

220. The Union of Gaseous Oxygen with Methyl Oleate, Linoleate, and Linolenate.

By F. D. GUNSTONE and T. P. HILDITCH.

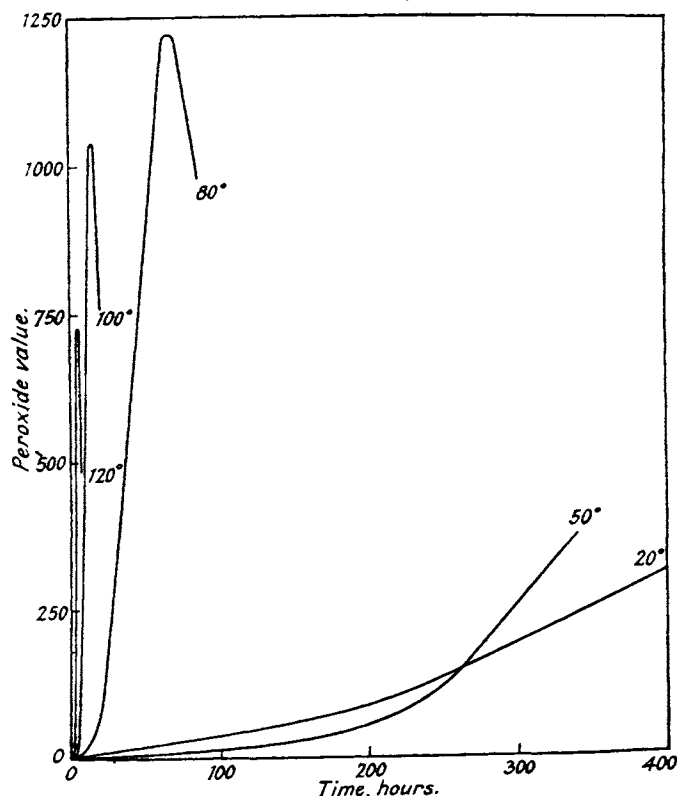
The autoxidation of methyl oleate in diffused daylight at temperatures between 20° and 130° has been followed by the changes in its peroxide and iodine values, and some of the autoxidised products have been further examined. The process is very slow at 20° and somewhat faster at 50°, but from 80° onwards it becomes very rapid and apparently differs in character from the oxidation at lower temperatures. At the higher temperatures there is development of considerable free acidity, which was shown to be due mainly to oxidative breakdown at the unsaturated group and consequent production of mono- and di-carboxylic acids (including those of the C₈ as well as of the C₉ series).

Autoxidation of methyl linoleate at 20°, 50°, and 80° proceeds with increasing rapidity, but the temperature-coefficient appears to be more constant in this case than with methyl oleate. In all three experiments, and in the autoxidation of methyl linolenate at 20°, the development of conjugated diene unsaturation to a maximum and its subsequent decline was observed to be parallel with the formation of peroxides.

The relative rates of autoxidation of methyl oleate, linoleate, and linolenate at 20° were 1 : 12 : ca. 25, the presence of the system $-\text{CH}:\text{CH}-\text{CH}_2-\text{CH}:\text{CH}-$ causing a marked increase in ease of union with oxygen.

It has been shown (Atherton and Hilditch, *J.*, 1944, 105) that autoxidation of methyl oleate at 120° differs in several respects from its autoxidation at 20°.

FIG. 1.
Autoxidation of methyl oleate.



At the higher temperature the action is extremely rapid, compared with that at 20°. Examination of the final products obtained indicated, in the case of the ester autoxidised at 20°, the presence of oxygenated groups on the 8th and 11th atoms of the carbon chain, as well as at the 9th and 10th carbon atoms; whereas less evidence of attack other than at the 9th and 10th carbon atoms (the position of the ethenoid bond) was observed in the product of autoxidation at 120°. The relationship between the development of peroxide value and the corresponding fall in iodine value suggested that at 120° the autoxidation involved both the mechanism put forward by Farmer and Sutton (*J.*, 1943, 119) and also, to some extent, direct addition of oxygen at the double bond.

