shortenings from the standpoint of reversion, both organoleptically and by carbonyl index determinations. Since the shortenings were deodorized and stabilized, they were substantially bland in taste and odor. They showed no development of reversion odors or flavors after heating in an oven at 60°C. for six days. Their original carbonyl index values of from 45 to 55 showed no increase after this oven-aging.

To establish whether or not the hydrogenation and stabilization treatments were responsible for protecting these shortenings from reversion, some shortenings in which these treatments were omitted were tested organoleptically and by the determination of carbonyl index values after oven-aging. Samples prepared similarly, but not hydrogenated, had detectable odors of reversion after oven-aging, and their carbonyl index was raised to 66. When the antioxidant was omitted from this type of shortening as well as the hydrogenation, the original carbonyl index value of 50 rose to 117 after oven-aging, and more pronounced reversion could be detected organoleptically. These experiments indicated that slight hydrogenation and the use of antioxidants are effective in stabilizing shortenings containing tallow against reversion.

Summary

Experimental shortenings were prepared from various mixtures of tallow and cottonseed oil. Three series of shortenings were produced by somewhat different procedures: a) mixtures of tallow and cottonseed oil were hydrogenated and then catalytically rearranged; b) mixtures of hydrogenated tallow and cottonseed oil were rearranged; and c) mixtures of hydrogenated tallow and cottonseed oil were rearranged in the presence of 0.43% glycerine.

Certain combinations and treatments of tallow and cottonseed oil produced shortenings which compared reasonably well with standard vegetable shortenings.

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Isomerization During Hydrogenation. III. Linoleic Acid

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IT HAS BEEN WELL ESTABLISHED that, during the hydrogenation of linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid) to a monoene, the product formed is a mixture of isomeric acids (7). It has been shown that the mixture is composed of not only the *cis* and *trans* geometrical isomers but also positional isomers which may be formed by saturation of either of the double bonds in the chain and also by migration of the bonds during the hydrogenation reaction (5).

The data presented in the first report in this series, on octadecenoic acids (3), showed that both geometrical and positional isomerizations occurred at the same time by a half hydrogenation-dehydrogenation reaction.

When the reaction was investigated further by the hydrogenation of a conjugated diene system (*cis*-10, *cis*-12-octadecadienoic acid), it was found that hydrogenation took place with equal ease in the 1,2, 1,4, and 3,4 positions of the diene system (2).

The present extension of the study is concerned with the diene system whose double bonds are separated by a methylene group.

Experimental

Linoleic acid and methyl linoleate were prepared from crude safflower-seed oil by saponification or ester interchange followed by low-temperature crystallization and separation of remaining monounsaturated acids or esters by treatment with urea as described by Swern (11). The acid (and ester) prepared in this way is essentially pure (over 95%) when saponification of the oil is carried out in dilute (below 5%) alcoholic KOH at room temperature for 24 hrs. However, even with the most careful handling, the linoleic acid always contained a small percentage of an isomer with a double bond at the 8 position. This isomer is believed to be present in the original safflower-seed oil since the ester, in which only a catalytic amount of alkali was present during the ester interchange, contained the 8 isomer. Also the isomer was not detected in cottonseed oil treated in the same manner. The acid and ester were prepared by crystallization instead of by bromination-debromination (9) since the debrominated material contained large amounts of positional and geometric isomers and less than 75% of the 9,12-octadecadienoic acid.

Hydrogenations under pressure were carried out in a Parr medium-pressure hydrogenation apparatus. Hydrogenations at atmospheric pressure with poor hydrogen dispersion were performed as described previously (3).

The catalyst was nickel formate reduced in cottonseed oil. No attempt was made to remove saturated material before use.

The percentage of isolated *trans* isomers was determined as described in the first paper of this series (3).

The fatty-acid composition of partially hydrogenated products was determined by A.O.C.S. methods Cd 1-25 and Cd 7-48 (rev. May 1951) after correction of the iodine value for conjugated double bonds as suggested by Feuge *et al.* (7).

Positional isomers were determined by chromatographic separation of the dibasic acids produced by

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oxidative scission (3). It was necessary to use a silicic acid column mixed with citrate buffer of pH 7.8 to separate the acids, which came out in the order monobasic acids, then 12-, 11-, 10-, and 9-carbon dibasic acids.

