Reactions of Chlorine Dioxide with Unsaturated Compounds

II. Methyl Oleate

BENGT O. LINDGREN and CARL MAGNUS SVAHN

Wood Chemistry Department, Swedish Forest Products Research Laboratory, Stockholm Ö, Sweden

The chlorine dioxide oxidation of methyl oleate yields α-unsaturated ketones, α-chloroketones, the dichloro addition product, chlorohydrines, allyl chlorides, β-diketones, epoxide, and C_8 and C_9 fragmentation products.

In the first part of this series,[1] the chlorine dioxide oxidation of cyclohexene was described. This paper deals with the oxidation of methyl oleate, a process which has technical applications in, for example, the pulping industry.

The analogous reaction between chlorine dioxide and triolein has been studied by Leopold and Mutton.[2] They have analysed the reaction mixture for its content of chloro, carbonyl, and other chemical groups.

RESULTS

In this study, an excess of methyl oleate was generally used (Expts. I and II) to minimise attack on the initial products of the reaction. The oxidation was performed in the absence (Expt. I) and in the presence (Expt. II) of water. The two experiments gave reaction mixtures with somewhat different compositions.

The reaction mixtures from the two experiments were divided by silicic acid chromatography into the fractions described in Tables 1 and 2. The following products were obtained in an almost pure state: methyl *threo*-9,10-dichloro-octadecan-1-oate, an α-chloroketone mixture, a mixture of α-unsaturated ketones, a chlorohydrine mixture, and a β-diketone mixture. The identifications of the fractions were carried out as follows.

The α-chloroketone mixture was identical with a mixture of equal amounts of methyl 10-chloro-octadecan-9-on-1-oate and methyl 9-chloro-octadecan-10-on-1-oate. The latter material was obtained by chromic acid oxidation of

Table 1. Fractions from the experiment performed in the absence of water (Expt. I). Chromatography on a silicic acid column with light petroleum-ethyl ether (4/1 v/v) as solvent.

Fraction No.	$\%^a$	Elution vol. ml $\times$ 10^{-1}	Constituent
1a	53	108 — 132	Methyl oleate Allyl chlorides Methyl octadecadienoates Methyl 9,10-dichloro-octadecanoate
1b	6	153 — 165 }	Methyl 9-chloro-octadecan-10-on-oate
1c	11	165 — 186 }	and 10-chloro-octadecan-9-on-oate
1d	2	186 — 225	
1e	4	225 — 300	β-Diketones
1f	1	300 — 345	
1g	7	345 — 450	α-Unsaturated ketones
1h	1	450 — 495	
1i	8	495 — 690	Methyl 9-chloro-octadecan-10-ol-oate and 10-chloro-octadecan-9-ol-oate
1k	1	690 — 900	

a Percentage of the reaction mixture (w/w).

Table 2. Fractions from the experiment performed in the presence of water (Expt. II). Chromatography on a silicic acid column with light petroleum-ethyl ether (4/1 v/v) as solvent.
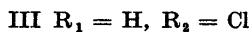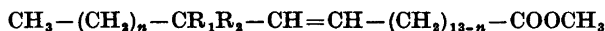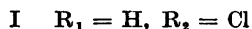
Fraction No.	$\%^a$	Elution vol. ml $\times$ 10^{-1}	Constituent
2a	54	75 — 90	Methyl oleate Methyl octadecadienoates Methyl 9,10-dichloro-octadecanoate
2b	3	90 — 96	Methyl 9,10-dichloro-octadecanoate
2c	12	96 — 159	Methyl 9-chloro-octadecan-10-on-oate and 10-chloro-octadecan-9-on-oate Methyl 9,10-epoxy-octadecanoate β-Diketones α-Unsaturated ketones
2d	7	159 — 180 }	α-Unsaturated ketones
2e	5	180 — 210 }	
2f	9	210 — 300	Methyl 9-chloro-octadecan-10-ol-oate and 10-chloro-octadecan-9-ol-oate

a Percentage of the reaction mixture (w/w).

the mixture of the corresponding chlorohydrines and its chemical nature was determined by its NMR and mass spectra.