The oxidation of methyl oleate, methyl linoleate, and methyl linolenate by oxygen at various temperatures from 20° upwards has now been further examined.

Autoxidation of Methyl Oleate.—The purification of oleic acid from linoleic acid was effected by crystallisation from acetone at about -40° . A source of oleic acid was chosen in which the latter was accompanied by as small a proportion as possible of linoleic acid. Animal fats such as beef tallow fulfil this condition, but for the immediate purpose a sufficient supply of the seed fat of *Allanblackia floribunda*, which contains but little linoleic acid, was available and was utilised. The mixed acids of this fat consist of saturated 60.2, oleic 39.4, and linoleic 0.4% (Meara and Zaky, *J. Soc. Chem. Ind.*, 1940, 59, 25), and from them two batches of purified methyl

oleate were prepared as described below (p. 840). One of these (168 g., iodine value 80.4) was used in the present experiments; it contained a small proportion of saturated esters, but was almost entirely free from methyl linoleate. Autoxidations were effected at room temperature (ca. 20°) and at 50°, 80°, 100°, 120°, and 130°.

The increase in peroxide value during autoxidation is plotted against time in Fig. 1. The course of the oxidation at different temperatures is similar in that an "induction period" is followed by a more rapid increase in peroxide value to a maximum followed, in turn, by an equally rapid fall in peroxide value. The iodine value drops slowly at first and then more rapidly and regularly. There is also development of free acidity, especially notable in autoxidations at 80° and above.

At the higher temperatures the action was markedly exothermic. An oil bath temperature about 3–5° below that of the ester undergoing oxidation at 100°, 120°, or 130° sufficed to maintain the desired autoxidation temperature.

Up to 50° the action is steadily accelerated by temperature, but from 80° upwards the temperature

coefficient is very much greater than at lower temperatures, and it is evident that an action of essentially different character from that at lower temperatures comes into play. The different character of the autoxidation may be illustrated by the times taken to reach a peroxide value of 500 at various temperatures :

Temperature	20°	50°	80°	100°	120°
Time (hours)	ca. 600	ca. 380	37	9	2.5

The practice, much favoured in technical control of oxidative rancidity, of predicting the stability of fats and fatty products to atmospheric exposure at the ordinary temperature from "accelerated" oxidation tests conducted at 100° or even higher, appears somewhat dubious; since the oxidising action seems to be essentially different, as judged from the abrupt change in the temperature coefficient from about 50° onwards. Whilst accelerated tests at the higher temperatures may indeed in many instances serve a useful purpose as an approximate guide, the present data offer confirmation that these tests do not rest on a sound theoretical basis, and thus reinforce the doubts recently expressed as to their complete validity (cf. Lea, Moran, and Smith, *J. Dairy Res.*, 1943, 13, 162; Banks, *J. Soc. Chem. Ind.*, 1944, 63, 8; Hilditch, *Chem. and Ind.*, 1944, 68).

In Table I the data are further illustrated with reference to the rate of increase of peroxide and acid values, and decrease of iodine value (measured over the approximately linear portions of the graphs), and to the maximum peroxide and acid values attained.

TABLE I.
Autoxidation of methyl oleate.

	20°.	50°.	80°.	100°.	120°.	130°.
Induction period (hours)	120	210	20.5	4.5	1.0	0.5
Maximum peroxide value attained	—	—	1220	1040	730	450
Time (hours) to attain maximum peroxide value	—	—	68	15	4	2
Rate of increase of peroxide value (units per hour)	1.2	2.9	28	110	330	450
„ decrease of iodine value (units per hour)	0.009	0.03	1.7	5.5	9.0	10.0
„ increase of acid value (units per hour)	—	—	1.5	7.5	9.3	9.8
Final acid value attained	0.5	5.2	48.9	56.1	43.3	43.9
Time (hours) to attain final acid value	604	609	83	20	7.3	6.0

As the temperature is increased, not only is the induction period diminished and the rate of oxidation increased, but the maximum peroxide value also decreases; in other words, secondary transformations of the peroxidic compounds first formed also proceed at increasing speed. In the autoxidations at 20° and 50° the maximum peroxide figures had, however, not been reached after 740 and 340 hours respectively.

