TABLE VI

Antioxidant	Lecithin added, %	Lovibond color value 5.25" column					
		Original			Irradiated		
		Y	R	B	Y	R	B
Control lard	0	13	2.2	2.2	12	2.2	1.8
Control lard + Fe[a]	0	16	4.5	2.0	16	4.7	2.1
BHA .01% + Fe[a]	0	18	4.6	2.4	20	5.5	2.1
BHA .01% + Fe[a]	0.01	14	2.8	1.5	14	3.6	1.0
PG .003% + Fe[a]	0	16	5.3	3.5	16	5.0	2.2
PG .003% + Fe[a]	0.01	18	5.5	3.4	16	5.0	2.5
CA .002% + Fe[a]	0	16	4.5	4.1	15	4.4	2.0
CA .002% + Fe[a]	0.01	16	3.6	3.0	16	4.2	2.0
BHA .01% + Fe[a] PG .003% +	0	24	5.5	3.2	26	6.0	2.5
BHA .01% + Fe[a] PG .003% +	0.01	20	5.0	3.6	20	6.2	3.6
BHA .01% + PG .003% + Fe[a] CA .002% +	0	20	5.1	3.4	20	5.3	3.3
BHA .01% + PG .003% + Fe[a] CA .002% +	0.01	13	2.8	1.5	20	7.0	6.0

[a] Fe—5 p.p.m.

ples were irradiated for 66 hours at room temperature as described previously. The colors before and after irradiation are shown in Table V.

The effects of the presence of lecithin with the other antioxidant ingredients and the effects of irradiation are demonstrated clearly. Propyl gallate apparently did not contribute to the blue color formation when used alone. Antioxidants A and B with lecithin added to the lard contributed blue colors after irradiation which were quite comparable to those provided by C.

These results then required one further test to learn the ingredients contributing to the photoactivated blue color in lard. Lard was contaminated with iron as described before. The lard was treated with BHA, PG, and CA and with the combinations of these ingredients both with and without added lecithin. The Lovibond color values are shown in Table VI.

This test showed that no one ingredient or combination of antioxidant ingredients was responsible for the photoactivated blue color in lard. It revealed that lecithin and iron are necessary components for the production of the photoactivated blue color in a lard system containing BHA, PG, and CA.

Summary

1. A study has been made of factors causing blue colors in antioxidant treated lards.

2. The formation of blue-colored lards or of blue-black sludges in lard storage tanks is due to reaction of propyl gallate in the antioxidant with iron contamination in the lard.

3. The solubility of the antioxidant mixture in lard is not a factor in the formation of blue-colored lard.

4. A new cause of blue-colored lard has been discovered. This is a photoactivated blue color resulting from irradiation of antioxidant treated lard. The blue color was developed in lard treated with BHA, propyl gallate, and citric acid only when lecithin was present and the lard was contaminated with iron. The state of oxidation of the lard did not contribute to these colors.

REFERENCES

1. Kraybill, H. R., Dugan, L. R. Jr., Vibrans, F. C., Swartz, VeNona, and Bondi, Vera, American Meat Institute Foundation *Bull. No. 4*, (1949).

2. Kraybill, H. R., Dugan, L. R. Jr., Beadle, B. W., Vibrans, F. C., Swartz, VeNona, and Rezabek, Helen, J. Am. Oil Chemists' Soc., *26*, 449-453 (1949).

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Modification of Vegetable Oils. XV. Formation of Isomers During Hydrogenation of Methyl Linoleate[1]

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IN the hydrogenation of normal linoleic acid (cis-9, cis-12-octadecadienoic acid) or its esters, linoleic acid tends to be hydrogenated to an oleic acid before hydrogenation to the saturated or stearic acid commences;[3] that is, the reaction tends to be selective. Moore, Richter, and Van Arsdel (13) first discovered this fact on determining the composition of hydrogenated cottonseed oils. Later investigators (7, 17) confirmed the discovery. Since then numerous investigations of the hydrogenation of linoleic acid and its esters have been made. Hilditch and Vidyarthi (8) concluded that on hydrogenation of methyl linoleate no methyl stearate is produced until 90% of the methyl linoleate has been transformed into methyl oleate. Bailey (3), in an analysis of hydrogenation data on cottonseed oil, found that under very nonselective operating conditions the ratio of hydrogenation rates for linoleic acid and oleic acid (combined as glycerides) is about 4:1. For very selective operating conditions this ratio is about 50:1.

It is generally believed that in the hydrogenation of linoleic acid esters the bond farthest removed from the ester linkage tends to be reduced first. Suzuki and and Inoue (19) found that hydrogenating 1 mole of normal methyl linoleate with 1 mole of hydrogen produced oleates having the double bond in the 9:10 position. Similar experiments with isolinoleic acid (10) also showed that the bond farthest removed from the ester linkage was hydrogenated first. In another investigation (15) it was found that in the hydrogenation of isomeric oleic acids the highest rate was observed when the single bond was farthest removed from the carboxyl group.

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[3] The terms linoleic acid, methyl linoleate, etc., will be used in the general sense and will refer to any octadecadienoic acid and its esters unless indicated otherwise. In a similar manner the terms oleic acid, methyl oleate, etc., will refer to any octadecenoic acid and its esters. The term normal will be used in referring to naturally-occurring cis-9, cis-12-octadecadienoic acid, and cis-9-octadecenoic acid and their esters.

