202. *The Reaction of* N-*Bromosuccinimide with Methyl Oleate and Other Vegetable-oil Derivatives.*

By Donald A. Sutton and J. Dutta.

N-Bromosuccinimide reacts with methyl oleate to give an oil which can be molecularly distilled without decomposition, and contains an appreciable proportion of the dibromo-substitution product. The oil reacts with chromatographic alumina; allyl bromide itself does not similarly react but 3-bromo*cyclo*hexene undergoes a vigorous decomposition. The bromo-substitution products from linoleic ester, linolenic ester, and linseed oil are unstable; they cannot be molecularly distilled without decomposition. The work has a bearing on a current hypothesis which states that the reaction between olefins and *N*-bromosuccinimide is a free-radical reaction.

The reaction between *N*-bromosuccinimide and methyl oleate was first investigated by Ziegler and his co-workers (*Annalen*, 1942, **551**, 80), who reported that the product obtained from equimolecular proportions of the reactants was an oil (assumed to be a monobromo-derivative) which could not be distilled or smoothly transformed by dehydrobromination into the diene ester. It was found that products containing larger amounts of combined bromine could readily be made when greater proportions of *N*-bromosuccinimide were employed. Teeter (*J. Amer. Oil Chem. Soc.*, 1948, **25**, No. 7, 243) treated *N*-bromosuccinimide with methyl linoleate and with the mixed methyl esters of soya-bean oil fatty acids; * he found that the brominated esters were somewhat unstable and recommended that the preparation should be carried out at a fairly low temperature (70°). Teeter also investigated the reaction of the brominated esters with sodium methoxide and with sodium and cuprous cyanides.

The present work on the reaction between methyl oleate and *N*-bromosuccinimide was undertaken because the expected monobromo-derivatives (I) and (II), or a mixture of both, was required for a synthesis in connection with a research into the thermal polymerisation of drying oils.

$CH_3\cdot[CH_2]_6\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot[CH_2]_6\cdot CO_2Me$ Methyl oleate. $\rightarrow$

$CH_3\cdot[CH_2]_6\cdot CHBr\cdot CH{:}CH\cdot CH_2\cdot[CH_2]_6\cdot CO_2Me$
Methyl 10-bromoheptadec-8-enecarboxylate
(11-bromo-Δ^9-oleate).
(I.)

$CH_3\cdot[CH_2]_6\cdot CH_2\cdot CH{:}CH\cdot CHBr\cdot[CH_2]_6\cdot CO_2Me$
Methyl 7-bromoheptadec-8-enecarboxylate
(8-bromo-Δ^9-oleate).
(II.)

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* The chief components of this mixture are linoleic acid (*ca.* 50%) and oleic acid (*ca.* 30%).

The course of the substitutive bromination has, in addition, a considerable theoretical interest, for Waters (*Nature*, 1944, **154**, 772; *J.*, 1946, 409) considers that *N*-bromosuccinimide reacts with olefins after the homolytic fission of a covalent carbon–hydrogen bond :

$$\cdot CH_2\cdot CH{:}CH\cdot \longrightarrow \cdot\underset{\bullet}{C}H\cdot CH{:}CH\cdot \xrightarrow{N\text{-Bromosuccinimide}} \cdot CHBr\cdot CH{:}CH\cdot$$

so that the reaction is essentially of the free-radical type. If this is the mechanism of reaction, then the number of possible monobromo-isomerides from methyl oleate is four, since the intermediate free-radical forms could isomerise as in autoxidation processes (compare Farmer, Koch, and Sutton, *J.*, 1943, 541; Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 236) and lead to the formation of (III) and (IV) in addition to (I) and (II).

$$CH_3\cdot[CH_2]_6\cdot\underset{\bullet}{C}H\cdot CH{:}CH\cdot CH_2\cdot[CH_2]_6\cdot CO_2Me$$
$$\upharpoonleft\downharpoonright$$
$$CH_3\cdot[CH_2]_6\cdot CH{:}CH\cdot\underset{\bullet}{C}H\cdot CH_2\cdot[CH_2]_6\cdot CO_2Me$$
$$\downarrow$$
$$CH_3\cdot[CH_2]_6\cdot CH{:}CH\cdot CHBr\cdot CH_2\cdot[CH_2]_6\cdot CO_2Me$$

Methyl 8-bromoheptadec-9-enecarboxylate
(9-bromo-Δ^{10}-oleate).
(III).

