TABLE II

Melting Points of Cis- and Trans-Octadecenoic Acids and the Dihydroxy Derivatives of the Latter

Octadecenoic Acid	m.p. °C.	Octadecenoic Acid	m.p. °C.	Dihydroxy Acid	m.p. °C.
Cis 6-	30 -30.2	Trans 6-	52.8-53.0	Trans 6-	121-121.5
Cis 7-	12.5-13.1	Trans 7-	44.2-44.5	Trans 7-	130.5-131
Cis 8-	22.8-24.2	Trans 8-	50.5-50.7	Trans 8-	117.5-118
Cis 9-	13.3-13	Trans 9-	44.0	Trans 9-	130-130.5
Cis 11-	10.5-12[a] 14.5-15.5	Trans 11-	43.6-44.0	Trans 11-	127.5-128

[a]Ahmad and Strong (2).

trans-7-octadecenoic acids and their 7,8-dihydroxystearic acid derivatives, and cis- and trans-8-octadecenoic acid derivatives and their 8,9-dihydroxystearic acid derivatives.

3. A new series of intermediate reaction products has been reported although these compounds were not fully characterized. These compounds include hexamethylene bromochloride, hexamethylene iodochloride, 1-chloro-6-heptadecyne, and 1-chloro-7-heptadecyne.

4. The extinction coefficients at 10.36 microns of the cis and trans-6-, 7-, 8-, 9-, and 11-octadecenoic acids have been calculated and compared.

5. The melting points of the cis- and trans-octadecenoic acids and their dihydroxy derivatives were shown to exhibit alternating patterns.

Addendum

After the present work was completed, we received a communication from W. F. Huber of the Procter and Gamble Company with a copy of a paper they were submitting to another journal, describing synthesis of a more extended series of octadecenoic acids, including 7- through 12- and 17-octadecenoic acids. Except for the 17-acid, the pattern of synthesis was essentially that of Ahmad and Strong. After examining Dr. Huber's paper, we feel that publication of our results is warranted because of certain novel and improved details of our synthesis of the 7- and 8-acids and our infra-red data. In view of his results it does not seem necessary to continue our work, as planned, which included synthesis of 10-octadecenoic acid.

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Modification of Vegetable Oils. XI. The Formation of Trans Isomers During the Hydrogenation of Methyl Oleate and Triolein[1,2]

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THE formation of isomeric oleic acids during the hydrogenation of vegetable oils has been the subject of considerable speculation and experimental work, but the phenomena involved are not well understood. It is recognized that the extent to which isomeric oleic acids are present in a plastic fat is of considerable practical importance. In margarine oils, for example, a high content of solid iso-oleic acid glycerides is highly desirable while in shortenings the reverse is true.

During hydrogenation of oils containing oleic and/or polyethenoid acids, both positional and geometric isomers of oleic acid are produced, and several investigators have concluded that both types are present in partially hydrogenated monoesters of oleic acid. Moore (7) examined ethyl oleates which had been partially hydrogenated in the presence of palladium and nickel catalysts and concluded that the solid iso-oleic acids were composed of $\Delta^{9,10}$-, $\Delta^{11,12}$-, and possibly $\Delta^{10,11}$-iso-oleic acids. The $\Delta^{9,10}$ isomer was considered to be elaidic acid, and the two positional isomers probably also possessed trans configurations. Hilditch and Vidyarthi (5) reported that hydrogenation of methyl oleate gave in addition to some elaidic acid, both $\Delta^{8,9}$- and $\Delta^{10,11}$-oleic acids. Moore (7) found that hydrogenation of ethyl oleate resulted in a definite ratio (*ca.* 10:15) of liquid oleic to solid iso-oleic acids. Somewhat later Hilditch and Jones (4) reported the results of an investigation similar to that of Moore but using partially hydrogenated cottonseed and olive oils instead of ethyl oleate. They found no constant proportion of solid to liquid oleic acids but instead a gradual accumulation of iso-oleic acids up to a point corresponding to the maximum observed by Moore, followed by a decline.

Mazume (6) investigated the hydrogenation of methyl oleate and concluded that large amounts of iso-oleic acids were formed during the initial stages of hydrogen addition, followed by a gradual transformation into oleic acid on further hydrogenation.

Recently Swern and co-workers (10, 12) described an infra-red spectrophotometric method for the determination of *trans*-octadecenoic acids and esters in the

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[1] Report of study made under the Research and Marketing Act of 1946.

[2] Presented at the 24th Fall Meeting of the American Oil Chemists' Society, San Francisco, Calif., Sept. 26-28, 1950.

