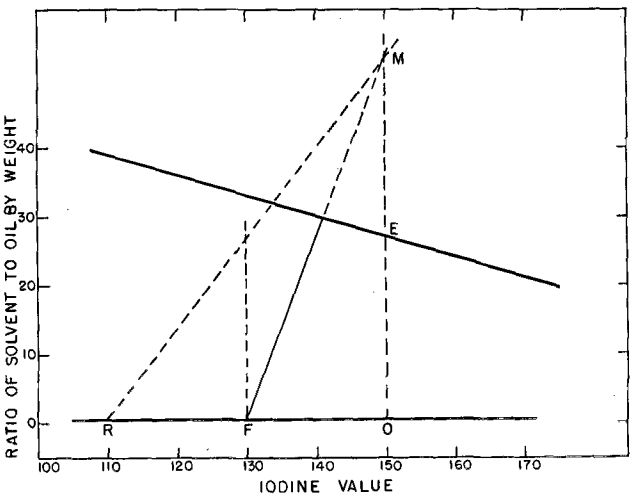

FIG. 8. Determination of minimum reflux ratio and solvent to oil ratio for hypothetical separation, using 6 parts H_2O per 100 parts acetone.

set: a) minimum reflux and solvent to oil ratio with an infinite number of stages and b) minimum number of stages with infinite reflux and solvent to oil ratio. The operating point, M, for minimum reflux, Figure 8, is located as the intersection of a vertical line through the iodine value of the extract and the tie line whose raffinate has the iodine value of the feed. The minimum reflux ratio, ME/EO, is 1.0. The minimum solvent to oil ratio, the solvent to oil ratio at which a line joining M to R crosses the iodine value of the feed, is 26:1. For the condition of minimum number of stages the operating points are at infinite distances from the iodine value axis so that lines joining raffinate points to the operating points are vertical.

TABLE II

Relation Between Water Content of Solvent and Minimum Limits for Extraction

Parts H_2O per 100 parts acetone	Min. reflux ratio	Min. solvent to oil ratio	Min. number of stages
6.0	1.0	26	3.7
5.5	1.1	21	3.8
5.0	1.2	17	4.0
4.5	1.6	14	4.2
3.5	3.2	13	6.2

Table II shows the minimum reflux ratio, solvent to oil ratio, and number of stages for various water contents of the solvent. There is a steady decrease in the minimum solvent to oil ratio required down to 4.5 parts water per 100 parts acetone with only a relatively small increase in the reflux ratio and number of stages. From 4.5 to 3.5 parts water however the small gain in decreased solvent requirement is more than offset by a sharp increase in the number of stages. The optimum water content appears therefore to be about 4.5 parts per 100 parts acetone. The effect of varying the reflux ratio on the number of stages and solvent to oil ratio required for this water content is shown in Table III. Optimum conditions here would depend on an economic balance between cost of capital equipment and cost of solvent recovery.

TABLE III

Effect of Reflux Ratio on Solvent to Oil Ratio and Number of Stages Required for 4.5 Parts Water per 100 Parts Acetone

Reflux ratio	Solvent to oil ratio	Number of stages
1.6	14	Infinite
2.0	15	9.4
3.0	20	7.0
4.0	25	5.0
Infinite	Infinite	4.2

Summary

It has been shown that useful fractionations of soyabean and linseed oils can be made, using a selective solvent consisting of 3 to 7 parts of water per 100 parts acetone. Equilibrium diagrams were determined for soybean oil, using 3.5 and 6 parts water per 100 parts acetone, and for linseed, using 5 parts water per 100 parts acetone. Operation of a packed column, 2-in. in diameter, 20 ft. high, showed that consistent H.E.T.S. values were obtained, using the above diagrams, and gave an average H.E.T.S. of 3.1 ft. for ¼-in. berl saddles and 5.9 ft. for ½-in. raschig rings.

The use of the equilibrium diagrams is illustrated by application to a hypothetical separation.

Acknowledgment

The authors wish to acknowledge their indebtedness to G. T. Westbrook for assistance in operating the pilot plant column.

