl eleostearate was studied by observing the kinetics of the reaction and separating the primary oxidation products. The results indicate that an eleostearate free radical adds oxygen to the 1,2, 1,4, or 1,6 position of the triene system to produce polymers through peroxide bridges.

Autoxidation of Methyl Oleate, Methyl Stearolate, and Methyl 9,10-Dideuteroöleate^{1,2}

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THE past decade has seen notable progress in understanding the nature of the autoxidation of fats and oils. Many of these advances have been made by studying the autoxidation of pure compounds which have led to postulations regarding the mechanisms involved in this complex phenomenon. Swern, Scanlan, and Knight (1) and Täufel and Rothe (2) have reviewed these theories. More recently a number of notable contributions have been made to the knowledge of the mechanism of the autoxidation of fats, and these will not be reviewed here.

It has been often reported that water is formed during the autoxidation process, and it was thought that perhaps some information of value might result when fat derivatives containing deuterium were studied and the resulting water characterized for deuterium content. Such studies might give information concerning the induction period, peroxidation, polymerization, and fragmentation of the molecule giving rise to rancidity. Accordingly this paper will deal with the autoxidation of methyl 9,10-dideuteroöleate, a mono-olefin where the olefinic hydrogens (on carbons 9,10) have been replaced by deuterium. In another paper there will be reported the autoxidation of 8,8,11,11-tetradeutero-cis-9-octadecene, a mono-olefin where the hydrogens, on the carbons 8 and 11, α to the double bond, have been replaced by deuterium. In both instances the corresponding compounds containing no deuterium are also to be reported.

Since the deuterioöleate was prepared from stearolic acid, the autoxidation of this compound and its methyl ester was also studied.

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Some investigations have been carried out on the nature of the non-aqueous volatile matter from the autoxidized compounds which were reported by Deatherage and Mattill (3) to contain a high concentration of peroxidic oxygen.

Materials

The substrates, "reduced" oleic acid, "reduced" methyl oleate, methyl 9,10-dideuteroöleate, stearolic acid, and methyl stearolate used for the autoxidation studies were prepared according to the methods described by Khan, Deatherage, and Brown (4) whereas those designated as "crystallized" oleic acid and "crystallized" methyl oleate were prepared according to the methods of Brown and Foreman (5). The characteristics of the different substrates were:

Reduced oleic acid: B.P., 183-184° at 1.8-2.0 mm.; I. N. (Iodine Number), 89.4; $n^{20} = 1.4600$; hydrogen uptake, 1.00 mole H_2 per mole.

Reduced methyl oleate: B.P., 171-172° at 1.9-2.0 mm.; I. N., 85.1; $n^{20} = 1.45215$; hydrogen uptake, 1.00 mole H_2 per mole.

Methyl 9,10-dideuteroöleate: B.P., 173-174° at 1.8-2.0 mm.; I. N. 84.7; $n^{20} = 1.45186$, $n^{26} = 1.4492$; deuterium content, 5.05 atoms per cent of hydrogen and deuterium (theory 5.55).

Stearolic acid: M.P. 46.0-46.5°; I. N., 89.5; $n^{20} = 1.4510$, $n^{21.5} = 1.4484$; hydrogen uptake, 1.98 moles H_2 per mole (theory, 2 moles). Freezing point curve, carbon and hydrogen analysis, and ozonolysis confirmed the purity of the material as 9-octadecenoic acid.

Methyl stearolate: B.P., 174-175° at 2.6-3 mm.; I. N., 86.2; hydrogen uptake, 2.00 moles H_2 per mole; $n^{20} = 1.4562$, $n^{22.5} = 1.4435$.

Crystallized oleic acid: M.P., 13.3-13.4°; I. N., 89.99; $n^{20} = 1.4600$.

Crystallized methyl oleate: B.P., 171-172° at 1.9-2.0 mm.; I. N., 84.97; $n^{20} = 1.4521$.

Hydroxy heptyl peroxide, 95%; methyl amyl ketone peroxide, 95%; and t-butyl hydroperoxide, 60%. These were donated by the Lucidol Division, Novadel-Agene Corporation.