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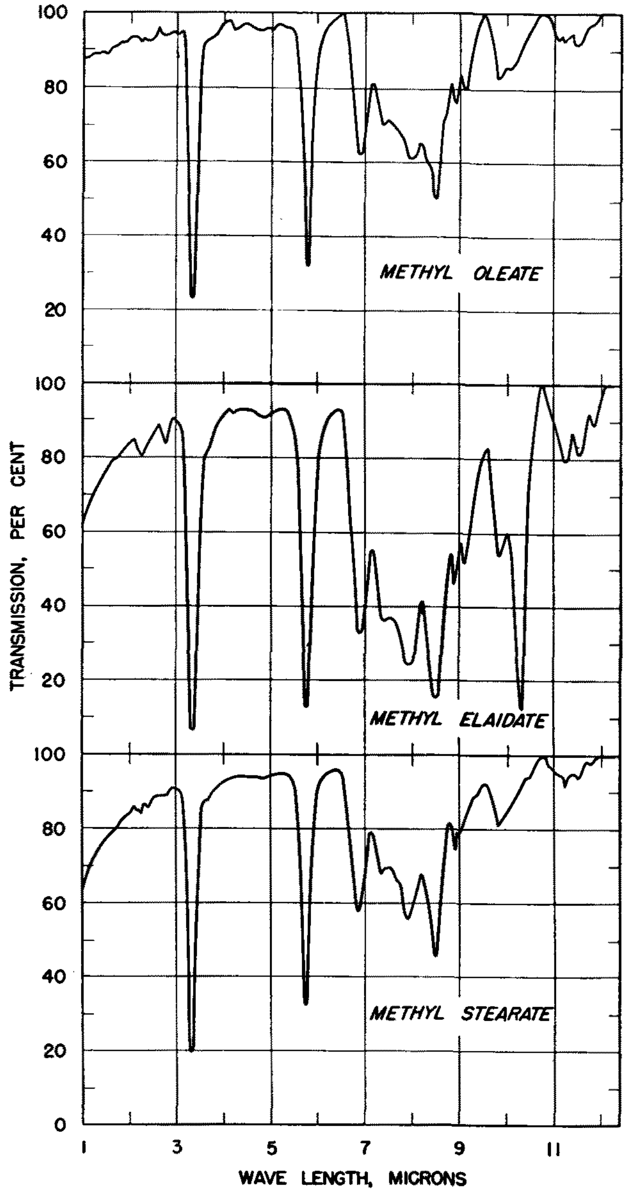


FIG. 1. Infra-red absorption spectra of chloroform solutions of methyl oleate, elaidate, and stearate.

presence of *cis*-octadecenoic and saturated acids and esters. This new technique is well suited for following the course of the hydrogenation of fats and oils and their derived acids and esters, and it has been applied in the present investigation to the hydrogenation of methyl oleate and triolein.

Materials

With the exception of tristearin all of the methyl esters and triglycerides used in this work were prepared from refined, bleached, and deodorized pecan oil containing approximately 79% oleic, 16% linoleic, 3% palmitic, and 2% stearic acids.

Crude methyl oleate was prepared from pecan oil by interesterifying the oil with methanol in the presence of sodium methylate. The reaction product was acidified, washed, and dried, then freed of methyl linoleate by three crystallizations from acetone at —60°C., using 15 ml. of acetone per gram of ester. The monoesters of the saturated acids were removed by two crystallizations from acetone at —37°C. using 10 ml. of acetone per gram of ester. This procedure, which is a simplification of that described by Wheeler and Riemenschneider (14), yielded a methyl oleate having an iodine value of 84.5 (theoretical, 85.62). The product contained approximately 97% methyl oleate, 0.7% methyl linoleate, and 2% of a mixture of methyl palmitate and stearate. It was stored under hydrogen at a low temperature to protect it from oxidation prior to use.

The triolein was prepared from the methyl oleate by reacting the latter with less than the equivalent amount of glycerol, using lithium hydroxide as a catalyst (3). After removal of the catalyst the crude glyceride was purified by vacuum-steam distillation to remove the excess methyl oleate and part of the diglycerides, after which the product was fractionally crystallized from petroleum naphtha to remove additional diglycerides. The final product had a hydroxyl value of 15 and a Wijs iodine value of 86.7.

Methyl elaidate was prepared by isomerizing the methyl oleate by heating it with 0.3% of powdered selenium at 200°C. for three hours under purified nitrogen, followed by distillation and five fractional crystallizations from acetone at —40°C. (10 ml. of acetone per gram of monoester). The final product melted at 10.25°C. and had the theoretical iodine value of 85.6. Its melting point curve, as determined by Smit's procedure (11), showed a melting range of only 0.05, indicating an exceptionally high purity.

Except for the distillation step, trielaidin was prepared from the methyl elaidate by the procedure used to prepare triolein from methyl oleate. The trielaidin was purified by repeated crystallization from acetone at —14°C. (10 ml. acetone per gram of solute). The final product had an iodine value of 85.9 (theoretical, 86.0) and a hydroxyl value of 15 and was free of peroxides.

The methyl stearate and tristearin used in this investigation were prepared in connection with a determination of their thermal properties and were therefore of a greater degree of purity than required for the present work.