If these were the only reactions occurring, iso-oleic acids would not be formed. Partial hydrogenation of the normal linoleic acid combined in natural glyceride oils produces however relatively large proportions of high-melting iso-oleic acids (21, 23). These iso-oleic acids appear early in the course of the reaction. Possibly some are positional isomers of cis-9 oleic acid produced either by hydrogenation of the 9:10-double bond of normal linoleic acid or the wandering of the double bond in the oleic acid which is produced during hydrogenation. However it is generally assumed that the high-melting iso-oleic acids are geometrical isomers of cis-oleic acids, that is, they possess the trans configuration. The latter assumption is supported by the fact that as a group the trans isomers of 6- through 12-oleic acid possess melting points appreciably above those for the corresponding cis isomers (9).

The object of the present investigation was to obtain additional information concerning the mechanism of the hydrogenation of methyl linoleate. The latter was hydrogenated under various operating conditions, and the formation of trans isomers and conjugated methyl linoleate followed spectrophotometrically. Cottonseed oil was progressively hydrogenated in one experiment for comparison with observations made on methyl linoleate.

Experimental

Materials. The methyl linoleate used in the experiments was prepared from refined and bleached cottonseed oil. The oil was interesterified with methanol in the presence of sodium methylate. The methyl esters, after being washed with dilute acetic acid, distilled water, and then dried, were dissolved in acetone (75 grams per liter) and fractionally crystallized and filtered at −75°C. The filtrate was reduced to one-half of its original volume and again filtered at −75° C. The acetone was removed from the second filtrate and one part of the residue or crude methyl linoleate was mixed with 2.5 parts (by volume) of commercial hexane, cooled to −75°C., and filtered. The methyl linoleate in the filtrate then was distilled under vacuum at approximately 180°C., to yield the final product, which possessed an iodine value of 166.3, a peroxide value of 0.8, and a free fatty acid content of 0.3%.

The refined and bleached cottonseed oil used in one experiment was obtained from a commercial source.

A commercial nickel catalyst, which had been prepared by electrolytic precipitation and dry reduction (2), was used. The hardened coconut oil in which the catalyst was originally suspended was removed and replaced by methyl linoleate.

Hydrogenation Apparatus and Procedure. The apparatus and procedure described in a previous publication (6) were used. A 70-g. batch of the methyl linoeate or cottonseed oil to be hydrogenated was placed together with the desired amount of catalyst in a closed test tube (38 mm. by 215 mm.). While the charge was under hydrogen, the test tube and charge were heated in an oil bath to the desired operating temperature; and the hydrogenation was performed by bubbling 0.015 cubic foot (425 ml.) of hydrogen per minute through the charge. The temperature was maintained constant by raising or lowering the position of the tube in the oil bath. The degree of hydrogen dispersion in the charge was varied by changing the type of tip on the hydrogen inlet tube. A small perforated glass bulb was used as the tip when a relatively low degree of dispersion was desired while a small fritted glass cylinder was used for a high degree of dispersion. Samples withdrawn during the course of a hydrogenation were filtered immediately to remove the catalyst and stored under hydrogen.

Infrared Analysis. In determining the percentage of nonconjugated trans isomers in the various samples, a modification of the infrared spectrophotometric method of Shreve *et al.* (18) and Swern *et al.* (20) was employed. Chloroform was used as the solvent because it was found to be preferable in several respects (14).

The infrared spectra were obtained with a Beckman IR-2T [4] automatic recording spectrophotometer housed in a room maintained at 23°C. and 20% relative humidity. The temperature of the instrument was maintained at 25 ± 0.1°C. by circulating through it water from a constant temperature bath. All measurements were made by the quantitative differential method, that is, measurement of chloroform solutions against pure chloroform.

The percentage of nonconjugated trans isomers, as methyl elaidate or trielaidin, in the hydrogenated samples was calculated from the following equation:

$$\% \text{ Trans} = \frac{100\,(a_{\text{ob.}} - a_{\text{av.}})}{a_{\text{trans}} - a_{\text{av.}}}$$

where the a terms are specific extinction coefficients at 10.3 microns; $a_{\text{ob.}}$ is the extinction coefficient for the hydrogenated sample, a_{trans} is the extinction coefficient for either methyl elaidate or trielaidin, depending on the nature of the hydrogenated sample, and $a_{\text{av.}}$ is a weighted average calculated from the extinction coefficients of the original and completely hydrogenated products. Values used for the specific extinction coefficients at 10.3 microns were: normal methyl linoleate, 0.062; normal methyl oleate, 0.037; methyl stearate, 0.031; methyl elaidate, 0.361; cottonseed oil, 0.085; completely hydrogenated cottonseed oil, 0.065; trielaidin, 0.398.

This formula may be applied to calculation of the percentage of trans isomers even though some of the trans bonds may be present in nonconjugated linoleates since it has been shown (11) that trans-9, trans-12-methyl linoleate possesses a specific extinction coefficient at 10.3 microns of very nearly twice that for methyl elaidate.

This formula cannot be applied to calculation of the percentage of trans isomers when the trans bonds are part of a conjugated system. Such bonds were not taken into consideration in arriving at the percentages of trans isomers which will be reported.

No attempt was made to determine the amount of trans bonds in the conjugated linoleates present in some of the samples because no suitable method of analysis exists. Jackson *et al.* (11) have shown that the infrared spectra of trans-trans conjugated linoleate and cis-trans conjugated linoleate are characterized by absorption bands at 10.12 and 10.18 microns, respectively. When both are present in a sample, the bands merge. Furthermore nothing is known about the infrared spectrum of cis-cis conjugated linoleates.