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TABLE I
 Induction Periods and Oxygen Consumption for Various Substrates

Substrate	Source	Impurities, especially dienes	Induction period (hrs.)	Autoxidation time	Moles oxygen consumed per mole substrate
Methyl oleate.....	Crystallized	?	18	91.0	0.345
Methyl oleate.....	Crystallized (treated with charcoal)	?	16	247.5	2.168
Methyl oleate.....	Crystallized (treated with charcoal)	1% linoleic acid added after 78th hour	16	126.0	0.865
Methyl oleate.....	Crystallized	1% autoxidized methyl oleate, Per. No. 571	0	56.0	0.878
Methyl oleate.....	From methyl stearolate by reduction	Nil	33	154.8	1.655
Methyl 9,10-dideuterooleate.....	From methyl stearolate by reduction	Nil	128	370.8	1.883
Methyl 9,10-dideuterooleate.....	From methyl stearolate by reduction	1% linoleic acid added	22	185.0	1.672
Oleic acid.....	From stearolic acid by reduction	Nil	7	81.0	0.772
Oleic acid.....	Crystallized	?	10.4	66.3	0.980
Methyl stearolate.....		Nil	0	89.5	2.30
Stearolic acid.....		Nil	0	113.0	1.81

Methods

For the autoxidation studies the methods and techniques were those reported by Deatherage and Mattill (3) wherein oxygen is slowly bubbled through the substrate at 75°C. and the volatile materials are caught in dry ice traps. In addition to this, some studies were conducted by incubation in air and oxygen at 65° and 75°

For iodine number determinations Wijs' (1/2 hour) method (6) was used and for carbonyl analysis the method of Findley (7) was used.

For deuterium analysis the non-aqueous materials were subjected to the standard semi-micro combustion similar to that described by Niederl and Niederl (8), and the water formed was collected in dry ice traps. This water and the water from autoxidation of the substrates were analyzed for deuterium by Prof. Herrick Johnston and his associates in the Department of Chemistry. Their methods consisted of converting the water to a mixture of hydrogen and deuterium gas, which was examined using a mass spectrograph.

Polarographic studies on some of the autoxidation products were done as described by Quackenbush, *et al.* (9, 10).

Results and Discussion

In Table I data are tabulated on the induction periods and total oxygen absorbed by various substrates when allowed to autoxidize at 75°. (As used in this paper, the induction period is the time required for oxygen absorption to begin.) There is a definite induction period with both oleic acid and methyl oleate confirming the findings of Greenbank and Holm (11) and Gunstone and Hilditch (12). The induction period for the acid is shorter than for the ester. With methyl oleate, prepared by crystallization, the induction period was shorter than for the ester prepared by the reduction of methyl stearolate, perhaps indicating a trace of linoleate in the "crystallized" ester. This indicated that separation of methyl oleate from methyl stearate and methyl stearolate is more effective than the separation from methyl linoleate. The addition of a small amount of autoxidized methyl oleate reduced the induction

period of purified methyl oleate to 0. The addition of 1% linoleate or stearolate shortened the induction period of methyl oleate.

When the induction period of methyl 9,10-dideuterooleate are compared with that of methyl oleate, a rather striking difference is seen. The replacement of the olefinic hydrogen atoms with deuterium causes a prolongation of the induction period. Even when 1% linoleic acid is added to the deuterooleate, there is an induction period comparable to the pure methyl oleate. The involvement of the olefinic hydrogen