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Isomerization During Hydrogenation. I. Oleic Acid[1]

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IT HAS BEEN well established that partial hydrogenation of monounsaturated fatty acids is accompanied by the formation of several isomeric acids. Moore (9) isolated solid isomers from partially hydrogenated ethyl oleate and found that both geometrical isomerization and migration of double bonds to the 10 and 11 positions had occurred. Also Hilditch and Vidyarthi (7) found that partial hydrogenation of methyl oleate gave *trans* isomers as well as positional isomers with the double bond in the 8 and 10 posi-

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tions. The more recent work of Boelhouwer *et al.* (4) demonstrated that during the hydrogenation of unsaturated acids large amounts of positional isomers are formed with the double bonds in either geometrical configuration. However, in spite of their commercial importance and the considerable amount of experimental work in this area, the mechanisms of the isomerization reactions are not well understood.

Recently two new analytical techniques have become available for the quantitative study of unsaturated fatty acid isomerization. Infrared spectrophotometric inspection of samples (10) permits the determination of *trans*-alkenoic acids or esters in the presence of the *cis* isomers and saturated acids. Oxidative cleavage of the unsaturated fatty acids followed by quantitative separation of the dicarboxylic acids by the partition chromatographic method permits an accurate estimation of positional isomers (6). These two techniques were applied in the present investigation of isomerization during hydrogenation of oleic acid, elaidic acid, and methyl oleate.

Experimental

Oleic acid was prepared from olive oil by saponification at room temperature with 3–5% alcoholic KOH. A series of low temperature fractional crystallizations, followed by distillation, produced a material containing approximately 98% octadecenoic acids. However various preparations differed in 9-octadecenoic acid content; the lowest contained 84% and the highest 98% of this positional isomer. The latter sample was prepared by saponifying the olive oil with 3% KOH. The remaining octadecenoic acids in these samples consisted of the 8- and 10-positional isomers in approximately equal amounts.

Trans-9-octadecenoic acid was prepared by elaidinizing oleic acid with nitrogen oxides at room temperature followed by crystallization at −5° from pentane-hexane. The acid was purified further by three recrystallizations from acetone followed by distillation. The acid had an iodine value of 89.6, the f. p. 42.8°, and a *trans*-9-octadecenoic acid content of 96.5%. The impurities were the *trans*-8- and 10-octadecenoic acids in about equal amounts.

The hydrogenations were carried out in two ways. A Parr medium pressure apparatus was employed, which had the heating jacket replaced by a thermoregulated oil bath. This permitted close temperature control of the hydrogenations. In order to obtain isomerization without extensive hydrogenation, one hydrogenation was carried out with poor hydrogen dispersion by the method described by Feuge *et al.* (5). The catalyst was a commercial preparation of nickel formate which had been reduced in cottonseed oil. No attempt was made to remove the hardened oil from the catalyst before use. Samples were withdrawn periodically during the hydrogenations, filtered, and stored under nitrogen at 0° until analyzed.

Trans isomers were determined by a slight modification of the infrared spectrophotometric method of Swern *et al.* (10). The spectra of carbon disulfide solutions of the samples were obtained with a Baird Associates double beam instrument, and the *trans* content was calculated by the base line method as described by Jackson and Callen (8).

The positional isomers in the partially hydrogenated samples were determined by ozonolysis of the unsaturated acids to yield a mixture of mono- and dicarboxylic acids followed by a quantitative determination of each dicarboxylic acid in the mixture.

Ozone was selected as the oxidizing agent since it was found that considerable degradation of dibasic acids occurred when potassium permanganate in acetone was used as the oxidant. Two- to 3-g. samples of the partially hydrogenated acids were dissolved in 50 ml. of dry methyl acetate. If esters were being analyzed, saponification and isolation of the free fatty acid was carried out prior to oxidation. This prevented any loss of dibasic acids that might occur if saponification were carried out after oxidation. Ozone was passed into the solution until the bromine test for unsaturation was negative. Ten ml. of 30% hydrogen peroxide were added, and the solution was allowed to stand at room temperature for at least 24 hrs. The solvent was removed by distillation, and the sample was dried under vacuum by heating on a steam bath. The mixture of mono- and dicarboxylic acids was dissolved in chloroform in a volumetric flask and diluted to 100 ml. Five-ml. aliquots of this solution were chromatographed by the procedure described by Higuchi *et al.* (6). However it was found that higher pH buffer solutions were necessary to separate the 11- and 10-carbon dibasic acids. Therefore it was necessary to employ two columns for each sample. The first, containing 1 M. citrate buffer at pH 6.8 as the stationary aqueous phase, separated the monocarboxylic acids followed by the 11-, 10-, 9-, and 8-carbon dicarboxylic acids. The second, containing citrate buffer at pH 5.4, separated the 10-, 9-, 8-, and 7-carbon dicarboxylic acids from the other acids. The chloroform-butanol mixtures were added to the chromatographic tube by an automatic device described by Allen and Eggenberger (1), and 7-ml. fractions of eluate were collected by an automatic fraction collector. Each fraction was titrated with 0.03 N alcoholic KOH to a phenolphthalein end-point. The titration plotted against the fraction number resulted in a series of peaks as shown in Figure 1. The area under each peak after subtraction of the blank titration is a measure of the dibasic acid present in the sample. Each dibasic acid was calculated as the mole percent-