$$CH_3\cdot[CH_2]_6\cdot CH_2\cdot CH{:}CH\cdot\underset{\bullet}{C}H\cdot[CH_2]_6\cdot CO_2Me$$
$$\upharpoonleft\downharpoonright$$
$$CH_3\cdot[CH_2]_6\cdot CH_2\cdot\underset{\bullet}{C}H\cdot CH{:}CH\cdot[CH_2]_6\cdot CO_2Me$$
$$\downarrow$$
$$CH_3\cdot[CH_2]_6\cdot CH_2\cdot CHBr\cdot CH{:}CH\cdot[CH_2]_6\cdot CO_2Me$$

Methyl 9-bromoheptadec-7-enecarboxylate
(10-bromo-Δ^{8}-oleate).
(IV.)

In the case of methylene-interrupted unsaturation, such as occurs in linoleic and linolenic esters, isomerisation of the intermediate free-radical forms would lead to formation of brominated compounds containing a system of conjugated double bonds. Thus linoleic ester could give rise to (V) and (VI) as a result of double-bond movement in the free radical :

$$CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Et \nearrow CH_3\cdot[CH_2]_4\cdot CHBr\cdot CH{:}CH\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Et$$

Ethyl linoleate.

Ethyl 12-bromoheptadeca-8 : 10-dienecarboxylate
(13-bromo-$\Delta^{9:11}$-linoleate).
(V.)

$$CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Et \searrow CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH{:}CH\cdot CHBr\cdot[CH_2]_7\cdot CO_2Et$$

Ethyl 8-bromoheptadeca-9 : 11-dienecarboxylate
(9-bromo-$\Delta^{10:12}$-linoleate).
(VI.)

Double-bond movement of the kind visualised above has not been recorded in the great majority of the cases of reaction between olefins and *N*-bromosuccinimide investigated since 1942 (Djerassi, *Chem. Reviews*, 1948, **43**, 271). In the present work it was found that the products obtained when *N*-bromosuccinimide reacted with linoleic ester, linolenic ester, and linseed oil contained conjugated unsaturation, but the amounts of conjugated compounds present (estimated by ultra-violet spectroscopy) were not large. The triene conjugation observed in the case of bromo-linoleic ester prepared in boiling carbon tetrachloride was not present in large amount; bromo-linoleic ester prepared under mild conditions (similar to Teeter's) contained no triene conjugation and no band near 232 mμ characteristic of diene conjugation but developed some triene conjugation when heated at 100°. The above data can be accounted for by the hypothesis that the bromo-ester readily undergoes an allylic rearrangement similar to that recorded by Karrer and Ringli in the case of brominated diallyl (*Helv. Chim. Acta*, 1947, **30**, 863, 1771), followed by partial dehydrobromination. These facts do not lend support to Waters's views.

In a typical experiment, methyl oleate reacted with an equimolecular proportion of *N*-bromosuccinimide in boiling carbon tetrachloride for 4½ hours to give an oil containing some two-thirds of the theoretical amount of combined bromine. The oil was comparatively stable; no hydrogen bromide was evolved during its preparation or subsequent molecular distillation at 78°. Although the overall percentage of combined bromine was less than that required for the pure monobromo-derivative, the product contained an appreciable proportion of the dibromo-compound as was shown by fractionation in a falling-film molecular still (Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, **65**, 164). By molecular distillation at 78° the oil was divided into a distillate (*ca.* 80%) and a residue (*ca.* 20%); the bromine content of the latter (28·7%) corresponded to a mixture containing some 53% of the dibromo-compound (presumably 7 : 10-dibromoheptadec-8-enecarboxylic ester) and 47% of the monobromo-compound. The distillate probably also contained some dibromo-ester, since the fractionating efficiency of falling-film stills is poor, and, in a distillation at 86° of another batch of the bromo-ester, a distillate with a bromine content (23·9%) higher than that required for the monobromo-compound (21·3%) was obtained. It was found that the succinimide had not been completely removed from the total reaction product by filtration from carbon tetrachloride solution, since some of it distilled under the conditions used. A specimen of the molecularly distilled oil was oxidised with permanganate in acetone and yielded a mixture from which suberic, azelaic, and octoic acids were isolated and identified. Some part of the azelaic acid would result from oxidation of the methyl oleate remaining in the oil; the formation of suberic and octoic acids is consistent with the presence of both monobromo-esters (I) and (II) which would also yield some azelaic and nonoic acids :

$$\text{(I)} \xrightarrow{\text{KMnO}_4} CH_3\cdot[CH_2]_6\cdot CO_2H + CO_2H\cdot[CH_2]_7\cdot CO_2Me$$

$$\text{(II)} \xrightarrow{\text{KMnO}_4} CH_3\cdot[CH_2]_7\cdot CO_2H + CO_2H\cdot[CH_2]_6\cdot CO_2Me$$

The above oxidative scission products could also arise from monobromo-esters (III) and (IV) if these were present.