Since only one double bond may be located by dibasic-acid analysis, one series of samples was subjected to monobasic-acid analysis in order to locate the second double bond. The mixture of partially hydrogenated fatty acids was ozonized, the ozonide was decomposed with aqueous H_2O_2 in the usual manner, and the solvent was removed by distillation on a steam bath. The mixture of mono- and dibasic acids was dried by azeotropic distillation with benzene, the dried sample was dissolved in chloroform, and aliquots were used for chromatographic analysis. The dibasic acids were determined as described, and the monobasic acids were separated on a column of silicic acid mixed with 2*N* glycine that had been brought to the proper pH with NaOH (6). It was necessary to employ two columns, one using glycine buffer at pH 10.15, which separated the 9-, 8-, and 7-carbon monobasic acids, and one buffered at pH 9.4, which separated the 8-, 7-, and 6-carbon monobasic acids. The positions of the double bonds were calculated from the mole percentage of mono- and dibasic acids as described in a previous publication (1).

Results and Discussion

The fatty-acid compositions of the samples obtained during the several hydrogenations are shown in Figures 1, 2, and 3. Figure 1 shows the course of hydrogenation of linoleic acid at 5 lbs. pressure and 120°, with 0.5% Ni catalyst, under efficient agitation. This hydrogenation was somewhat non-selective as shown by the formation of considerable saturated material before all the dienoic acid had disappeared. In contrast, Figure 2 shows very selective hydrogenation. This reaction was conducted at 5 lbs. pressure and 180°, with 0.5% Ni catalyst, under good agitation. Thus a 60° increase in reaction temperature permitted almost complete hydrogenation of diene to monoene before any completely saturated material was formed. The hydrogenation of methyl linoleate (Figure 3) at 220°, 0.5% Ni, and atmospheric pressure, with poor hydrogen dispersion, also showed very good selectivity. This is to be expected as it has been shown (4) that selectivity is increased by higher temperatures and lower pressures.

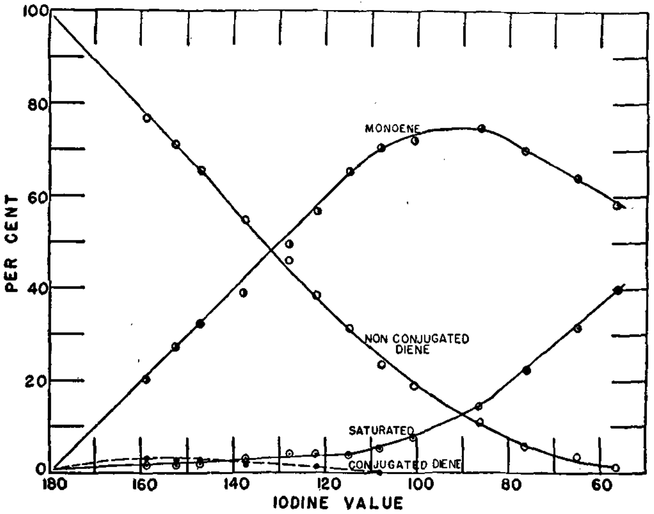


FIG. 1. Fatty acid composition of hydrogenated linoleic acid. Hydrogenated at 120°, 5 lbs. press., 0.5% Ni catalyst with efficient agitation.

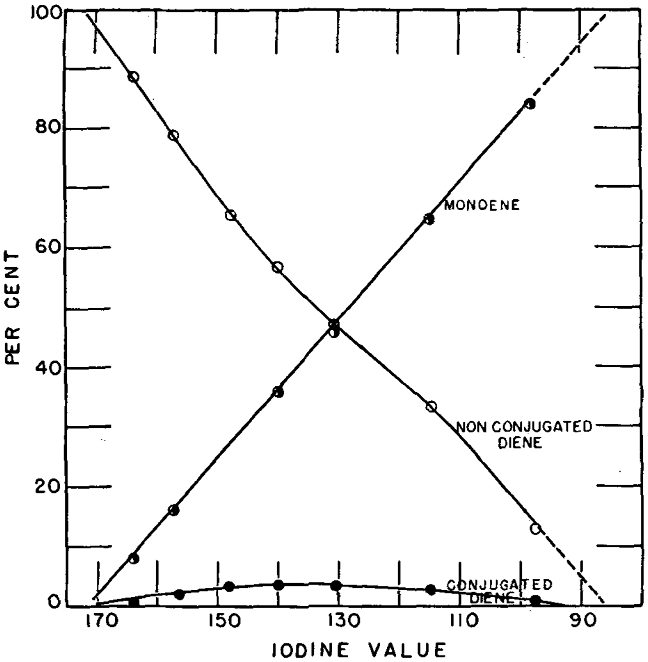


FIG. 2. Fatty acid composition of hydrogenated linoleic acid. Hydrogenated at 180°, 5 lbs. press., 0.5% Ni catalyst with efficient agitation.

