An excerpt from Chemical Week magazine, February 2, 1952 issue, reads as follows:

"As Bristol-Myers' Louis B. Dobie put it: 'One man's stearic should be the same as another's. A difference in iodine value or in the stearic-palmitic ratio is critical for some products.'

"Speaking only for use in toiletries, Dobie pointed out that while manufacturers don't expect it, the producer of a new fatty acid mixture or derivative who has conducted clinical test on it 'has his foot inside the sales door'."

If any conclusion is to be drawn from all of these facts, one must consider them in the light of the length of time fractionally fatty acids have been on the market in appreciable quantities. From 1935 to 1951 the market for fractionally distilled fatty acids has increased from nothing to about one hundred million pounds per year. This represents about 15% of the domestic production, and this percentage is increasing rapidly when considering new European plants of U.S.A. design. Therefore a fractional distillation plant may be considered a form of insurance of future markets as users of fatty acids set more and more rigid specifications.

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The Chemistry of Polymerized Oils. II.[1] Dehydro-Polymers of Methyl Linoleate and Methyl Stearate

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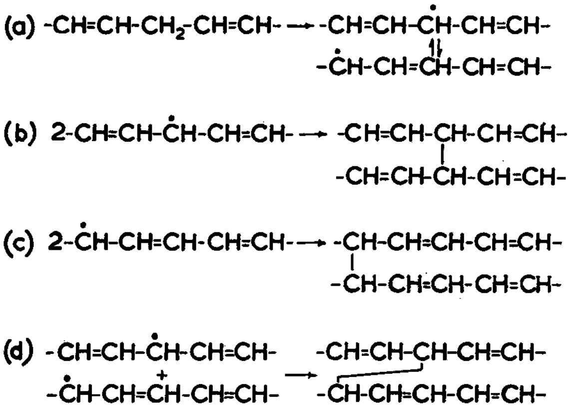
FARMER and Moore (6) investigated the reaction between a variety of olefinic and saturated hydrocarbons and various peroxides [*cf.* also Raley, Rust, Vaughan, and Seubold (15, 16)]. For example, cyclohexene was converted to a mixture of dehydro-polymers when heated with di-tert.-butyl peroxide, the tert.-butoxy radicals formed by symmetrical fission of the peroxide being converted into tert.-butyl alcohol by abstracting hydrogen atoms from cyclohexene and cyclohexene dehydro-polymer molecules. We decided to study the methyl linoleate/di-tert.-butyl peroxide reaction since this seemed likely to be relevant to the researches being carried out in this laboratory (8, 11, 19) into the chemistry of both heat-polymerized and peroxidized oils. Thus the present study may have relevance to the secondary reactions of autoxidation which occur when the initially formed peroxides react with olefinic centres. Also it is relevant to the chemistry of stand oils since Sunderland has proposed (18) that the inter-chain linkages in these are single carbon-carbon bonds giving structures analogous to those outlined in schemes (b), (c), and (d) below. During this work it became necessary to study briefly methyl stearate also. We hope to report further on the structural chemistry and technical application (17) of the reaction at a later date.

From the mechanism elucidated by Farmer and Moore (6) and by analogy with the free-radical double bond rearrangement which occurs during autoxidation (1, 5), it was anticipated that the reaction product from di-tert.-butyl peroxide and methyl linoleate would consist of dehydro-polymers, some of which would contain conjugated diene unsaturation. For example, free radical attack on the central methylene group of the pentadiene system could result in the formation of dehydro-dimers as follows:



$$\text{(a)}\ -CH{=}CH{-}CH_2{-}CH{=}CH- \longrightarrow -CH{=}CH{-}\dot{C}H{-}CH{=}CH- \rightleftharpoons -\dot{C}H{-}CH{=}CH{-}CH{=}CH-$$

$$\text{(b)}\ 2\text{-}CH{=}CH{-}\dot{C}H{-}CH{=}CH- \longrightarrow \begin{array}{l} -CH{=}CH{-}CH{-}CH{=}CH- \\ \qquad\quad\ \ | \\ -CH{=}CH{-}CH{-}CH{=}CH- \end{array}$$

$$\text{(c)}\ 2\text{-}\dot{C}H{-}CH{=}CH{-}CH{=}CH- \longrightarrow \begin{array}{l} -CH{-}CH{=}CH{-}CH{=}CH- \\ \ \ | \\ -CH{-}CH{=}CH{-}CH{=}CH- \end{array}$$

$$\text{(d)}\ \begin{array}{l} -CH{=}CH{-}\dot{C}H{-}CH{=}CH- \\ \qquad\qquad + \\ -\dot{C}H{-}CH{=}CH{-}CH{=}CH- \end{array} \longrightarrow \begin{array}{l} -CH{=}CH{-}CH{-}CH{=}CH- \\ -CH{-}CH{=}CH{-}CH{=}CH- \end{array}$$

· Denotes free radical.