The mixture of the α-unsaturated ketones was recognised by its UV, IR, NMR, and mass spectra, all of which agreed with its being composed of methyl octadecen-on-oates. The magnetic coupling constant between the olefinic protons was found to be 16.5 cps, indicating a *trans* configuration for the double bonds.[3]

The four isomers which can be expected to be formed from methyl oleate are (II) and (IV), n being 6 and 7. Direct oxidation of the allylic positions gives (II, $n = 7$) and (IV, $n = 6$), and a combination of allylic oxidation and allylic rearrangement, (II, $n = 6$) and (IV, $n = 7$).

$$CH_3-(CH_2)_n-CH=CH-CR_1R_2-(CH_2)_{13-n}-COOCH_3$$

$$I \quad R_1 = H, \ R_2 = Cl$$
$$II \quad R_1 + R_2 = O$$

$$CH_3-(CH_2)_n-CR_1R_2-CH=CH-(CH_2)_{13-n}-COOCH_3$$

$$III \quad R_1 = H, \ R_2 = Cl$$
$$IV \quad R_1 + R_2 = O$$

The β-diketones (most likely the 8,10- and 9,11-diones) were isolated *via* their copper complex and were characterised by UV and IR spectra.

The dichloro compound (methyl *threo*-9,10-dichloro-octadecan-1-oate) and the chlorohydrine mixture (methyl *threo*-9-chloro-10-hydroxy-octadecan-1-oate and *threo*-10-chloro-9-hydroxy-octadecan-1-oate) were identified by comparison with authentic samples.

Other substances were present in the fractions but they were not isolated. The fraction of recovered methyl oleate contained small amounts of chloro substances. If the reaction was performed in the absence of water (Expt. I), a part of the chloro groups that had been introduced reacted with silver ions under the mild conditions characteristic for chloro groups in allylic positions.[4] The expected isomers in the allyl chloride mixture are (I) and (III), n being 6 and 7.

The presence of allyl chlorides was not observed when the reaction was carried out in the water emulsion (Expt. II).

As shown by UV and GLC, the methyl oleate fractions also contained methyl esters of acids with two conjugated double bonds.

One of the substances in the reaction mixture moved with the same rate as methyl *erythro*-9,10-epoxystearate on a GLC examination.

The nature of the C_8 and C_9 cleavage products was investigated using the unfractionated reaction mixtures. In Expts. I and II, the yields of cleavage products were very low. A larger amount of cleavage (about 2 %) occurred if equimolar amounts of the reactants were used (Expt. III).

The following cleavage products were recognised by GLC: octanal, nonanal, caprylic and pelargonic acids (determined as the methyl esters), methyl hydrogen suberate and methyl hydrogen azelate (determined as the dimethyl esters). The C_8 and C_9 compunds were produced in about equal proportions. Their formation shows that the methyl oleate chain is cleaved through the 8—9, 9—10, or 10—11 bonds. In the experiment with equimolar amounts of reactants (Expt. III), formation of carbon dioxide was observed.

DISCUSSION

Leopold and Mutton [2] found that the oxidation mixture from triolein contains equimolar amounts of chloro and carbonyl groups, small amounts of epoxy and hydroxyl groups as well as traces of free carboxyl groups. They assumed from their results that the main reaction involves a cleavage of the

methyl oleate chain but they also discussed the possibility of α-chloroketone formation. The results of this investigation indicate that the chain is cleaved only to a small extent.