Attempts to separate the individual monobromo-esters (I) and (II) in a pure state from the molecularly distilled oil by chromatography on activated alumina were unsuccessful because the adsorbent reacted with the brominated ester and removed most of the combined bromine. Two products of the chromatographic experiments were isolated; they were apparently hydroxy-oleic esters, but the positions of the hydroxyl groups were not determined. Examination of one product by infra-red spectroscopy showed that it gave a band at a wave-length of 2·9 μ characteristic of a hydroxyl group and similar in intensity to the corresponding band given by methyl ricinoleate. The other product was hydrogenated, and the saturated ester formed was converted into the corresponding acid; examination of the latter in a Langmuir trough showed that it gave a monolayer film of the gaseous type very similar to that given by a pure specimen of 12-hydroxystearic (11-hydroxyheptadecanecarboxylic) acid in our laboratories and also similar to that of 3(?)-hydroxystearic acid (Fosbinder and Rideal, *Proc. Roy. Soc.*, 1933, **143**, *A*, 61).

It is possible that the hydroxy-oleic ester is formed as a result of reaction between the bromo-ester and aluminium hydroxide present in the chromatographic alumina. Allyl bromide itself does not react with activated alumina at room temperature, but 3-bromo*cyclo*hexene undergoes a vigorous reaction.

Linoleic and linolenic esters were also brought into reaction with *N*-bromosuccinimide in boiling carbon tetrachloride solution. In agreement with Teeter (*loc. cit.*), it was noted that fumes of hydrogen bromide were evolved during the reaction; molecular distillation of the products could not be achieved owing to their instability. As has been stated above, these brominated esters contained some conjugated unsaturation; *e.g.*, brominated linoleic ester having 13·6% of combined bromine contained 10% of conjugated triene compounds (assuming that the pure conjugated triene would give $\varepsilon = 47,000$ at $\lambda_{\text{max.}} = 270$ mμ). Brominated linoleic ester prepared under milder conditions had an absorption band of moderate intensity at 258 mμ which is not characteristic of acyclic diene or triene conjugation; this product developed 11% of triene conjugation after an hour's heating at 100°.

Linseed oil similarly gave off fumes of hydrogen bromide when it reacted with *N*-bromosuccinimide. The product was an oil which had film-forming properties. By saponification and concomitant dehydrobromination, the oil yielded a mixture of fatty acids which was appreciably more unsaturated than the original linseed oil and contained considerable amounts of conjugated polyenes.

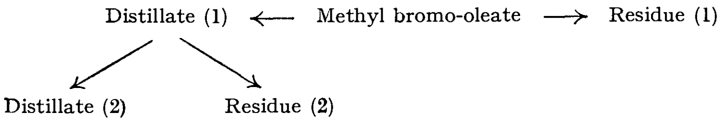
EXPERIMENTAL.

Units used.—Iodine value (I.V.) = g. of iodine per 100 g. of substance based on the amount of iodine chloride taken up by the substance in one hour by the Wijs method.

Acid value (A.V.) = mg. of potassium hydroxide equivalent to 1 g. of substance.

Bromination of Methyl Oleate.—Methyl oleate (30 g., 0·11 mole; I. V. 89), prepared from olive oil by Hilditch's method (" The Chemical Constitution of Natural Fats," 2nd edn., Chapman and Hall, London, 1947, p. 398), was dissolved in redistilled " AnalaR " carbon tetrachloride (150 c.c.), and *N*-bromosuccinimide (23 g. containing 0·10 atom of reactive bromine) was added. The whole was heated under reflux on a water-bath for 4½ hours in a slow stream of pure nitrogen with frequent shaking; there was apparently no evolution of hydrogen bromide. The solution was then cooled and filtered from succinimide at the water-pump; solvent was removed from the filtrate by distillation and finally in a vacuum to leave an orange-red liquid (30 g.) as residue; $n_D^{25°}$ 1·4670, $d_{4°}^{25°}$ 0·9986 (Found: Br, 14·65; I.V., 68·0. Calc. for $C_{19}H_{35}O_2Br$: Br, 21·3%; I.V., 67·7).