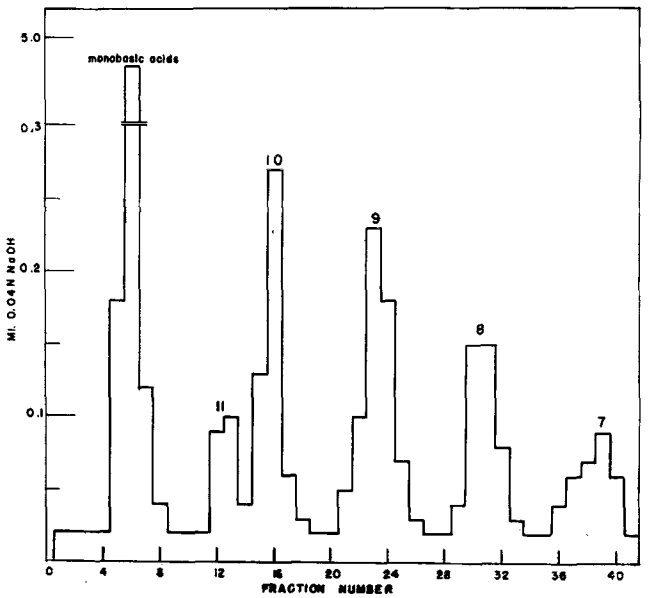


FIG. 1. Partition chomatogram of mixture of acids. Numbers on peaks are chain lengths of the dibasic acids.

age of the total dibasic acids, which gives directly the mole percentage of each positional isomer present in the unsaturated portion of the partially hydrogenated fatty acid.

Results and Discussion

The isomerizations that occurred during the hydrogenation of oleic acid, elaidic acid, and methyl oleate are shown in Figures 2, 3, and 4, respectively. It is evident that as the hydrogenation proceeded, the double bonds in the unsaturated portion of the sample were migrating along the chain as shown by a decrease in the 9-octadecenoic acid and an increase in the 8-, 10-, 7-, and 11-isomers. The amounts of 8- and

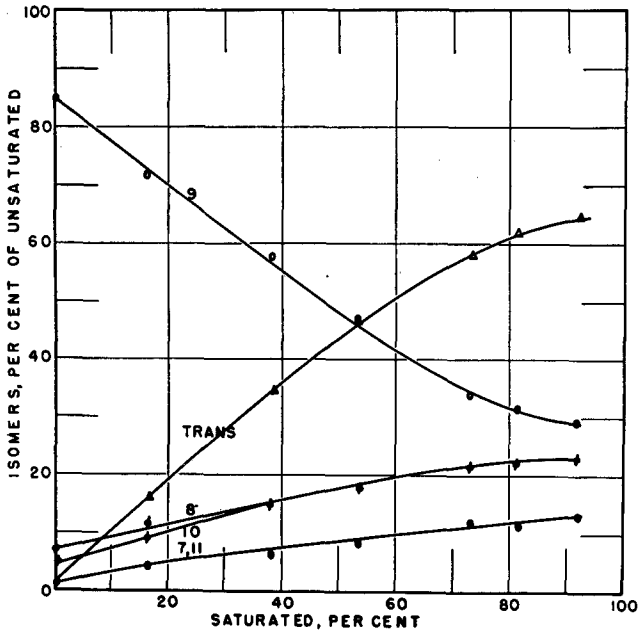


FIG. 2. Isomerization during hydrogenation of oleic acid at 150°, 5 pounds' pressure and 0.25% Ni. Numbers on curves show double bond position.