In addition to (b), (c), and (d), it is possible that other less activated methylene groups in the linoleate molecule may be attacked. For example, attack could occur on the methylene group situated next to the ester group since Kharasch and his co-workers have shown (9, 10) that the free radical reaction of diacetyl peroxide with acetic, iso-butyric, and monochloroacetic acids results in attack at the α-position. However (10) dilauryl peroxide and dibenzoyl peroxide did not yield succinic acid when thermally decomposed in the presence of acetic acid, whereas Farmer and Moore found that cyclohexane was attacked at 140°C. by tert.-butoxy radicals to give di-cyclohexyl and higher hydrocarbons. The total reaction product is also likely to contain dehydro-trimers and higher species and these could partly result from purely thermal further intramolecular and intermolecular reaction.

To eliminate as many confusing possibilities as feasible it was decided to study first the dehydro-dimer fraction of a peroxide/linoleate total reaction product

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[1] Part I. Joubert and Sutton, this journal, *29*, 287 (1952).

which had been formed by heating the two components together for a moderate time only.

Harrison and Wheeler (7) studied the reaction between di-tert.-butyl peroxide and the vinyl and allyl esters of linoleic acid and demonstrated that conjugated diene was present in the polymeric products. The main features of Harrison and Wheeler's study of the reaction of allyl and vinyl linoleate are strikingly analogous to those which arise from Farmer and Moore's findings on hept-l-ene.

Bradley (2) mentioned some experiments in which di-tert.-butyl peroxide was successfully used in small percentages as a catalyst for the preparation of styrene/oil co-polymers. This deserves further investigation in view of the recent opinion of Falkenburg, Hill, and Wolff (4) that benzoyl peroxide does not act as a co-polymerization catalyst.

For the sake of brevity the word "dehydro" is hereafter omitted where no ambiguity can arise.

Experimental

The Rate of Formation of Conjugated Diene Groups from Methyl Linoleate. A single batch of a solution of di-tert.-butyl peroxide (13) in pure methyl linoleate[2] was prepared, the peroxide linoleate molar ratio being 0.248/1.00. Small quantities of the solution were placed into separate pyrex tubes which were cooled in liquid air, evacuated to 10^{-4} mm. pressure, and sealed. The tubes were heated in a wax bath at 134° ± 1°C. for various times. After withdrawal from the bath the tubes were opened and the volatiles (residual peroxide and tert.-butyl alcohol) were removed by pumping out to 10^{-4} mm. at room temperature. Each of the heated samples exhibited the ultra-violet absorption maximum near 235 mμ characteristic of conjugated diene unsaturation, and no other maxima were present. The intensity of absorption increased steadily with time for some 20 hours and then slowly decreased. The refractive index (n_D^{30}) rose from the value of 1.4569 for pure methyl linoleate to 1.4649 after 27 hours.

Similar experiments using different molar ratios were carried out at the same temperature. An increased peroxide/linoleate ratio resulted in an increased initial rate of conjugated diene formation and eventually in gelation when the molar ratio used was 1.65/1.00.

The results of these experiments are given in Table I.

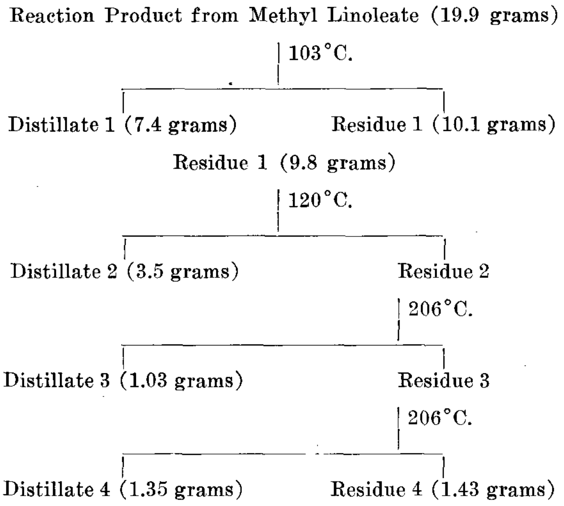
TABLE I
Characteristics of Total Product from Methyl Linoleate

Peroxide/ linoleate molar ratio	Time of heating (hours)	$E_{1\,cm.}^{1\%}$ [a] 2350 A.U.	n_D^{30}
0.248	2	31	....
0.248	4	62	1.4600
0.248	5.7	83	1.4616
0.248	12	134	1.4647
0.248	15.7	143	1.4648
0.248	22.2	150	....
0.248	27	136	1.4649
0.27	10	155	....
0.415	2.2	74	....
0.415	15.6	176	....
0.952	2.2	120	1.4649
0.952	15.6	193	1.4819
1.65	1.9	187	1.4720
1.65	7.8[b]	....	....