The infrared absorption spectrum of the methyl linoleate used as starting material is reproduced in

[4] The mentioning of this name does not constitute a recommendation of the Department of Agriculture of this instrument over those of any other manufacturers.

TABLE I

Progressive Hydrogenation of Methyl Linoleate

Operating conditions	Sample No.	Hydrogenation time	Iodine value	Total linoleate	Total oleate	Stearate	Conjugated linoleate	Non-conjugated trans isomers as elaidate	Non-conjugated trans isomers basis total oleate
		minutes		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Run No. 1	0	0	166.3	93.0	6.9	0.1	0.47	0.0	.....
Temperature, 150°C.	1	16	140.1	59.5	43.8	−3.3	0.95	20.3	.....
Catalyst concentration,	2	32	117.2	33.6	69.1	−2.8	0.49	37.7	.....
0.25% Ni	3	48	95.1	8.1	94.7	−2.9	0.06	51.4	54.3
Hydrogen dispersion,	4	68	77.6	0.0	90.7	9.3	0.01	53.2	58.6
fritted glass tip	5	88	65.6	.....	76.6	23.4	0.01	49.9	65.2
	6	113	52.6	.....	61.5	38.5	.....	48.8	79.3
	7	153	33.0	.....	38.6	61.4	.....	32.2	83.4
	8	193	18.6	.....	21.7	78.3	.....	19.2	88.5
	9	198	18.0	.....	21.0	79.0	.....	18.3	87.2
Run No. 2	1	7	135.0	61.2	34.3	4.4	10.35	24.4	.....
Temperature, 200°C.	2	14	113.6	37.0	58.2	4.8	8.07	42.7	.....
Catalyst concentration,	3	21	98.2	13.0	88.4	−1.4	1.71	59.1	.....
0.25% Ni	4	31	80.9	0.0	94.5	5.5	0.02	62.1	65.7
Hydrogen dispersion,	5	41	67.4	.....	78.8	21.2	0.01	56.4	71.6
fritted glass tip	6	54	48.2	.....	56.3	43.7	.....	41.2	73.2
	7	71	23.4	.....	27.4	72.6	.....	21.3	77.8
	8	101	4.8	.....	5.6	94.4	.....	3.5	62.5
	9	131	2.0	.....	2.3	97.7	.....	2.3	100.0
Run No. 3	1	18	137.4	64.8	30.0	5.2	16.55	27.1	.....
Temperature, 200°C.	2	36	114.7	41.2	50.9	7.8	17.40	47.9	.....
Catalyst concentration,	3	54	97.9	17.2	76.6	3.1	8.54	66.1	.....
0.25% Ni	4	77	79.8	0.0	93.3	6.7	0.03	79.6	85.3
Hydrogen dispersion,	5	100	60.8	.....	71.0	29.0	0.02	51.0	71.8
Perforated glass bulb	6	129	34.7	.....	40.5	59.5	.....	29.7	73.4
	7	160	9.2	.....	10.7	89.3	.....	8.8	82.2
	8	189	1.1	.....	1.3	98.7	.....	1.4	107.5
Run No. 4	1	8	146.3	70.5	29.0	0.6	5.10	22.5	.....
Temperature, 200°C.	2	16	130.4	50.5	50.6	−1.1	4.13	39.8	.....
Catalyst concentration,	3	26	114.4	30.6	72.0	−2.6	1.43	56.1	.....
0.05% Ni	4	36	102.2	16.1	87.0	−3.1	0.46	70.5	81.1
Hydrogen dispersion,	5	48	91.4	4.5	97.6	−2.2	0.12	78.6	80.6
fritted glass tip	6	63	83.0	0.4	96.2	3.4	0.02	77.6	80.7
	7	78	75.5	0.0	88.2	11.8	0.01	72.0	81.6
	8	108	54.7	.....	63.9	36.1	.....	45.1	70.6
	9	138	34.2	.....	40.0	60.0	.....	29.2	73.0

Figure 1. The 9-11 micron region of the spectra of several samples removed during the course of the hydrogenation of methyl linoleate is reproduced in Figure 2.

Examination of the infrared spectra of the various hydrogenated samples revealed that the absorption at 10.3 microns, which is characteristic for the trans

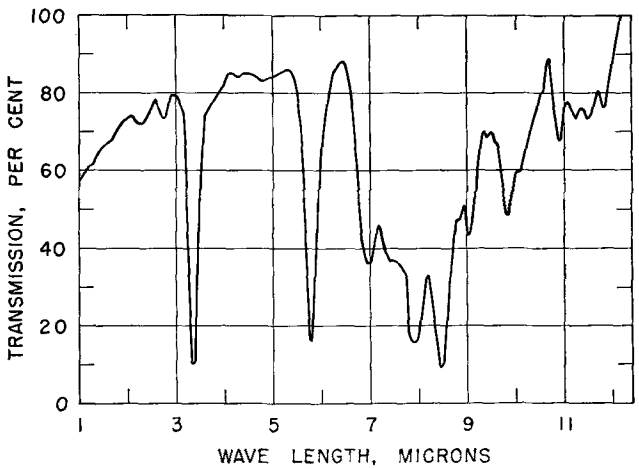


FIG. 1. Infrared absorption spectrum of methyl linolcate used in the hydrogenations.

bond, except as noted above, was not affected by the fact that the samples contained a mixture of trans isomers. The transmission minima at 10.3 microns were as sharp as the minimum of methyl elaidate, and there was no evidence of shifting of the minimum. The absorption at 10.1 microns, which is shown in these spectra (Figure 2) is characteristic of diene conjugation (at least of some types) and should not be confused with the absorption at 10.3 microns.