The falls in iodine value at 20° lie between the declines calculated on the respective assumptions that peroxide formation occurs (i) exclusively at a $-\text{CH}_2-$ group adjacent to a double bond and (ii) exclusively at a double bond. At the higher temperatures this relation holds in the early stages of the action, but later the observed fall in iodine value exceeds that which would result from direct addition of oxygen to a double bond; this is merely the consequence of disappearance of peroxides by secondary actions, the peroxide values at this stage no longer being indicative of the total quantity of peroxides formed during the autoxidation. It is at this stage, also, that the development of free acidity becomes very marked.

Composition of the Products of Autoxidation of Methyl Oleate.—We have examined the products obtained by disruptive oxidation (with potassium permanganate in acetone solution) of some of the autoxidised esters. After autoxidation at 20°, we have confirmed the previous observation of Atherton and Hilditch (*loc. cit.*) that suberic and octoic acids are formed in addition to azelaic and nonoic acids, indicating attack by oxygen on $-\text{CH}_2-$ groups adjacent to the double bond in methyl oleate. This process is still operative to some extent when methyl oleate is autoxidised at 100° or 120°, but in addition direct attack on the ethenoid bond seems to take place. Removal, prior to disruptive oxidation of the autoxidised esters, of the acidic products formed during autoxidation at the higher temperatures showed that scission into mono- and di-carboxylic acids also occurs to some marked extent at these temperatures; minor quantities of other products such as dihydroxystearic acid, a compound of apparent formula $\text{C}_{18}\text{H}_{32}\text{O}_8$, and aldehydes(?) of low molecular weight are also produced.

Autoxidation of Methyl Linoleate.—A specimen of methyl linoleate (iodine value 173.2, calc. 172.8) was autoxidised at 20°, 50°, and 80°. As with methyl oleate, after a (very short) induction period the peroxide value steadily rose, and increase in temperature led to an increase in the rate of peroxide formation but to a decrease in the maximum peroxide value obtained. With methyl linoleate, however, development of peroxides is accompanied throughout by development of diene conjugation. The amount of the latter increases *pari passu* with that of the peroxides, but reaches a maximum somewhat before the maximum peroxide value is attained, and thereafter steadily declines. This is of course fully in accordance with the view of Farmer, Koch, and Sutton (*J.*, 1943, 541) that the initial action is one of detachment of a hydrogen atom from the central $-\text{CH}_2-$ group in the unsaturated system, leaving a grouping $-\text{CH}:\overset{|}{\text{C}}\text{H}-\text{CH}:\text{CH}-$ which may undergo rearrangement to $-\text{CH}_2-\text{CH}:\text{CH}-\text{CH}:\text{CH}-$ or its hydroperoxide.

The changes in peroxide value and diene conjugation at the three temperatures of autoxidation are shown graphically in Fig. 2, whilst a further general indication of the course of the autoxidations is given by the summarised data in Table II.

FIG. 2.
Autoxidation of methyl linoleate.