[a] Ethyl alcohol solvent.
[b] Gelled.

The gels resulting from heating together the 1.65/1.00 peroxide/linoleate molar ratio for 7.8, 12.7, and 18.1 hours were extracted separately with ether in a soxhlet apparatus giving 33%, 23%, and 8% of ether soluble fractions respectively. The ether insoluble residues were, in each case, rubbery materials.

Isolation and Examination of the Linoleate Dehydro-Dimer Fraction. A solution of 3.581 g. of the peroxide in 26.103 g. of methyl linoleate (molar ratio, 0.276/1.00) was sealed up in a bulb at 10^{-4} mm. pressure and heated for 10 hours at 134°C. The bulb was opened, and the volatiles were pumped off under 1 mm. pressure into a trap cooled in liquid air. Volatiles (2.3 g.) were recovered and distilled to give tert.-butyl alcohol (1.6 g., b.p. 77°C./650 mm.), which was identified as its phenyl urethane m.p. 135°C. undepressed in m.p. when admixed with an authentic specimen (Found: N, 7.06%. Calc. for $C_{11}H_{15}O_2N$: N, 7.25%). Some of the non-volatile oil remaining was distilled in a falling film molecular still according to the following scheme:



Data obtained for the above fractions are recorded in Table II.

Distillates 1 and 2 were chiefly monomeric linoleate, Distillates 3 and 4 were chiefly dehydro-dimer, and Residue 4 contained higher polymers. Calculation of the composition of Distillates 3 and 4 and of Residue 4, assuming that not more than two polymeric species occur in any one fraction, gives the following: Distillate 3, 93% dimer, 7% monomer; Distillate 4, 77% dimer, 23% trimer, and Residue 4, 100% trimer. The monomer fraction was freed from traces of dimer by

TABLE II
Characteristics of Fractions from Methyl Linoleate Reaction Product

Fraction	$E_{1\,cm.}^{1\%}$ 2350 A.U.[a]	Hydrogenation value[b]	%C and %H[c]	Mol. Wt.[d]	n_D^{30}
Total non-volatile oil	155	......	....	......	....
Distillate 1	< 10	......	....	......	....
Distillate 2	< 10	1.94	C, 77.25; H, 11.75	305	1.4580
Distillate 3	374	1.86	C, 77.8 ; H, 11.4	546	1.4768
Distillate 4	396	1.90	C, 77.7 ; H, 11.5	632	1.4775
Residue 4	371	2.03	C, 77.3 ; H, 11.4	891	1.4838

[a] Ethyl alcohol solvent.
[b] In double bonds per C_{18} chain; using Adams' platinum catalyst in glacial acetic acid.
[c] Calc. for methyl linoleate: C, 77.5; H, 11.65%; for dehydrodimer: C, 77.8; H, 11.3%.
[d] Menzies-Wright ebullioscopic method (12) in benzene solution.

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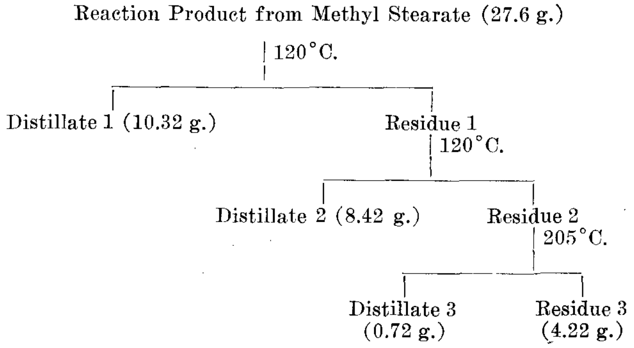
[2] I.V. = 173.0; prepared by debromination of hexabromostearic acid by the Hormel Research Foundation, Austin, Minn.

redistillation through a short column at 0.5 mm. pressure to give a distillate of iodine value = 173 (theoretical value = 172.4) (Found: C, 77.6; H, 11.9%).