If compared with the oxidation of cyclohexene,[1] it is evident that the same types of substances are formed from methyl oleate as from cyclohexene. An exception is in the formation of the dienic compounds which were found only in the reaction mixture from methyl oleate. They may be secondary products formed by hydrogen chloride elimination from the allyl chlorides either during the reaction or during the fractionation and analysis. This may explain why the yield of the allyl chlorides is much lower from methyl oleate than from cyclohexene.
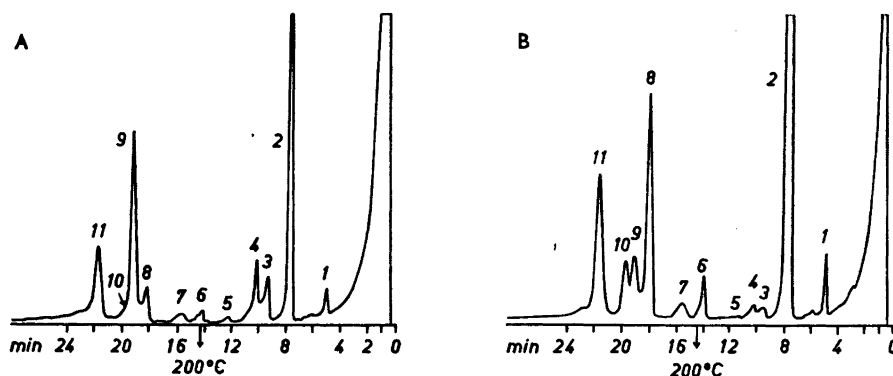

Fig 1. GLC of the reaction mixture from methyl oleate and chlorine dioxide. A) Non-aqueous conditions. B) Aqueous suspension.
The chromatotagram was run on a column with 1 % of XE−60 (General Electric Co, Waterford, N. Y.) on silanized Gas-Chrom P. The temperature was raised linearly from 150°C to 200°C for 15.6 min and then kept constant.
The peaks are: 1) Methyl palmitate. 2) Methyl oleate. 3−4) Methyl dienoates. 5) Methyl trienoates? 6) The epoxide. 7) Unknown compound(s). 8) The α-unsaturated ketones. 9) The α-chloroketones. 10) The dichloro compound. 11) The chlorohydrines.

From the weights of the fractions (Tables 1 and 2) and the peak areas of the GLC patterns (Figs. 1a and 1b) it can be seen that the α-unsaturated ketones, the chlorohydrines and the α-chloroketones are the main reaction products. The relatively low content of α-chloroketones (compare the GLC in Figs. 1a and 1b, and the TLC in Fig. 2) and the absence of allyl chlorides (see above) when the oxidation was carried out in water suspension is probably the result of the easy hydrolysis of these substances.

The mechanism of the chlorine dioxide reaction was discussed in the earlier paper.[1] It was assumed that the α-unsaturated ketones and chlorides are formed via allyl radicals. Autoxidation also proceeds *via* this type of radical. The α-unsaturated hydroperoxides formed by autoxidation of methyl oleate have the *trans* configuration. [5] The *trans* configuration of the α-unsaturated ketones obtained by the chlorine dioxide oxidation thus agrees with their postulated formation via allyl radicals. The *cis-trans* rearrangement during

Front

Fig. 2. TLC of the reaction mixture from the methyl oleate and chlorine dioxide. A) Non-aqueous conditions. B) Aqueous suspension. C) Reference mixture.

The chromatogram was run on Merck silicic acid G using light petroleum-diethyl ether (80 : 20 v/v) as solvent. The spots were developed by heating the plate at about 105°C after spraying with sulphuric acid-diethyl ether (1/4 v/v).

The spots are: 1) Methyl oleate. 2) The dichloro compound. 3) The α-chloroketones. 4 — 5) Material containing β-diketones. 6) The epoxide. 7) The unsaturated ketones. 8) The chlorohydrines.
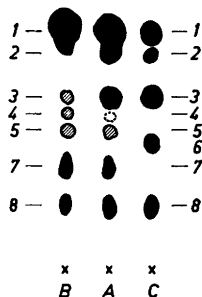
allylic homolytic chlorination has recently been studied by Walling and Thaler on some simpler systems.[6]

EXPERIMENTAL

General. Methyl oleate was purified by fractional low-temperature recrystallisations and distillation.[7] As estimated by GLC, the sample obtained was about 98 % pure, the main impurities being the esters of palmitic (1 %) and linoleic (less than 0.5 %) acids.

