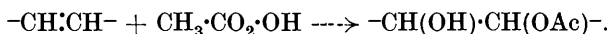


CCV.—*A Quantitative Study of the Oxidation of Methyl Oleate and Elaidate by Hydrogen Peroxide in Presence of Acetic Acid.*

By THOMAS PERCY HILDITCH and COLIN HENRY LEA.

BÖESEKEN (*Rec. trav. chim.*, 1926, **45**, 842; 1927, **46**, 622) has recently stated that perbenzoic and peracetic acids convert ethylenic groupings into dihydroxylated or glycol residues, but that the mode of action differs with each reagent: perbenzoic acid almost invariably causes the initial production of an oxido- or glycide derivative, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ -\text{CH}-\text{CH}- \end{array}$, whereas peracetic acid and the ethylenic grouping unite to yield the monoacetyl derivative of a glycol:



We have observed (J., 1927, 3114) that treatment of an acetic acid solution of unsaturated glycerides with hydrogen peroxide produced glycerides, not only of dihydroxystearic acid, but also of the latter in a monoacetylated form.

As we had in mind the possibility of employing the hydrogen peroxide-acetic acid oxidation as an aid in the study of glyceride constitution, we considered it desirable to make a more thorough examination of the analogous oxidation of methyl oleate and elaidate, which leads ultimately to the formation of the isomeric 9:10-dihydroxystearic acids melting respectively at 95° and 132° (Hilditch, J., 1926, 1828).

In order to detect any oxido-compounds present we have followed the procedure of Steger and van Loon (*Rec. trav. chim.*, 1927, **46**, 706), who have shown that oxido-methyl esters are hydrolysed by alcoholic potash in the cold without alteration of the oxido-ring system. The acids thus obtained from the original oxidation product were submitted to systematic fractional crystallisation from ether at 0°, which led to the separation of a very large proportion of the solid acids. In every instance the products obtained by us melted, without purification, within a few degrees of the melting points of the respective dihydroxystearic acids, and far above those of the oxido-stearic acids (Table II).

We are therefore convinced that no oxido-compounds result from these oxidations whether carried out at the ordinary temperature or at 95°, but there is, at the same time, definite evidence of the concurrent formation of three types of oxidation product varying in amount according to the temperature of oxidation:—

(i) Simple *dihydroxystearic esters* are produced in appreciable quantities, especially at the lower temperature. They separated from the oxidation mixture as a crystalline deposit and were isolated by crystallisation from acetone at 0°. The yields obtained represent minimum values, since it is quite probable that a small quantity of the dihydroxystearic ester remains behind in the mother-liquor.

(ii) *Acetylated dihydroxystearic esters* are only produced to the extent of about 50% of the total product at room temperature, but in much larger amount as the temperature is increased. The percentage of acetic acid combined in the original oxidised ester was determined, and hence was calculated the total amount of mono-acetylated dihydroxystearic ester present, since we concur with Böeseke (*loc. cit.*) in regarding the formation of partially acetylated derivatives as largely due to the direct addition of peracetic acid to the double bond. (We may state here that the presence of peracetic acid in the reaction mixture was evidenced in all cases by the characteristic odour; also, the opinion that oxidation proceeds by way of peracetic acid is reinforced by our observations that the presence of ferrous or manganous salts markedly retards, instead of accelerating, the oxidation of the unsaturated esters—compounds which tend to reduce peracetic acid restrain the conversion into dihydroxystearic derivatives. Further, although methyl dihydroxystearate is acetylated to some extent when heated at 95° for 4 hours with acetic acid of the net concentration present in the oxidations, this action is by no means sufficient to account for the observed acetyl content of the oxidation products.)

(iii) An *oily product* is also formed—like the dihydroxy-ester, in greater amount at lower temperatures. It has all the properties characteristic of an unsaturated fatty oil or ester which has been exposed to atmospheric oxidation, and in our opinion is largely made up of a compound in which molecular oxygen is held very loosely in direct combination with the unsaturated system. It instantly liberates iodine from acidified potassium iodide solution and on heating to about 100° under reduced pressure froths violently and evolves small quantities of acrid vapour with an acid reaction and the well-known accompanying odour of fatty acids of medium molecular weight. It differs from the ordinary air-oxidised fatty oil in one respect, namely, that after heat treatment in a vacuum (which also destroys its activity towards acidified iodide solution) it definitely increases in iodine absorption, *i.e.*, a certain proportion of ethylenic compound is regenerated; we are not aware that this early stage of oxygen attachment has yet been observed in the case of air-oxidised films of unsaturated fats.

