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Reactions of Fatty Materials With Oxygen. XV.[1] Formation of 9,10-Dihydroxystearic Acid and Cleavage Products in the Oxidation of Oleic Acid and Methyl Oleate in Acetic Acid[2]

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THE prolonged autoxidation of unsaturated fatty materials in the absence of solvents leads eventually to highly viscous products through which efficient dispersion of oxygen is extremely difficult (11). The obvious solution, namely, use of a diluent, is complicated by the problem of finding an "inert" material. Consideration of possible "inert" solvents, as well as examination of the literature, indicated that glacial acetic acid most nearly meets the requirements and, in addition, it possesses the characteristic of accelerating autoxidation reactions (1, 5, 13).

This paper describes the results obtained in the autoxidation of oleic acid and methyl oleate at 25-30°, 65°, and 115-120°C. in acetic acid solution with cobalt acetate (or occasionally cobalt oleate) as the catalyst. Samples were withdrawn at suitable time intervals, the acetic acid was recovered, and the non-volatile residue was worked up to isolate 9,10-dihydroxystearic acid, short-chain cleavage products (mono- and dibasic), unoxidized and monohydroxy materials, and polymers.

Experimental

Materials Used. The oleic acid and methyl oleate (composition: oleic, 94-98%; linoleic, 0.3%; saturates, 2-6%) were prepared from olive oil (7). Cobaltous acetate and glacial acetic acid were analytical reagent grade. Cobaltous oleate was prepared from purified oleic acid as described previously (11).

Autoxidation Procedure. A typical experiment at 65° is described in detail. (Tables I, II, and III summarize the results obtained at 25-30°, 65°, and 115-120°). A solution consisting of 1,000 g. of oleic acid (or methyl oleate), 10.1 g. of cobaltous acetate (or 33 g. of cobaltous oleate), and 2,000 ml. of glacial acetic acid was prepared in a 5-l., three-neck flask equipped with a thermometer, a reflux condenser, and two fritted discs immersed in the solution. A vigorous stream of air or cylinder oxygen was passed through the solution while the temperature was maintained at 65°. Samples of the solution (ca. 450-500 ml.) were withdrawn at suitable time intervals for isolation and analysis of oxidation products.

The acetic acid was recovered under reduced pressure and the residue analyzed. The oxidation was stopped when the iodine number became substantially constant (5-10); this usually required 150-250 hours at 65°. The peroxide values were negligible throughout.

The residue was refluxed for six hours with an excess of 6 *N* aqueous sodium hydroxide, acidified while hot with 6 *N* sulfuric acid, and stirred vigorously. A dark brown viscous oil separated. After the mixture had cooled to room temperature, it was treated with ether and the aqueous layer was reextracted. The combined ether solutions, in which a considerable quantity of insoluble white solid was suspended, was washed three times with small quantities of water to remove excess sulfuric acid and salt. These washings were reextracted with ether, and all ether solutions were then combined. The ether:solute ratio was approximately 3:1 at this point. The ether solution was cooled to 0 to 5° and filtered, and the solid was washed once with a small amount of cold ether. The precipitate was substantially pure high-melting 9,10-dihydroxystearic acid, m.p. 129-130° and neutralization equivalent, 317-323. A mixed melting point with an authentic sample, m.p. 130-131°, showed no depression. The yield was 12-17%, depending on the oxidation time (Table II). [An additional 1-2% of slightly impure high melting 9,10-dihydroxystearic acid, m.p. 120-123°, could be obtained by evaporation of the ether, solution of the residue in acetone (5 ml. per g. of solute) and cooling to —20°, followed by recrystallization of the precipitate from 95% ethanol at 0°.]

The dark-brown viscous residue obtained after recovery of the ether was converted to methyl esters by refluxing for eight hours with a large excess of anhydrous methanol (sulfuric acid catalyst). These esters were distilled from a Claisen flask to a maximum pot

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[1] Paper XIV is reference 10.

[2] Presented at the Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Nov. 2-4, 1953.