Chlorine dioxide was synthesised, purified and analysed as described earlier.[1]

If not otherwise stated, IR and NMR spectra were measured in carbon tetrachloride solutions, and UV spectra in ethanol solutions. The magnetic field in the NMR runs was 60 Mc.

The yields are reported in mole percentage of the added methyl oleate. As about half of the methyl oleate was recovered at the end of both runs, the yields calculated on the amount of the reacted ester are about double of those reported below.

Expt. I. The oxidation carried out in the absence of water

A stream of nitrogen containing chlorine dioxide (1.00 g, 15 mmole) was passed through methyl oleate (7.00 g, 24 mmole) for 23 h. The temperature rose to slightly above room temperature during the reaction.

Aldehydes. The reaction mixture was analysed for aldehydes by GLC using a poly-diethylene glycol succinate column at 125°C. The column was back-flushed after 10 min. Two peaks of about equal area were observed. The retention times were the same as those for authentic samples of octanal (retention time, 4.2 min) and nonanal (6.2 min). The area of the peaks corresponds to a yield of the aldehydes of less than 0.01 %.

Acids. From a part of the reaction mixture (2.0 g), dissolved in ether, the acids were collected by extraction with a 2 % aqueous solution of sodium carbonate. The acid fraction (14 mg, 0.7 % of the weight of methyl oleate) was esterified with methanolic hydrogen chloride and the products were examined by GLC on a poly-butandiol succinate column. The temperature was kept at 150°C for 3 min, then increased linearly for 5.3 min to 205°C, where it was kept constant. Peaks with the same retention times as those for authentic samples of the methyl esters of caprylic (1.6 min), pelargonic (2.3 min), suberic (9.7 min), azelaic (10.8 min), and oleic acids (15.6 min) were observed. Oleic acid was the main component, the other substances were present only in traces. As oleic acid

was not formed during the more severe conditions used in Expt. III below, the methyl oleate in this case must be unchanged starting material. This is also likely because the separation of the carbonate solution and the ether was unsatisfactory owing to the formation of an emulsion.

The main constituents. The reaction mixture was analysed for its main constituents by GLC on a nitrile silicone column. The results are shown in Fig. 1A. Fig. 2A shows the result of a TLC analysis.

A part of the reaction product (5 g) was chromatographed on a column of silicic acid (1770 ml, Mallinckrodt, activated by heating for 2 h at 120°C) using light petroleum (b.p. 30—60°C)-diethyl ether (4/1 v/v) as solvent.

The fractions (1a—1k) are described in Table 1. The total recovery of added material was 94 %. The following compounds were found in the fractions.

Methyl oleate. The main component of fraction 1a was indistinguishable by TLC and GLC from this compound.

Allyl chlorides (probably I and III, n being 6 and 7). Fraction 1a contained about 3 mg of chlorine linked to allylic positions as determined according to Teeter and Jackson [4] on 0.1 g portions. This figure corresponded to a yield of 0.8% of methyl chloro-octadecenoates. In a GLC analysis they are probably transformed into dienic compounds.

Methyl octadeca-dien-oates (probably $\Delta^{7,9}$, $\Delta^{8,10}$, and $\Delta^{9,11}$). The retention times of the peaks 3 and 4 in Fig. 1A agree with those expected for methyl octadeca-dien-oates with conjugated double bonds. The substances giving the peaks 3 and 4 were also present in fraction 1a, the UV spectrum of which had a maximum at 231 mμ. The maximum of the alkali-isomerised linoleic acid, which is a mixture of conjugated dienoic acids, is at 232 mμ.[8]

TLC did not separate the dienic substances from the 9,10-dichloro derivative (Fig. 2A). The presence of dienes was indicated, however, by a violet-brown spot which developed after a short period of heating at 105°C of the sulphuric acid-ether sprayed plates. The 9,10-dichloro compound gave a yellow-brown spot after further heating.