A repetition of the above peroxide/linoleate reaction followed by molecular distillation gave a dehydro-dimer fraction of similar carbon and hydrogen analysis and hydrogenation value and with an $E^{1\%}_{1\,cm.}$ at 235 mμ of 420 in fair agreement with the $E^{1\%}_{1\,cm.}$ values in Table II. The recovered monomer and dehydro-dimer fractions from this preparation were submitted to alkali isomerization by the method of Mitchell, Kraybill, and Zscheile (14), giving $E^{1\%}_{1\,cm.}$ values at 235 mμ of 770 and 445, respectively (based on the weight of ester taken), after 25 minutes at 180° ± 0.5°C.

The Reaction of Di-tert.-butyl Peroxide with Methyl Stearate. A solution of the peroxide in pure methyl stearate (molar ratio, 0.276/1) was sealed up in an evacuated glass bulb and heated for 10 hours at 134° C. exactly as in the case of the methyl linoleate experiment described above. The volatiles removed by pumping into a liquid air trap at the conclusion of the reaction were shown to consist chiefly of tert.-butyl alcohol by the same method as before (b.p. and formation of phenylurethene derivative). The residual product (a solid at room temperature) was fractionated in a falling film molecular still as follows:



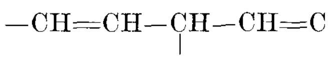
Distillates 1 and 2 were solids (m.p. 38.5-38.7°C.), Distillate 3 was solid (m.p. 38.8-48.5°C.), and Residue 3 was a viscous oil which solidified on cooling to 4°C. The molecular weight of Residue 3 was 997, corresponding to a mixture of 55% trimer and 45% tetramer, if it be assumed that only these species are present (Found: C, 77.2; H, 12.3%. Calc. for $(C_{19}H_{36}O_2)_n$: C, 77.0; H, 12.24%). Distillate 3 had a molecular weight of 465, corresponding to a mixture of 28% monomer and 72% dimer, assuming that only two species are present (Found: C, 76.5; H, 12.7%). Both Distillate 3 and Residue 3 were slightly unsaturated, the iodine values being 10 and 18 respectively, but neither showed any selective ultra-violet absorption.

Discussion

The results obtained are, in general, those which could be anticipated by analogy with Farmer and Moore's results. It has not been rigidly proven that the behavior exhibited by methyl linoleate and methyl stearate is, in every detail, identical with that expected and the details so far lacking in this exploratory investigation are discussed in the following paragraphs. In particular, the alkali isomerization result for the linoleate dehydro-dimer does not conform to expectations, but this may be capable of explanation and therefore does not necessarily invalidate the general theme.

Methyl Linoleate. Formation of conjugated diene groups by rearrangement of the pentadiene system occurs at a rapid rate from the beginning of the reaction. The concentration of these groups reaches a maximum and then slowly decreases. The formation of conjugated diene groups has already been discussed on page 53 (reaction scheme [a]). Their gradual loss must occur because the rate of destruction by thermal treatment eventually becomes greater than their rate of formation. Tert.-butyl alcohol was shown to be the main product from the peroxide, but the technique used would not have detected traces of acetone reported by Farmer and Moore to be a minor product. The total non-volatile oil contained a) monomeric linoleate still in the unconjugated form,[3] b) dehydro-dimer with an $E^{1\%}_{1\,cm.}$ value of about 400, with the expected carbon and hydrogen percentages, and with an average unsaturation of nearly four double bonds per molecule, and c) higher dehydro-polymers with an $E^{1\%}_{1\,cm.}$ value of 371, with the expected carbon and hydrogen percentages and with the original unsaturation. Thus tert.-butoxy radicals are not incorporated to any appreciable extent into the linoleate system. The retention of substantially the original unsaturation in the dehydro-polymers is as expected; the figures for Distillates 3 and 4 (Table II) are 5-7% low, possibly owing to a minor degree of intramolecular cyclization. Some caution must be exercised in the quantitative interpretation of the $E^{1\%}_{1\,cm.}$ values for the dehydro-dimer since it is not known whether published values (*cf.* 3) for C_{18} conjugated diene acids can be directly applied to these C_{36} acid derivatives, but if such values are used, approximately 40% of the total unsaturation is in the conjugated diene form. The absorption maximum is at a slightly longer wave length (235 mμ) than that of Δ10:12 linoleic acid (232 mμ). Taken at its face value, the figure of 40% is significantly lower than the 67% conjugation produced by free radical double bond rearrangement during autoxidation (1, 5). The higher polymers also possess a considerable percentage of conjugated diene groups (Residue 4, Table II).