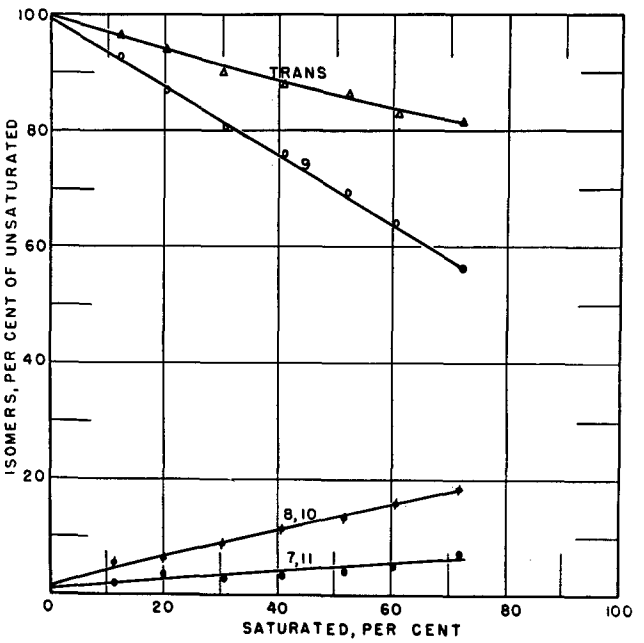


FIG. 3. Isomerization during hydrogenation of elaidic acid at 150°, 5 pounds' pressure and 0.25% Ni. Numbers on curves show double bond positions.

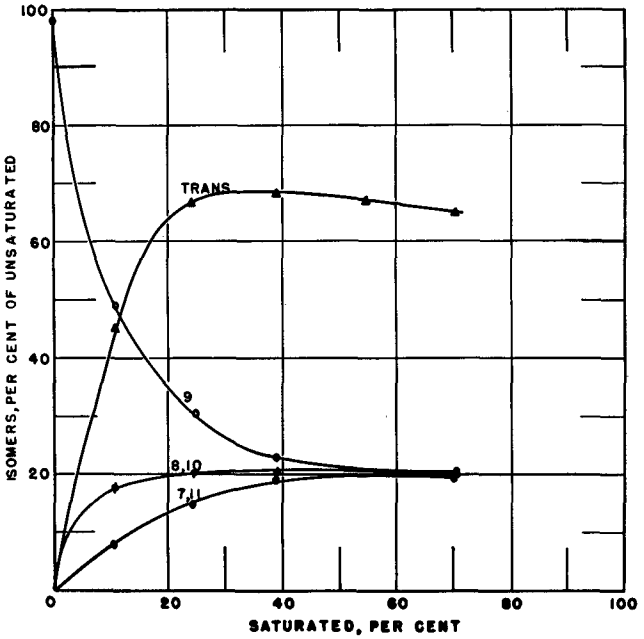
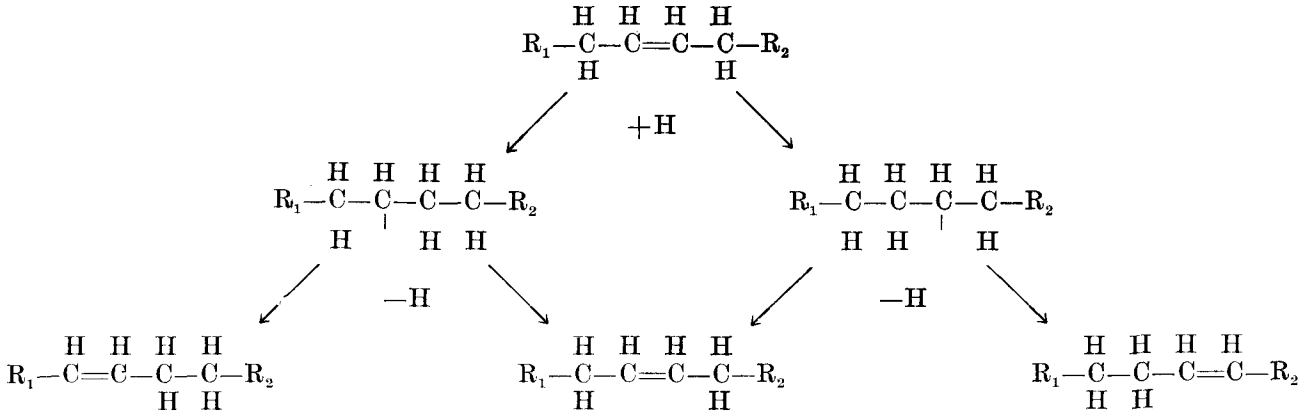


FIG. 4. Isomerization during hydrogenation of methyl oleate at 200°, atm. pressure, 0.25% Ni with poor hydrogen dispersion. Numbers on curves show double bond positions.