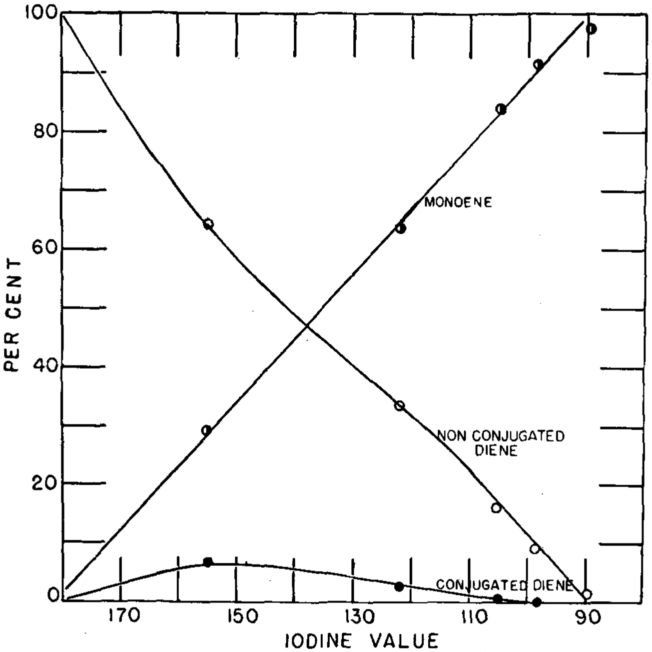


FIG. 3. Fatty acid composition of hydrogenated methyl linoleate. Hydrogenated at 220°, atm. press., 0.5% Ni catalyst with poor hydrogen dispersion.

Formation of Positional Isomers. The positional isomers formed during the hydrogenations are shown in Figures 4, 5, and 6. The numbers of the curves designate the position of the double bond nearer the carboxyl group if more than one double bond is present. For example, at 100% diene content, where the figure shows 100% 9 isomer, there are actually double

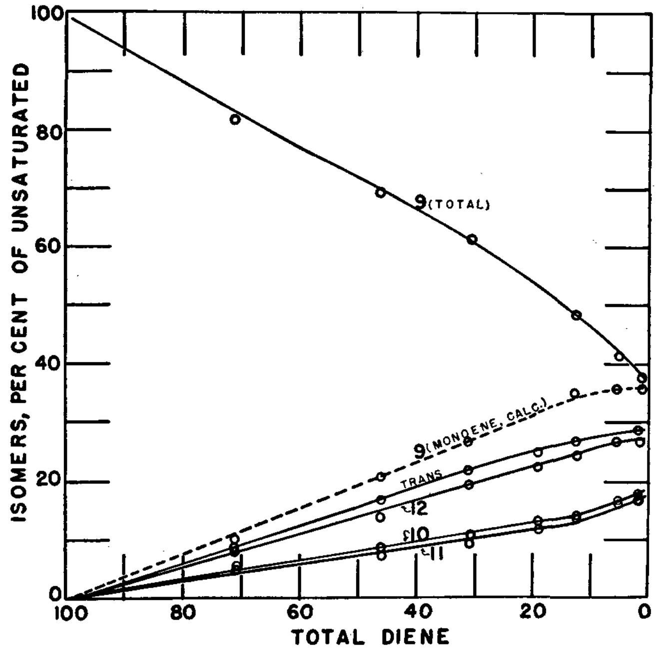


Fig. 4. Isomerization during hydrogenation of linoleic acid at 120°, 5 lbs. press., 0.5% Ni. Numbers on curves indicate double bond positions.