After hydrolysis of the original product, followed by removal of as much dihydroxystearic acid as possible by solution in ether and subsequent heating at 100° under reduced pressure to remove acetic acid, the oily substance shows no reaction to acid potassium iodide solution and has an apparent saponification equivalent of the order of 220—245; ultimate analysis gave figures in agreement with the addition of two atoms of oxygen per ethylenic linkage [Found : C, 68.4; H, 10.6. Calc. for $C_{17}H_{33}(O_2) \cdot CO_2H$: C, 68.8; H, 10.8%. Calc. for $C_{17}H_{33}(OH)_2 \cdot CO_2H$: C, 68.4; H, 11.4%]. In this condition, the material closely resembled in its apparent equivalent and general properties the "neutral oxidised ester" obtained by E. F. Armstrong and one of us (*J. Soc. Chem. Ind.*, 1925, **44**, 44r) as the first stage in the oxidation of methyl oleate by potassium permanganate in acetone solution. It is within our knowledge that a very similar substance results when oleic acid is "blown," *i.e.*, heated in a current of oxygen at about 130—140°; a decline in the rate of absorption of oxygen sets in when about one molecule of the latter has been absorbed per molecule of oleic acid, and the product is a viscid liquid which has an apparently low equivalent, but contains little or no dihydroxystearic acid, and does not break down to any great extent into the normal scission products of disruptive oxidation when submitted to the action of alcoholic alkali.

The formation of this oily residual material in the present instance is therefore most probably conditioned by the relatively slow introduction into the oleate or elaidate molecule of molecular oxygen (produced *in situ* by slow decomposition of some of the hydrogen peroxide) in the form of a very unstable molecular or "peroxide" complex, $\begin{array}{c} O_2 \\ \diagup \quad \diagdown \\ -CH-CH- \end{array}$. Its isolation is of some interest from the standpoint of the investigation of "drying" oils, a subject which is, however, too remote from our present theme for further discussion here.

The results may be summed up by saying that, in addition to the last-mentioned compound (which is definitely not a dihydroxystearic acid), oxidation of methyl oleate by hydrogen peroxide in acetic acid leads by two different processes to the exclusive production of derivatives of the same dihydroxystearic acid, m. p. 95°; whereas that of methyl elaidate similarly yields exclusively derivatives of the isomeric form, m. p. 132°. Since Böeseken and Belinfante (*Rec. trav. chim.*, 1926, **45**, 917), using perbenzoic acid, have obtained similar end-products from oleic and elaidic esters, it is clear that whether oxidation proceeds *via* an oxido-compound (perbenzoic acid) or not (hydrogen peroxide in acetic acid) oleates yield the dihydroxy-acid, m. p. 95°, and elaidates give rise to the isomeride,

m. p. 132°. These facts are difficult to reconcile with the view of these workers that inversion takes place during hydration in an acidic medium of the oxido-compound, subsequent to the actual oxidation. They appear rather to afford further cumulative evidence for the view expressed by one of us (J., 1926, 1828) that the acid of m. p. 95°, for example, is produced without intramolecular rearrangement by the oxidation of oleic acid, so that the formation of the isomeric acid of m. p. 132° by alkaline permanganate oxidation of oleic acid must involve an inversion.

This opinion, which is in apparent conflict with the generalisations of Lapworth and Mottram (*Mem. Manchester Lit. Phil. Soc.*, 1927, **71**, 63), has also been criticised by Böeseken and Belinfante (*loc. cit.*) on the grounds that oxidation by permanganate does not normally involve any change of configuration. The latter objection rather misses the point of the suggestion made in the earlier communication, namely (*loc. cit.*, p. 1830) that "inversion" takes place *during oxidation in an alkaline medium*. In order to obtain good yields of dihydroxystearic acid by oxidation of sodium oleate by aqueous permanganate, it is imperative to employ a marked excess of alkali: Lapworth and Mottram (J., 1925, **127**, 1628) recommend the use of equal weights of sodium hydroxide and oleic acid, *i.e.*, about seven times the amount of the former necessary to neutralise the oleic acid. We have had many opportunities from time to time with various acids of the oleic series to confirm the necessity for this precaution, and find that the use of a comparatively slight (*e.g.*, twofold or less) excess causes the production of indefinite and sometimes only semi-solid products. Marked alkaline conditions are, then, essential for the quantitative production of dihydroxystearic acid (m. p. 132°) from oleic acid, or the corresponding (m. p. 95°) acid from elaidic acid.