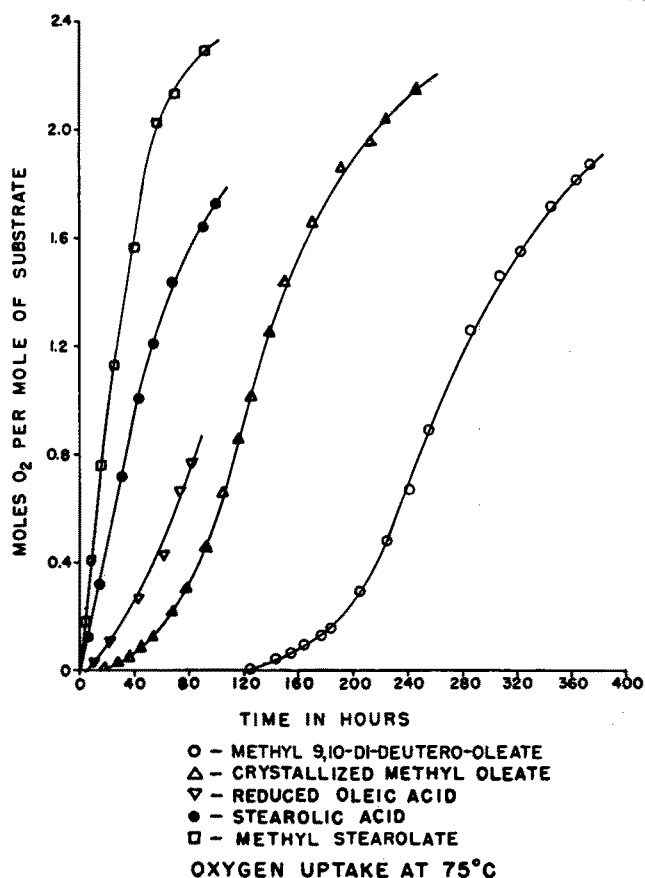


FIG. 1.

atoms or other substituents and the double bond appears to be definitely related to the onset of autoxidation. [Cf. Farmer (13, 14), Gunstone and Hilditch (15), Bolland and Gee (16).]

Neither stearic acid nor methyl stearolate has an induction period. Apparently the effect of the triple bond is to accelerate the autoxidation reaction. This is in decided contrast with the simple addition of ozone and the halogens which are much slower to react than in the case of the corresponding olefins. This contrast between autoxidation and addition reactions indicates a fundamental difference between the two phenomena.

The curves of oxygen consumption are shown in Figures 1-3; in Table I total oxygen consumption is given. These data indicate that the olefinic substrates are somewhat similar in their autoxidative behavior even though the induction periods may be shortened or lengthened by the procedures noted. The oxygen absorption of methyl oleate and methyl 9,10-dideuterooleate follow almost identical patterns except that the oxygen absorption curve is displaced approximately 100 hours by the long induction period. It is also noted that oleic acid absorbs less oxygen than the corresponding ester, a fact which confirms the reports of others (3, 17). Contrast be-

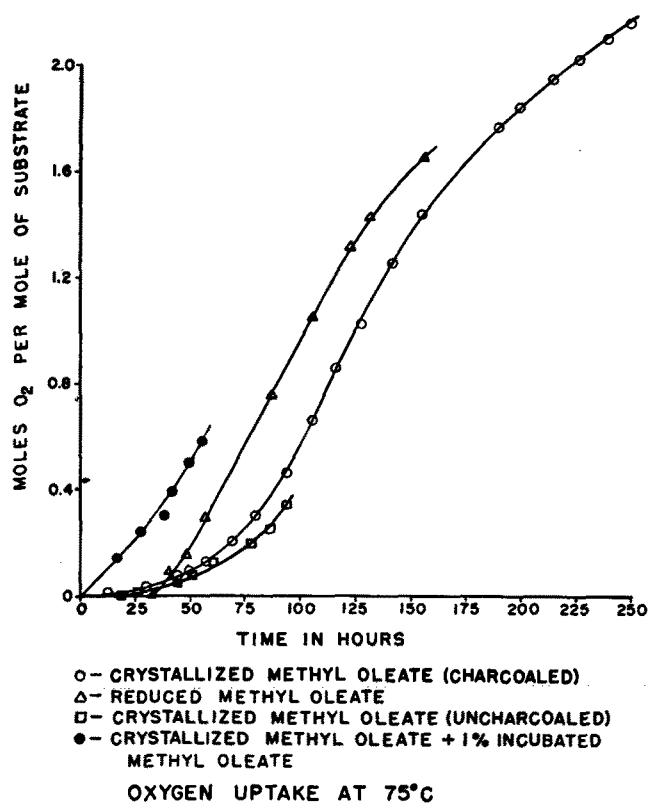


FIG. 2.