Composition of Products. The composition of the methyl linoleate and hydrogenated methyl linoleate samples was calculated in terms of total methyl linoleate, conjugated methyl linoleate, total methyl oleate, and methyl stearate from the iodine value and content of polyunsaturated fatty acids, as determined by Methods Cd 1-25 and Cd 7-48 (rev. May 1951) of the American Oil Chemists' Society (1). The results of the calculations, together with the operational data for the various hydrogenation experiments, are recorded in Table I.

The iodine values listed in the table do not reflect the true amount of unsaturation in the samples in those instances where diene conjugation occurs because conjugation reduces the iodine value of an oil as determined by the A.O.C.S. method. Wherever iodine values were used in the interpretations of the results, they were corrected by assuming that for each 1% of conjugated linoleate in a sample the experimentally-determined iodine value was 0.5 unit below the theoretical. This assumption is supported by hydrogen-iodine values determined by analytical hydrogenation of selected samples. The percentages of stearate content calculated with the corrected iodine values no longer showed a decrease with progressive hydrogenation during the early stages of hydrogenation.

The small negative values for stearate shown in Table I are the result of one or a combination of two factors: limited accuracy of the experimental method and the presence of linoleate isomers in which the double bonds are separated by more than one methylene group. In the methods of analysis employed these linoleate isomers would appear as oleates hav-

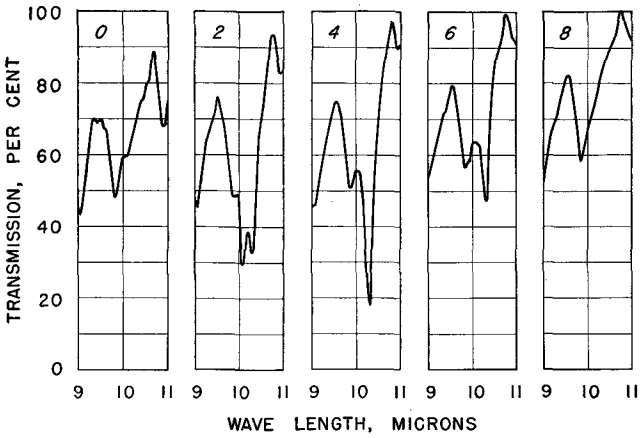


FIG. 2. Infrared absorption spectra of progressively hydrogenated methyl linoleate. Original methyl linoleate (O) and samples Nos. 2, 4, 6, and 8 of hydrogenation Run No. 3.

ing twice the accepted iodine value of oleates. This would be reflected in a higher than actual value for oleate and consequently a lower than actual for stearate, which is obtained by the difference.

Data and results of the calculation for the hydrogenation of cottonseed oil are recorded in Table II.

TABLE II

Cottonseed Oil Progressively Hydrogenated Under One Atmosphere of Hydrogen at 200°C., Using 0.25% of Nickel and a Low Degree of Hydrogen Dispersion

Sample No.	Hydrogenation time	Iodine value	Conjugated trilinolein	Trans isomers as trielaidin
	minutes		*per cent*	*per cent*
0	0	108.2	0.27	0.00
1	12	104.2	0.86	0.37
2	24	98.7	2.22	0.84
3	36	94.4	2.82	1.17
4	48	90.1	2.92	1.67
5	60	84.9	2.68	2.18
6	72	80.4	2.10	2.62

Amount and Source of Diene Conjugation

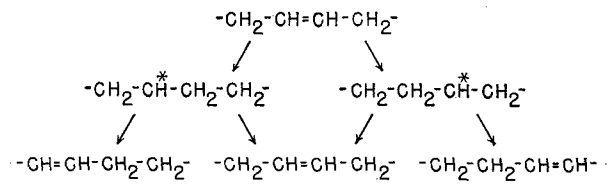
The relatively large amounts of conjugated linoleate, up to 17.4%, found in some of the hydrogenated samples, Table I, are far greater than would be expected from a survey of the literature on hydrogenation. It had been concluded heretofore that only minor amounts of diene conjugation are produced during the hydrogenation of linoleic acid esters. The conclusion that diene conjugation occurs to a minor degree during hydrogenation may be more nearly correct when hydrogenation of glycerides is under consideration. From Tables I and II it is evident that the hydrogenation of cottonseed oil produced a maximum of only 2.92% of diene conjugated components under operating conditions which produced 17.4% of diene conjugated components in the methyl linoleate. This may be owing in part to the lower concentration of combined linoleic acid in the cottonseed oil. However it appears that under a given set of operating conditions diene conjugation develops faster when linoleic acid is combined as the methyl ester than when it is combined as the triglyceride, possibly because the triglyceride has a larger molecular size and hydrogenates more slowly, which in turn changes the course of the reaction.

It has been generally assumed heretofore that conjugation occurring during hydrogenation is at least partly independent of the presence of hydrogen since it may be induced by heat in the presence of a hydrogenation catalyst (12, 16, 22). With the aid of the results recorded in Tables I and II it can be shown that this assumption is improbable. Radlove *et al.* (16) found that heating the methyl esters of soybean oil for 4 hours at 210°-220°C. with 6% of nickel in the form of a nickel-on-diatomaceous earth catalyst produced 12.2% of diene-conjugated methyl esters. When methyl linoleate was hydrogenated, Run No. 2, Table I, much milder conditions than those reported by Radlove resulted in 17.4% of conjugation.

