37. *The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part IV. The Isolation and Constitution of Photochemically-formed Methyl Oleate Peroxide.*

By Ernest Harold Farmer and Donald A. Sutton.

Methyl oleate absorbs oxygen readily at 35° to give a peroxide, which can be isolated, but not completely freed from other substances, by continuous molecular distillation of the product. This somewhat impure peroxide consists mainly of mono-hydroperoxide, but contains a little di-hydroperoxide together with some peroxide transformation product. The mono-hydroperoxide retains the olefinic unsaturation of the oleic ester intact, and is doubtless formed by substitution of the ·OOH group in the oleic chain at one or other of the methylene groups adjacent to the double bond. The mono-hydroperoxide can be hydrogenated to give methyl hydroxystearate, or reduced by aluminium amalgam to give methyl hydroxyoleate.

Another method for the separation of hydroperoxide from unchanged ester (which can be used with moderate success where the total quantity of material involved is comparatively small) consists in the selective adsorption of the peroxide on alumina.

Oleic acid has been selected for study as being the mono-olefinic counterpart of the unconjugated diene and polyene acids forming the drying-oil group. Because of its mono-olefinic character, oleic acid undergoes autoxidation much less readily than do the more unsaturated long-chain acids : hence, to produce a reasonable rate of oxygen absorption it is necessary to resort either to reaction at temperatures considerably above room temperature (preferably with a catalyst present) or to reaction under ultra-violet illumination. Careful studies have been made by Skellon (*J. Soc. Chem. Ind.*, 1931, **50**, 382 T) and by Ellis (*ibid.*, 1925, **44**, 401 T) of the products (all non-peroxidic) formed in the thermal reaction under various conditions; nevertheless, there is as yet no clear account of the course actually followed in this reaction, which presumably, like photo-oxidation, includes peroxidation and peroxide decay as consecutive stages. The progress of photochemical oxidation can be easily followed in the early stages of reaction, and the clear-cut results obtained may perhaps serve as a guide to the elucidation of the course pursued in the catalysed and uncatalysed thermal reactions. In order to avoid complications arising from the interaction of the carboxyl group of oleic acid with the primary products of autoxidation, free oleic acid has been replaced for the present purpose by its methyl ester.

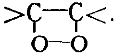
Isolation of Peroxido-oleic Ester.—Methyl oleate absorbs oxygen with reasonable rapidity under ultra-violet illumination at temperatures little above room temperature; but unavoidably, after the early stages of reaction have been passed, the amount of peroxide decay which sets in increases progressively. Hence, in order to retain the possibility of isolating a reasonably pure primary oxidation product, it is necessary to restrict oxidation to an oxygen intake of about 1·5% : success in isolating the pure peroxide must then depend on ability to fractionate the resulting dilute solution of peroxido-ester in unchanged oleic ester. Two processes for fractionating this mixture have been examined, *viz.*, continuous molecular distillation at 65° and chromatographic analysis.

Continuous molecular distillation by the procedure described by Farmer and Van den Heuvel (*ibid.*, 1938, **57**, 24) has given good results, two passages of the partly autoxidised ester through the still serving to remove unchanged ester by volatilisation, leaving a peroxidic residue having the correct analysis, the correct peroxidic oxygen content, and the correct unsaturation for a mono-olefinic *hydroperoxide*, $C_{17}H_{32}(OOH){\cdot}CO_2Me$. The completeness with which this residue retains the unsaturation of the original ester, however, varies a little from experiment to experiment, as is shown by hydrogenating samples of the products, whereby figures varying from 1·97 to 1·86 mols. of hydrogen consumed have been observed $[C_{17}H_{32}(OOH){\cdot}CO_2Me \xrightarrow{2H_2} C_{17}H_{34}(OH){\cdot}CO_2Me + H_2O]$. Various of these saturated hydrogenation products have been investigated after saponification, and it is clear that, although the overall composition of the free acid invariably agrees closely with that required for hydroxystearic acid, yet the acid is never entirely homogeneous. The major and the minor components of this mixed acid, however, cannot be easily or economically separated by fractional crystallisation owing to their similar solubilities, although systematic crystallisation has shown that the sample of peroxido-ester requiring 1·86 mols. of hydrogen for reduction and saturation contained a little stearic acid, much (certainly 50%, probably well over 70%) of a hydroxy-acid agreeing in composition and active hydrogen value with *mono-hydroxystearic acid*, and a little acid which appeared from its analytical values to be a mixture of dihydroxy- and epoxy-stearic acid. When a further (slightly purer) sample of the hydroperoxido-ester was reduced with aluminium amalgam, to destroy the peroxide groups $[C_{17}H_{32}(OOH){\cdot}CO_2Me \xrightarrow{2H} C_{17}H_{32}(OH){\cdot}CO_2Me + H_2O]$, an unsaturated ester approximating in analysis and unsaturation to methyl hydroxyoleate was obtained; this product almost certainly contained small amounts of oleic, dihydroxyoleic, and oxidostearic esters.