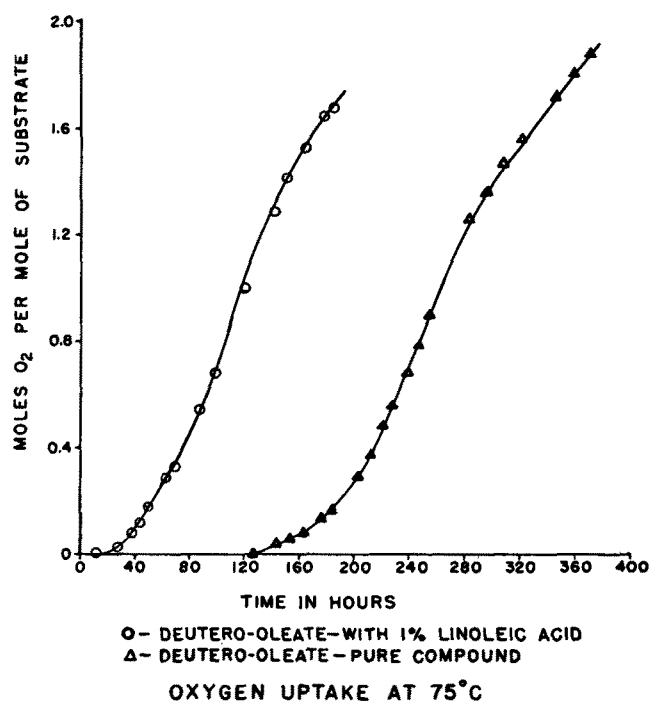


FIG. 3

tween the olefinic and acetylenic substrates is seen when the rate and amounts of oxygen absorbed are compared. Methyl stearolate and stearic acid absorbed more oxygen and at a faster rate. But here also, as with the olefinic substrates, the acid absorbed less oxygen and at a lower rate than did the ester.

Table II shows some of the characteristics of the autoxidation residues. In general, these data concur with the results of Deatherage and Mattill (3) on methyl oleate. It is noteworthy that the characteristics of the residues from the oleate and the deuterio-oleate are quite similar. Some carbonyl is found in the residues of the olefinic substrates, but the amount is not great.

There was considerable polymerization when both methyl stearolate and stearic acid were allowed to autoxidize, for the substrates became quite viscous—the acid somewhat more than the ester. There was a relatively large amount of carbonyl oxygen in these residues, which were quite yellow in color, yet no diketostearic acid was isolated. The degree of unsaturation remaining in the autoxidation residues from stearic acid and its ester was somewhat high when compared to that from the oleates. Considerable acid and ester groups were present, but only small amounts of peroxide and hydroxyl group were found. These observations indicate some fundamental differences in the over-all pattern of reactions in the acetylenic compounds as compared with the olefinic substrates.

TABLE II
Autoxidation Residues

Substrate	Millimoles Per Gram of Residue					
	—COOH	—COOC—	—CH=CH—	=C=O	—O—	—OH
Pure methyl oleate (crystallized).....	1.25	3.64	0.394	0.88	0.258	1.37
Pure methyl oleate (reduced).....	1.23	5.05	0.429	0.94	0.551
Methyl 9,10-dideuterooleate + 1% linoleic acid.....	0.870	0.567
Pure methyl 9,10-dideuterooleate.....	1.34	4.25	0.461	0.97	0.326	1.89
Methyl stearolate.....	2.21	5.29	2.17	2.40	0.246	0.47
Stearic acid.....	4.42	2.28	2.59	2.49	0.983	0.48

Data concerning the volatile products of autoxidation are shown in Table III. Water appears as an important autoxidation product accounting for one out of four or five atoms of the oxygen absorbed for the methyl oleate and slightly less for stearolic acid and its methyl ester. When the autoxidation reactions were interrupted during the earlier stages, the ratio of water to oxygen absorbed was higher, indicating that water is formed at an early stage of the au-

TABLE III
Volatile Autoxidation Products

Substrate	H ₂ O moles per mole of substrate	CO ₂ moles per mole of substrate	Non-aqueous volatile products	
			Grams per mole of substrate	Peroxide content, milli-moles/g.
Methyl oleate (crystallized)...	0.826	0.022	56.1	3.63
Methyl oleate (reduced).....	0.757	0.013	25.8	3.52
Methyl 9,10-dideuteriooleate + 1% linoleic acid.....	0.792	0.000	25.8	3.67
Methyl 9,10-dideuteriooleate...	0.960	0.027	43.5	3.71
Methyl stearolate.....	0.846	0.133	25.1	3.79
Stearolic acid.....	0.635	0.106	21.3	2.78

toxidation process. Furthermore, when the amount of methyl oleate was increased six-fold without changing the flow rate of the oxygen, the amount of water formed per mole of substrate remained the same but not the non-aqueous volatile matter, which was diminished proportionately. Furthermore in this instance even though the amount of oxygen absorbed and water formed per mole were unchanged, there was more polymerization, as indicated by a marked increase in viscosity.