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TABLE I

Yields of Products Obtained in Autoxidation of Oleic Acid at 25-30° in Acetic Acid

Oxidation time, hours	High-melting 9,10-dihydroxystearic acid			Cleavage products and unoxidized material[a]			Unoxidized and hydroxy material[b]				Polymeric residue[c]	
	Yield %	Neut. equiv.	M.P., °C.	Yield %	Sapon. no.	Iodine no.	Yield %	Sapon. no.	Iodine no.	Hydroxyl oxygen, %	Yield %	Mol. wt.[d]
100	6	312	128	33	210	50	43	212	70	0.2	18	935
200	8	320	127	58	220	44	14	237	60	0.5	20	865
300	4	316	127	21	230	43	55	248	64	0.6	22	865
400	6	317	125	25	230	32	52	250	64	1.7	16	1,780
500	16	315	127	30	237	32	34	238	44	1.8	20	820
1,000	11	310	130	23	374	17	45	240	51	1.9	19	2,600

[a] Boiling range, 60°/4-160°/0.4 mm.
[b] Boiling range, 140°/0.05-200°/0.1 mm.
[c] Non-volatile at a pot temperature of 230°/0.1 mm.
[d] Determined ebullioscopically in chloroform.

TABLE II

Yields of Products Obtained in Autoxidation of Oleic Acid at 65° in Acetic Acid

Oxidation time, hours	High-melting 9,10-dihydroxystearic acid			Cleavage products and unoxidized material			Unoxidized and hydroxy material				Polymeric residue	
	Yield %	Neut. equiv.	M.P., °C.	Yield %	Sapon. no.	Iodine no.	Yield %	Sapon. no.	Iodine no.	Hydroxyl oxygen, %	Yield %	Mol. Wt.
16	12	321	130	48	304	40	16	206	34	4.1	22	540
32	17	321	130	48	365	23	13	217	31	4.8	20	860
64	16	320	130	58	393	16	9	216	26	5.6	16	845
128	13	323	130	64	414	11	9	232	24	5.6	12	......[a]
256	12	317	129	68	433	8	8	256	32	4.2	11	......

[a] Insoluble.

TABLE III

Yields of Products Obtained in Autoxidation of Oleic Acid in Boiling Acetic Acid (115-120°)

Oxidation time, hours	High-melting 9,10-dihydroxystearic acid			Cleavage products and unoxidized material			Unoxidized and hydroxy material			Polymeric residue	
	Yield %	Neut. equiv.	M.P., °C.	Yield %	Sapon. no.	Iodine no.	Yield %	Sapon. no.	Iodine no.	Yield %	Mol. Wt.
4	2	326	129	81	199	79	8	210	66	8	1,090
8	3	......	129	74	211	73	9	213	71	14	......[a]
16	4	321	130	72	210	70	9	208	47	15	1,055
32	7	320	128	62	236	59	6	217	51	24	855
64	9	321	129	50	317	34	14	210	47	26	800
128	11	320	129	43	356	22	11	231	40	31	735

[a] Insoluble.

temperature of 230°/0.1 mm. Two overhead fractions, b.p. 60°/4-160°/0.4 mm. and 140°/0.05-200°/0.1 mm. were taken. Results are summarized in Table II. Maximum yields of cleavage products were 64-68%; polymer yields were 11-22%.

Discussion

Tables I, II, and III summarize the results obtained in the oxidation of oleic acid at 25-30° (room temperature), 65°, and 115-120° (the reflux temperature of the reaction mixture), respectively.

At an oxidation temperature of 65° the yield of high-melting 9,10-dihydroxystearic acid remains fairly constant between 12-17% (Table II). At 25° (Table I) and 115-120° (Table III) the yield is lower during the oxidation periods studied. At 115-120° the yield increases from 2% after 4 hours of oxidation to 11% after 128 hours; at 25-30° the yield appears to reach a maximum of 16% after 500 hours and then drops.

The best yields (64-68%) of cleavage products are also obtained at 65° (Table II). Examination of the iodine and saponification numbers of the cleavage products obtained after 256 hours of oxidation indicates that unoxidized material probably does not exceed 10% of this fraction. On the other hand, at room temperature (Table I) or the boiling point (Table III) the yields of cleavage products are considerably lower. At 100° the results are substantially the same as at 65°, but the oxidation time is shorter.