Further evidence that hydrogenation is necessary to induce diene conjugation was obtained by repeating the hydrogenation procedure represented in Table II except that nitrogen instead of hydrogen was bubbled through the oil. After 4 hours the diene conjugation was still at its original low level of 0.27%, indicating that under the operating conditions used hydrogen was necessary to induce conjugation.

An indication that the content of positional isomers other than conjugated was low is given by the small negative values of stearate calculated to be present in those hydrogenated samples (Table I) in which linoleate has almost disappeared. Such samples would be expected to contain the highest concentration of the relatively-slow-to-hydrogenate, nonconjugatable isomers, that is, linoleate isomers in which the double bonds are separated by more than one methylene group.

The mechanism by which positional isomers are produced during hydrogenation is still a subject of speculation. According to Blekkingh (4) hydrogenation at the surface of a nickel catalyst can be effected by either molecular or atomic hydrogen, and the formation of positional isomers is a side reaction of the latter type of hydrogenation. The positional isomers are claimed to be formed by partial hydrogenation to one of two possible groups containing a free valency followed by a partial dehydrogenation to form either an isomer or to reform the original group:



This explanation, when coupled with Blekkingh's theory concerning geometrical isomers (5), fits the fact, as will be shown below, that the formation of positional and geometrical isomers proceeded by different mechanisms.

For practical purposes the above reaction mechanism may be considered to be irreversible during the early stage of hydrogenation of normal methyl linoleate. A shift of one of the bonds toward the other would produce a stable conjugated isomer. A shift of one of the bonds away from the other would produce a relatively unreactive isomer and would practically remove it from reaction during the early stage of hydrogenation.

Relative Reaction Rates of Linoleates

The contents of conjugated linoleate found during the course of each of the hydrogenations represented in Table I are compared graphically in Figure 3. It is evident that under the operating conditions em-

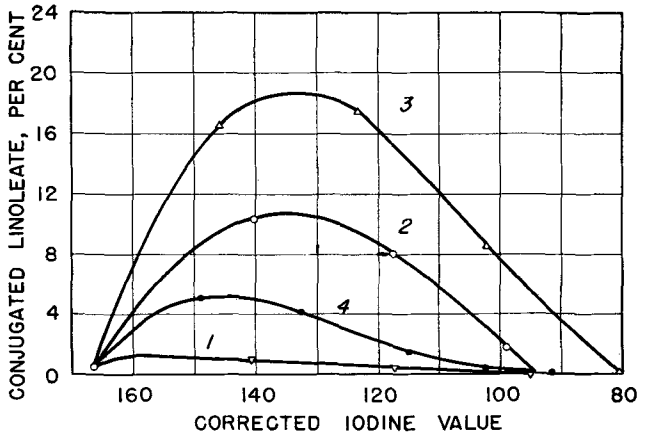
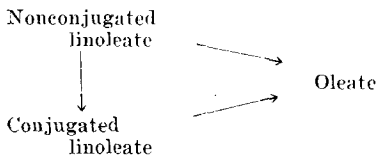


FIG. 3. Diene conjugation *vs.* corrected iodine value for progressively hydrogenated methyl linoleate. Curve numbers refer to hydrogenation experiments listed in Table I.

ployed the maximum content of conjugated linoleate increased as the temperature and catalyst concentration increased and as the rate of hydrogen dispersion decreased.

The proportion of linoleate undergoing conjugation under the various operating conditions and the relative rates of hydrogenation of conjugated and nonconjugated linoleates were calculated for each hydrogenation run from plots of corrected iodine value *vs.* contents of conjugated and nonconjugated linoleates. The calculations were made by a modification of a procedure described by Bailey (3) and were based on the following course of simultaneous and consecutive reactions occurring during hydrogenation of normal methyl linoleate:



It was assumed that when the hydrogenation proceeds by an infinitesimal amount each of the three reactions indicated proceeds by an amount equal to the concentration of the reacting product multiplied by a reactivity constant. It was further assumed that the reactions are irreversible and that the formation of a small amount of nonconjugatable linoleate did not significantly affect the kinetics of the reaction. Under these conditions the following equations apply:

$$L_t = Le^{-k_L t}$$

$$D_t = De^{-k_D t} + LF_D\left(\frac{k_L}{k_D - k_L}\right)\left(e^{-k_L t} - e^{-k_D t}\right)$$

where,
L = % nonconjugated linoleate at start of hydrogenation
L_t = % nonconjugated linoleate after time t
D = % conjugated linoleate at start of hydrogenation
D_t = % conjugated linoleate after time t
F_D = fraction of L going to conjugated linoleate
k_L = relative reaction rate of nonconjugated linoleate (total rate of two reactions)
k_D = relative reaction rate of conjugated linoleate.

In applying the above equation, only the values for D and L were known. A value for k_L was assumed since relative reaction rates were desired. Using arbitrarily chosen values of t, values of F_D and k_D were determined by trial and error so that for a given content of nonconjugated linoleate, the calculated contents of conjugated linoleate coincided as closely as possible with the experimentally determined contents of conjugated linoleate.

It is evident from Figure 4 that constants were found which fitted the experimental data quite closely, at least for the hydrogenations which produced relatively large percentages of conjugated linoleate.