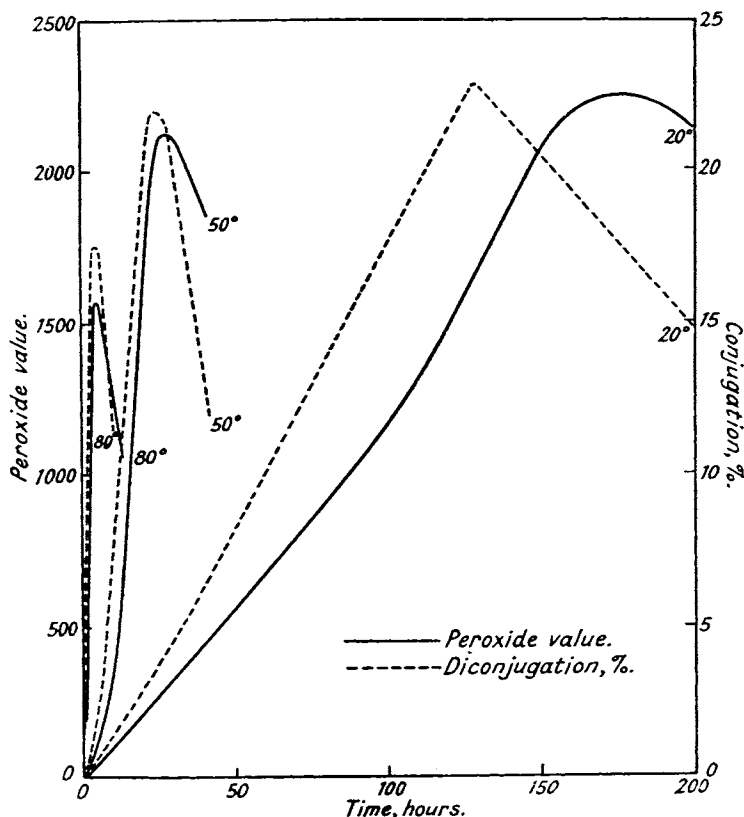


TABLE II.
Autoxidation of methyl linoleate.

	20°.	50°.	80°.
Maximum peroxide value attained	2250	2125	1573
Time to reach maximum peroxide value (hours)	175	28	4.5
Maximum percentage diconjugation attained	22.8	22.0	17.6
Time to reach maximum % diconjugation (hours)	129	24	4.5
Time for iodine value to drop 10 units (hours)	73	13	1.1
Time for iodine value to drop 50 "	143	24	5.9
Final acid value reached "	*	34.5	20.7
Time to reach final acid value (hours)	262	44	9.4

* The acid value of the final product of autoxidation at 20° was not measured until 3 months after the experiment had closed, when it was 58.6.

The times taken to reach a peroxide value of 1500 at 20°, 50°, and 80° were respectively 121, 19, and 4 hours. The temperature-coefficient thus appears to be more constant over the whole of this range than with methyl oleate, in which a much increased rate of oxidation sets in above 50°. The reaction is strongly exothermic; the heating-bath temperatures necessary to maintain the autoxidising methyl linoleate at 50° and at 80° were respectively 40–43° and 63–67°.

In the early stages of autoxidation of methyl linoleate, the observed fall in iodine value is nearer to that caused by hydroperoxide formation at a methylene group than to that due to attachment of oxygen at a double bond. The observed drop in iodine value soon, however, approaches and surpasses that calculated on the latter assumption (and more rapidly than is the case with autoxidised methyl oleate). This is to be expected since, in addition to progressive failure of the peroxide values to indicate the total quantity of peroxides produced (in consequence of secondary changes in some of the latter), there are increasingly significant proportions of conjugated diethenoid ester formed, and these will not register their true iodine value under the conditions of analysis (Wijs' reagent).

The results of disruptive oxidation of the autoxidised products (p. 841) suggest that peroxidation is exclusively confined to the $-\text{CH}_2-$ group situated between the two ethenoid bonds of the linoleic chain, *i.e.*, in the system, $\text{CH}_3\cdot[\text{CH}_2]_3-\overset{14}{\text{CH}_2}-\overset{13}{\text{CH}}\cdot\overset{12}{\text{CH}}-\overset{11}{\text{CH}_2}-\overset{10}{\text{CH}}\cdot\overset{9}{\text{CH}}-\overset{8}{\text{CH}_2}-[\text{CH}_2]_6-\text{CO}_2\text{Me}$, attack by oxygen is so much concentrated