Hydrogenation Apparatus and Procedure

All hydrogenations were conducted in test tubes (38 mm. by 215 mm.) immersed in a constant temperature oil bath. The test tubes were closed by rubber stoppers carrying a thermometer, a hydrogen inlet tube reaching to the bottom, a hydrogen outlet tube, and an additional tube (35-mm. length of 16-mm. tubing), which was closed by a small rubber stopper except during withdrawal of samples for analysis. The flow of hydrogen into the sample was kept constant by a system of valves and pressure regulators, and the amounts of hydrogen entering and leaving the apparatus were measured by wet gas meters.

A commercial nickel catalyst of the supported type, prepared by electrolytic precipitation (1) and suspended in hardened coconut oil, was used. The hardened coconut oil was removed and replaced by the product to be hydrogenated.

All of the hydrogenations were carried out under the same conditions, which were as follows: A 70-g. batch of methyl oleate or triolein was placed in the test tube and the ester, catalyst, and hydrogen mixed and agitated by bubbling the hydrogen through the material at a fairly rapid rate. This was accomplished

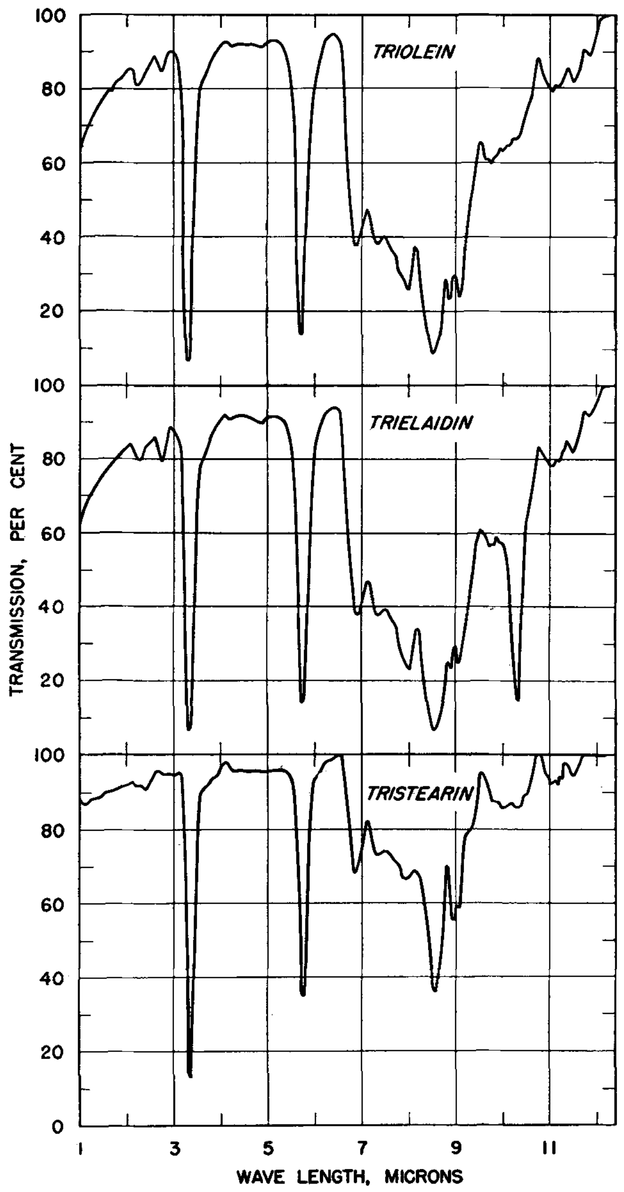


Fig. 2. Infra-red absorption spectra of chloroform solutions of triolein, trielaidin, and tristearin.

by introducing the hydrogen at atmospheric pressure at the rate of 0.015 cubic feet (425 ml.) per minute. The temperature was maintained constant by adjusting the depth to which the test tube was immersed in the constant temperature bath. Samples of 7 to 8 grams each were withdrawn periodically by inserting a pipette through the sampling tube. All of the samples were stored under hydrogen until analyzed. The presence of some dielaidin, indicated by the hydroxyl value, had no detectable effect on the absorption coefficient or measurable effect on the hydrogenation.

Spectrophotometric Analysis

In the present investigation slight modifications of the infra-red spectrophotometric method of Swern *et al.* (10, 12) were employed. Chloroform was substituted for the carbon disulfide as solvent because the former was found to be preferable in several respects (8).

All spectra used in the present investigation were obtained with a Beckman IR-2 infra-red spectrophotometer maintained in a room at 23° C. and 20% relative humidity. The temperature of the instrument was maintained at 25 ± 0.1°C. by circulating through it a hydrocarbon medium from a constant temperature bath. All measurements were made by the quantitative differential method, that is, measurement of chloroform solutions of the methyl esters and triglycerides against pure chloroform (9).

Additional details concerning the method of analysis as applied in the present investigation are described elsewhere (8).

The spectral absorption curves (percentage of transmission *vs.* wave length) for methyl oleate, elaidate, and stearate are shown in Figure 1, and those for triolein, trielaidin, and tristearin are shown in Figure 2.