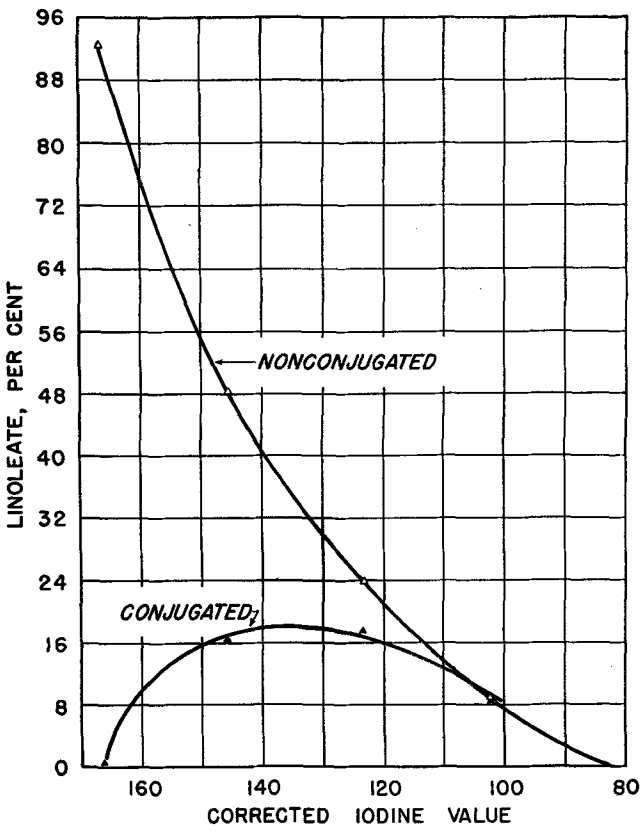


FIG. 4. Linoleate contents *vs.* corrected iodine value for progressively hydrogenated methyl linoleate, Run No. 3. Curve for nonconjugated linoleate and plotted points represent experimentally determined compositions. Curve for conjugated linoleate is calculated from relative reaction rates listed in Table III.

In the calculations described above the constant k_L is the overall constant for the relative reaction rate of nonconjugated linoleate. With the aid of the constant F_D this overall rate can be resolved into rates for nonconjugated linoleate to oleate and nonconjugated linoleate to conjugated linoleate. These resolved values, together with the other values which were determined, are listed in Table III.

Trans Isomers

In Figure 5 the concentration of nonconjugated trans bonds *vs.* corrected iodine value is plotted for each of the hydrogenation runs represented in Table I. From this plot it is evident that, for the operating conditions employed (Table I), decreasing the rate of hydrogen dispersion had about the same effect on trans isomer formation as decreasing the catalyst concentration. Both increased the rate of formation and maximum amount of trans isomers formed. Decreas-

TABLE III

Relative Reaction Rates in the Hydrogenation of Methyl Linoleate and Fraction of Original Linoleate Undergoing Conjugation

Run No.[a]	Fraction of non-conjugated linoleate to conjugated linoleate	Relative reaction rate		
		Non-conjugated linoleate to oleate	Non-conjugated linoleate to conjugated linoleate	Conjugated linoleate to oleate
1	0.05	1	0.06	3.7
2	0.60	1	1.5	7.5
3	0.77	1	3.3	8.7
4	0.34	1	0.52	6.0

[a] Operating conditions for each run given in Table I.

ing the temperature decreased the rate of formation and maximum amount of trans isomers.

Changing the operating variables did not produce the same effect in the rate of formation of trans isomers and conjugated linoleate. Trans isomers were produced at the greatest rate during Run No. 4, but in this run conjugated linoleate was produced at the next to lowest rate. Obviously the two reactions are not directly related.

In previous hydrogenation experiments with normal methyl oleate (6) the formation of trans isomers was much more rapid than the formation of methyl stearate during the early stages of hydrogenation until an equilibrium of cis-trans isomers was attained, after which the amount of trans isomers decreased linearly as hydrogenation proceeded. In the hydrogenation of methyl linoleate an analogous reaction did not occur since the maximum amount of trans isomers was not attained in the early stages of hydrogenation. The above statement is, of course, dependent upon the recognized fact that at equilibrium the number of trans bonds in elaidinized methyl linoleate is greater than that in elaidinized methyl oleate. According to the elaidinization mechanism proposed by Blekkingh (5), the trans bonds in elaidinized methyl linoleate amount to 64.7% of the total number of double bonds. Expressed as percentage of methyl elaidate in Figure 5, this equilibrium concentration would be 129.4. On the basis of the experimental evidence it may be concluded that elaidinization of the normal methyl linoleate was not a major factor in any of the hydrogenation reactions.

Some trans bonds in all probability were formed in the course of conjugation of a portion of the methyl

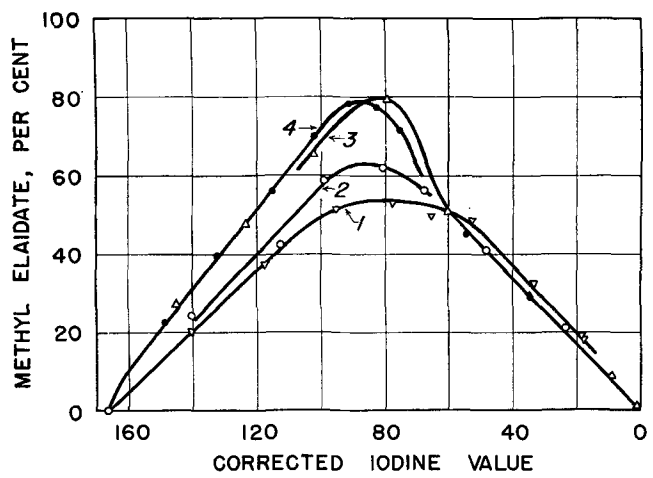


FIG. 5. Content of nonconjugated trans isomers, as methyl elaidate, *vs.* corrected iodine value for progressively hydrogenated methyl linoleate. Curve numbers refer to hydrogenation runs listed in Table I.

linoleate during hydrogenation. As stated before, there is no suitable method for determining the amount of such trans bonds; however it appears that they were not a major factor in establishing the total amount of nonconjugated trans bonds present at any particular time during hydrogenation. The rate of formation of nonconjugated trans isomers was highest for Run 4 which had the next-to-lowest rate of conjugation. In Run 1 only 5% of the linoleate was conjugated in the course of hydrogenation yet trans isomers were produced at a high rate, the equivalent of approximately 50% of methyl elaidate being present at the point where the last of the linoleate disappeared.

