Isomers of Linoleic Acid. Infrared and Ultraviolet Properties of Methyl Esters[1]

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THE data to be reported resulted from studies on the mechanism of thermal polymerization of methyl linoleate and its isomers, particularly the isomeric structures of the unpolymerized recovered monomers, and the effect of isomeric structure of the starting monomers on the rates and mechanism of thermal polymerization.

The linoleic[2] acids considered in this paper are those with the double bonds in the 9, 10, 11, or 12 positions since they are related to the naturally occurring acids, or to acids made from natural acids. Four cis, trans isomers of non-conjugated, 9,12 linoleate are possible: cis-9, cis-12; cis-9, trans-12; trans-9, cis-12; and trans-9, trans-12. Four cis-trans isomers of conjugated, 10,12 linoleate are possible: cis-10, cis-12; cis-10, trans-12; trans-10, cis-12; and trans-10, trans-12. Similarly, four isomers of conjugated, 9,11 linoleate are possible: cis-9, cis-11; cis-9, trans-11; trans-9, cis-11; and trans-9, trans-11.

Naturally occurring or normal linoleic acid is generally believed to be cis-9, cis-12, octadecadienoic acid. Treatment with selenium at 210° changes it to the crystalline trans-9, trans-12 linoleic acid, known as linolelaidic acid. Non-conjugated linoleic with one double bond cis- and one double bond trans- has apparently not been previously prepared pure enough for definite identification and characterization.

Kass and Burr (4) isolated a liquid acid which probably contained a substantial amount of cis-trans linoleic acid since it afforded a pair of tetrahydroxy stearic acids on hydroxylation (alkaline permanganate) which, according to McKay and Bader (8), could only originate from a cis-9, trans-12 linoleic acid.

Conjugated linoleic acids can be formed by isomerizing non-conjugated linoleic acids, by the action of catalysts such as nickel, anthraquinone, sulfur dioxide, or alkali at elevated temperatures. Nichols, Herb, and Riemenschneider (11) have made a most elegant study of the conjugated isomers resulting from alkali isomerization of cis-9, cis-12 linoleic acid. They presented convincing evidence, on theoretical and experimental grounds, that the products are predominantly cis-9, trans-11 and trans-10, cis-12 linoleic acids, and they isolated each in a fairly pure form. The formation of a cis-cis conjugated linoleate from cis-cis non-conjugated linoleate was excluded by them.

Preparation of Materials

I. Debromination methyl linoleate was made from tetrabromostearic acid, m.p. 115°, by debromination with zinc in methanol and sulfuric acid (5), followed by distillation through a short Vigreaux column. I.V. = 171.4 (Theory 172.4). It showed a slight band at 968 cm^{-1} indicating some trans double bond.

II. Crystallized methyl linoleate was made by esterifying debromination linoleic acid which had been crystallized 12 times from Skelly F at —65 to —60°, according to Mathews, Brode, and Brown (7). M.P. of acid = —4.3°. The distilled methyl ester showed I.V. = 172.0. It showed no trans double bonds by infrared and is presumably pure cis-9, cis-12 linoleate.

III. Methyl linolelaidate was made by esterifying linolelaidic acid. Linolelaidic acid was made by isomerizing debromination linoleic acid with 1% selenium for 6 hours at 210°. The crude acids were vacuum distilled and then crystallized three times from acetone (4 cc./g.) at —40° and four times (10 cc./g.) at —20°. Yield 14%, m.p. 28-29°; m.p. 28-29° according to Kass and Burr (4). The distilled methyl esters showed: m.p. —7.8; n_D^{30} = 1.4562; sp. α at 231 mμ = 4.8; I.V. (Rapid Wijs) = 166.9; I.V. (hydrogenation) = 175.5 (theory 172.4). Infrared absorption at 968 cm^{-1} was very nearly twice that of methyl elaidate. It is presumably pure trans-9, trans-12 linoleate.

IV. The non-conjugated methyl esters of dehydrated castor oil acids (Woburn Isoline Supra) were separated from the conjugated esters by fractional distillation in a Podbielniak Hyper-Cal column. The non-conjugated C_{18} ester fraction, which boils lower than the conjugated ester (15), was obtained in 54% yield, with an iodine value of 155, corresponding to 80% of linoleate. Sp. α at 231 mμ was 1.0, indicating about 1% of conjugated linoleate. This non-conjugated linoleate should be a mixture of cis-9, trans-12 and cis-9, cis-12 (11). Infrared spectrum showed a moderately strong band at 968 cm^{-1}, characteristic of isolated trans double bonds.