Methyl threo-9,10-dichloro-octadecan-1-oate. GLC showed the presence of this substance in fraction 1a. The retention time of an authentic sample of the dichloro compound [9] correspond to point 10 in Fig. 1A. According to the method of Teeter and Jackson,[4] fraction 1a contained about 41 mg of chlorine in α-dichloro groups. This corresponds to a yield of 3 % of the dichloro substance.

Methyl 9-chloro-octadecan-10-on-1-oate and *methyl 10-chloro-octadecan-9-on-1-oate.* Fraction 1c was indistinguishable by TLC, GLC, NMR, and IR from a mixture (prepared as described below) of the two α-chloro-ketones. (Found: Cl 10.0. Calc. for $C_{19}H_{35}ClO_3$: Cl 10.2).

The mass spectra of the two samples showed the expected molecular peaks (m/e 346 and 348, the ratio of the peak heights being 4) and two large fragment peaks, m/e 141 [assigned to $CH_3-(CH_2)_7-CO^+$ from the 9-chloro compound] and m/e 185 [$CH_3OCO-(CH_2)_7-CO^+$ from the 10-chloro compound]. In both samples, the heights of the fragment peaks were the same.

The samples gave the following proton magnetic signals: $\delta = 0.90$ ppm (triplet) for CH_3-CH_2-, 1.33 ppm (multiplet) for $-CH_2-$, 2.29 ppm (triplet, $J_c = 6.5$ cps) for $-CH_2-COOCH_3$, 2.67 ppm (triplet, $J_c = 7$ cps) for $-CH_2-CO-CHCl-$, 3.69 ppm (singlet) for $-COOCH_3$, and 4.27 ppm (triplet, $J_c = 6.5$ cps) for $-CHCl-CO-$.

The two α-chloroketones also constituted the major part of fraction 1b (TLC and GLC). The weights of 1b and 1c correspond to a yield of about 14 %.

The mixture of the two α-chloroketones was prepared from the mixture of the corresponding chlorohydrines [10] by chromic acid oxidation. The same procedure was used as described for the oxidation of a methyl hydroxystearate mixture.[11] (Found: Cl 10.5. Calc. for $C_{19}H_{35}ClO_3$: Cl 10.2). The synthesis requires that the isomers be present in the proportion 1:1.

β-Diketones. Fraction 1e gave a red colour reaction with a solution of ferric chloride in chloroform-pyridine and a blue precipitate with cupric acetate in methanol. After recrystallisations from ether, the copper complex melted at 85°C. After regeneration with dilute hydrogen chloride a yellow oil, which darkened on handling and storage, was obtained. It had absorption maxima in a carbon tetrachloride solution at 1520—1620 cm^{-1} (broad and strong peak) and 1705 cm^{-1} (weak peak). In a potassium bromide plate or as the oil, the maxima were at 1610 cm^{-1} and 1700 cm^{-1}. Its UV maximum in an ethanol

solution was at 276 mμ, ε being 10 700 (10^{-4} M solution), and in a 0.5 M methanolic potassium hydroxide solution at 296 mμ, ε being 18 000 M).(10^{-4} These data agree with those reported for nonadecan-9,11-dion-1-oic acid [12] [UV maximum in ethanol at 275 mμ, ε being 10 500 (10^{-4} M), and in an ethanolic potassium hydroxide solution at 296 mμ, ε being 22 800 (10^{-4} M)] and for acetyl-acetone (IR maxima at 1530—1640 and at 1709 cm^{-1}).