On the other hand, the opposite isomerides (m. p. 95° from oleic acid and m. p. 132° from elaidic acid) have been exclusively produced by six distinct processes, namely, oxidation *via* the oxido-esters (perbenzoic acid), the direct formation of dihydroxystearic esters and the production of monoacetylated dihydroxystearic esters (present communication), and the three older methods referred to in the previous paper (J., 1926, 1831).

Hence, until rigorous experimental proof to the contrary is available, it appears reasonable to suppose that the dihydroxystearic acid which is formed by so wide a variety of methods is the one more nearly related to the monoethylenic acid from which it emanates.

EXPERIMENTAL.

The methyl oleate and methyl elaidate employed in these experiments were carefully purified specimens prepared as described in the previous communication (J., 1926, pp. 1833, 1834). The same procedure was applied in general to each oxidation, and the experimental data can consequently be presented to a certain extent in a summarised form (Table I).

Oxidation of the Unsaturated Esters.—(i) *At atmospheric temperature.* The ester (20 g.) was mixed with glacial acetic acid (200 c.c.), and a solution of 35% perhydrol (26.5 c.c.) added; the solution remained homogeneous and was set aside for 3 days; further perhydrol (13.5 c.c.) was then added, and the mixture left for a further 7 days at room temperature.

(ii) *At higher temperatures.* A similar solution in acetic acid was placed in a conical beaker immersed in a water-bath which was maintained at 75–80° or 95° in different experiments. Perhydrol (20 c.c.) was added at the commencement, with a further addition of 20 c.c. after 2 hours, after which the mixture was maintained hot for several hours.

At the conclusion of the oxidation, the cooled solution was poured into a cold 7% aqueous ammonia solution (*ca.* 1000 c.c.) with vigorous stirring, after which the product was extracted as rapidly as possible by means of ether. After thorough washing with dilute ammonia and then with water, the oxidised products were recovered from the ether and usually dried finally by heating at 100° in a vacuum for a short time. This procedure led to the regeneration of a certain proportion of unsaturated ester as described on p. 1577, and it was necessary, in order to determine the degree of unsaturation of the oxidised material, to dry the ethereal solution over anhydrous sodium sulphate and remove the last traces of solvent under reduced pressure at as low a temperature as possible.

The changes accompanying the increase in iodine value on heating under reduced pressure included the evolution of small quantities of vapour which possessed an acrid odour and an acid reaction to litmus paper, but which did not attack starch-iodide paper (absence of peracetic acid); the consequent loss in weight was small.

In order to eliminate the possibility of error through retention of hydrogen peroxide by the ester, a "blank" oxidation was carried out on a specimen of methyl palmitate with the following results:—

	Iodine value.	Starch-iodide test.
Original ester	0.5	—
After oxidation, dried at 40° for 7 minutes <i>in vacuo</i>	0.6	Slight +ve.
After oxidation, dried at 100° for 2 hours <i>in vacuo</i> ...	0.9	Negative.

TABLE I.
Oxidation of methyl oleate and elaidate (20 g.) at various temperatures.

No.	Ester oxidised.	Temp.	Time.	Oxidised ester.		Iodine value.		Mean saponification equivalent.
				Wt.	Appearance.	Dried <i>in vacuo</i> below 45°.	After 100° <i>in vacuo</i> .	
1	Methyl oleate.	15-20°	10 days	20.5	Very soft, semi-solid.	2.9	11.4	231.5
2	" "	75-80	9 hours	19.2	Pale-coloured oil, containing quantities of crystalline material.	Not estd.	5.9	208.1
3	" "	95	4½ "	19.2			-0.7	4.8
4	Methyl elaidate	15-20	10 days	20.0	Somewhat soft, solid mass.	Not estd.	11.1	225.1
5	" "	95	4½ hours	16.8	Solidified rapidly.	0.8	4.9	202.6

TABLE II.

No. of expt.	Dihydroxy-ester isolated.		Acetyl content.		Solid acids obtained				Deficit* of dihydroxy-acid.		Oily residue.	
	%.	M. P.	CH ₃ ·CO, %.	As mono-acetyl ester, %.	%.	M. P.	from separated salts.	from solution.	%.	M. P.	%.	Sap. equiv.
1	15	62-63°	6.4	56	35.0	88-89.5°	{ 19.6 3.2	{ 83-85° 83-85	13	?	42	245.6
2	-	-	8.2	71	43.7	87-89	{ 18.0 3.8	{ 81-84 73-76	?	?	35	247.1
3	6	63-65	8.9	77	44.9	88-89	{ 18.8 5.8	{ 79-81 79-81	16	?	30	-
4	22	98-99	5.4	46	50.2	125-126	{ 12.5 14.8	{ 122-123 120-122	6	?	37	210.9
5	12	100-101	8.2	71	56.4	125-126.5	{ 14.8	{ 120-122	15	?	29	228.8

* The deficit is probably due in part to dihydroxy-acid retained in the oily product. Some diacetylated ester may also be produced by subsequent acetylation of the hydroxy-esters.