It is difficult to interpret quantitatively the alkali isomerization result for the dehydro-dimer since it is not known to what extent the pentadiene system



$$-CH{=}CH-\underset{|}{C}H-CH{=}CH-$$

[reacton schemes (b) and (d), of formulae] would be isomerized under the conditions used, and neither is it known to what extent the conjugated diene already present would be destroyed. By analogy with the behavior of Δ10:12 linoleic acid (3) it is possible that the destruction of diene groups will be relatively small. The small increase of the $E^{1\%}_{1\,cm.}$ value (from 420 to 445) does however indicate the presence, probably in small amount, of a system capable of being alkali-isomerized under the standard conditions. This matter requires further investigation.

The ready formation of gels from large peroxide/linoleate ratios is understandable since the various dehydro-dimer structures all have more than two hydrogen atoms potentially capable of detachment and hence the system can, on further reaction, give cross-linked networks.

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[3] The experimental alkali isomerization figure of 770 corresponds to a Δ9:12 linoleate content of 93%.

Farmer and Moore found good agreement between the yields of dehydro-polymers produced from cyclohexene and those calculated from the amount of peroxide used. In our case we should expect that each peroxide molecule is capable of converting two linoleate chains into free radicals so as to form one dehydro-dimer molecule, but it is not possible to check the stoichiometry of the total reaction unless the polymers are quantitatively resolved into dimer, trimer, etc. With the small quantities of linoleate used and the relatively large distillation losses it was impossible to check the stoichiometry except that it is calculated from the $E^{1\%}_{1\,cm.}$ values in Table II that the total product would contain 37% (*i.e.* 155/420x100/1) of dimer (if the latter only were formed) whereas complete expenditure of the peroxide to give dimer only would result in a 55% dimer content. Similarly complete expenditure of the peroxide could give a maximum of 41.5% of trimer as the only species. These figures are reasonable since the reaction is not complete in 10 hours.

Methyl Stearate. Using the same reaction conditions and peroxide/fatty ester molar ratio as in the preparation of linoleate dehydro-dimer, methyl stearate gives dehydro-polymers containing only a little dimer. Although the points of attack in the stearate molecule remain to be determined, it is clear from this experiment that linking can occur where olefinic double-bond activation is absent. Thus it is probable in the case of linoleate that linking occurs between positions which are, and are not, activated by the proximity of olefinic double bonds. The small percentage of dimer isolated from the stearate product may reflect the superior ease of attack (6) of tertiary α-methylidyne groups (—CHR—) as compared with secondary methylene groups ($-CH_2-$) so that the initially formed dimer is more readily attacked than the unchanged stearate. The case of stearate differs from that of linoleate where the dimer/higher polymers ratio is substantially higher.

The small amount of unsaturation present in the stearate polymers is analogous to that found in the dehydro-polymers of cyclohexane (6).

Carbon and hydrogen percentages of the dimer and higher polymers indicate that very little, if any, incorporation of tert.-butoxy radicals takes place in agreement with the fact that tert.-butyl alcohol is the main product from the peroxide.

Summary

a) Reaction of methyl linoleate with di-tert.-butyl peroxide yields tert.-butyl alcohol and dehydro-polymers of methyl linoleate as the main products.

b) The dehydro-dimers and higher dehydro-polymers of methyl linoleate contain conjugated diene unsaturation, thus indicating the involvement of the pentadiene system $-CH{=}CH-CH_2-CH{=}CH-$ in the reaction.

c) Methyl stearate yields dehydro-polymers on reaction with di-tert.-butyl peroxide, thus indicating that reaction can occur at points in the fatty acid chains not activated by the proximity of olefinic double bonds.

Acknowledgment

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The Solvent Extraction of Cottonseed

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COTTONSEED is a unique oil seed. It is more complex and is subject to more variation than any other oil seed. It is not strange, then, that the problems of solvent extracting this oil seed are greater and more numerous than for any other oil seed. Any other seed has one preferred method of handling. There are three distinct, commercially-proven methods of extracting cottonseed. Although exact comparative data are not available, it seems desirable to make a preliminary examination of the advantages and disadvantages of these three basic methods.

The most widely applied method of extracting cottonseed is to pre-press the cottonseed meats in a mechanical screw press or expeller, then to extract the pre-pressed and the prepared cake. Figure 1 shows a flow chart for this method. The cottonseed is first cleaned, de-linted, hulled, and the meats separated from a substantial part of the hulls. These meats are then put through a crushing roll, familiar to the cottonseed industry, and cooked. Dry meats will be humidified in the cooker or possibly even before the crushing rolls. Cooking will require from 30 to 60 minutes, and the cooked meats will be discharged at a moisture of from 5 to 8% and a temperature of 220 to 235°F. A majority of the oil is then pressed out in a continuous mechanical screw press.

The oil in the pre-pressed cake will vary in current practice from 9% oil up to 15%. The cake will be broken up in a cracking roll or cake granulator and