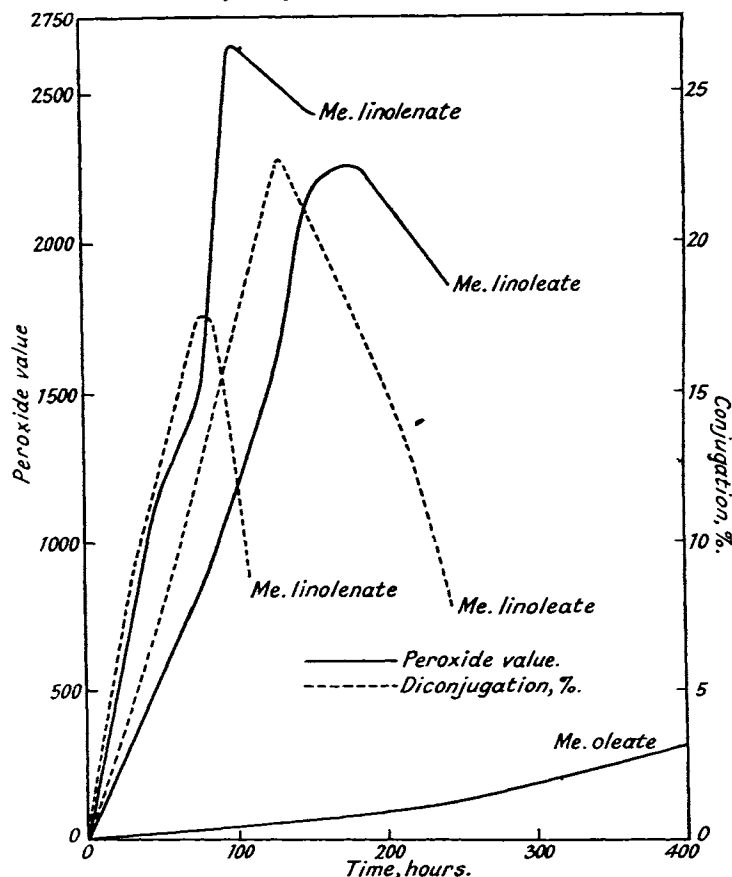
upon the methylene group at C_{11} that no perceptible products of attack at the groups at C_8 or C_{14} could be detected.

The free acids formed in the later stages of the autoxidation of methyl linoleate were mainly scission products arising from disruption of the $\Delta^9, 12$ -diethenoid system.

Autoxidation of Methyl Linolenate.—A specimen of methyl linolenate (iodine value 256.1, calc 261.0) was oxidised at 20° with the results summarised in Table III (p. 841). The development of di- and tri-ethenoid conjugation was similar to, but not so marked as, that first observed in the autoxidation of ethyl linolenate by Farmer, Koch, and Sutton (*loc. cit.*); these authors record that, when 1 mol. of oxygen had been absorbed per mol. of ester (in presence of ultra-violet radiation), 28.5% of diene and 4.5% of triene conjugation were detected.

The development of peroxides and of conjugated unsaturated esters resembles that observed with methyl linoleate at 20° , but the rate of autoxidation is more rapid. In both cases a maximum is reached, followed by a

FIG. 3.
Autoxidation of methyl oleate, linoleate, and linolenate at 20° .



decline, and the maximum of diene conjugation is passed before the peroxide value attains its maximum. The fall in iodine value in the earliest stages is closer to that demanded by hydroperoxide formation than that due to direct attachment of oxygen at a double bond, but becomes greater than the latter earlier than in the case of methyl linoleate, no doubt for the same reasons (cf. p. 838).

The development of peroxides and of diene conjugation is shown in Fig. 3, which also serves to compare the relative rates of autoxidation of methyl oleate, linoleate, and linolenate at 20° . The average rates of increase per hour in peroxide value of methyl oleate, linoleate, and linolenate during autoxidation at 20° were respectively 1, 12, and *ca.* 25 in the above experiments. The much more rapid autoxidation of methyl linoleate than of methyl oleate, and the relatively less increased rate of autoxidation of methyl linolenate over that of methyl linoleate illustrate further the ease with which the system $-\text{CH}:\text{CH}-\text{CH}_2-\text{CH}:\text{CH}-$, or rather its central $-\text{CH}_2-$ group, unites with molecular oxygen; interaction of oxygen with $-\text{CH}_2-$ groups adjacent to a single ethenoid bond, as in methyl oleate, is a relatively slow process.