The formation of relatively large amounts of 9,10-dihydroxystearic acid plus cleavage products at 65° (Table II) is necessarily accompanied by reduced yields of unoxidized, hydroxy, and polymeric materials, which is a desirable situation. On the other hand, at room temperature (Table I) and the boiling point (Table III) these last materials account for over 60% and 40%, respectively, of the starting material. Autoxidation at room temperature and the boiling point of acetic acid are therefore inefficient techniques for the preparation of 9,10-dihydroxystearic acid or cleavage products. At 65° however approximately 80% of the original oleic acid can be accounted for as desirable products. Since we have shown qualitatively (8) that the polymeric residue also yields cleavage products on reoxidation, the overall conversion is fairly high.

Separation of the cleavage products by conventional methods (saponification of the mixed methyl esters, acidification, steam distillation, reesterification with methanol, and fractional distillation) shows that they consist mainly of methyl esters of C_6-C_{12} mono- and dibasic acids. Unfortunately their precise chain-length distribution is not known because of handling losses and the relatively small quantities available by the time the analytical distillations were carried out. Based on the present data, methyl esters of C_8-C_{10} acids appear to predominate as would be expected (3, 9).

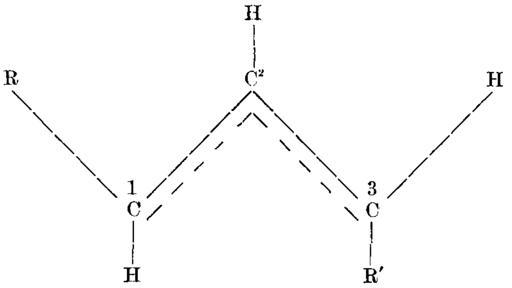
Oxidation at 65° proceeds more rapidly than at

25-30° or 115-120°. The surprisingly slow rate of oxidation at 115-120° is probably a consequence of the lowered solubility of oxygen in boiling acetic acid as well as the poor contact between oxygen and the substrate because of acetic acid vapor.

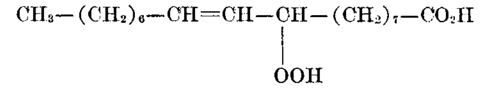
In general, the molecular weights of the polymeric residues are about 800-1,100 with occasional samples in the range of 1,800-2,600. Products partially insoluble in boiling chloroform were also encountered from time to time. No further examination of the polymeric residues was conducted.

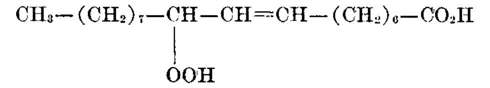
The 9,10-dihydroxystearic acid isolated from the saponified, acidified autoxidation mixture is the high-melting isomer, it has a sharp melting point, usually not below 128°, and its purity is obviously high. This is indeed surprising in view of the complexity of autoxidation reactions and the known shifting of double bonds which takes place.

The most likely precursor of high-melting 9,10-dihydroxystearic acid is *trans*-9,10-epoxystearic acid, which Ellis (3) has shown to be formed in about 20% yield by autoxidation of either oleic or elaidic acid. The fact that both a *cis* and a *trans* olefinic compound yield the same product is striking confirmation of our earlier proposal (6) that the majority of the radicals in the autoxidation of oleic (or elaidic) acid take the configuration shown below,

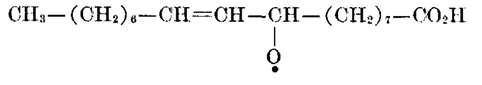


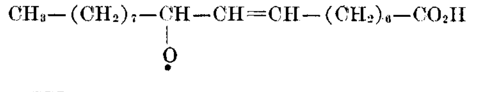
add oxygen at carbon atom 3 and become a *trans* hydroperoxide which would be a mixture mainly of 9-hydroperoxido-*trans*-10-octadecenoic acid (I) and 10-hydroperoxido-*trans*-8-octadecenoic acid (II) (10).