V. These non-conjugated esters, IV, were fractionally crystallized in an attempt to isolate the cis-9, trans-12 linoleate presumably present. The following procedure apparently accomplished the desired result: 200 g. of IV were dissolved in 1,800 cc. of acetone, cooled to —60° and filtered. The filtrate was cooled to —70° and filtered. The precipitate was dissolved in 1,800 cc. of acetone, cooled to —70°, and filtered. The filtrate material was separated from solvent to afford 48.5 g. with I.V. = 168.3. This material was crystallized from 240 cc. of acetone at —70°, and the precipitate was again crystallized from 240 cc. of acetone at —70°. The final precipitate, V, was 22 g., or 11% yield. It showed I.V. = 170.2, m.p. of acid = —6.3°, sp. α at 231 mμ = 1.0. It is believed to be fairly pure cis-9, trans-12 methyl linoleate. The following evidence is presented for the structure:

a) The infrared absorption at 900-1,000 cm^{-1} showed only one band at 968 cm^{-1}, the band characteristic of isolated, non-conjugated trans double bonds. The specific absorption at this frequency was very nearly the same as methyl elaidate and very nearly one-half that of methyl linolelaidate. This would indicate that it is either a cis-trans linoleate or a mixture (possibly eutectic) of equal parts of cis-cis and trans-trans lino-

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[2] The term linoleic acid will be used in the general sense as any *octadecadienoic acid. Specific isomers will be suitably identified as to* position and cis-trans configuration of the double bonds.

TABLE I

Infrared Bands of Methyl Linoleates in the 900-1,000 cm^{-1} Region

Material	Probable Configuration	948	968	982	988
I. Debromination linoleate[a]	c-9, c-12; and c/t-9, c/t-12	—	±	—	—
II. Crystallized linoleate[a]	c-9, c-12	—	—	—	—
III. Linolelaidate	t-9, t-12	—	++	—	—
IV. Non-conj. fraction of dehydrated castor ester	c-9, t-12; and c-9, c-12	—	+	—	—
V. Crystallized fraction from IV	c-9, t-12	—	+	—	—
VI. von Mikusch acid ester	t-10, t-12	—	—	?	+++
VII. Alk. conj. linoleate (II)	c-9, t-11; and t-10, c-12	+	—	+	?
VIII. Crystallized fraction of VII	t-10, c-12	+	—	+	?
IX. Alk. conj. linolelaidate	t-9, c/t-11; and c/t-10, t-12	+	± ?	?	++
X. Conj. fraction, dehydrated castor ester	c-9, c/t-11; and t-9, t-11	+	±	+	+
XI. Crystallized fraction A from X	t-9, t-11	—	—	?	+++
XII. Crystallized fraction B from X	c-9, t-11	+	± ? ?	+	?
XIII. Alk. conj. V	c-9, c/t-11; and t-10, t-12	+	—	?	++

[a] Also showed a weak band at 913 cm^{-1}.

leate. If it is a cis-trans linoleate, it is undoubtedly cis-9, trans-12, since the 9 double bond of recinoleic acid is cis.

b) The melting point diagram of cis-9, cis-12 linoleic acid (from II) and of trans-9, trans-12 linoleic acid (from III) was determined by the capillary melting point method. (Heating rate, 0.1° per minute, m.p. taken as disappearance of last crystal). It shows (Fig. 1) an eutectic at about 9.5% trans-9, trans-12 linolelaidic acid, melting at about —7°. The 50-50 mixture melts at +18°. The acid from V (the presumed cis-9, trans-12 linoleate) melted rather sharply at —6.3° while a 50% mixture with the above eutectic melted at —12.8°. V is therefore neither the 50-50 mixture indicated as a possibility by infrared, nor the eutectic of cis-9, cis-12 with trans-9, trans-12 linoleate.

c) Ultraviolet studies of alkali isomerization rates (cf. data below on ultraviolet studies) showed that it reached maximum conjugation, (specific α) in 150 minutes, whereas cis-9, cis-12 linoleate requires only 30 minutes, and trans-9, trans-12 linoleate requires 360 minutes. A 50-50 mixture of cis-9, cis-12 and trans-9, trans-12 linoleate requires 360 minutes and follows a curve quite different from V, but identical with that calculated for the mixture. It would be interesting to study the bromination products, and particularly the hydroxylation products of V, since the work of McKay and Bader (8) permits one to predict which pair of tetrahydroxy stearic acids should be obtained by hydroxylation of any cis-trans isomer of 9,12 linoleic acid. We hope to report on this later.