α-*Unsaturated ketones* (probably the *trans* isomers of II and IV, n being 6 and 7). Fraction 1g showed a carbonyl peak at 1680 cm^{-1}, a C=C band at 1630 cm^{-1} and a peak at 970 cm^{-1} probably due to the *trans* double bond. Its UV spectrum had a maximum at 224 mμ, ε being 13 800, *cf.* the UV maximum at 224 mμ, ε being 16 000, for *trans* heptadec-9-en-11-on-1-oic acid.[13]

The NMR spectrum showed the following signals: δ = 0.90 ppm (triplet) for CH_3- CH_2-, 1.35 ppm (multiplet) for $-CH_2-$, 2.18—2.60 ppm (groups of peaks) for the three methylene groups linked to $-COOCH_3$ and $-CO-CH=CH-$, 3.69 ppm (singlet) for $-COOCH_3$, 6.15 ppm (sextet composed of a doublet, J_c = 16.5 cps, and a triplet, J_c = 1.5 cps) for $-CO-CH=CH-$, 6.93 ppm (sextet composed of a doublet, J_c = 16.5 cps, and a triplet, J_c = 6.5 cps) for $-CO-CH=CH-$.

Electron impact showed that the mass number of the molecule ion was 310 in agreement with the molecular weight calculated for $C_{19}H_{34}O_3$. The spectrum showed the presence of many fragments. Their assignments were questionable as most of them can be ascribed to two or more isomers.

The total yield was about 7 %.

Methyl threo-*9-chloro-10-hydroxy-octadecan-1-oate and methyl* threo-*10-chloro-9-hydroxy-octadecan-1-oate.* Fraction 1i was indistinguishable by IR, TLC, and GLC from an authentic sample [8] of the mixture of these two chlorohydrines. The yield was about 7 %. (Found: Cl 8.6. Calc. for $C_{19}H_{37}ClO_3$: Cl 10.2).

Methyl erythro-*9,10-epoxy-octadecan-1-oate.* The retention time for peak 6 in Fig. 1A agrees with that of an authentic sample [14] of the epoxide.

Expt. II. The oxidation carried out in the presence of water:
Excess of methyl oleate

If not otherwise stated, the experiment was carried out as in Expt. I.

Purified methyl oleate (6.13 g, 21 mmole) was vigorously stirred in an aqueous chlorine dioxide solution (100 ml, 8.5 mmole of dioxide). The temperature rose from 13°C to slightly above room temperature. After 22 h, the oil was separated and combined with four ether extracts of the aqueous solution. The ether solution was dried and evaporated.

The reaction mixture contained octanal and nonanal, the yields being less than 0.01 % (GLC).

A part (1.15 g) of the reaction mixture yielded an acidic fraction (7 mg, 0.6 % of the weight of the methyl oleate), in wich caprylic, pelargonic, suberic, azelaic, and oleic acids were found in roughly equal portions (GLC of the methyl esters).

The results of GLC and TLC analyses of the reaction product are shown in Figs. 1B and 2B, respectively.

A part (3.50 g) of the reaction product was fractionated on a silicic acid column (940 ml). The fractions are described in Table 2. The total recovery of the added material was 89 %. The following compounds and isomer mixtures were found in the fractions.

Methyl oleate. It was the main component of fraction 2a.

Allyl chlorides. Fraction 2a contained no chlorine in allylic positions as determined according to Teeter and Jackson.[4]

Methyl octadeca-dien-oates. GLC of the reaction product showed the presence of the peaks (3 and 4 in Fig. 1B) attributed to methyl octadeca-dien-oates with conjugated double bonds.

Methyl threo-*9,10-dichloro-octadecan-1-oate.* Fraction 2b was found to be indistinguishable by TLC and GLC from this substance. (Found: Cl 19.3. Calc. for $C_{19}H_{36}Cl_2O_2$: Cl 19.2).

About 0.19 g of the dichloro compound was also found in fraction 2a by the method of Teeter and Jackson.

The total yield was about 7 %.