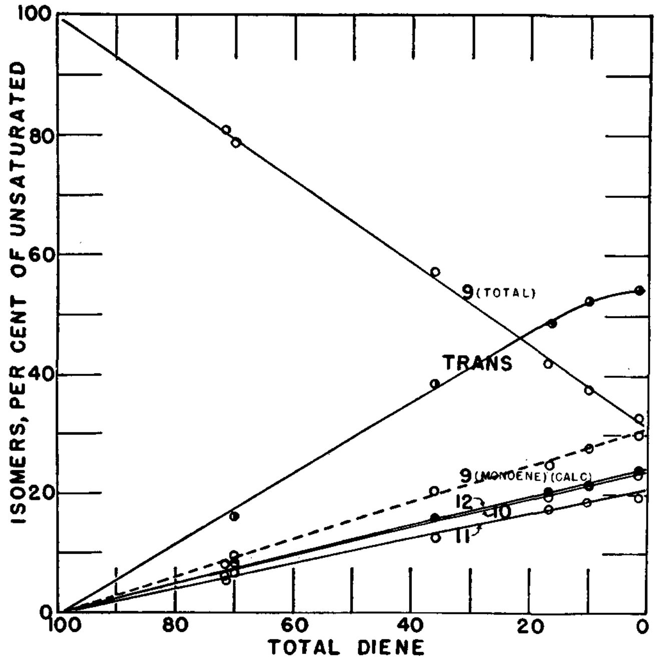


Fig. 5. Isomerization during hydrogenation of linoleic acid at 180°, 5 lbs. press., 0.5% Ni. Numbers on curves indicate double bond positions.

bonds at the 9 and 12 positions. As shown on the curves, as hydrogenation proceeds, there is a decrease in the total 9 isomer and an increase in the 10, 11, and 12 isomers. An estimation of 9 monoene may be made by subtracting the 9,12 diene determined by another method from the total 9. Also, if it is assumed that the 10, 11, and 12 isomers are all monoenes, the difference between their sum and the total monoene content will be the 9 monoene. The 9 monoene contents calculated by both methods are the same within experimental error. Calculated 9 monoene contents are shown on Fgures 4 and 5, whereas Figure 6 presents the 9 monoene content determined by the analysis of the monobasic acids produced by oxidative scission of partially hydrogenated methyl linoleate.

The question as to which of the two double bonds in linoleic acid is hydrogenated first has received some attention. It is generally believed that the bond farther from the carboxyl group has the greater reactivity. Suzuki and Inoue (10) found that when 1 mole of hydrogen was added to 1 mole of methyl linoleate, the oleate produced had the remaining bond in the 9 position. Examination of Figures 4 and 5 shows that more 9 than 12 monoene was produced as hydrogenation proceeded. Therefore the 12 bond in linoleic acid is hydrogenated faster than the 9 bond. In the third experiment (Figure 6) the two bonds are saturated at about the same rate. This change in relative reactivity of the two bonds could result from the differences in the conditions of hydrogenation, *i.e.*, higher temperature, lower pressure, poor hydrogen dispersion, or from the use of the ester instead of the free acid. However it is believed that esterification would have very little effect on any directing influence attributable to a carboxyl group seven carbons away from the reaction site. The drastic conditions of the hydrogenation of methyl linoleate are thought to have more influence on the reactivities of the two bonds. More investigation of this problem is needed before a clear explanation can be made.

Migration of the double bonds into the 10 and 11 positions during hydrogenation is shown in Figures 4, 5, and 6. During the less selective hydrogenation shown in Figure 4, the amounts of 10 and 11 octadecenoic acids formed were less than the 9 or 12, with slightly more 10 than 11. However, during the very selective hydrogenation shown in Figure 5, the amounts of 10 and 11 were practically equal to the 12 but did not exceed the 12. Even more drastic conditions of hydrogenation, as shown in Figure 6, did not increase the amounts of the 10 or 11 isomer above the 12.