A better result has been obtained by pressing high-vacuum distillation of the peroxidised methyl oleate to a point at which not merely the unchanged oleic ester but the main bulk of the peroxido-ester itself had distilled, since in this manner the last traces of unchanged oleic ester could be effectively and fairly economically segregated in a small first peroxido-ester fraction, leaving the main part of the distilled monoperoxido-ester almost uncontaminated by its secondary transformation products. It had been hoped to reduce this fairly pure peroxido-ester quantitatively to methyl hydroxyoleate, by means of aluminium amalgam, but this reagent in common with various other reducing agents (*e.g.*, ferrous sulphate) appears always to bring about a considerable degree of secondary change side by side with the desired reduction of hydroperoxide groups. Hence the peroxide-free reduction product proved to contain a proportion of material of higher oxygen content than hydroxyoleic ester: nevertheless, it gave on complete hydrogenation in presence of platinum, followed by saponification and crystallisation of the products, a 71% yield of hydroxystearic acid. This yield is regarded as a minimal one.

The monohydroxy-acid melted not very sharply at 60—65°, and, as might be expected, consisted (apparently) of two isomerides, since the bromostearic acid formed from it by the action of hydrogen bromide or phosphorus tribromide was always resolvable into two portions, one crystalline and one oily at room temperature. No attempt has yet been made to separate the isomeric hydroxy-acids, and to identify them with the 8- and 11-hydroxystearic acids (III and IV) * to which substitutive attack by oxygen at the methylene groups adjacent

$$C_8H_{17}\cdot CH{:}CH\cdot CH(OOH)\cdot[CH_2]_6\cdot CO_2Me \text{ (I.)} \xrightarrow{2H_2} C_{10}H_{21}\cdot CH(OH)\cdot[CH_2]_6\cdot CO_2Me \quad \text{(III.)}$$
$$C_7H_{15}\cdot CH(OOH)\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Me \text{ (II.)} \xrightarrow{2H_2} C_7H_{15}\cdot CH(OH)\cdot[CH_2]_9\cdot CO_2Me \quad \text{(IV.)}$$

to the double bond in oleic acid should (after complete reduction) give rise. The facts observed, however, furnish good grounds for tentatively formulating the monoperoxidation product of methyl oleate as a mixture of the forms (I) and (II), and they are inconsistent with its representation as a double-bond adduct containing the ring system .

Substitutive peroxidation similar to that discussed above doubless applies to the more highly unsaturated (and easily autoxidised) unconjugated acids or esters of the drying-oil series. With regard to open-chain *conjugated* acids (*e.g.*, elæostearic acid) and their esters, however, it might be supposed that these would resemble terpinene and various conjugated members of the sterol group (cf. Part I, p. 127) in combining additively with oxygen at the ends of their conjugated diene systems. So far, however, no such additive mode has been observed; Heinänen's conclusion (*Ann. Acad. Sci. Fennicae*, 1938, [A], **49**, 1) that methyl sorbate, $CH_3\cdot CH{:}CH\cdot CH{:}CH\cdot CO_2Me$, in diffused light, adds oxygen at the $\gamma\delta$-double bond is based on equivocal evidence, for it has been found in these laboratories that attack by oxygen probably occurs largely at the ε-carbon atom, so resembling the oxidation of sorbic acid to muconic acid in the animal body (Kuhn and Köhler, *Z. physiol. Chem.*, 1937, **247**, 197). Heinänen's abnormally high peroxide yields may be due to the fact, which he ignores, that sorbic ester, like peroxides, ordinarily liberates iodine from 65% hydriodic acid at 90° (Heinänen's conditions), and so invalidates the method of peroxide determination employed.