It is believed that the initial formation of nonconjugated trans isomers observed during the early stages in the hydrogenation of methyl linoleate is mainly the result of hydrogenating one double bond of the methyl linoleate and simultaneously converting the remaining double bond to the trans form. This reaction occurs in a fixed percentage of the total number of molecules of linoleate undergoing hydrogenation.

This belief is supported by the following experimental observations. In none of the analyses recorded in Table I did the content of trans isomers calculated as elaidate exceed the content of total oleates. During the first stage of each hydrogenation, when only methyl linoleate was being hydrogenated, the calculated content of methyl elaidate was in direct proportion to the amount of hydrogenation (Figure 5) even though the operating conditions varied considerably.

Confirmatory evidence for the above mentioned mode of trans isomer formation is given by the data obtained from the progressive hydrogenation of cottonseed oil (Table II). The cottonseed oil, which contained linoleic, oleic, and saturated acid glycerides equivalent to approximately 50%, 25%, and 25% by weight, respectively, was hydrogenated under such selective conditions that only the linoleic was hydrogenated over the range of iodine values shown in the table. From a plot of nonconjugated trans isomers, calculated as trielaidin, *vs.* iodine value (Figure 6) it is evident that the amount of trielaidin formed was in direct proportion to the amount of hydrogenation. The amount of nonconjugated trans isomer formed per unit drop in iodine value was only 0.18 as great as in the comparable hydrogenation of methyl linoleate.

The percentages of nonconjugated trans isomers formed during the first state of the hydrogenation of methyl linoleate provide another indication that the trans isomers formed resulted mainly from the hydrogenation of one double bond of the linoleate and the simultaneous conversion of the other to the trans form. The percentages found could not have been formed by the independent elaidinization of the cis isomers of oleic acid produced by hydrogenation. From Figure 5 it can be calculated that in Run No. 4 approximately 89% of the total oleate formed in the first stage of hydrogenation could have been in the form of trans isomers. This is well above the equilibrium concentration of 67%, which is attained rapidly during the hydrogenation of methyl oleate (6). For all 4 runs the constant rate of formation of trans isomers continued until practically all of the linoleate had disappeared, and the oleate commenced to hydrogenate. At this point the percentage of trans isomers on the basis of the total weight of reaction product

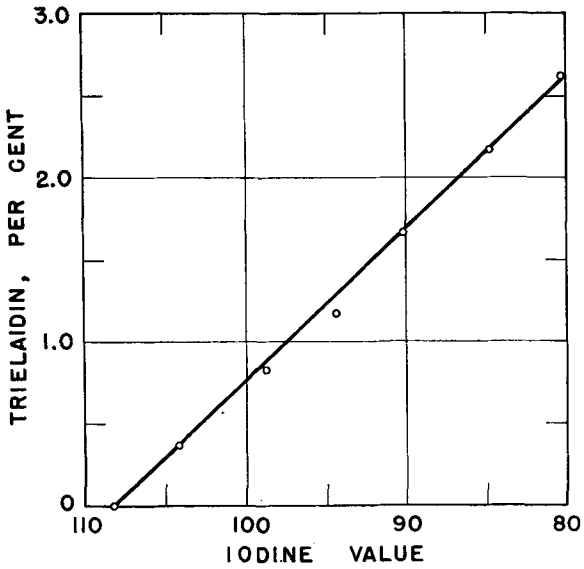


FIG. 6. Content of nonconjugated trans isomers *vs.* iodine value for progressively hydrogenated cottonseed oil.

was 54, 63, 80, and 80 for Runs Nos. 1, 2, 3, and 4, respectively. In Runs Nos. 3 and 4 the 80% concentration of trans isomers was so great that as soon as hydrogenation of the oleate began, a distinct shift commenced toward the trans-cis equilibrium concentration for elaidinized methyl oleate. The shift was indicated by the fact that between iodine values 60 and 80 (Figure 5) the percentage of methyl elaidate for Runs Nos. 3 and 4 decreased faster than the percentage of stearate increased, as indicated by the iodine value.

After the disappearance of the linoleate in each of the hydrogenations, both cis and trans isomers were hydrogenated, but no distinct equilibrium between cis and trans isomers was established as hydrogenation proceeded. This is in contrast to the fact that in the hydrogenation of methyl oleate a distinct equilibrium does occur (6) and the trans isomers comprise 67% of the total cis and trans isomers. Reference to the last column of Table I shows the percentage of trans isomers to be generally higher than 67%. Possibly the large amounts of trans isomers formed during the early stages of hydrogenation were positional isomers of normal methyl elaidate and were hydrogenated at different rates and consequently brought toward cis-trans equilibrium at different rates, that is, some trans isomers were relatively unaffected by hydrogenation until those which hydrogenated more readily were eliminated.