Whereas very little carbon dioxide was formed when the methyl oleates were autoxidized, slightly more than one mole of CO₂ per mole of substrate resulted from the autoxidation of the methyl stearolate and stearolic acid. The non-aqueous volatile matter from the oleates gave an intense and typical odor of rancidity and the Kreis reaction. This fraction from the acetylenic substrates had an odor somewhat similar to that from the oleates but gave no Kreis test.

The amount of non-aqueous volatile matter varied

somewhat according to the length of run. The peroxide content of this material was quite high, indicating a mean molecular weight of the volatile peroxides to be less than 300. It was noted that these peroxides appeared to be neutral and, on standing at room temperature, the peroxide content of the volatile matter decreased while the acid value increased.

In attempts to purify these peroxidic substances a number of somewhat impure crystalline preparations were obtained which could not be characterized. From these materials three preparations were made with the following melting points, peroxide numbers, and carbon hydrogen analyses respectively: 45-50°, 2800, 51.9%, 10.25%; 57-58°, 2200, 67.0, 12.0; 57-58°, 2100, 63.0, 7.0. It is of interest to note that these materials on polarographic study by the method of Quackenbush, *et al.* (9, 10) behaved similarly to commercial preparations of hydroxy heptyl peroxide and methyl amyl ketone peroxides and at the same time failed to give the Kreis test. In contrast, the crude volatile products gave intense Kreis reactions and on similar polarographic study showed marked differences from the commercial carbonyl peroxides. Consequently it appears that either the purification procedure altered the nature of the volatile products or that some of the major constituents were rejected in the purification. From the yields of the crystalline preparations the latter explanation may be correct.

Another important property of the non-aqueous volatile matter was brought out by studying the oxidation of methyl oleate by the volatile material, *t*-butyl hydroperoxide, methyl amyl ketone peroxide, and hydroxy heptyl peroxide, Table IV. The strong oxidizing power of the volatile matter is indicated by complete cleavage of methyl oleate when 1/2 mole of the oleate was used for each mole of active oxygen. However when an excess of methyl oleate was used, only a small amount of cleavage resulted and the high melting form of dihydroxystearic acid was formed when the incubated mixture was treated with acetic acid and saponified by the method of Deatherage and Mattill (3). This high melting isomer is the same as that reported by many investigators and confirmed

TABLE IV
Effects of Different Substances on Autoxidation of Methyl Oleate

Substance added	Treatment	Peroxide number	Dihydroxy derivative isolated	Degree of scission of methyl oleate
Nothing.....	Autoxidation at 75° with absorption of 2.16 moles O ₂ per mole	258.0	High melting + minor amounts of low melting	Considerable
Nothing.....	Incubated at 65° for 2 1/2 days in oxygen	71.2		
1% methyl stearolate.....	Incubated at 65° for 2 1/2 days in oxygen	213.0		
1% methyl stearolate.....	Incubated at 65° for 2 1/2 days in oxygen	638.0		
Methyl oleate + 1% methyl linoleate.....	Incubated at 65° for 2 1/2 days in oxygen	571.0		
Hydroxy heptyl peroxide, 1 mole per mole.....	Incubated at 75° for 4 days in air	35.2	Low melting	Considerable
Methyl amyl ketone peroxide, 1 mole per mole.....	Incubated at 75° for 4 days in air	122.0	Low melting (almost quantitative)	Small amount
<i>t</i> -Butyl hydroperoxide, 1 mole per mole.....	Incubated at 75° for 4 days in air	2610.0	Low melting (very small amount)	None
Volatile material from autoxidation of methyl oleate, 2 moles peroxide per mole.....	Incubated at 75° for 3 days in air	122.0	Nil	Complete
+ 1% volatile material from autoxidation of methyl oleate.....	Incubated at 75° for 4 days in air	102.0	High melting	Small amount