VI. The 10,12 linoleic acid of von Mikusch (17) was prepared by alkali isomerizing the non-conjugated esters of dehydrated castor oil (IV). The acid was isolated from the conjugated mixed acids by crystallizing 5 times (10 cc./g.) from Skelly B at —20°. M.p. 55.5°, sp. α at 230 mμ = 106.8. The acid was esterified with methanol (H_2SO_4 catalyst), and the recovered methyl ester was distilled and recrystallized from Skelly B (10 cc./g.) at —20°. M.p. = 24.0°; sp. α at 230 mμ = 105.9; n_D^{30} = 1.4698; I.V. (Woburn) = 175.4, I.V. (Rapid Wijs) = 129.4. This isomer is undoubtedly the trans-10, trans-12 linoleate (11, 18).

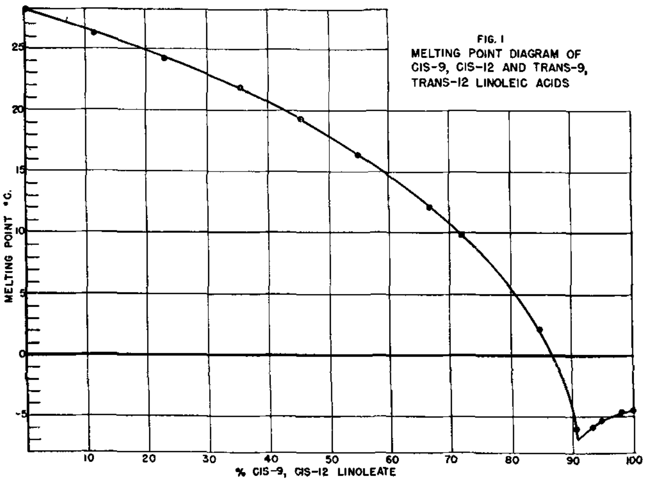


FIG. I MELTING POINT DIAGRAM OF CIS-9, CIS-12 AND TRANS-9, TRANS-12 LINOLEIC ACIDS

VII. Alkali conjugated linoleate was made as previously described (15) by alkali conjugation of I and esterification with methanol. It showed: I.V. (Woburn) = 180.0, I.V. (Rapid Wijs) = 146.1; sp. α at 230 mμ = 82.3; n_D^{30} = 1.4691. This is apparently a mixture consisting mostly of cis-9, trans-11 and trans-10, cis-12 linoleates (11).

VIII. Alkali conjugated linoleate, VII, was fractionally crystallized according to Nichols *et al.* (11). The 10,12 linoleate fraction (their compound 18 in Chart I), isolated was similar to theirs. It showed sp. α at 232 mμ = 97.7; m.p. —12° to —9°; I.V. (Woburn) = 182; I.V. (by hydrogenation) = 174.2; n_D^{30} = 1.4702. It appears that this material is essentially pure trans-10, cis-12 linoleate in view of the method of isolation and of the theoretical and experimental considerations of Nichols *et al.* (11).

IX. Alkali conjugated linolelaidate was made by the same method as VII except that the isomerization was extended to 6 hours (cf. ultraviolet studies below).

X. The conjugated methyl esters of dehydrated castor oil acids were prepared from the residue after fractional distillation of non-conjugated esters, IV, from the whole esters. The residue was vacuum-distilled through a short column to afford a product which showed sp. α at 232 mμ = 71.1; I.V. (Woburn) = 174.8; I.V. (Rapid Wijs) = 139.5. This is presumably cis-9, trans-11 and cis-9, cis-11 linoleate. However infrared data indicated that some conjugated trans-trans isomer was present (988 cm^{-1} band). A weak band at 968 cm^{-1} indicated some isolated trans double bond due to incomplete removal of non-conjugated isomers.

XI. Since infrared examination of X indicated some conjugated trans, trans isomer, the material was crystallized in an attempt to isolate it. X was crystallized 4 times from Skelly F at —60, once at 9 cc./g. and 3 times at 15 cc./g. The final precipitate, XI, obtained in 11% yield showed a single band characteristic of conjugated trans-trans linoleate. Sp. α at 231 mμ = 93.5.