Methyl 9-chloro-octadecan-10-on-1-oate and *methyl 10-chloro-octadecan-9-on-1-oate*. These isomers were constituents of fraction 2c (GLC, TLC and NMR).

Material containing β-diketones. The UV spectrum of fraction 2c had a maximum at 283 mμ and its IR spectrum (oil film in an Irtran cuvette) at 1610 cm^{-1} (strong peak) and 1695 cm^{-1} (weak peak). Among its proton magnetic signals one was at $\delta = 6.05$ ppm (singlet) maybe for $-CO-CH=COH-$ and another at $\delta = 15.68$ ppm (singlet) probably for $-CO-CH=COH-$. Positive tests for β-diketones were observed with the iron and the copper reagents.

α-Unsaturated ketones. Fraction 2d consisted of these substances. They formed the major part of fraction 2e (GLC and TLC) and were also found in fraction 2c (GLC, TLC and a UV maximum at 224 mμ). The total yield was about 12 %.

Methyl threo-9-chloro-10-hydroxy-octadecan-1-oate and *methyl threo-10-chloro-9-hydroxy-octadecan-1-oate*. Fraction 2f was indistinguishable by TLC, GLC, and IR from an authentic sample [8] of the mixture of these two chlorohydrines. The yield was about 8 %. (Found: Cl 9.8. Calc. for $C_{19}H_{37}ClO_3$: Cl 10.2).

Methyl erythro-9,10-epoxy-octadecan-1-oate. Both the reaction mixture and fraction 2c gave a GLC peak indistinguishable from the peak of an authentic sample.

Expt. III. The oxidation carried out in the presence of water:
Equimolar amounts of reactants

Methyl oleate (3.00 g, 10 mmole) was vigorously stirred with an aqueous solution (115 ml) of chlorine dioxide (10 mmole) under an atmosphere of nitrogen. After 60 h the solution was colourless and the oily layer light-yellow. The gas above the solution was flushed with nitrogen into a calcium hydroxide solution, in which a precipitate was formed.

The reaction mixture was extracted with ether and the material in the ether solution was separated into neutral (3.08 g) and acidic (0.06 g) components by extraction with a 5 % sodium carbonate solution.

The neutral and acidic fractions were analysed by GLC on nitrile and polyester columns, respectively, as described for Expt. I. The neutral fraction gave a GLC pattern essentially the same as that in Fig. 1B from Expt. II, and it contained only traces of octanal and nonanal. The acidic fraction contained the C_8 and C_9 acids but no oleic acid (no emulsion was formed, see Expt. I).

REFERENCES

1. Lindgren, B. O., Svahn, C. M. and Widmark, G. *Acta Chem. Scand.* **19** (1965) 7.
2. Leopold, B. and Mutton, D. B. *Tappi* **42** (1959) 218.
3. Jackman, L. M. *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, London 1959, p. 85.
4. Teeter, H. M. and Jackson, J. E. *J. Am. Oil Chemists' Soc.* **26** (1949) 535.
5. Knight, H. B., Eddy, C. R. and Swern, D. *J. Am. Oil Chemists' Soc.* **28** (1951) 188.
6. Walling, C. and Thaler, W. *J. Am. Chem. Soc.* **83** (1961) 3877.
7. Wheeler, D. H. and Riemenschneider, R. W. *Oil and Soap* **16** (1939) 207.
8. O'Connor, R. T. *J. Am. Oil Chemists' Soc.* **32** (1955) 616.
9. King, G. *J. Chem. Soc.* **1949** 1822.
10. Swern, D. *J. Am. Chem. Soc.* **70** (1948) 1235.
11. Fore, S. P. and Bickford, W. G. *J. Org. Chem.* **24** (1959) 920.
12. Nunn, J. R. *J. Chem. Soc.* **1952** 313.
13. King, G. *J. Chem. Soc.* **1951** 1980.
14. Findley, T. W., Swern, D. and Scanlan, J. T. *J. Am. Chem. Soc.* **67** (1945) 412.