Kuhn and Meyer (*Z. physiol. Chem.*, 1929, **185**, 193), who compared the rate of oxidation (catalysed by hæmin) of ethyl oleate and methyl linoleate, and of olive oil and linseed oil, state that the relative rates of oxidation of the mono-, di-, and tri-ethenoid fatty acid groups were respectively 1 : 12 : 100.

840 The Union of Gaseous Oxygen with Methyl Oleate, Linoleate, and Linolenate.

It will be shown in a subsequent paper that the onset of oxidative rancidity in edible fats is largely conditioned by the presence of linoleic, rather than oleic, glycerides, the peroxides formed by preferential autoxidation of the former catalysing the oxidation of the (usually predominant) oleic glycerides present. Since autoxidation of linoleic groups is accompanied by production of diene conjugation, the possibility of following the course of the oxidation by measurements of the extinction coefficient of the absorption band at 234 $m\mu$, as an alternative to other methods (*e.g.*, peroxide values), is at present being studied.

EXPERIMENTAL.

Preparation of Methyl Oleate.—The mixed fatty acids (428 g., iodine value 36.9) from *Allanblackia floribunda* seed fat (iodine value 34.5) were treated in boiling alcohol solution (4280 ml.) containing 1.5% acetic acid with lead acetate, (300 g.), and set aside at room temperature for some hours. They were thus resolved into mainly saturated (244 g. iodine value 1.6) and mainly unsaturated (184 g., iodine value 84.5) acids. The latter acids (175 g.) were then successively crystallised from acetone (900 ml.) at 0°, -15°, and -40° with the following results:

Separated at	0°	-15°	-40°	Soluble at -40°
Weight, g.	14.3	17.1	113.3	29.8
Iodine value	25.1	74.6	86.9	99.0

The material separated at -40° was converted into methyl esters which were distilled in a vacuum through an electrically-heated and packed fractionating column, when the following fractions were obtained:

Fraction No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	Residue.
Weight, g.	1.6	4.0	3.5	10.5	19.2	17.6	18.4	21.0	13.8	5.8
Iodine value	57.1	72.9	80.6	84.1	84.5	84.9	84.7	84.8	84.4	84.3

Fractions 4—9 (100.5 g.) were collected as part of the material to be used in autoxidation experiments; this represented a yield of approximately 55% of the oleic acid in the unsaturated acids obtained from the lead salt separation of the *Allanblackia* mixed fatty acids. Subsequently, if the iodine value of the unsaturated acids from the lead salt separation was not below 85, it was considered unnecessary to remove further saturated acids by crystallisation at 0° and -15°, and they were simply crystallised from acetone at -40° in order to retain in solution the small proportions of linoleic acid present in the original mixed acids. The later ester-fractionation served to separate residual methyl palmitate, but the methyl oleate finally obtained still contained a small proportion of methyl stearate, which was considered immaterial for the purpose of the autoxidation experiments, the important point being the complete removal of linoleic acid in the crystallisation process.

In the course of preparation of methyl oleate for autoxidation work, the following batches were obtained:

Fraction No.	1.	2.	3.	4.	5.	6.	7.	8.
Weight, g.	90	24	82	43.5	46	35	109	24
Iodine value	84.6	83.3	83.2	83.0	82.0	80.4	80.4	80.8

These were combined into two batches: nos. 1—5 (286 g., iodine value 83.4) and nos. 6—8 (168 g., iodine value 80.4); the latter was the material used in the present experiments.

Preparation of Methyl Linoleate.—Tetrabromostearic acid (m. p. 114—115°), prepared from the unsaturated acids of cottonseed oil, was debrominated in methanol with activated zinc dust and hydrochloric acid (Rollett, *Z. physiol. Chem.*, 1909, **62**, 410), and the methyl linoleate obtained purified by fractional distillation as above. The specimens employed had iodine values of 170.9, 172.9, and 173.2 (calc. 172.8).