XII. The conjugated trans-trans isomer in X could be removed by a treatment of its solution in methyl isobutyl ketone with urea (absence of 988 cm^{-1} band). This material was then crystallized twice from methanol, 20 cc./g., once at —65° and once at —72°. A 25% yield of product, XII, was obtained, which showed: sp. α at 232 mμ = 82.5; I.V. Woburn = 177.0; I.V. Rapid Wijs = 136.2; n_D^{30} = 1.4684; m.p. = —38° to —28°. This material is probably a somewhat impure cis-9, trans-11 linoleate. The cis-9, trans-11 linoleate of Nichols *et al.* (11) showed m.p. —56° to —49°, and sp. α = 85.1.

XIII. The cis-9, trans-12 linoleate (V) was isomerized 3 hours and converted to methyl ester. Sp. α 231 = 93.4.

Infrared Studies of Linoleate Isomers

A preliminary survey indicated that the region from 900 to 1,000 cm^{-1} was probably the most useful for characterizing the linoleate isomers. This region is associated with the bending frequency of hydrogen attached to an olefinic carbon. It was also found that the methyl esters were preferable to the free acids since the free acids showed a broad, fairly intense band at about 930 cm^{-1}, whereas the only band near this region shown by the esters was a very weak band at 1,020 cm^{-1}, which did not interfere with the sharp bands observed as characteristic of the linoleate isomers.

The instrument used was a Beckman IR-2 equipped with a special slit drive (16). The spectra were run in CS_2 solvent at 10% volume in a 0.1 mm. cell. The slit setting of the instrument was .44 to .55 mm. over this range. Amplification was set to show 100% transmission at 968 cm^{-1} with CS_2 in the cell.

The data to be presented are qualitative or semi-quantitative. We hope to report detailed quantitative data later. Table I shows the bands observed on the compounds described above. The four bands observed are 948, 968, 982, and 988 cm^{-1}. The 968 cm^{-1} band is well recognized as characteristic of isolated trans double bonds.

Non-conjugated esters. Debromination linoleate (I) contains a small amount of trans double bond, as indicated by the weak 968 cm^{-1} band and as suggested by Frankel and Brown (3). Recrystallized linoleate (II) shows no 968 cm^{-1} bands or any other strong band in this region. It did show a very weak band at 913 cm^{-1}. This band was found only in I, II, and IV which contain the cis-9, cis-12 linoleate. It is too weak to be useful analytically. Linolelaidate (III) shows only one intense band at 968 cm^{-1}. Methyl elaidate was also prepared and found to have a band at 968 cm^{-1} only. Approximate quantitative measurements on methyl elaidate checked the absorption coefficient for elaidate reported by Swern, Knight, Shreeve, and Heether (14). The absorption coefficient of the linolelaidate was very nearly twice that of the elaidate. The non-conjugated fraction of dehydrated castor oil esters (IV) and the crystallized fraction from it (V) showed only the 968 cm^{-1} band. The absorption coefficient of V was quite close to that of elaidate and very nearly one-half that of linolelaidate. This would be expected if V were the cis-9, trans-12 linoleate as proposed and if isolated trans double bonds are additive, as the data on linolelaidate indicated.

Conjugated esters. The ester of the von Mikusch acid (VI) showed only one very strong band at 988 cm^{-1}. This compound is undoubtedly trans-10, trans-12 linoleate, according to Nichols *et al.* (12) and von Mikusch (18). The 988 cm^{-1} band is therefore characteristic of trans-trans conjugated linoleates, and one would predict that the Mangold acid, trans-9, trans-11 (6, 18) would show the same band at 988 cm^{-1}.

Alkali conjugated normal linoleate (VII) showed two bands, at 948 and 982 cm^{-1}, both of them strong and sharp. At first it was thought that one of these might be due to a cis-trans conjugated linoleate and the other due to a cis-cis conjugated linoleate. However it now appears quite certain that these two bands are a doublet due to cis-trans (or trans-cis) conjugated linoleate. The evidence for this is as follows: a) Attempts to separate these bands in VII failed and produced only products which had both bands with essentially the same relative intensity. Methods used included crystallization, urea complex formation, and reaction with maleic anhydride. b) The crystallized fraction VIII, isolated from VII, had these bands in the same relative intensity and about the same intensity as VII. c) The theoretical and experimental work of Nichols *et al.* (11) indicates that conjugated cis-trans (or trans-cis) isomers should be the principal products of alkali isomerization of cis-cis non-conjugated linoleate.

The 988 cm^{-1} band, due to trans-trans conjugation, is very close to the 982 band of the 948-982 cm^{-1} doublet and is much stronger than the 982 cm^{-1} band. When either the 982 or 988 band is strong and the other is absent, the difference in position is real and definite, as in the compounds IV, V, and VI. When either band is quite strong, the other may be present to an appreciable extent without being detected. For this reason a question mark has been placed at 982 cm^{-1} when a strong 988 cm^{-1} band is observed, and the same at 988 cm^{-1} when a strong 982 cm^{-1} band was present (except compound X to be discussed later).