There was no frothing or evolution of acid vapour when the recovered ester was heated at 100° under reduced pressure.

Some parallel experiments were also made with two methyl esters consisting of mixtures of oleate and linoleate which had been stored for some time with partial access to air. Each gave a definite starch-iodide reaction and possessed the typical oxidised oil odour; the heat treatment caused a brief effervescence similar to that observed with the esters which had been treated with hydrogen peroxide, the evolved vapour being acid to litmus, whereas after heating the products ceased to liberate iodine from acidified iodide solution. The behaviour of the slightly air-oxidised esters was thus qualitatively parallel with those studied in the present work, but no definite alteration in their iodine values was observed after the heat treatment; apparently the absorbed oxygen, although still reactive to hydrogen iodide, was more firmly combined than in the oily part of the products obtained with hydrogen peroxide.

Separation of Free Dihydroxystearic Esters.—Portions of the original oxidised esters from experiments 1, 3, 4 and 5 were treated with a little acetone and set aside at 0° for some days; the crystalline deposit was filtered off and washed with a little cold acetone and the filtrates and washings were concentrated and again cooled at 0°. The weights and melting points (without further purification) of the successive crops are given in Table II.

The mixed solids separated from the oleate oxidations melted at 66—68° when mixed with methyl 9 : 10-dihydroxystearate (m. p. 70—71°), and the similar products from the elaidate melted at 102—102·5° on admixture with the isomeric methyl 9 : 10-dihydroxystearate (m. p. 105°); a single crystallisation of either group of esters furnished specimens which melted respectively at 69—70·5° and 103—103·5°. It is thus clear that the compounds in question were free dihydroxystearic, and not oxido-, esters.

Estimation of the Proportion of Acetylated Ester present.—Following the determinations of saponification equivalent on the original products, the solvent alcohol present was removed and the residue made acid with 2*N*-sulphuric acid (about 10 c.c. excess), after which it was distilled in steam until all acetic acid had been removed; the condensates were then titrated in the usual way.

In order to ascertain how far the presence of acetylated ester was due to acetylation of methyl dihydroxystearate, rather than to the intervention of peracetic acid, methyl 9 : 10-dihydroxystearate (m. p. 105°; 3·5 g.) was heated at 95° with a mixture of glacial acetic acid (30 g.) and water (6 g.) for 4 hours; the recovered product melted at about 95° [Found : sap. equiv., 278·4. Calc. for C₁₇H₃₃(OH)₂·CO₂Me,

330. Found : $\text{CH}_3\cdot\text{CO}$, 2.8%]. Acetylation had therefore occurred to the extent of about 24% (as monoacetyl derivative).

Hydrolysis of the Oxidised Esters and Separation of Dihydroxystearic Acids from the Oily Residue.—The original oxidised esters (ca. 15 g.) were mixed with cold $N/2$ -alcoholic potash (200 c.c.) and left at room temperature for 17—18 hours, followed by a period of 6—7 hours at 0° . A considerable deposit of crystalline potassium salt was acidified separately, and the melting point of the recovered acid determined without further purification. The acids recovered from the soluble potassium salts were separated from the oily product by crystallisation from 70% alcohol and finally from ether at 0° (compare Table II).

The melting points, even of the less pure fractions, are far above those given by Böeseken and Belinfante (*loc. cit.*) for the 9 : 10-oxido-stearic acids (52° and $60\text{--}61^\circ$, respectively). The melting points of mixtures of the respective products, as obtained, with the appropriate 9 : 10-dihydroxystearic acid were $89.5\text{--}90.5^\circ$ in the case of the oleate products and $127\text{--}128^\circ$ in that of acids from methyl elaidate.

Examination of the Oily Residues.—The general properties of these products (which were similar in each case, except that those from methyl elaidate were more viscous than those from methyl oleate) have already been dealt with (p. 1577).

THE UNIVERSITY, LIVERPOOL.

[Received, March 14th, 1928.]