Table I gives the molecular extinction coefficient for the various absorption maxima (dips) in the curves shown in Figures 1 and 2 and correlates them with molecular structure. The molecular extinction coefficient, ϵ, is defined by the equation, $\epsilon = d/cl$, where d is the optical density at the wavelength involved in the measurement, c is the concentration of the compound in moles per liter, and l is the cell length in centimeters.

TABLE I

Magnitude and Significance of the Molecular Extinction Coefficients of Compounds Involved in the Hydrogenations

Approximate location of band, microns	Significance of vibration	Molecular extinction coefficient, ϵ					
		Methyl oleate	Methyl elaidate	Methyl stearate	Triolein	Trielaidin	Tristearin
3.3	C—H stretching	219.3	234.2	232.9	619.5	628.4	677.2
5.7	C=O stretching	171.9	171.9	164.2	451.4	442.5	481.1
6.8	C—H bending	71.4	77.1	77.6	177.0	177.0	169.3
7.3	—CH_3 symmetrical deformation	53.4	56.3	53.7	150.5	150.5	142.6
7.9	C—O stretching	77.1	80.0	83.6	203.6	221.3	187.1
8.5	C—O stretching	112.6	112.6	110.4	460.2	451.4	454.4
8.9	C—C—O unsymmetrical stretching and possibly COOR stretching	41.5	41.5	41.5	221.3	239.0	267.3
10.3	C—H deformation at C=C double bond	11.0	107.0	9.2	62.0	352.3	57.9

It is evident from Figures 1 and 2 and Table I that the only significant difference in the infra-red spectra of the methyl esters or triglycerides lie in the extent of the absorption at 10.3 microns. Absorption in this region is a function of the concentration of trans ethylenic linkages, i.e., the concentration of *trans*-octadecenoic acids.

The specific extinction coefficient, a, at 10.3 microns was employed in calculating the proportion of trans isomers in the hydrogenated products. It differs from the molecular extinction coefficient in that the concentration factor used in calculating the coefficient is expressed in grams per liter instead of moles per liter. The specific extinction coefficients at 10.3 microns for the pure esters were: methyl oleate, 0.037; methyl stearate, 0.031; methyl elaidate, 0.361; triolein, 0.070; tristearin, 0.065; trielaidin, 0.398.

In calculating the amount of trans component in a hydrogenated sample the following equation was used:

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

where $a_{ob.}$ 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 $a_{av.}$ is a weighted average calculated from the extinction coefficient of the original and completely hydrogenated products. In calculating the value of $a_{av.}$ it was assumed the unsaturated portion of the sample was in the form of cis isomers.

It has been shown that positional isomers are formed during hydrogenation of derivatives of oleic acid, and it is known that such isomers have a small effect on the value of the extinction coefficient. However this effect was disregarded in calculating the percentage of trans component because of its small magnitude. From the data of Swern *et al.* (12) it can be shown that the extinction coefficients of petroselaidic acid (*trans*-$\triangle^{6,7}$-octadecenoic acid) and elaidic acid (*trans*-$\triangle^{9,10}$-octadecenioc acid) differ by less than 2%. The double bonds of the positional isomers obtained by hydrogenating oleic acid derivatives are close to their original positions, and the extinction coefficients for their trans forms are probably almost identical.

The percentage of trans component determined by the spectrophotometric method described above is believed to be accurate to within one or two percentage units.

Hydrogenation of Methyl Oleate

As the hydrogenation of methyl oleate or triolein proceeds, the infra-red absorption spectrum undergoes a pronounced change in the region of 9 to 11 microns as is evident in Figure 3. Curves A to J refer to methyl oleate hydrogenated at 200°C. using 0.25% of nickel catalyst and moderate agitation. Curves K to R are for triolein hydrogenated at 200°C. using 0.25% of catalyst and fairly intense agitation. In both series the initial curves (A and K) refer to the original, unhydrogenated esters.

The percentage of trans isomers formed at each stage of the hydrogenation of methyl oleate and triolein are shown in Table II and in each case correspond in designation to the infra-red absorption spectrum shown in Figure 3.