Preparation of Methyl Linolenate.—Hexabromostearic acid (m. p. 180—181°), prepared from the acids of linseed oil, was debrominated in pyridine solution with activated zinc dust (Kaufmann and Mestern, *Ber.*, 1936, **69**, 2684). The crude linolenic acid obtained was esterified with methanol in presence of 0.5% of sulphuric acid, and the neutral methyl ester distilled as above (iodine value: found 256.1, calc. 261.0).

Autoxidations.—The esters (25—50 g.) were placed in a 250 ml. three-necked flask, fitted with a mechanically driven (*ca.* 300 r.p.m.) glass stirrer, thermometer (with bulb immersed in the ester), inlet and outlet tubes. No metal surfaces were exposed within the apparatus, since at the higher temperatures volatile fatty acids were produced during the oxidation. A slow current of oxygen was passed through the ester during the experiments which were conducted in diffused daylight. In experiments above room temperature the flask was immersed in an oil-bath, the temperature of which was regulated so as to maintain the ester at the desired experimental temperature.

The conjugated unsaturation produced during autoxidation of methyl linoleate and linolenate was determined from the extinction coefficients of the absorption bands at 234 $m\mu$ and 268 $m\mu$. For this purpose solutions in purified cyclohexane were normally employed. In the later stages of oxidation, however, the products commenced to be difficultly soluble in cyclohexane, and, in some of the later experiments, solutions in alcohol were then found to be a useful alternative.

The abridged data in Tables I and II summarise the observations on methyl oleate and linoleate autoxidised at various temperatures. The full observations for autoxidation of methyl linoleate and linolenate at 20° are recorded, by way of illustration, in Table III.

With methyl linolenate, spectroscopic observations could not be carried out after 117 hours, owing to progressively diminishing solubility of the product in cyclohexane. The final product (after further standing for two months) had an acid value of 77.

Examination of Autoxidised Products.—**Methyl oleate.** The results obtained may be illustrated by reference to the product of autoxidation of methyl oleate at 100°, which had iodine value 17.6, peroxide value 764, and acid value 56.1. The product (17.0 g.) yielded material volatile in steam (1.2 g.), which consisted of approximately equal parts of acidic compounds (Found: equiv., 154.5. Calc. for $C_9H_{16}O_2$: equiv., 144; for $C_9H_{18}O_2$: equiv., 158) and of a neutral liquid with a fruity odour similar to that of octaldehyde or nonaldehyde, but no crystalline 2:4-dinitrophenylhydrazones could be obtained from it. The portion non-volatile in steam (acid value 59.7) gave 2.4 g. of acidic and 9.9 g. of neutral compounds. Of the acids, 1.5 g. were soluble in water and yielded on crystallisation a very small amount of suberic acid and larger quantities of azelaic acid; from the acids insoluble in water, a very small amount of an acid was obtained. This was analysed (Found: C, 74.9; H, 11.9. Calc. for $C_{10}H_{18}O_2$: C, 74.5; H, 11.7%), but its constitution was not further elucidated. The neutral product, non-volatile in steam, was hydrolysed and the resulting oily acids were crystallised from various solvents. The only crystalline product obtained was a very small amount of an acid, m. p. 63—67° (Found: C, 74.8; H 12.1%; equiv., 296), which appeared to be the same as that previously mentioned.

TABLE III.

Time (hours).	Peroxide value.	Conjugation.			Fall in iodine value.		
		Di-ethenoid, %	Tri-ethenoid, %	Iodine value (Wijs).	Observed.	Calc.*	Calc.†
<i>Autoxidation of methyl linoleate.</i>							
0.0	0	0	—	173.2	—	—	—
37.0	423	5.8	—	168.5	4.7	13.1	2.4
92.5	1174	16.1	—	157.5	15.7	36.3	6.5
132.4	1731	22.7	—	137.4	35.8	53.5	9.6
178.2	2210	18.7	—	99.1	74.1	68.3	12.2
188.8	2211	15.9	—	90.5	82.7	68.4	12.3
211.3	2155	13.7	—	80.4	92.8	—	—
242.4	1850	8.1	—	65.5	107.7	—	—
262.4	1355	4.5	—	58.5	114.7	—	—
<i>Autoxidation of methyl linolenate.</i>							
0.0	11	0.6	—	256.1	—	—	—
16.5	459	4.9	—	244.5	11.6	15.5	3.8
32.6	872	9.9	—	230.0	26.1	29.4	7.3
49.7	1185	12.6	0.6	216.5	39.6	40.0	9.9
83.2	1674	17.6	0.6	165.6	90.5	56.5	13.9
98.8	2655	12.2	0.3	132.8	123.3	89.5	22.1
117.2	2383	7.3	0.4	106.0	150.1	—	—
143.3	2300	Not determined.		76.6	179.5	—	—
162.4	2484	„	„	76.4	179.7	—	—