Distillation of the Methyl Bromo-oleate.—The product (30 g.) was subdivided by distillation in a falling-film molecular still (Farmer and Sutton, *loc. cit.*) at 78° according to the following scheme:



The fractions had the following properties:

Fraction.	Weight, g.	Br, %.	Other properties.
Original methyl bromo-oleate	30	14·65	As given above
Residue (1)	4·5	28·7	—
Distillate (1)	20	—	—
Residue (2)	11	15·0	I.V. 69·6; $n_D^{25°}$ 1·4673; $d_{4°}^{25°}$ 0·9888
Distillate (2)	6·3	5·05	—

During the first distillation of the total methyl bromo-oleate some succinimide distilled and adhered to the wall of the still. The bromine content of residue (1) indicated the presence of dibromo-oleic ester (see p. 940), whereas residue (2) and distillate (2) contained unbrominated methyl oleate.

A second batch of methyl bromo-oleate was divided into a distillate (55 g. Found: Br, 12·0%) and a residue by molecular distillation at 78°; the residue was again subdivided at 86° into a second distillate (10 g. Found: Br, 23·9%) and a final residue (24 g.). The bromine content of the second distillate indicated the presence of distilled dibromo-ester.

Permanganate Oxidation of Distilled Methyl Bromo-oleate.—A portion of residue (2) (8·5 g.) was dissolved in acetone (90 c.c.), and the solution heated under reflux on a water-bath for 4 hours, during which potassium permanganate (50 g.) was added in small portions. The acetone was removed by distillation and finally in a vacuum to leave a solid residue which was decolorised by addition of sodium metabisulphite solution. To the decolorised solution was added sufficient aqueous sulphuric acid to render it acid to Congo-red; the organic acids present were then extracted by ether, and the aqueous layer was retained (*A*, see below). The ethereal extract was washed several times with aqueous potassium carbonate; the alkaline washings were combined, acidified, and ether-extracted. The final ethereal solution was thoroughly washed with water to remove mineral acid, and it was then dried and evaporated to yield a mixture of acids (4·1 g.) (Found: A.V., 341) which was fractionated by distillation under 2 mm. pressure through a short column to yield the folowing fractions, the residue being discarded:

Fraction.	Weight, g.	B. p.	A.V.	Fraction.	Weight, g.	B. p.	A.V.
(i)	0·4	95—100°	463	(iii)	0·6	110—135°	378
(ii)	0·3	100—110	409	(iv)	1·2	135—170	321

Fraction (iv) was a mixture containing the half-esters of suberic and azelaic acids, which were obtained and identified thus: Some of fraction (iv) (0·9 g.) was saponified by refluxing with a 10% solution of potassium hydroxide in ethyl alcohol (50 c.c.) for 2 hours; the bulk of the alcohol was removed by distillation, and the remaining solution was poured into water, acidified with dilute sulphuric acid, and thoroughly extracted with ether. The extract was washed, dried, and evaporated to yield a solid mixture of acids which was recrystallised from chloroform to give m. p. 134—138° and then from ethyl acetate to give suberic acid of m. p. 140—142° (mixed m. p. 141—143° in admixture with an authentic specimen, m. p. 143°). On evaporation of the filtrate from the chloroform recrystallisation, a solid was obtained which was recrystallised from ethyl acetate to give azelaic acid, m. p. 97—100° (mixed m. p. 99—101° in admixture with an authentic specimen, m. p. 104°).

Fraction (ii) contained *n*-octoic acid; it was converted into its *p*-bromophenacyl ester (Moses and Reid, *J. Amer. Chem. Soc.*, 1932, **54**, 2101), which, recrystallised from dilute alcohol, had m. p. 61—62° (Found: C, 56·3; H, 6·3. Calc. for $C_{16}H_{21}O_3Br$: C, 56·3; H, 6·2%) (mixed m. p. 62—64° in admixture with an authentic specimen, m. p. 65°).