Alkali conjugated linolelaidate (IX) showed strong bands at 948 and 988, the latter much stronger. This indicates that both trans-trans and cis-trans conjugated isomers are present. Nichols *et al.* (11) predicted that 9-trans, 11-cis; 9-trans, 11-trans; 10-cis, 12-trans; and 10-trans, 12-trans isomers would result from alkali isomerization of linolelaidate. Our results confirm their predictions as far as they can be interpreted, that is, we have found trans, trans, and cis-trans (or trans-cis) conjugated isomers as predicted.

Presumably the cis-cis conjugated linoleate structure has no separate strong bands in this region, or else it is not present to any large extent in the products which we have studied so far. The isolation of a pure cis-cis conjugated linoleate presents some interesting problems of synthetic and isolation procedures.

The conjugated fraction of dehydrated castor esters X showed a fairly strong band at 948 cm^{-1}, indicating cis-trans conjugation. It showed a very weak band at 968 cm^{-1}, presumably due to incomplete removal of non-conjugated trans isomers. It also showed a broad band between 982 and 988 cm^{-1}, due to both 982 cm^{-1} and 988 cm^{-1} bands in approximately equal intensity, indicating conjugated trans-trans as well as cis-trans isomers. Since the 988 cm^{-1} band of conjugated trans-trans is much more intense than the 982 cm^{-1} band, it is estimated that the cis-trans conjugated linoleate is the predominant isomer in X. That the broad 982-988 cm^{-1} band was due to both bands was confirmed by separation from it of fraction XI, showing only the 988 cm^{-1} trans-trans band and of fraction XII, showing sharp bands at 948 and 982 similar to those shown by VII and VIII.

The presence of a conjugated cis-trans (cis-9, trans-11) linoleate in dehydrated castor esters is to be expected since the Δ 9 double bond in recinoleic acid is cis. The presence of a trans-trans isomer would not be expected. However we have found that conjugated cis-trans linoleate (VII) isomerizes to trans-trans conjugated forms rather rapidly at temperatures above 200°. The monomers recovered from polymerization of VII at 270° showed a strong band at 988 cm^{-1}, and other evidence indicates that this shift occurs at even lower temperatures. It therefore appears that the trans-trans conjugated linoleate found in X could be formed from a cis-trans isomer by the action of heat, either in the dehydration operation or during the fractional distillation.

Alkali conjugation of V (cis-9, trans-12) produced a material (XIII) containing both cis-trans and trans-trans conjugated isomers, also as predicted by Nichols *et al.* (11).

Figure 2 is given to illustrate the appearance of the infrared curves of typical examples. This figure was made from actual curves by mechanical tracing so as to expand the wave-length scale and make the differences in wave-length more obvious.

Summary of Infrared Data

1. The 968 cm^{-1} band characteristic of isolated trans double bonds is approximately additive since linolelaidate has about twice the absorption of elaidate and a cis-trans linoleate has about the same absorption as elaidate.

2. Trans-trans conjugated linoleate is characterized by a band at 988 cm^{-1}.

3. Cis-trans conjugated linoleate is characterized by a doublet at 948 and 982 cm^{-1}.

4. Confirmation has been made of the predictions of Nichols *et al.* (10) as to isomers produced by alkali isomerization as far as the infrared data can be interpreted.

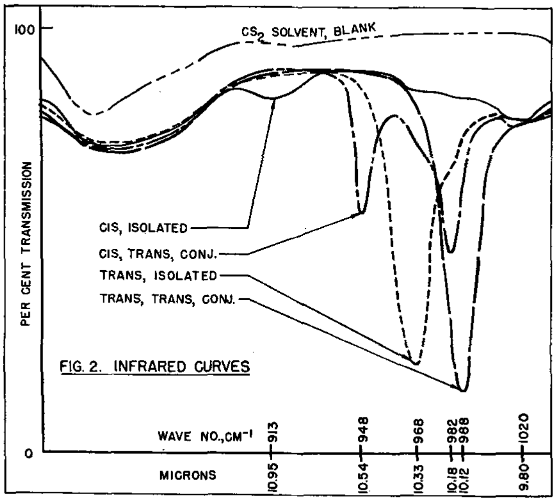


FIG. 2. INFRARED CURVES

Ultraviolet Absorption of Linoleate Isomers

Pure non-conjugated linoleate is essentially transparent in the near ultraviolet while conjugated linoleate absorbs strongly at 230-233 mμ. Alkali conjugation of normal cis-9, cis-12 linoleate has been made the basis of analytical methods (1, 2, 9).