* Calculated for assumption of union of 1 mol. O₂ with one double bond.

† Calculated for assumption of union of 1 mol. O₂ at one —CH₂— group.

The product of autoxidation of methyl oleate at 120° (iodine value 28.3, peroxide value 482, acid value 43.2) was similarly examined, the portions volatile in steam being similar to those found in the above experiment. After hydrolysis of the neutral, not-volatile-in-steam portion, very small proportions of 9:10-dihydroxystearic acid, m. p. 92—93°, were isolated in addition to small amounts of the acid, m. p. 63—65° (Found: C, 74.6; H, 12.0%). Another portion of the oily neutral product (8.2 g.) was oxidised in acetone with potassium permanganate, but was not completely attacked, 38% of unoxidised material being recovered; from the dibasic acids produced (2.2 g.) both suberic (0.2 g., m. p. 132—138°) and impure azelaic (0.6 g., m. p. 92—94°) acids were isolated.

Methyl linoleate. With methyl linoleate autoxidised at 20°, the products were further examined after 90 hours (peroxide value 1174, iodine value 157.5) and 262 hours (peroxide value 1355, iodine value 58.5). After 90 hours autoxidation, the product (27 g.) was dissolved in ligroin and passed over a column of silica gel. The eluates from the upper part of the column (6.4 g.) had a mean peroxide value 1618 (range 1163—1830), and a mean iodine value 71.6 (range 83.0—55.7), whilst those from the lower part (2.7 g.) had a mean peroxide value of 722 and a mean iodine value 107.7. The unabsorbed material (17.9 g.) was mainly unaltered methyl linoleate (iodine value 166.8—170.0, mean peroxide value 26).

The material adsorbed on the upper part of the column (5.7 g.) yielded, after oxidation in acetone with potassium permanganate, a mixture of dicarboxylic (2.5 g.) and monocarboxylic (1.0 g.) acids. The dicarboxylic acids gave azelaic acid on crystallisation, but no indication of the presence of suberic acid was obtained. Distillation of the methyl esters of the monocarboxylic acids yielded fractions with equivalents varying between 126 and 132 (Calc. for methyl hexoate: equiv., 130).

The final product obtained after 262 hours autoxidation at 20° was examined with regard to its content of free acids (acid value 58.5). From 6.0 g. there were obtained 0.8 g. of steam-volatile material and 5.2 g. of material non-volatile in steam. The volatile portion contained some neutral liquid compounds, but was mainly acidic (equiv., 123.8; iodine value, 9.2). The acid portion was mainly solid but had the sharp smell of acetic or propionic acid; a small amount of crystals was obtained (from ligroin) which had m. p. 90—94° (equiv., 116). The nature of the solid acid was not ascertained. The definite iodine value of the steam-volatile acids is surprising, and points to the presence of some small proportion of an unidentified unsaturated acid of low molecular weight. The portion non-volatile in steam consisted of about 75% of a viscous neutral liquid, about 17% of water-soluble acids and about 8% of acidic matter insoluble in water. The water-soluble acids were mainly azelaic acid (m. p., after crystallisation, 97—101°).

We are indebted to the Colonial Products Research Council for permission to publish the results in this paper, and for a grant to one of us (F. D. G.); and to Professor R. A. Morton for the use of a spectrograph.

THE UNIVERSITY, LIVERPOOL.

[Received, July 2nd, 1945.]