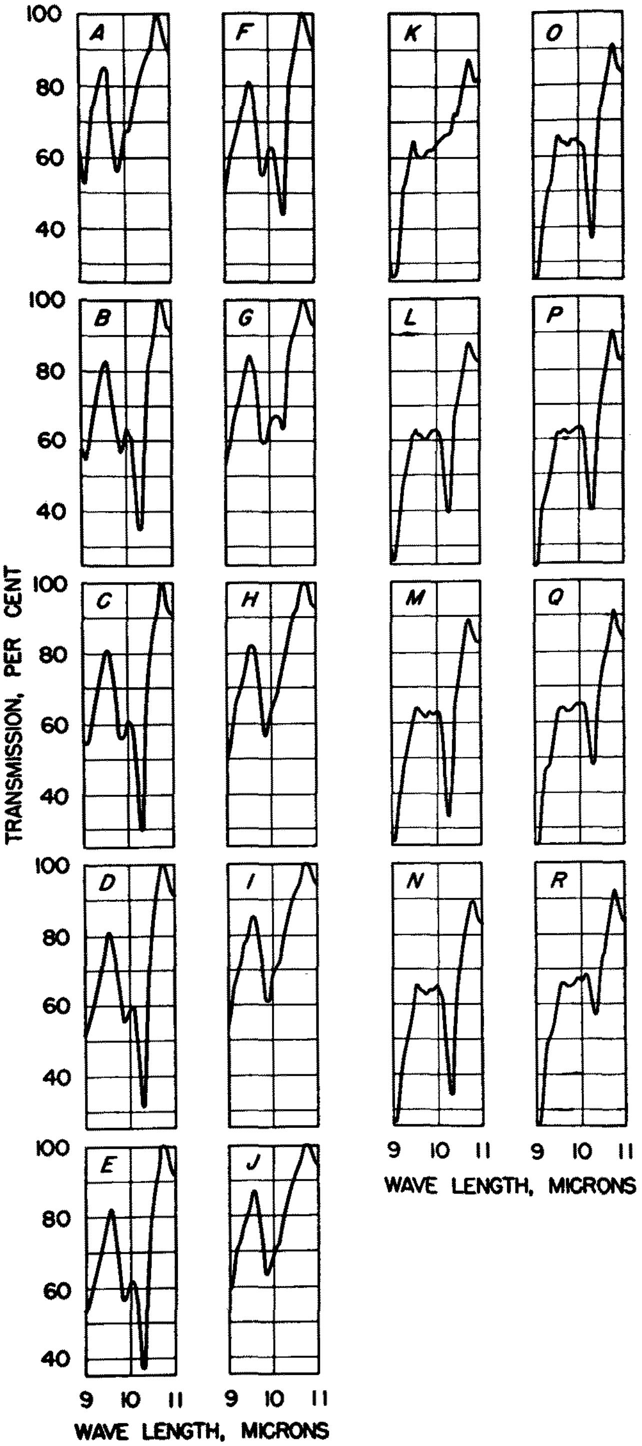


FIG. 3. Infra-red absorption spectra of progressively hydrogenated methyl oleate (curves A-J) and triolein (curves K-R).

The effect of temperature on the formation of trans oleates was established by hydrogenating a batch of the methyl ester at 150°, 175°, and 200°C. The iodine values, content of trans isomers, and compositions were determined for samples withdrawn during the hydrogenations. The variation of the content of trans isomers as a function of stearate formation for each of the hydrogenation temperatures is shown in Figure 4. Curves for the reaction time as a function of stearate formation for each of the hydrogenation temperatures are also shown in Figure 4.

It is evident that at the start of the hydrogenation the trans isomers form at a very rapid rate, which increases as the temperature increases. At the be-

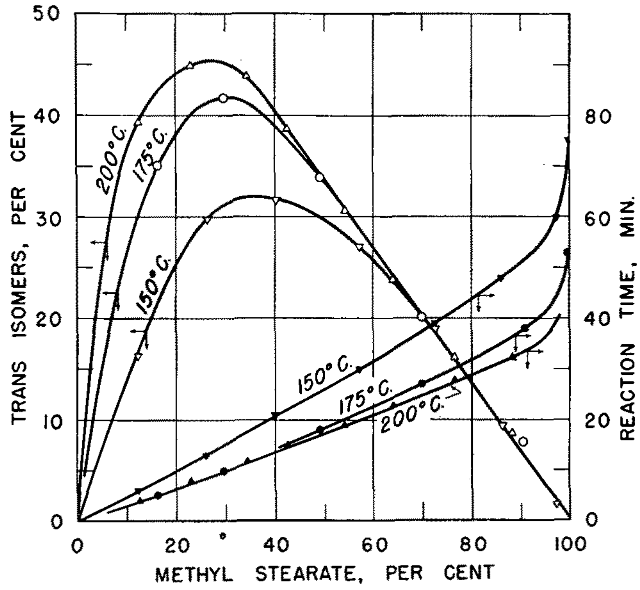


FIG. 4. Effect of temperature on the formation of trans isomers during the hydrogenation of methyl oleate with 0.25% nickel catalyst and good dispersion of hydrogen.

ginning of the reaction, when the hydrogenation is 10% complete, the concentration of trans isomers is found to be 14% for the reaction at 150°C., 26% for that at 175°C., and 36% for that at 200°C. Further examination of Figure 4 reveals that eventually all of the reactions reach a stage where the decrease in trans isomers is proportional to the increase in methyl stearate, that is, the ratio of trans to cis isomers has reached equilibrium. Calculated from the straight line portion of the curves, the proportion of trans compounds present at equilibrium is 67%, based on the total amount of unsaturated esters present. This percentage is identical with that occurring during elaidinization with sulfur or selenium.