10-octadecenoic acids were found to be practically equal, as were the amounts of 7 and 11. This is in contrast to the report by C. Boelhouwer *et al.* (4) to the effect that the double bond tended to migrate away from the alkoxy carbonyl group. It is believed that in this previous work some of the shorter chain dibasic acids were lost in the water phase during the separations after the saponification of the oxidized esters. The subsequent analysis of the remaining dibasic acids would therefore show a higher percentage of longer chain dibasic acids, indicating a shift of the double bond predominantly away from the alkoxy carbonyl.

The extent of positional isomerization at any degree of hydrogenation depends upon the conditions of hydrogenation. For example, oleic acid hydrogenated at 150° and 5 lbs. pressure, to a stearic acid content of 40%, contained 56% of the 9-octadecenoic acid in the unsaturated portion, whereas methyl oleate hydrogenated to the same degree at 200° and atmospheric pressure with very poor hydrogen dispersion contained only 22% of the 9-isomer in the unsaturated portion. Figure 5 shows the extent of positional isomerization as expressed by the ratio of the 9 to the 8 acid as a function of the percentage of 9 present after hydrogenation. The data from the various hydrogenations were found to fall on the same curve, indicating that the same mechanism of isomerization is operating during the hydrogenation of the different materials under different conditions.

Further examination of Figure 5 shows that as the amount of 9 decreases, the amount of 8, or 10 which is not shown but is equal to the 8, increases until the ratio of 9:8 approaches but does not go below 1. This result suggests an equilibrium between the various isomers which may be explained by the addition of a hydrogen atom to one carbon of the double bond followed by elimination of a hydrogen atom to reform a double bond (2). This mechanism is illustrated as follows:



Addition of a hydrogen atom to a double bond may occur at either carbon to form either of two different radicals which has an unsaturated center on either of the two carbons. If a hydrogen atom is then eliminated from a carbon next to the free radical center, a double bond is reformed. However this double bond may be in the original position or in the adjacent position because either of the hydrogens adjacent to the free radical center may be removed. In this way either a positional isomer is formed or the bond in the initial position is regenerated. If this reaction sequence is applied to the 9-octadecenoic acid (oleic acid), the first hydrogenation-dehydrogenation reaction would produce the 8-, 9-, and 10-isomers. The 8-isomer may then react to give the 7, 8, and 9, and similarly the 10 may produce the 11, 10, and 9. If these reactions proceed by first order kinetics, the 8 or 10 acids can never exceed the 9. As the 8 and 10 are produced from the 9, they may also react to produce the 9. Similarly the 7 will always be less or equal to the 8 and the 11 less than the 10. The experimental evidence agrees quite well with this theory.

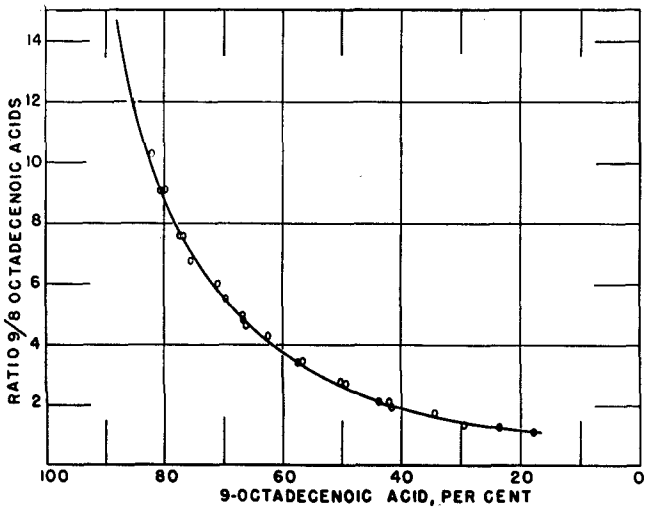


FIG. 5. Relationship of ratio of 9/8-octadecenoic acids to 9-octadecenoic acids present during hydrogenation of octadecenoic acids and esters.