$$CH_3-(CH_2)_6-CH{=}CH-\underset{\displaystyle OOH}{\underset{|}{C}H}-(CH_2)_7-CO_2H \qquad (I)$$

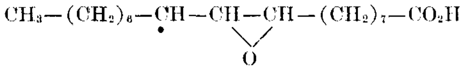

$$CH_3-(CH_2)_7-\underset{\displaystyle OOH}{\underset{|}{C}H}-CH{=}CH-(CH_2)_6-CO_2H \qquad (II)$$

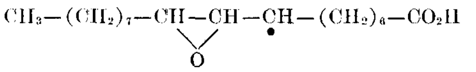
Cleavage of the —O—O— bond would yield HO· and RO· (III and IV). This type of unimolecular peroxide decomposition would be expected when hydroperoxide concentration is low (1a), as is the case when cobalt salts are present.


$$CH_3-(CH_2)_6-CH{=}CH-\underset{\underset{\bullet}{O}}{\underset{|}{C}H}-(CH_2)_7-CO_2H \qquad (III)$$


$$CH_3-(CH_2)_7-\underset{\underset{\bullet}{O}}{\underset{|}{C}H}-CH{=}CH-(CH_2)_6-CO_2H \qquad (IV)$$

Both III and IV, merely by a shift of one π-electron of the double bond to couple with the odd electron on oxygen, could form the oxirane ring in the 9,10-position as shown (V and VI).


$$CH_3-(CH_2)_6-\underset{\bullet}{C}H-\underbrace{CH-CH}_{O}-(CH_2)_7-CO_2H \qquad (V)$$


$$CH_3-(CH_2)_7-\underbrace{CH-CH}_{O}-\underset{\bullet}{C}H-(CH_2)_6-CO_2H \qquad (VI)$$

Reacquisition of a hydrogen atom by V or VI would yield the identical compound, namely, *trans*-9,10-epoxystearic acid, the product actually isolated when solvent is absent (3). In acetic acid however *trans*-9,10-epoxystearic acid is converted by ring opening to the hydroxyacetoxy compound which yields high-melting 9,10-dihydroxystearic acid on hydrolysis.

This reaction scheme also accounts for the isolation of triol, reported by earlier works for other systems (4), since the reacquisition of the HO· by V or VI followed by hydrolysis would yield a trihydroxy compound.

It should not be concluded however that high-melting, 9,10-dihydroxystearic acid is the sole dihydroxy compound formed although there is no doubt that it predominates. It has been shown by us (11), as well as by others (3, 12), that low-melting 9,10-dihydroxystearic acid is also formed. In the present investigation a 0.5-1% yield of low-melting 9,10-dihydroxystearic acid, m.p. 92° (a mixed melting point with an authentic specimen, m.p. 95°, was not depressed), was obtained from the fraction consisting of unoxidized and hydroxy material (Tables I, II, III) by saponification, acidification, and crystallization of the mixed acids successively from acetone and alcohol at 0°.

The isolation of only minor quantities of low-melting 9,10-dihydroxystearic acid strongly suggests that the formation of oxirane compounds does not occur by an epoxidation reaction between a peroxide and an olefinic compound. If epoxidation were an important reaction, appreciable quantities of *cis*-9,10-epoxystearic acid (solvent-free system) or low-melting 9,10-dihydroxystearic acid (acetic acid system) would be isolated since oleic acid, a *cis* compound, is the predominant olefinic species present during the major portion of the autoxidation reaction, and epoxidation is known to be stereospecific. Furthermore elaidic acid cannot be present to any significant extent since we have shown (10) that the bulk, if not all, of the *trans* components formed during the autoxidation of oleic acid are *trans* peroxides and not the simple *trans* olefinic compound. Recently we have obtained more direct evidence that elaidic acid is not formed in significant quantities by demonstrating that the products isolated from the urea complexes obtained in separating unoxidized material from peroxides (in solvent-free autoxidation systems) are substantially free of *trans* materials (2).

Summary

The autoxidation of oleic acid and methyl oleate in acetic acid solution at 25-30°, 65°, and 115-120° with a cobalt salt as catalyst has been studied. Samples were withdrawn at intervals and the oxidation products were analyzed and then separated into high-melting 9,10-dihydroxystearic acid, cleavage products, unoxidized and hydroxy materials, and polymers.