TABLE II

Iodine Value and Corresponding Percentage of Trans Isomers for Partially Hydrogenated Methyl Oleate and Triolein

Methyl oleate			Triolein		
Sample[a]	Iodine value	Trans isomers,%	Sample[a]	Iodine value	Trans isomers,%
A	84.5	......	K	86.7	......
B	75.0	42.2	L	74.9	27.4
C	66.5	48.9	M	63.9	37.7
D	57.9	42.0	N	54.6	38.2
E	48.3	37.6	O	43.8	31.7
F	33.5	26.2	P	35.2	25.4
G	15.3	11.8	Q	24.2	17.4
H	0.9	1.2	R	14.7	10.2
I	0.2	0.9			
J	0.1	0			

[a] The sample designation corresponds to that for the infra-red absorption curves shown in Figure 3.

The effect of the degree of dispersion of the gaseous hydrogen on the formation of trans isomers during hydrogenation was determined by a procedure similar to that used to determine the effect of temperature. The degree of dispersion (not the rate) of the gas phase was varied by changing the type of distributor at the end of the hydrogen inlet tube. For the low degree of dispersion this distributor consisted of a glass bulb, 10 mm. in diameter, perforated by five small holes. For the high degree of dispersion the distributor consisted of a coarse porosity, fritted glass cylinder 12 mm. in diameter and 10 mm. high. With the latter distributor the reaction mixture assumed a foamy appearance. Curves 1 and 2 of Figure 5 which represent low and high degrees of dispersion, respectively, show that isomers form more rapidly as the degree of hydrogen dispersion decreases. The curves of the reaction time *vs.* content of methyl stearate show that the rate at which gaseous hydrogen was absorbed by the methyl esters must have been appreciably different in the two hydrogenations. These curves also show that the order of reaction was essentially zero, indicating that the rate of solution of hydrogen in the esters predominantly determined the over-all rate of reaction. The coincidence of curves 1 and 2 at contents of methyl stearate in excess of 35% is proof that the degree of dispersion of hydrogen has no effect on the ratio of trans to cis isomers formed once equilibrium is reached. The percentage of trans isomers, based on the content of total monounsaturated constituents, is again observed to be 67%.

The influence of catalyst concentration on the formation of trans isomers is shown in Figure 6, from which it may be seen that the trans isomers form at a greater rate as the concentration of catalyst increases. By referring to Figure 4 it is seen that increasing the catalyst concentration from 0.05% to 0.25% when the reaction temperature is 175°C. has the same effect as increasing the temperature from about 160° to 175°C. when the catalyst concentration is 0.25%. Figure 6 also shows that the catalyst concentration does not affect the equilibrium ratio of trans to cis isomers.

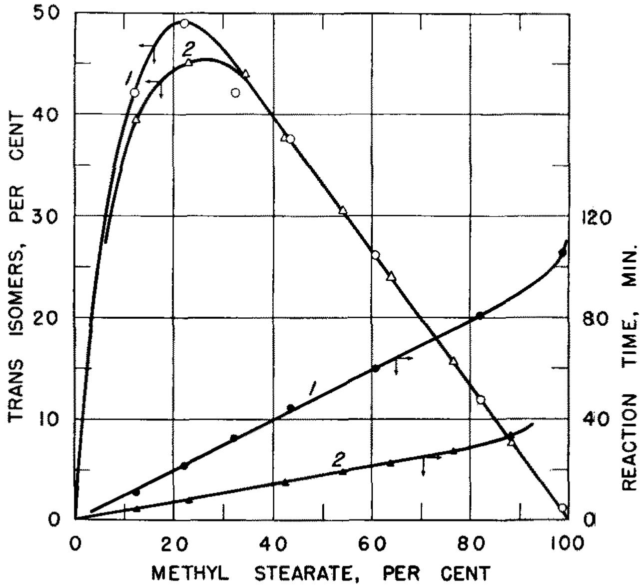


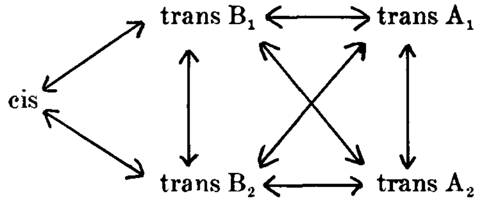
FIG. 5. Effect on trans isomer formation during hydrogenation of methyl oleate at 200°C., 0.25% nickel catalyst, and 1) poor dispersion of hydrogen and 2) good dispersion of hydrogen.

The formation of trans isomers does not occur in the absence of hydrogenation as was shown in one experiment in which 0.25% of nickel catalyst was added to methyl oleate and the mixture heated to 200°C. and agitated by bubbling purified nitrogen through it. All of the samples, withdrawn after one, two, three, and four hours, contained exactly 2.2%

of trans isomers, probably as a result of hydrogen adsorbed on the catalyst at the beginning of the experiment. After this amount of hydrogen had reacted, no more trans isomers formed. These results agree with those of Moore (7), who found that solid iso-oleic acids are not formed in the absence of hydrogen but differ from those of Waterman and Vlodrop (13) and several others, who observed such isomers to be formed at high temperatures.