Relationship of Positional and Geometrical Isomerization

The relationship of the geometrical and positional isomerization that occurs during a hydrogenation of oleic acid and methyl oleate is shown by Figure 6 and for elaidic acid by Figure 7. These plots of the percentages of positional *vs.* geometrical isomers show that the amount of the geometrical isomers that are formed during hydrogenation are proportional to the amount of the positional isomers. As shown by Figure 6, if the *cis*-9 isomer is the starting material, the total 9 decreases and 8 (or 10 which is not indicated but is the same as the 8) increases in proportion to the *trans* until the equilibrium point of the *cis-trans* interconversion is reached, *i.e.*, 2:1 *trans-cis*. At this point the ratio of the 9:8 positional isomers is close to one. Similarly Figure 7 shows that the same results are obtained if the *trans*-9-isomer is hydrogenated. The 9 decreases and the 8 increases until the 9:8 ratio is close to one and the *trans:cis* ratio is 2:1. Thus it seems evident that the two types of isomerization take place at the same time and with either configuration of the double bond.

The amount of each positional isomer that is in the *trans* configuration was determined by a separation of the *trans* acids from the *cis* by acetone crystallization, followed by a determination of the positional isomers present in the purified *trans* fraction. The

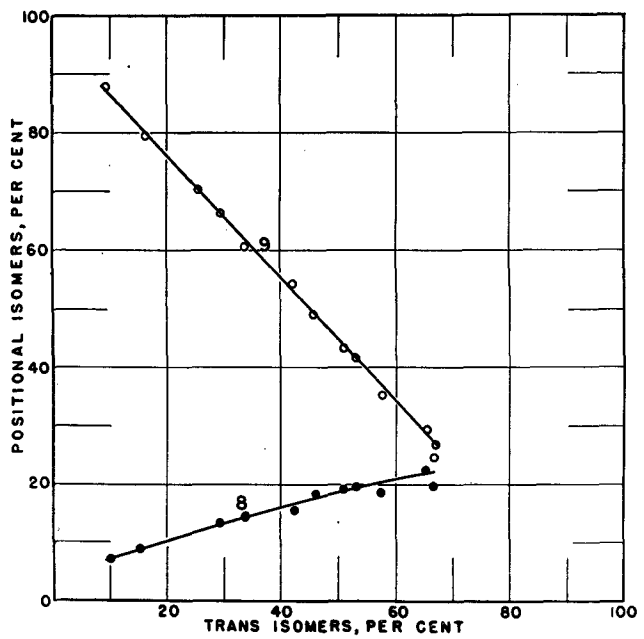


FIG. 6. Relationship of positional isomers and geometrical isomers formed during the hydrogenation of oleic acid and methyl oleate.

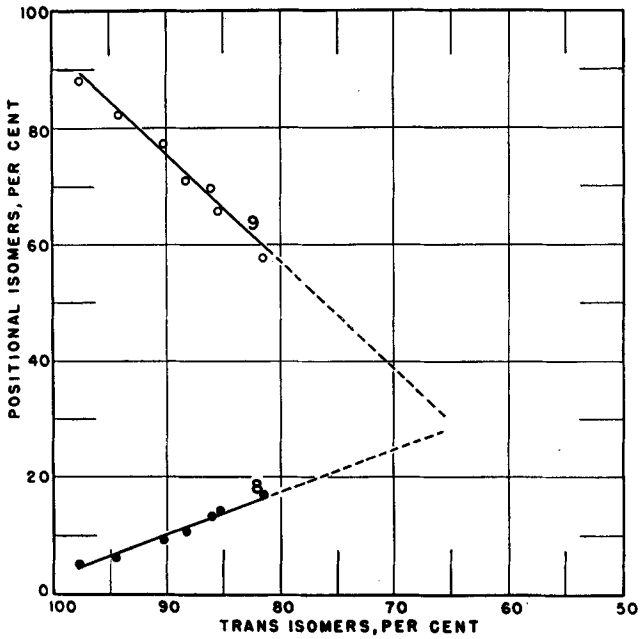


FIG. 7. Relationship of positional isomers to geometrical isomers formed during the hydrogenation of elaidic acid.

mole fraction of each positional isomer present in the pure *trans* multiplied by the total *trans* in the sample shows the amount of each positional isomer having the *trans* configuration. A typical analysis is shown in Table I. The second column of Table I shows the