Summary

Methyl linoleate was prepared from cottonseed oil and progressively hydrogenated in 4 experiments using temperatures at 150° and 200°C., catalyst concentrations of 0.05 and 0.25% nickel, and a high and low rate of hydrogen dispersion at atmospheric pressure. Cottonseed oil was progressively hydrogenated in one experiment for comparative purposes.

The hydrogenated methyl linoleate was analyzed for content of total linoleate, conjugated linoleate, total oleate (including trans isomers), and nonconjugated trans isomers (as methyl elaidate).

It was found that the amount of diene conjugation increased as the temperature and catalyst concentrations increased and as the degree of hydrogen dispersion decreased. Conjugation induced by heat and the nickel catalyst was not a factor. All conjugation was the direct result of hydrogenation.

The maximum content of diene conjugated linoleate found experimentally ranged from 0.95% when hydrogenation was conducted at 150°C., with 0.25% nickel, and a moderate degree of hydrogen dispersion to 17.4% when hydrogenation was conducted at 200° C., with 0.25% nickel, and a low degree of hydrogen dispersion. In the former experiment 5.7% of the original linoleate was conjugated in the course of hydrogenation as compared to 77% in the latter. The relative rate of hydrogenation for conjugated linoleate was 3.7 to 8.7 times as great as that for nonconjugated linoleate.

The maximum amount of nonconjugated trans isomers formed during hydrogenation increased as the temperature increased and as the catalyst concentration and degree of hydrogen dispersion decreased.

The amount of nonconjugated trans isomers formed during the first stage of hydrogenation when only linoleate was reacting was directly proportional to the amount of hydrogenation. It was concluded that during this stage nonconjugated trans isomers resulted from the hydrogenation of one of the double bonds of the linoleate and the simultaneous conversion of the other into the trans form. In one hydrogenation apparently 89% of the oleate formed in the first stage contained trans bonds.

In the second stage of hydrogenation after the linoleate disappeared, the percentage of trans isomers on the basis of the total amount of oleate tended to remain well above the equilibrium concentration of 67% for elaidinized methyl oleate. It was concluded that the various trans isomers formed in the early stage of hydrogenation were converted to stearate at different rates and that some tended to remain unchanged while the others were elaidinized to a 67% equilibrium.

REFERENCES

1. American Oil Chemists' Society, Official and Tentative Methods, 2nd ed., edited by V. C. Mehlenbacher, Chicago, 1946.
2. Bailey, A. E., "Industrial Oil and Fat Products," 2nd ed., pp. 721-722, New York, Interscience Publishers Inc. (1951).
3. Bailey, A. E., J. Am. Oil Chem. Soc., *26*, 644-648 (1949).
4. Blekkingh, J. J. A., Discussions Faraday Soc., *1950*, No. 8, 200-201.
5. Blekkingh, J. J. A., Bull. Soc. chim. France, *1950*, 278-282.
6. Feuge, R. O., Pepper, M. B. Jr., O'Connor, R. T., and Field, E. T., J. Am. Oil Chem. Soc., *28*, 420-426 (1951).
7. Hilditch, T. P., and Moore, C. W., J. Soc. Chem. Ind., *42*, 15-17 T (1923).
8. Hilditch, T. P., and Vidyarthi, N. L., Proc. Roy. Soc. London, *A122*, 563-570 (1929).
9. Huber, W. F., J. Am. Chem. Soc., *73*, 2730-2733 (1951).
10. Inoue, Y., and Suzuki, B., Proc. Imp. Acad. Tokyo, *7*, 15-18 (1931).
11. Jackson, J. E., Paschke, R. F., Tolberg, W., Boyd, H. M., and Wheeler, D. H., J. Am. Oil Chem. Soc., *29*, 229-234 (1952).
12. Mattil, K. F., Oil & Soap, *22*, 213-215 (1945).
13. Moore, H. K., Richter, G. A., and Van Arsdel, W. B., J. Ind. Eng. Chem., *9*, 451-462 (1917).
14. O'Connor, R. T., Field, E. T., and Singleton, W. S., J. Am. Oil Chem. Soc., *28*, 154-160 (1951).
15. Pigulevskii, G. V., and Antamonov, P. A., J. Gen. Chem. (USSR), *12*, 510 (1942).
16. Radlove, S. B., Teeter, H. M., Bond, W. H., Cowan, J. C., and Kass, J. P., Ind. Eng. Chem., *38*, 997-1002 (1946).
17. Richardson, A. S., Knuth, C. A., and Milligan, C. H., Ind. Eng. Chem., *16*, 519-522 (1924); *17*, 80-83 (1925).
18. Shreve, O. D., Heether, M. R., Knight, H. B., and Swern, Daniel, Anal. Chem., *22*, 1261-1264 (1950).
19. Suzuki, B., and Inoue, Y., Proc. Imp. Acad. Tokyo, *6*, 266-268 (1930).
20. Swern, Daniel, Knight, H. B., Shreve, O. D., and Heether, M. R., J. Am. Oil Chem. Soc., *27*, 17-21 (1950).
21. Tyutyunnikov, B., and Rholodovskaya, R., Masloboino Zhirovoe Delo, *1929*, No. 5, 53-61.
22. Waterman, H. I., and van Vlodrop, C., Rec. trav. chim., *57*, 629-636 (1938).
23. Zinovev, A., and Kurochkina, N., Masloboino Zhirovol Delo, *11*, 308-312 (1935).

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