Nichols *et al.* (11) have shown that alkali isomerization of cis-9, cis-12 linoleate produces cis-trans conjugated isomers which have maxima at longer wave lengths and have lower absorption values than the previously known pure trans, trans conjugated linoleates.

Riemenschneider, Herb, and Nichols (13) reported that pure normal methyl linoleate (cis-9, cis-12), prepared by chromatographic absorption, showed sp. *a* 232 = 86.5 (91.0 calc. as acid), while the pure methyl ester prepared by them via crystallization showed sp. *a* = 90.5 calculated for the acid or 86.0 for the methyl ester, when alkali isomerized (KOH-glycerol, 180°, 30 minutes). This value is some 4% higher than the value (87.1 calcd. to acid) reported by Mitchell *et al.* (9) for methyl linoleate made by debromination, without crystallization (isomerized in KOH-glycol, 180° 25 minutes). Riemenschneider *et al.* (13) comment on the probable presence of cis-trans isomers and the possible errors in using debromination linoleate as a standard. They also state that cis, cis linoleic acid isomerizes with alkali about 20 times as fast as the trans-trans linolelaidic acid and that the latter (trans, trans) showed sp. *a* 231 at mμ = 16.5, compared to 89.0 at 233 mμ for the former (KOH-glycerol, 180°, 30 minutes).

In view of these facts a systematic study of the alkali isomerization of methyl linolelaidate was made in connection with a study being made on its thermal polymerization. It was found that the linolelaidate required 6 hours (KOH-glycol, 180°) (7) to reach a maximum absorption (at 231 mμ) whereas normal cis, cis linoleate reaches its maximum (at 233 mμ) in 24-45 minutes.

The alkali isomerization data are shown in Table II and Figure 3. The crystallized cis-cis linoleate (II) reaches a value of 87.5 at 25 minutes, 89.2 in 30 minutes, and a maximum value of 89.7 in 45 minutes, and then decreases to 84.8 in 360 minutes. These values

TABLE II

Alkali Isomerization of Methyl Linoleates (180° in KOH-Glycol. Sp. *a*, 1 cm., 1 g. per 1,000 cc. at Indicated Max. Wave Lengths)

Time. minutes	cis-9, cis-12 Linoleate II		trans-9, trans-12 Linoleate III		cis-9, trans-12 Linoleate V		1-1 Mixture of II and III		
	233 mμ		231 mμ		231 mμ		232 mμ		
	obs.	corr.	obs.	corr.	obs.	corr.	obs.	corr.	calc.
0 (orig.)	0.1	0	4.8	0	1.0	0	2.6	0	
10	70.2	70.2							
15	82.1	82.1					46.6	45.3	45.6
20	84.3	84.3							
25	87.5	87.5	23.2	19.3	58.0	57.6			
30	89.2	89.2					55.9	54.5	55.8
40			32.0	28.4	74.1	73.8			
45	89.7	89.7							
60	89.4	89.4	43.5	40.5	81.0	80.8	65.8	64.5	64.9
90					85.1	85.0			
120			64.7	62.1	86.1	86.0	75.6	74.8	75.3
150					87.0	86.9			
180	87.1	87.1	77.5	76.1	86.3	86.2	81.7	81.1	81.6
210					86.6	86.5			
240			84.8	83.6	86.8	86.7			
300	86.1	86.1	88.5	87.5					
360	84.8	84.8	90.0	89.1	84.7	84.6	86.2	85.6	86.9
420			88.9	88.0					
480			89.0	88.1					
600			87.5	86.6					

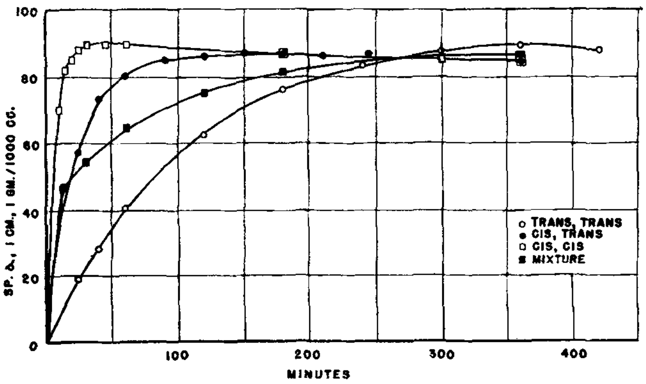
for the ester are somewhat higher than those reported by Mitchell *et al.* (9) and by Riemenschneider *et al.* (13) for comparable times.