TABLE V
 Partition of Deuterium From Autoxidized Methyl 9,10-Dideuteroöleate

Substrate	Deuterium Content—Atoms Per Cent of Hydrogen and Deuterium				
	Original substrate		Water formed by autoxidation of substrate at 75°	Autoxidized residue of substrate	Volatile product from autoxidation of substrate at 75°
	Analysis	Theory			
Methyl 9,10-dideuteroöleate.....	5.05	5.55	5.46	4.78	3.25
Methyl 9,10-dideuteroöleate + 1% linoleic acid.....		5.50	5.77	4.05	3.06

here to result from the autoxidation of oleates. In contrast, it will be seen from Table IV that *t*-butyl hydroperoxide and methyl oleate were essentially unchanged when mixed and allowed to stand at 75°; and when methyl oleate and methyl amyl ketone peroxide or hydroxy heptyl peroxide were incubated at 75°, the low melting dihydroxystearic acid resulted. These facts again illustrate the peculiar character of these volatile materials which are so typical of rancid fats. Table IV also brings out another fact worthy of mention, and that is the pro-oxygenic properties of the volatile peroxides and methyl stearolate.

It has been found that the volatile peroxidic compounds can be reduced to carbonyl compounds and a number of 2,4-dinitrophenylhydrazones have been prepared but not characterized. This might suggest that there may be some relation, perhaps as precursors, between the volatile peroxides and the aldehydes reported by Swift, *et al.* (18, 19), Schepartz and Daubert (20), and by Brekke and Mackinney (21).

When methyl 9,10-dideuteroöleate was allowed to autoxidize with and without linoleic acid, only small differences appeared except for the induction period. This was true for the deuterium content of the various fractions, Table V, as well as shape of the curves of oxygen absorption, Figs. 1 and 3. The deuterium analyses which tended to give slightly low results for this type of study did not show a high deuterium content for any of the fractions. It is apparent that the ratio of deuterium to hydrogen in the water, residue, or non-aqueous volatile matter did not change markedly from the ratio in the initial methyl 9,10-dideuteroöleate. This appears to indicate that no large or significant amount of water comes from the olefinic hydrogens. The amount of deuterium in the water indicates apparently that some water comes from the olefinic hydrogens and that most of the hydrogens come from other positions along the carbon chain. There appears to be a slight shift in the deuterium concentration from the substrate and residue to the water. This might arise from oxidative cleavage at the 9,10 position giving labile deuterium atoms which might migrate to the water phase. It is well known that some cleavage with the formation of 9 carbon compounds, such as pelargonic acid, does take place. The deuterium in the water, of course, could come from direct attack at the double bond since it is thought (13, 14, 15, 16, 17) that such oxidative attack initiates and precedes the hydroperoxidation at the α -position. If this is true, and our results on the induction periods of methyl oleate and deuterioöleate appear to support this postulate, one might expect some oxidation to continue to some degree at the 9 and 10 positions and give rise to the deuterium in the water. At best the use of the deuterioöleate to study the mechanism of water formation and rupture of the carbon-carbon or carbon-hydrogen bond has given inconclusive results.

Summary

A comparative study of the autoxidation of methyl oleate, methyl 9,10-dideuteroöleate, methyl stearolate, and stearolic acid has re-emphasized the complexity of the autoxidation phenomenon. The autoxidation of the acetylenic compounds indicates the importance of peroxidation of the active methylene group as compared to the addition of oxygen at the unsaturated linkages. The importance of olefinic hydrogens and the role of the double bond with respect to the induction periods and possible addition reactions has been brought out by the studies on the autoxidation of the deuterioöleate. Consequently it appears that during autoxidation of methyl oleate, oxidative attack is initiated at the olefinic position and then at α -methylene position and that water formation occurs shortly thereafter. At least some of the hydrogen of the water formed during autoxidation comes from the olefinic hydrogens.

It appears that most of the non-aqueous volatile cleavage products arising from a rupture of a carbon to carbon bond are peroxidic in character. The nature of these volatile peroxides appears different from several commercially available organic peroxides since they are capable of oxidizing methyl oleate in a manner to yield the high melting form of dihydroxystearic acid whereas peracids and some peroxides under similar conditions give only the low melting isomer.

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