It should be noted that the conditions of temperature, catalyst concentration, etc., which favor an increased rate of trans isomer formation during the hydrogenation of methyl oleate are the same conditions which favor increased selectivity during the hydrogenation of fats and oils. Selectivity is defined here as the preferential saturation of polyethenoid acids over monoethenoid acids.

In the light of observations made by Blekkingh (2) the fact that an equilibrium mixture of trans and cis isomers consisting of 67% trans is always reached during the hydrogenation of methyl oleate has several interesting implications. Blekkingh pointed out that a double bond in an unsaturated fatty acid derivative can occur in five transitional forms, which can be designated as trans A_1, trans A_2, trans B_1, trans B_2, and cis. Under the influence of an elaidinization catalyst the forms cis and trans B are directly interchangeable while the forms trans A cannot be changed directly into cis, or vice versa. All trans forms however are interchangeable. In other words, the following reactions occur:



When the probabilities of all possible transitions are equal, the ratio of trans to cis, at equilibrium, will be 2:1; that is, 67% of the double bonds will be in the trans form.

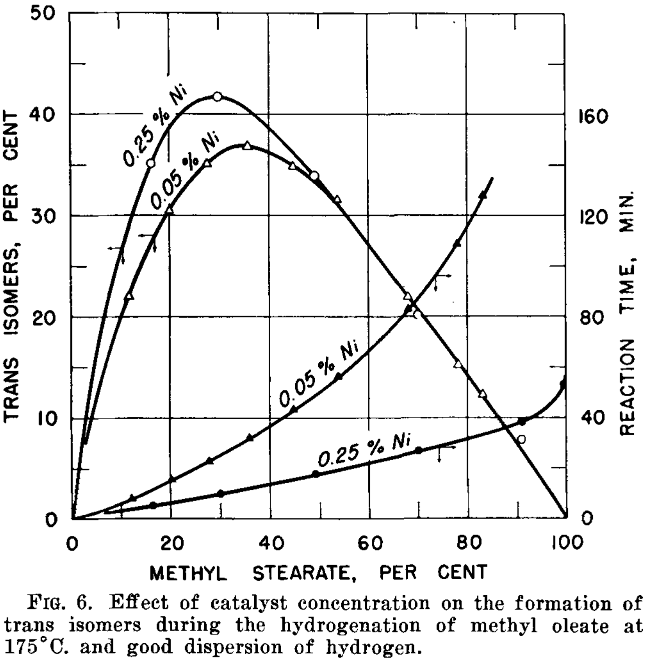


FIG. 6. Effect of catalyst concentration on the formation of trans isomers during the hydrogenation of methyl oleate at 175°C. and good dispersion of hydrogen.

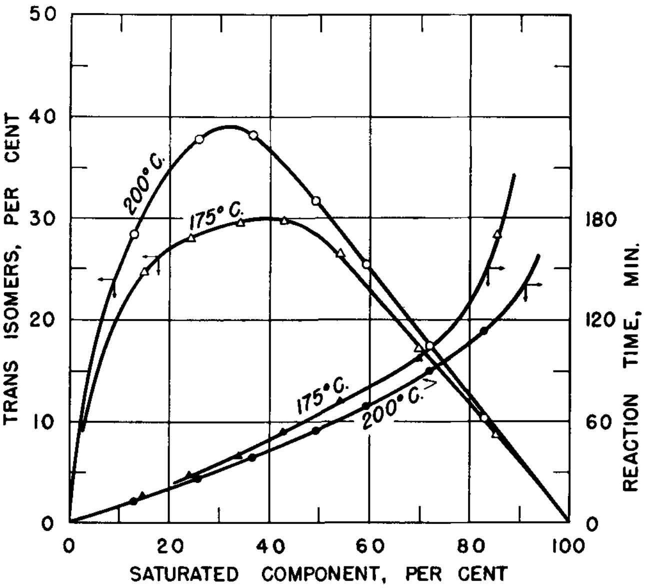


FIG. 7. Effect of temperature on the formation of trans isomers during the hydrogenation of triolein with 0.25% nickel catalyst and good dispersion of hydrogen.

Since the equilibrium ratio of trans to cis isomers attained during the hydrogenation of methyl oleate is 2:1, it must be concluded that all positional and geometric isomers in the partially hydrogenated product react with equal ease. Not only are they adsorbed and desorbed from the nickel catalyst with equal readiness, but they also hydrogenate with equal readiness. If the probabilities of reaction were not equal for all of the isomers, the theoretical equilibrium ratio would seldom be attained in a given hydrogenation and almost certainly would not be attained under varying conditions of temperature, catalyst concentration, and degree of dispersion of hydrogen.