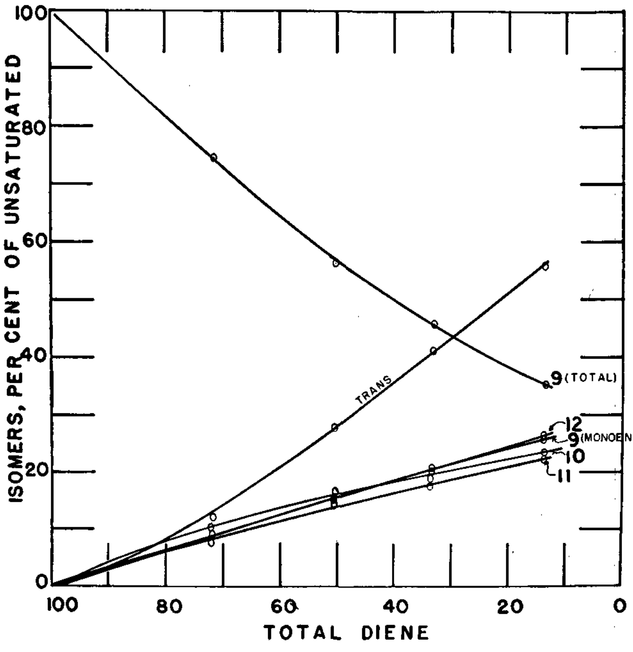
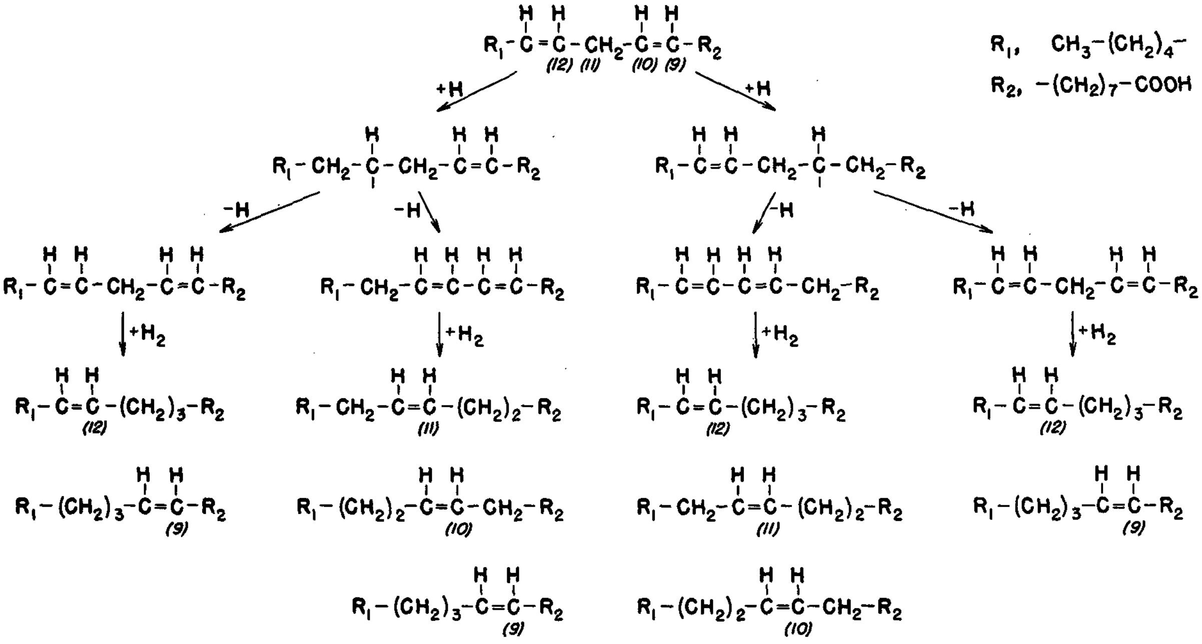


Fig. 6. Isomerization during hydrogenation of methyl linoleate at 220°, atm. press., 0.5% Ni with poor hydrogen dispersion. Numbers on curves show double bond positions.

From this it appears that the last two hydrogenations were operating under some sort of equilibrium conditions. The formation of appreciable amounts of conjugated diene during hydrogenation lends support to the view that the methylene-interrupted diene system first shifts to a conjugated system before hydrogenation takes place. This would account for the presence of the bonds at the 10 and 11 positions since the 9,12 system could produce both 9,11 and 10,12 conjugated dienes. Hydrogenation of these conjugated bonds would then produce the isomeric monoenoic acids found. It has been shown however (2) that during the hydrogenation of a conjugated diene system, the hydrogen adds 1,2, 1,4, and 3,4 with equal ease. Thus, if the normal linoleic (9,12) produced only 9,11 and 10,12 conjugated diene in equal amounts in the first step of the reaction, addition of hydrogen to the 9,11 would produce the 9, the 10, and the 11 monoenes in equal amounts while the 10,12 would give the 10, the 11, and the 12 in equal amounts. Therefore determination of the positional isomers would show twice as much 10 or 11 as 9 or 12. Since hydrogenation even under drastic conditions did not show this ratio of positionally isomeric monoenes, it must be concluded that all the pentadiene system did not shift to a conjugated diene before hydrogenation. From the approximately equal amounts of positional isomers found during a selective hydrogenation, only roughly two-thirds of the diene shifts to a conjugated system.