Fraction (i) probably contained succinic acid (from its high acid value and positive fluorescent test after fusion with resorcinol); this acid presumably came from traces of succinimide still remaining in the distilled bromo-ester. Succinic acid was isolated from the aqueous liquor (*A*, above) thus: the liquor was continuously extracted with ether in a liquid–liquid extractor, and the extract was evaporated to yield succinic acid, m. p. 182—183° (Found: C, 41·3; H, 5·3; A.V., 930. Calc. for $C_4H_6O_4$: C, 40·6; H, 5·1%; A.V., 950) (mixed m. p. 183—185° in admixture with an authentic specimen, m. p. 185°), which gave a strongly fluorescent solution after fusion with resorcinol.

Attempted Chromatography of Methyl Bromo-oleate on Activated Alumina.—A sample of undistilled brominated methyl oleate (12 g.) (Found: Br, 18·3%) was dissolved in redistilled "AnalaR" light petroleum (100 c.c.; b. p. 40—60°) and passed through a column (12½″ × 1¼″) of activated alumina (Savory and Moore's "Mayfair A" brand, standardised according to Brockmann). Two yellow-brown bands appeared, and the column was developed and eluted by washing with a 2% solution of ethyl alcohol in light petroleum. Three separate portions of filtrate were collected: (*a*) the portion below the lower band, (*b*) the lower band, and (*c*) the upper band. Portion (*a*) gave 2·8 g. of an oil (Found: C, 77·2; H, 12·3; Br, 0·6%); (*b*) gave 1·9 g. of an oil, and (*c*) gave 2·3 g. of an oil. The whole of (*b*) and (*c*) was chromatographed on more alumina in two separate columns (11″ × ¾″) and each split into two more bands, thus :

(*b*) ↗ (*b*, i) Upper band (0·6 g. Found : Br, 0·96%)
(*b*) ↘ (*b*, ii) Lower band (0·8 g. Found : Br, 4·3%)

(*c*) ↗ (*c*, i) Upper band (1·8 g. Found : Br, 0·6%)
(*c*) ↘ (*c*, ii) Lower band (0·2 g. Found : Br, 1·47%)

Some of (*c*, i) (1·0 g.) was again treated on a column of alumina (8¼″ × ⅞″) but was not further resolved.

Examination of two of the chromatographic products. The portion (*b*, i) was examined in a Perkin–Elmer infra-red spectrometer; it gave a band at a wave-length of 2·9μ characteristic of the hydroxyl grouping and of similar intensity to that found in methyl ricinoleate.

A sample (0·544 g.) of the final product from (*c*, i) was dissolved in methyl alcohol and hydrogenated in the presence of Adams's catalyst (0·544 g. absorbed 40 c.c. of hydrogen at N.T.P., corresponding to I.V., 83·5. Calc. for monohydroxyoleic ester, $C_{19}H_{36}O_3$: I.V., 81·5). The saturated ester was isolated and then saponified by one hour's heating under reflux with a 10% solution of potassium hydroxide in methyl alcohol to yield the corresponding saturated acid, which was recrystallised from acetone. The recrystallised saturated acid (Found : C, 72·4; H, 11·9; Br, 0·0; A.V., 191·4. Calc. for $C_{18}H_{36}O_3$: C, 71·95; H, 12·1%; A.V., 186·5) (m. p. 68—69°), which was used for Langmuir trough experiments, gave a depression of m. p. in admixture with stearic acid. A portion of the recrystallised saturated acid was converted into the methyl ester (m. p. 40—41°) by reaction with diazomethane in ethereal solution [Found : *M* (Menzies–Wright ebullioscopic in benzene), 328. Calc. for $C_{19}H_{38}O_3$: *M*, 314·4).

Attempted Chromatography of Allyl Bromide.—Allyl bromide (2 g.) in ether (100 c.c.) was passed through a column of alumina (8″ × ⅞″); evaporation of the filtrate yielded unchanged allyl bromide.

Attempted Chromatography of 3-*Bromo*cyclo*hexene.*—3-Bromo*cyclo*hexene (10 g.), made from *cyclo*hexene by the method of Zielger *et al.* (*loc. cit.*), in light petroleum (100 c.c.; b. p. 40—60°), was passed down a column of alumina (20″ × ⅞″). As the solution travelled down the column the alumina became warm and turned blue. The column was washed with a 2% solution of ethyl alcohol in light petroleum (500 c.c.) and the filtrate was evaporated to yield a viscous red-brown liquid (Found : C, 74·8; H, 8·6; Br, 13·6%), apparently of polymeric complexity.