The trans, trans linolelaidate (III) shows a value of 19.3 in 25 minutes and reaches its maximum of 89.1 in 360 minutes. The cis-trans isomer (V) shows a value of 57.6 in 25 minutes, reaches a maximum of 87.0 in 150 minutes, and shows a value of 84.7 in 360 minutes. This behavior in itself is an indication that V is a cis-trans isomer. Since infrared data on V indicated the possibility that it could be a 50-50 mixture of II and III, such a mixture was made and isomerized. The observed values were very close to those calculated for the mixture but quite different from those for V.

Nichols, Riemenschneider, and Herb (10) reported sp. α at 231 mμ = 100 for linolelaidic acid or 95.2 calculated to methyl ester, during alkali isomerization. However they did not state the time at which this value was observed. Their maximum value for sp. α of 95.2 (calculated to the ester) was presumably estimated by extrapolation of their data beyond 4 hours and is some 6 units higher than our observed maximum at 6 hours. They showed a graph of a logarithmic function of sp. α vs. time up to 4 hours for linolelaidic acid. From this graph it is estimated that at 4 hours sp. α = 74.0, and at 6 hours it is estimated as 85.1 by extrapolation (calculated to methyl esters). These values are lower than our values at the same time intervals. They used KOH-glycerine and the free acid while we used KOH-glycol and the methyl ester. While these discrepancies cannot be completely explained at the present time, our data confirms theirs in a general way in showing that the linolelaidate isomerizes much more slowly than cis, cis linoleate. The cis-trans linoleate (V) is intermediate in isomerization rate between cis-cis and trans-trans linoleate, as expected.

Since naturally occurring linoleic acid is cis-cis, the present findings are not of great importance in spectral analyses of linoleic acid in natural oils. However in a study of the thermal polymerization of methyl linoleate (12) it was found that recovered monomer (distilled from the polymerized mixture) contained as much as 20% of a material which did not analyze as either conjugated linoleate or normal linoleate by the ordinary spectral methods. It was noted that this material must be largely an isomeric linoleate (particularly in the monomers from the earlier stages of reaction) judging from the iodine values. When these same monomers were isomerized for 6 hours, the values for sp. α were considerably greater than those for 25 minutes previously reported, and a reasonable materials balance could be made when the total nonconjugated linoleate was calculated from the 6-hour values. It is evident that non-conjugated cis, trans or trans, trans linoleates were formed rather rapidly at bodying temperatures and that they were responsible for the apparent isolinoleate indicated by the 25-minute isomerization analyses. Infrared data on these monomers confirmed the presence of trans double bonds.

FIG. III
ALKALI ISOMERIZATION OF LINOLEATES



A more detailed consideration of the rate curves of the pure linoleate isomers (II, III, IV) leads to a method of estimating them in mixtures. Since each isomer conjugates with alkali at a different rate, it is possible to set up three simultaneous equations for the observed sp. α at three different times of alkali isomerization. The data in Table I are for the wave-lengths of maximum absorption. To be strictly valid for simultaneous equations, the same wave-length should be used. A wave-length of 232 mμ was chosen as suitable. These three equations can be solved for each component. For example, using the values at 25 minutes, 50 minutes, and 360 minutes for the pure isomers, the derivation is as follows:

k_1 = observed sp. α[3] after 25 minutes
k_2 = observed sp. α[3] after 60 minutes
k_3 = observed sp. α[3] after 360 minutes
x = weight fraction of cis, cis nonconjugated linoleate
y = weight fraction of trans, trans nonconjugated linoleate
z = weight fraction of cis, trans nonconjugated linoleate

Observed sp. α at 232 mμ, 1 cm., 1 g./liter (EtOH)

Minutes	x	y	z
25	87.2	19.0	57.4
60	88.7	40.1	80.4
360	84.8	88.4	84.1

whence

$$k_1 = 87.2x + 19.0y + 57.4z$$
$$k_2 = 88.7x + 40.1y + 80.4z$$
$$k_3 = 84.8x + 88.4y + 84.1z$$

and

$$x = 0.0450k_1 - 0.04189k_2 + 0.00933k_3$$
$$y = 0.00773k_1 - 0.02971k_2 + 0.02313k_3$$
$$z = -0.05351k_1 + 0.07347k_2 - 0.02183k_3$$

Applying these equations to the known mixture of 50% x and 50% y, the results were x = 46.0%, y = 47.0%, and z = 6.1%. This accuracy is about what would be expected since small errors in the experimentally determined values are amplified in the calculations which involve differences between the various values determined experimentally. However this method is the only one now available for estimating the proportions of such isomers in mixtures.