The best yields of desired oxidation products were obtained at 65°. Yields of pure 9,10-dihydroxystearic acid, m.p. $\geqq 128°$, were 12-17% and cleavage products

64-68%, thus accounting for about 80% of the starting material. At 25-30° and 115-120°, yields of the above-mentioned products were low.

A mechanism is proposed which accounts for the formation of *trans*-9,10-epoxystearic acid from both oleic and elaidic acid autoxidized in the absence of solvent, and the consequent isolation of high-melting 9,10-dihydroxystearic acid when acetic acid is the solvent.

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The Effect of Extended Storage on the Properties of Tung Oil

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THE storage of tung oil for periods in excess of one year has been reported (2, 4, 5, 6, 7, 9, 10, 11) by several investigators. These reports are separable generally into two categories: a) small samples of oil stored under laboratory conditions with chemical and physical characteristics determined after varying periods of storage (5, 6, 7, 11); b) commercial quantities of oil stored under conditions that obtain in the trade, but with few or none of the characteristics of the stored oil reported (2, 4, 9, 10).

Some important points of agreement are evident in these investigations: a) storage containers should be either air-tight, or the exposed surface of the oil should be blanketed with an inert gas; b) storage containers should have a minimum of head space; c) authenticated instances of isomerization (accompanied without exception by extensive polymerization) are attributable to contamination of the oil during transportation, transfer, or storage. The contaminative material when identified invariably contains sulfur or iodine.

Because the oil storage problem is perennial in the domestic tung industry, a controlled storage experiment was designed with the purpose of gathering data that would support or negate some of the generalizations rife, (*i.e.*, stored oil isomerizes spontaneously, tung oil is difficult to store, etc.).

Experimental

Oil was stored in 1-gal. containers, tin-coated inside and closed with friction type (pressed in) lids, which for all practical purposes are air-tight. The tung oil used in the tests was taken directly after filtration at the mill in carefully cleaned and dry storage containers.

Three common storage conditions were simulated: a) unsheltered tank storage where containers were exposed to the direct rays of the sun throughout the day and to the prevailing atmospheric temperature the rest of the time; b) sheltered tank storage where samples were protected from the direct rays of the sun but exposed to the prevailing atmospheric temperature; c) indoor tank storage with reasonably constant temperature (20°-38°). Containers filled to within one-half inch of the top and others half-filled were stored under each condition for the purpose of determining the effect of head-space in the container. At the unsheltered location two sets of samples were stored, one set in containers painted a dull black, the other in containers coated with a highly reflective paint.

Examined on the practical basis of reproducibility in the hands of different analysts at widely spaced intervals of time, such commonly measured and reported characteristics for tung oil as iodine value, diene value, saponification value, unsaponifiable matter, etc., are of doubtful value. Under the conditions imposed by an extended storage experiment, index of refraction, gel time at 282°C., acid value, and viscosity are reliable, measurable with both accuracy and precision, and, considered collectively, quite adequate to characterize tung oil from the standpoint of quality. These measurements therefore were made at intervals over a three and one-half year period on the samples stored under various conditions. The official methods of the American Oil Chemists' Society (1) were used for refractive index (Method Ka 4-47), acid value (Method Ka 2-47), and viscosity (Method Ka 6-48); and the method of the American Society for Testing Materials (3) with modified equipment (13) for the gel time. Each stored sample was opened, and a sample of 24-40 ml. was withdrawn at each sampling. The refractive indices were determined at 5890 Å and 4358 Å (at 25°C.), but only the values determined at the former wave-length and the differences (dispersion) are tabulated. Results are given in Tables I and II.

Results and Discussion

The effects on tung oil of outdoor storage are surprisingly mild even though the tests were carried out in the southern part of the United States.

Storage containers with exterior coatings of a reflective paint show little, if any, superiority to their non-reflectively coated counterparts.

Tung oil in well-filled containers kept well throughout the three and one-half year period regardless of storage location and at the termination of the experiment, and met the A.S.T.M. specifications (3) for tung oil.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.