Hydrogenation of Triolein

Exactly the same procedures were employed in the hydrogenation of triolein as were described for methyl oleate. The effect of varying the temperature of hydrogenation of triolein is shown in Figure 7. In this case the percentages of trans isomers and saturated component were calculated from spectrophotometric data and iodine values as trielaidin and tristearin, respectively.

As in the case of methyl oleate the infra-red absorption spectrum in the region of 9 to 11 microns undergoes a marked change during the progressive hydrogenation of triolein (Figure 3, K-R) at 200°C.

Comparison of Figures 4 and 7 indicates that the rates of hydrogenation and of trans isomer formation are greater for a given temperature with methyl oleate than with triolein. Actually the rate at which triolein hydrogenated during the greater portion of the reaction was approximately one-third that of methyl oleate under similar conditions.

The most important difference in the hydrogenation of methyl oleate and triolein is observed in the equilibrium ratio of trans to cis isomers. Whereas the concentration of trans isomers of the partially hydrogenated methyl oleate always reached equilibrium at 67%, calculated on the basis of total unsaturated constituents, the trans isomers in partially hydrogenated triolein came to equilibrium somewhere below this value. At 200°C. this equilibrium was 62% while at 175°C. it was 57%.

The ratio of trans isomers at equilibrium was further verified by hydrogenation of samples of refined cottonseed oil to iodine values of 22 and 35. These samples were hydrogenated in a stainless steel hydrogenator under a pressure of 15 p.s.i.g., a temperature of 177°C., catalyst concentration of 0.1%, and mechanical agitation. The samples were found to contain 58-59% of trans components, calculated on the basis of total unsaturated constituents.

Summary

1. During the hydrogenation of methyl oleate, trans isomers are formed at a very rapid rate. As much as 38% of trans isomers formed while the first 10% of methyl stearate was formed.

2. The rate of formation of trans isomers in methyl oleate undergoing hydrogenation is increased by increasing the temperature, increasing the catalyst concentration, and decreasing the degree of dispersion of the hydrogen.

3. The hydrogenation of methyl oleate always resulted in the establishment of an equilibrium between cis and trans isomers, and irrespective of the conditions employed the concentration of trans isomers was always 67%, calculated on the basis of total unsaturated constituents.

4. It is concluded that all of the iso-oleic acids formed during the hydrogenation of methyl oleate adsorb hydrogen at the same rate as oleic acid and are adsorbed and desorbed from the nickel catalyst with equal ease.

5. Trans isomers are formed at a slightly lower rate during the hydrogenation of triolein than in the case of methyl oleate.

6. Partial hydrogenation of triolein also results in the establishment of an equilibrium between cis and trans isomers of oleic acid but at values of less than 67% of trans constituents (based on the total unsaturated constituents) observed with methyl oleate. The equilibrium concentration was found to vary with the conditions of hydrogenation and was found to be 62% at 200°C. and 57% at 175°C.

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Viscosity of Potassium Soap-Potassium Silicate Mixtures[1]

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IN 1949 Merrill and Getty (13) reported data on the solubility, pH's, and detergent properties of mixtures of potassium coconut oil soap with two potassium silicates. They concluded that the addition of potassium silicates to potassium soaps resulted in equivalent or better detergency and at appreciable savings in cost. The effect was particularly obvious in hard water. Since potassium soaps are commonly sold as liquids or pastes, it is important to know what effect silicate additives will have on the viscosity of the mixture. This paper is a report on that phase of the problem.

While there are many published references on the effects of additives on the viscosity of soap solutions (1-3, 5-9, 11, 12, 15-17, 19), no data have been found which are strictly comparable with the present work. Most of the published references are concerned with a) pure soaps, usually sodium soaps, b) low concentrations of soap and additives, c) higher working temperatures, and d) the effect of organic additives which were often used.

Thus in recent years Angelescu and co-workers have investigated the effects of cresols and other phenolic compounds on sodium and potassium stearate and palmitate and other pure soaps (1-3). Philippoff has studied the viscosity and elasticity of low concentrations of potassium laurate and other derivatives of dodecane (16, 17). Neiman in 1947 published viscosity data on the system potassium palmitate-water-isoamyl alcohol at 50°C. (15). Freundlich and Kores have also done work on the viscosity and elasticity of solutions of pure soaps (6, 7).

About 25 years ago King, and later McBain, Willavoys, and Heighington did work on the effect of NaCl and other sodium salts on the viscosity palmitate solutions (11, 12). They found that the addition of electrolytes increased the viscosity to a maximum value many hundred times greater than that of the original soap solution. Further additions decreased the viscosity almost as rapidly until the salting-out concentration was reached. In both of these studies viscosities were measured by falling ball method at a working temperature of 80°C.

Merrill (14) has shown that a liquid soap containing 33% soap corresponding to potassium laurate can be mixed in all proportions with a potassium silicate containing 38.7% solids with a silica-to-alkali mole ratio of 3.2:1.

In the present investigation commercial potassium paste soaps and commercial potassium silicates have been used. Thus the data have direct value for manufacturers and users of liquid potassium soaps.

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