EXPERIMENTAL.

Oxidation of Methyl Oleate.—Methyl oleate (99 g.), derived by esterification of carefully purified oleic acid, was placed without solvent in a Pyrex flask mounted on a shaking machine and connected with an oxygen reservoir. At first, the air in the flask was replaced by oxygen; afterwards, the flask was shaken at a sufficiently rapid speed to ensure good agitation, and at the same time it was irradiated by light from an ultra-violet lamp (Hanovia U.V.S. 500). The temperature in the flask was maintained at about 35°, and during about 4 hours 1134 c.c. of oxygen (18° and 755 mm.) were absorbed. This oxygen intake amounted to 1·51% by weight of the oxidation product, and immediate determination of the peroxidic oxygen content of the latter (method of Bolland *et al.*, *Trans. Inst. Rubber Ind.*, 1941, **17**, 29) gave the value 1·29%, or 85% of the total observed oxygen intake. Several similar oxidations with fresh portions of methyl oleate gave exactly comparable results.

The oxygenated ester (99·4 g.), containing much unchanged methyl oleate, was distilled at 10^{-5} mm. pressure in a Watermann type of continuous molecular still (procedure of Farmer and Van den Heuvel, *loc. cit.*), the heating surface being maintained at 65°. The distillate (64·9 g.) had P.O.C. (for definition, see J., 1942, 133) 0·197%, representing 0·13 g. of peroxidic oxygen, and the residue (32·9 g.) left in the still had P.O.C. 3·25%, representing 1·07 g. of peroxidic oxygen. The total oxygen present in peroxidic form in distillate and residue was thus 1·20 g., and account being taken of the manipulative loss of 1·6 g. (due mainly to hold-up in the still), the recovery of peroxidic oxygen was *ca.* 95%. Hence the proportion of non-peroxidic oxygen in the peroxidised ester owing its presence to peroxide decay during the oxidation or during distillation was comparatively small. The residue (residue 1) was redistilled at 10^{-5} mm. pressure, giving distillate 2 (16·7 g.) having P.O.C. 0·34% and residue 2 (14·9 g.) having P.O.C. 6·3%, and then the residue 2 was redistilled, giving distillate 3 (4·6 g.) having P.O.C. 0·64%, and residue 3 (9·6 g.) having P.O.C. 9·84%. The residue 3 appeared from analysis to be substantially pure *methyl hydroperoxido-oleate* [Found: C, 69·1; H, 10·85; O (diff.), 20·05; P.O.C., 9·84; active H, expressed as ·OH, 4·7. $C_{19}H_{36}O_4$ requires C, 69·4; H, 11·05; O, 19·54; P.O.C., 9·76; ·OH, 5·18%]. The unsaturation (average) of the hydroperoxido-ester as determined from the iodine value amounted to $|\overline{\overline{_{1}}}$ per 329 g. of ester (Calc.: $|\overline{\overline{_{1}}}$ per 328 g.); the unsaturation as determined by hydrogenation was $|\overline{\overline{_{0\cdot985}}}$. In a similar oxidation the residue 3 had P.O.C. 9·50% (theory, 9·76%) and gave comparable figures on analysis.

Hydrogenation of the Hydroperoxido-ester.—The ester (1·8773 g.) was dissolved in absolute alcohol (100 c.c.), and shaken with hydrogen in presence of Adams's catalyst (0·1 g.). Reaction was complete in about 15 mins., 253 c.c. of hydrogen (N.T.P.) being absorbed (Calc.: 257 c.c.). The catalyst was removed at the centrifuge, and the hydrogenated ester isolated by evaporating the solvent. The residue, a white solid, m. p. 26°, was saponified by heating it under reflux for 1½ hours on a steam-bath with excess of potassium hydroxide (alcoholic). The hydrolysis product, isolated in the usual manner, was a white solid acid, m. p. 54°, having very nearly the correct empirical composition for monohydroxystearic acid: it proved, however, on crystallisation from acetone to be non-homogeneous, the fractions varying somewhat in m. p. and in composition.