Bromination of Ethyl Linoleate.—Ethyl linoleate (8·4 g., 0·0273 mole), prepared by debromination of tetrabromostearic acid (*Org. Synth.*, **22**, 45), and *N*-bromosuccinimide (5·1 g. containing 0·028 atom of reactive bromine) were heated under reflux with frequent shaking in redistilled "AnalaR" carbon tetrachloride (50 c.c.) on a water-bath for 4½ hours under a slow stream of nitrogen. Hydrogen bromide was evolved towards the end of the refluxing; the mixture was cooled and filtered at the water-pump, the filter being washed with three 10-c.c. portions of carbon tetrachloride. The filtrate was freed from solvent in a vacuum and left a brown oil (9·1 g.) (Found : Br, 13·6; I.V., 117. Calc. for $C_{20}H_{35}O_2Br$: Br, 20·7%; I.V., 131); $n_{\mathrm{D}}^{25°}$ 1·4820. Ultra-violet spectroscopic examination indicated that 10·2% of conjugated triene compounds was present.

The brominated ester was also prepared under mild conditions following Teeter (*loc. cit.*) : ethyl linoleate (10 g.; 0·0326 mole), *N*-bromosuccinimide (5·8 g. containing 0·0326 atom of reactive bromine), and benzene (10 c.c.) were heated together and stirred at 70—75° for 25 minutes. After cooling, light petroleum (20 c.c.) was added and the succinimide was filtered off; the filtrate was evaporated in a vacuum, leaving a brown oil (12·2 g.) (Found : Br, 19·2%; I.V., 111), $n_{\mathrm{D}}^{25°}$ 1·4870, which gave on ultra-violet spectroscopic examination $\lambda_{\max.}$ 258·0 mμ, $\varepsilon_{\max.} = 5800$ (assuming $M = 387$). The oil was heated for one hour at 100° in a slow stream of nitrogen and then gave a band at 269 mμ, the intensity of which corresponded to the presence of 11·4% of conjugated triene compounds; the development of the 269 mμ absorption masked the original 258 mμ band.

Attempted Molecular Distillation of Bromolinoleic Ester.—Hydrogen bromide was evolved when the bromo-ester was heated at 100° in a pot still under 10^{-4} mm. pressure.

Bromination of Ethyl Linolenate.—Ethyl linolenate (10·6 g., 0·0345 mole), prepared by debromination of hexabromostearic acid (*Org. Synth.*, **22**, 82), and *N*-bromosuccinimide (6·2 g. containing 0·0345 atom of reactive bromine) were heated under reflux with frequent shaking in redistilled "AnalaR" carbon tetrachloride (52 c.c.) for 4 hours; a copious evolution of hydrogen bromide occurred during the last 3 hours. The product, recovered exactly as in the case of bromo-linoleic ester described above, was a dark brown liquid (13·4 g.) which could not be distilled under 10^{-4} pressure without decomposition.

Bromination of Linseed Oil.—Alkali-refined linseed oil (10 g., 0·0125 mole) (Found : I.V., 177; A.V., 0·7) and *N*-bromosuccinimide (12·7 g. containing 0·070 atom of reactive bromine) were heated in boiling carbon tetrachloride solution for 4 hours as in the previous brominations; a copious evolution of hydrogen bromide occurred during the last 3 hours. The product (12·6 g.) was a dark brown viscous liquid (Found : Br, 18·8%; I.V., 93·5) which dried overnight to a hard film when spread on flat aluminium panels.

Reaction of Brominated Linseed Oil with Alkali.—Brominated linseed oil (10 g.), obtained as described above, was heated under reflux on a water-bath with a 20% solution of potassium hydroxide in ethyl alcohol (50 c.c.) for one hour. The bulk of the alcohol was removed by distillation and the residual solution was poured into water, acidified, and ether-extracted to yield a semi-solid mixture of fatty acids (6 g.) [Found : Br, 0·98%; A.V., 185; I.V. (Wijs) 143; I.V. (by hydrogenation), 214]. Ultra-violet spectroscopic examination indicated that a total of 33% of conjugated compounds were present, *viz.*, diene, 13%; triene, 12%; tetraene, 8%.

Analyses are by Mr. C. Whalley, spectroscopic work by Mr. N. H. E. Ahlers, and Langmuir-trough experiments by Mrs. W. Ribchester.

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THE PAINT RESEARCH STATION,
WALDEGRAVE ROAD, TEDDINGTON.

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