TABLE I

Unsaturated Fatty Acid Composition of Partially Hydrogenated Oleic Acid

Double Bond Position	Total Unsat. (42.5% Trans) %	100% Trans %	Trans % of Total Unsat.	% Positional Isomer in Trans Form
11	7.0	11.2	4.7	67.2
10	15.7	23.0	9.8	62.5
9	54.5	31.6	13.4	24.6
8	15.8	23.0	9.8	62.0
7	7.0	11.2	4.7	67.2

positional isomers present in the *cis-trans* mixture (42.5% *trans*), the next, the percentage of positional isomers in the pure *trans*. The fourth column shows the percentage of each isomer in the total sample that was *trans* (42.5%). The fifth column shows the percentage of each positional isomer in the *trans* form, $\frac{\text{column four}}{\text{column two}} \times 100$. The values in this column suggest that each new positional isomer is composed of *cis-trans* in a 1:2 equilibrium ratio.

The analysis of several samples which contained different amounts of *trans* revealed that the pure *trans* contained positional isomers in about the same ratio as shown in column three, Table I. Also the percentage of the positional isomers in the pure *trans* and in the mixed *cis-trans* at the point at which *cis-trans* equilibrium is reached were found to be the same. This indicates that, at the point at which the equilibrium is attained, each positional isomer, including the 9-isomer, is composed of a 1:2 mixture of *cis* and *trans*. The results of the analysis for the percentage of *trans* 9 that is formed during hydrogenation of oleic acid is shown in Figure 8. This shows that as the hydrogenation and isomerization proceeds and the total 9-isomer decreases, the percentage of *trans*-9 increases to a maximum of 2:1 *trans-cis*. If the half hydrogenation-dehydrogenation concept is applied to explain the simultaneous occurrence of both types of isomerization, it is evident that after

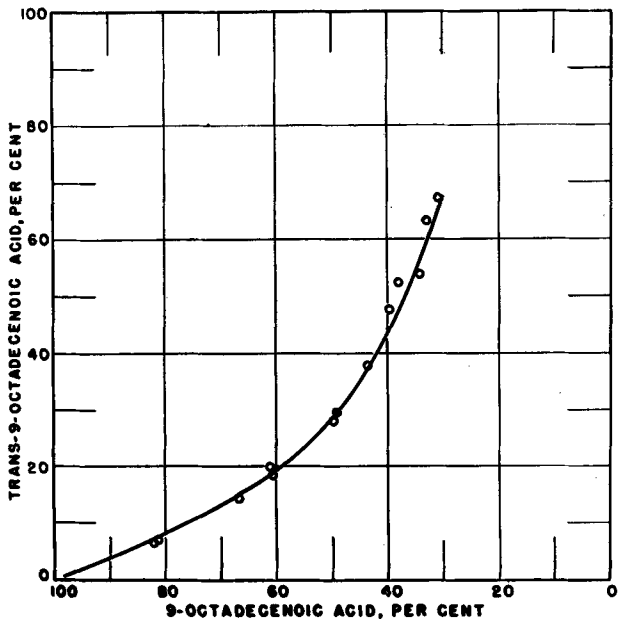


FIG. 8. Trans-9-octadecenoic acid formation during the hydrogenation of oleic acid.

the hydrogen atom is added to one carbon of the double bond, a system with free rotation is formed. Subsequent removal of a hydrogen atom will form the double bond in either the *cis* or the *trans* forms. If the theory of five transitional forms as postulated by Blekkingh (3) is applied, the new positional isomers are composed of *trans-cis* in a 2:1 ratio. However, since the bonds may be reformed in the original position, the same ratio of *trans* is also formed in the original position. Therefore *cis-trans* equilibrium of the bond in the original position, the 9 position in oleic acid, is not reached until the point at which as much 9 is being formed from the 8 and 10 as is being displaced to the 8 and 10 positions. However further hydrogenation accompanied by isomerization will not change the *cis-trans* ratio because each positional isomer is at *cis-trans* equilibrium but it will cause the bonds to migrate further along the chain with the consequence that the amounts of positional isomers will become more nearly equal. This is illustrated in Figure 4 in which the isomerization was carried far past the point of equilibrium. Although not shown, there was considerable 12- and 6-octadecenoic acids in the most saturated sample of this hydrogenation. The original geometrical configuration of the bond which goes through the hydrogenation-dehydrogenation sequence does not determine the new configuration since the bonds that are reformed are always composed of the 2:1 *trans-cis* mixture. This is evident from the comparison of the isomerizations of oleic and elaidic acids. Also the data support the view of Feuge *et al.* (5) that isomerization during hydrogenation does result in a 2:1 *trans-cis* equilibrium and that all

geometric and positional isomers react with equal ease. If the probabilities of reaction of all the isomers were not equal, the theoretical equilibrium ratio proposed by Blekkingh (3) would seldom, if ever, be attained under varied conditions of temperature, catalyst concentration, and dispersion of hydrogen.