Repetition of the experiment with a new sample of peroxido-ester on double the former scale gave by absorption of 93% of the calculated amount of hydrogen a product of m. p. 26°. This after saponification gave a crude acid (2·9 g.) of m. p. 54—55°, having the correct empirical composition for monohydroxystearic acid (Found: C, 72·25; H, 12·0. Calc. for $C_{18}H_{36}O_3$: C, 72·0; H, 12·0%). This was resolved by fractional crystallisation from acetone into five fractions, *viz.*: (A) 0·9 g., m. p. 63°; (B) 0·83 g., m. p. 58—60°; (C) 0·21 g., m. p. 56—58°; (D) 0·32 g., m. p. 44°; (E) 0·56 g.,

---

* The 8-acid is as yet unknown; the 11-acid, although reported in the literature, has been obtained by means which render its constitution and homogeneity uncertain (cf. Tomecko and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 526).

m. p. 43—44°. The first was subdivided by recrystallisation from acetone into three parts (Ai, Aii, and Aiii), and the first of these parts into four sub-parts, Ai(*a*), Ai(*b*), Ai(*c*), and Ai(*d*). The analytical figures obtained were as follows :

Fraction.	Wt., mg.	C, %.	H, %.	Fraction.	Wt., mg.	C, %.	H, %.	Fraction.	Wt., mg.	C, %.	H, %.
Ai(*a*)	31	74·9	12·55	Aii	198	72·65	12·2	C	210	70·55	11·7
Ai(*b*)	90	75·15	12·55	Aiii	218	71·9	11·95	D	323	70·5	11·35
Ai(*c*)	114	74·85	12·55	B	830	72·2	12·1	E	563	70·25	11·35
Ai(*d*)	121	73·25	12·25								

$C_{18}H_{36}O_2$ requires C, 76·1; H, 13·0%. $C_{18}H_{36}O_3$ requires C, 71·95; H, 12·1%. $C_{18}H_{36}O_4$ requires C, 68·3; H, 11·4%.

The fractions Ai(*a*—*c*) were clearly mixtures of monohydroxystearic acid with stearic acid, having an average empirical composition of $C_{18}H_{35\cdot9}O_{2\cdot28}$, and therefore containing about 30% of hydroxystearic acid and 70% of stearic acid. The active hydrogen value found for fraction Ai(*a*) was 0·50%; the value corresponding to $C_{18}H_{35\cdot9}O_{2\cdot28}$ is 0·45%. The fractions Aii, Aiii, and B, which constituted more than half the total material, were substantially pure *monohydroxystearic acid.* The last of these fractions gave an active hydrogen value of 0·64%, thus agreeing with the calculated value for hydroxystearic acid (0·66%). Fractions D and E had nearly the same empirical formula, $C_{18}H_{34\cdot6}O_{3\cdot5}$, the oxygen value in which pointed to the presence of a mixture of mono- and di-oxygenated stearic acid, and the rather low hydrogen value indicated that the mono-oxygenated acid was an oxido- rather than a hydroxy-stearic acid. The analytical figures for carbon and hydrogen, and the active hydrogen value (Found : 0·618%) agreed with those for a mixture composed of 55% of oxido-acid and 45% of dihydroxystearic acid (Calc. : C, 70·55; H, 11·45; active H, 0·616%).

A portion (0·19 g.) of the monohydroxystearic acid (fraction Aiii), m. p. 58—59°, was dissolved in 5 c.c. of glacial acetic acid contained in a narrow Carius tube, and the solution treated with excess of dry hydrogen bromide for 1 hour. The tube was sealed and then heated at 75° for 3 hours. From the product, on cooling, some crystals separated : these represented $<10\%$ of the whole and proved to be unchanged hydroxystearic acid (Found : C, 69·9; H, 11·9%); they were convertible by phosphorus tribromide into a crude semi-solid bromide (Found : Br, *ca.* 22·5%). From the filtrate, on standing, crystals (i) separated at the surface, and an oily solid (ii) at the bottom. These were separated, washed, dried, and analysed. Both (i) and (ii) proved to be nearly pure bromostearic acid [Found : (i) C, 59·7; H, 9·45; Br, 19·9; (ii) C, 59·55; H, 9·55; Br, 20·4. Calc. for $C_{18}H_{35}O_2Br$: C, 59·5; H, 9·65; Br, 22·0%]. The semi-solid bromo-acid yielded solid and oily forms on filtration, the latter in greater amount. Repetition of the bromination also gave liquid and solid forms of the bromo-acid, and it appears likely that one of these was derived from 8-hydroxy- and the other from 11-hydroxy-stearic acid.