The use of the 6-hour isomerization value as the final value in developing the equations was based on the fact that trans, trans linolelaidate required 6 hours to reach a maximum value. It is evident from Figure 3 that all three isomers have very nearly the same value of sp. α after 285 minutes. It would there-

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[3] Corrected for conjugation originally present.

fore be more suitable to use this value rather than the 6-hour value in future work. Total non-conjugated linoleate could be calculated directly from this value. The value for sp. α at 232 mμ at $4\frac{1}{2}$ hours is estimated graphically to be 86.0. The formulae for calculating x, y, and z, taking k_3 as 86.0 for all isomers at 285 minutes are as follows:

$$x = 0.04568k_1 - 0.04353k_2 + 0.01020k_3$$
$$y = 0.00941k_1 - 0.03378k_2 + 0.02530k_3$$
$$z = -0.05509k_1 + 0.07730k_2 - 0.02388k_3$$

It is obvious that the method is only an approximation since it involves values of sp. α taken at times when it is changing rapidly and involves differences between values determined at different times of reaction. All values reported are averages of at least two determinations. Duplicate determinations occasionally varied as much as two units. Any modification of technique which would give better reproducibility would certainly improve the accuracy of the method.

This method is based on the assumption that the isomers used to establish the constants are of known purity and that cis, trans isomers with one cis and one trans double bond would behave identically whether the trans double bond were at the 9, or 12 position. The purity of the cis-9, trans-12 linoleate is probably the one most subject to suspicion. An independent method of checking its purity and of preparing other pure cis, trans or trans, cis isomers would be desirable.

The observed values and calculated equations are, of course, specific for the conditions of temperature, reagents and conditions used: KOH, glycol, 180°C. (9), and the use of methyl esters.

Compound IV, the non-conjugated fraction of dehydrated castor oil esters, showed 32.5% cis, cis, 41.5% cis, trans and 2.7% trans, trans nonconjugated linoleate. Infrared data approximately checked with this amount of trans double bonds. This shows that the new double bond formed in dehydration is about equally cis and trans.

Monomers recovered from the progressive thermal polymerization of non-conjugated linoleate isomers have also been examined. Those from normal cis, cis, linoleate showed rapid formation of cis, trans isomers with very little trans, trans isomer, and rapid disappearance of cis, cis isomer as the cis, trans isomer is formed. Monomers from linolelaidate also showed formation of appreciable amounts of cis, trans isomer, but very little cis, cis isomer. The thermal isomerization of trans, trans to cis, trans linoleate is apparently less extensive than that of cis, cis to cis, trans linoleate. A monomer from polymerization of cis, trans linoleate (V) showed almost no cis, cis, or trans, trans isomer. It thus appears that the cis, trans nonconjugated linoleate isomer is the form which most readily forms and accumulates during thermal polymerization.

Thus, although the present work does not greatly affect the interpretation of spectral analyses for linoleate in natural oils, it does point out that materials which have been subjected to conditions of heat or catalysis which could cause cis-trans shifts, require special conditions for spectral analysis if gross errors are to be avoided. It will be interesting to compare the alkali isomerization of normal cis, cis, cis linolenate with the known trans, trans, trans elaidolinolenic acid, and the unknown cis, trans isomers if, and when, they become known. The extension of infrared and ultraviolet studies to the non-conjugated and conjugated linolenates is under way by us now. It is hoped that the present work and extensions of it will provide useful tools of research for following the isomeric changes involved in operations on unsaturated oils such as heat-bodying, distillation, and resin formation, where conditions prevail which undoubtedly lead to cis-trans and position isomerization of the polyene acid present.

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Correction

The second paragraph of the section under Conclusions for the paper entitled "The Deposition of Lime Soap on Fabrics During Washing," by Knowles, Berch, and Schwartz, which appeared on page 161 of the April 1952 issue of the Journal of the American Oil Chemists' Society, should have read as follows:

1. Peptizing power, as exemplified by the Nessler tube test, is not a realistic index of the extent to which a surfactant will prevent firm deposition. A good peptizing agent will however minimize the loose deposition resulting from a filtration effect, and this is of importance in many practical situations.