The data also indicate that the concentration of hydrogen in the oil and therefore on the catalyst surface influences the comparative rates of saturation and isomerization of the double bond. For example, the hydrogenation shown in Figure 2, carried out under pressure with efficient agitation, thus producing a high concentration of hydrogen on the catalyst, reached isomerization equilibrium just before complete saturation occurred. However Figure 4 shows that in the hydrogenation in which the hydrogen concentration on the catalyst was low, isomerization occurred at a much greater rate than hydrogenation. This can be explained by the hydrogenation-dehydrogenation concept. If there is a very high concentration of hydrogen on the catalyst surface, the chance of a hydrogen being taken off a half-hydrogenated molecule before another is added is less than in a system in which the concentration of hydrogen on the catalyst is low. Therefore, under conditions in which all of the active catalyst is kept saturated with hydrogen, no isomerization would occur. But, also, without some hydrogenation no isomerization will occur. Therefore it is believed that an exchange reaction between the catalyst and the unsaturated material takes place as the half-hydrogenation-dehydrogenation concept would indicate.

Summary

It was found that during the hydrogenation of octadecenoic acids, migration of the double bonds takes place equally in each direction. The positional isomers that are formed are composed of the 1:2 equilibrium mixture of *cis* and *trans*. A partial hydrogenation-dehydrogenation theory may be applied to explain the simultaneous formation of both positional and geometrical isomers.

Acknowledgment

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The Mbocayá Palm: An Economic Oil Plant of Paraguay

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THE MBOCAYA PALM (*Acrocomia totai* Mart.) is one of about 25 species of spiny palms belonging to the genus *Acrocomia*, which abounds from the West Indies and Mexico to Paraguay and Argentina and encompasses a climatic range from tropical to temperate. From the economic and utilitarian point of view the mbocayá is of greater importance to Paraguay than any other of the 10 or more species of indigenous palms. It is closely related to, and difficultly distinguishable from *A. sclerocarpa* Mart., which is said to occur over a wide area of Brazil. It has been referred to in the literature by a variety of common names (Paraguay: mbocayá, mbocayá Cayiete; Bolivia: cayara, totai; Brazil: grou-grou, mbocayá-ubá, mocaje, mucujá, noz do Paraguay; elsewhere: Paraguay palm; totai palm). Unfortunately mbocayá, or variants thereof, has been applied to at least five and perhaps more species of palms (19). In Paraguay the palm is frequently referred to as coco, cocotero-paraguayo, and occasionally as coquito del Paraguay. These names are unfortunate because the palm and its fruit are totally dissimilar to the true coconut palm *(Cocus nucifera)*.

Because of the confusion of names and identities of the *Acrocomias* some of the previously reported chemical analyses of the fruit and oil of *A. totai* cannot be relied on as they refer to *A. sclerocarpa* or some other species.[2] In 1920 Junelle (12) commented on this confusion as follows: "et la confusion est facilité par le fait que les fruits de tous ces *Acrocomia* sont sphériques et que, d'autre part, tous ces *Acrocomia* portent, en Amérique du Sud, le nom indigéne de *mocaja* ou *mbocaya.*" This confusion still persists as reference to the latest monograph (8) on fats and oils reveals. *A. sclerocarpa* of Brazil was described by Martins in 1824 and *A. totai* of Paraguay and Bolivia in 1847, and the genus *Acrocomia* was the subject of a monograph by Bailey (3) in 1941.

The mbocayá palm has many uses (1, 19, 22), most of which are not germane to the present report, and their mention is therefore omitted here. They are however discussed in another article by this author (16) together with much additional information concerning this palm.

Although almost all parts of the mbocayá palm are important in the rural economy of Paraguay, it is the

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[2] The analysis reported for Paraguay kernels (*Acrocomia* sp.) by Bray and Elliott (6) almost certainly pertains to *A. totai*.