A portion of the slightly impure hydroxystearic acid, m. p. 58—60° (0·3 g.), was heated on a steam-bath for 1 hour with excess of chromic oxide (0·2 g.) dissolved in 5 c.c. of glacial acetic acid. The product, precipitated when the acid solution was poured into water, proved to be only partly oxidised. The mixed product gave a crude semicarbazone, m. p. 71—74°, but the small amount available could not be wholly freed from hydroxy-acid and from sodium salts.

Reduction of the Hydroperoxido-ester with Aluminium Amalgam.—A new sample of methyl hydroperoxido-oleate (23·2 g.) was prepared by continuous molecular distillation of an oxidation product from pure methyl oleate (258·6 g.) in which the incorporated oxygen amounted to 1·06% of the whole (Found : C, 69·5; H, 11·05; P.O.C., 9·57. Calc. for $C_{19}H_{36}O_4$: C, 69·4; H, 11·05; P.O.C., 9·76%). A portion of this sample (9·5 g.) was added to amalgamated aluminium foil contained in a 500 c.c. flask, completely covered with moist ether. Vigorous refluxing of the solvent occurred in the early stages of reaction, and after 22 hours the ethereal liquor contained only a trace of peroxide. The ethereal liquor was filtered and the aluminium hydroxide well washed with acetone in an endeavour to elute any adsorbed reduction product. The filtrate yielded 7 g. of colourless, mobile, slightly hygroscopic oil which, when completely freed at reduced pressure from solvent, gave figures showing rather too high an oxygen content and too low an unsaturation for pure methyl hydroxyoleate (Found : C, 72·5; H, 11·55; $|\overline{\overline{0\cdot85}}$. Calc. for $C_{19}H_{36}O_3$: C, 73·05; H, 11·55%). Some secondary change had apparently accompanied reduction.

Distillation of the Hydroperoxido-ester.—A sample of methyl oleate (200 g.) was oxidised to an uptake of *ca.* 1·19% and distilled at 10^{-4} mm. as before. This time, however, after the unchanged ester had been segregated so far as possible in five operations, the residue was itself distilled, so that any relatively non-volatile materials (*e.g.*, secondary transformation products of mono- and di-hydroperoxides) could be eliminated. The procedure was the following : oxidation product $\longrightarrow D_1 + R_1 \xrightarrow{65^\circ} D_2 + R_2 \xrightarrow{65^\circ} D_3 + R_3 \xrightarrow{65^\circ} D_4 + R_4 \xrightarrow{91^\circ} D_5 + R_5 \xrightarrow{91^\circ} D_6 + R_6$, the residues R_3, R_4, R_5, and R_6 having the P.O.C. values 7·13, 9·53, 10·2 and 8·7% respectively, and the distillate D_6 having P.O.C. 9·68%. The final distillate D_6 had C, 69·25; H, 10·95%, and the final residue R_6 had C, 68·05; H, 10·7%, the former thus showing correct values for methyl hydroperoxido-oleate, and the latter (with too high an oxygen content, and too low a peroxide content) manifestly containing some proportion of secondary oxidation products. The survival of peroxidic oxygen in each of the distillations 1—6 varied from 88 to 98% of the amount present before distillation, the variation from one operation to another being probably more apparent than real, reflecting the range of experimental error ($\pm 5\%$) in the method of peroxide determination employed. Reduction of the peroxide groups in a portion of the final residue R_6 by means of zinc dust and acetic acid (mixed with some acetone) gave a peroxide-free, oily product showing roughly the expected unsaturation and composition having regard to its original peroxide content (Found : C, 70·65; H, 10·6%; $|\overline{\overline{1}}$ per 310 g.); the crude reduction product, however, was rather less mobile than methyl hydroxyoleate and hence possibly contained some proportion of bimolecular condensation product.

Reduction and Hydrogenation of the Distilled Hydroperoxido-ester.—The distilled ester (distillate D_6) was reduced as before with aluminium amalgam and the peroxide-free unsaturated ester (methyl hydroxyoleate) so obtained proved as on the previous occasion when aluminium amalgam was the reagent to have an unduly high oxygen content (Found : C, 72·4; H, 11·55%). Hydrogenation of the impure ester in presence of Adams's catalyst (0·71 mol. uptake) [*] gave correspondingly impure methyl hydroxystearate as a white solid, m. p. 26—27° (Found : C, 70·7; H, 11·8. Calc. for $C_{19}H_{38}O_3$: C, 72·55; H, 12·15%). The bulk of the impurity was removed when the ester was saponified with excess of alcoholic sodium hydroxide and the free acid precipitated by acidifying the product and diluting it with water; under these conditions the most highly oxygenated component remained dissolved in the mother-liquors and the nearly pure hydroxystearic acid (m. p. 55—56°) was obtained as a white crystalline powder closely resembling stearic acid (Found : C, 71·6; H, 12·05. Calc. for $C_{18}H_{36}O_3$: C, 71·95; H, 12·1%). By fractional crystallisation of the crude hydroxystearic acid from acetone, 60% separated at once as colourless crystals, m. p. 60—65°, of correct composition (Found : C, 71·8; H, 12·0; active H, 0·71. Calc. : active H, 0·67%), leaving a sticky, semi-solid acid (Found : C, 70·35; H, 11·6%) which gave on recrystallisation from aqueous acetone a further 11% of hydroxystearic acid, m. p. 60—65° (Found : C,

---

[*] The unexpectedly low uptake is attributed to the inadvertent use of an aged specimen of catalyst.

71·75; H, 11·95%), and a semi-solid acid of rather higher oxygen content, which could not be satisfactorily crystallised further. The total yield of hydroxystearic acid isolated from the distilled peroxido-ester was thus 71%.

Reduction of the Hydroperoxido-ester with a Ferrous Salt.—A mixture of hydroperoxido-ester (5·6 g.; P.O.C., 9·76%), sulphuric acid (2 c.c. of *d* 1·84 in 100 c.c. of water) and ferrous ammonium sulphate (30 g.) was shaken at room temperature for 20 hours. The light brown mobile oil in the resulting mixture was taken up in ether, washed several times with water, and dried over anhydrous sodium sulphate. It weighed 4·2 g. and still contained peroxidic oxygen (P.O.C. 1·6%) (Found : C, 70·6; H, 10·9%). A second portion of hydroperoxido-ester when treated similarly had P.O.C. 1·5% (Found : C, 70·25; H, 10·85%). Reduction of the peroxide groups to hydroxyl by this method was thus small, although the bulk of the peroxidic oxygen was redistributed.

Separation of the Hydroperoxido-ester by Chromatographic Adsorption.—A sample of peroxidised methyl oleate (16·7 g.) containing 1·14% of incorporated oxygen was dissolved in 800 c.c. of light petroleum and passed slowly through a column of alumina (35 cm. × 2 cm.) which had been previously washed with 100 c.c. of glacial acetic acid and then with 220 c.c. of light petroleum. The adsorbate was washed with more light petroleum until the filtrate gave a positive test for peroxide (50 c.c. used). The receiver, containing 850 c.c. of light petroleum and unoxidised ester (Filtrate I), was then changed, and the washing continued first with more light petroleum (50 c.c.) and then with 150 c.c. of methanol (Filtrate II). The filtrate I was found to contain only a negligible amount of peroxide, and it gave on evaporation 14·7 g. of unchanged methyl oleate. The filtrate II, when evaporated below 50°, gave 1·9 g. of oil, having P.O.C. 8·67%. If it is assumed that the whole of the oxygen originally incorporated was in peroxidic form, the recovery of peroxidised ester by the chromatographic method was 87%.

We thank Dr. W. T. Chambers for carrying out the analyses.

The British Rubber Producers' Research Association,
48, Tewin Road, Welwyn Garden City, Herts.

[*Received, November* 28*th*, 1942.]