The isomerization may be explained by the half hydrogenation-dehydrogenation mechanism similar to the reaction sequence that is believed to operate during the hydrogenation of monoenes. The reactions may be shown as follows:



In these reaction sequences the first atom of hydrogen adds to the 9 or 13 position in the pentadiene system. Removal of a hydrogen atom can produce two isomeric dienes since either of the hydrogens adjacent to the free-radical center may be removed. This process will produce the original pentadiene plus a conjugated diene. Since either end of the pentadiene may add a hydrogen atom, there will be two different conjugated dienes produced. Addition of one mole of hydrogen to this mixture will then produce the isomeric monoenes found. It is believed that the hydrogen atom adds to the end of the pentadiene system because there was very little increase in 8 or 13 monoenes during the hydrogenation and isomerization reactions. Although a small increase in the 8 monoene was found, this is believed to be due to a minor side reaction and the main reaction sequence takes place as indicated.

In hydrogenation under non-selective conditions (Figure 4) the rate of hydrogenation is greater than the rate of isomerization. This difference in rate is believed to be due to the concentration of hydrogen at the catalyst surface. If the catalyst maintains a high concentration of hydrogen as a result of high pressure, low reaction temperature, and low catalyst concentration, the rate of hydrogenation should be higher than the rate of isomerization; and since less of the more reactive conjugated dienes are produced, the reaction will be less selective. Conversely high reaction temperature, low pressure, and high catalyst concentration will decrease the hydrogen concentration on the catalyst and thus increase the ratio of isomerization to hydrogenation, which will increase selectivity. This hypothesis is in agreement with the view of Hilditch (8) that the selectivity of hydrogenation is a function of the active methylene group. If there are two or more methylene groups between the double bonds, it would be necessary for the molecule to go through several isomerization reactions to form a reactive conjugated diene. This would be very unlikely as the molecule would probably be hydrogenated completely before the several isomerization reactions could occur.

Formation of trans Isomers. During hydrogenation some isomers containing isolated *trans* double bonds are formed. The amount of these isomers is shown in Figures 4, 5, and 6. Non-selective hydrogenation results in a rather low amount of *trans* whereas selective hydrogenation produces large amounts. Thus it can be deduced that the formation of *trans* isomers depends on the reaction conditions.

The positional isomers in the *trans* form were determined after separation of the *trans* acids from

TABLE I

Monoenoic Fatty Acid Composition of Partially Hydrogenated Linoleic Acid

Double Bond Position	% Total Unsaturated	% *Trans* Fraction	% Total Unsaturated in *Trans* form	% Positional Isomer in *Trans* form
Non-Selective Hydrogenation (120°, 5 lbs. pressure, 0.5% Ni)				
	(33% *Trans*)			
12	28.6	22.0	7.3	25.6
11	14.6	25.1	8.4	57.5
10	16.5	32.1	10.7	65.0
9	40.3	20.8	7.0	17.4
Selective Hydrogenation (220°, atm. pressure, 0.5% Ni, poor H_2 dispersion)				
	(55.2% *Trans*)			
12	25.1	22.6	12.5	50.0
11	19.8	24.0	13.3	67.2
10	23.1	31.0	17.1	74.0
9	32.0	22.4	12.3	38.7

the *cis* by acetone crystallization. The mole fraction of each positional isomer present in the pure *trans* multiplied by the percentage of *trans* in the original sample gives the percentage of each positional isomer in the total sample in the *trans* form. The results of the analyses of a non-selective and a selective hydrogenation are shown in the table.

Inspection of column 3 reveals that although the two samples contain very different amounts of total *trans*, the amounts of a positional isomer in the *trans* portions of the two samples are equal within experimental error.

The last column, which shows the percentage of each positional isomer in the *trans* form

$$\left(\frac{\text{Column four}}{\text{Column two}} \times 100\right)$$

supports the view that half hydrogenation-dehydrogenation of a double bond during hydrogenation results in a *trans,cis* mixture of the new double bonds (3) and in geometrical isomerization of the double bonds in the original positions as well. Comparison of the *trans* contents of the 9 and 12 monoenes of the two samples shows that selective hydrogenation produces more 9 and 12 *trans* monoenes than does non-selective hydrogenation. Since positional isomerization under selective conditions is greater, it follows that geometrical isomerization of the bonds in the original positions is also greater under such conditions. This relationship of positional and geometrical isomerization follows from the half hydrogenation-dehydrogenation concept. When a hydrogen atom adds to a pentadiene system with subsequent removal of a hydrogen to reform a diene, three positionally isomeric dienes are possible. Each of the two conjugated isomers may be in two geometrical forms, whereas the nonconjugated isomer may appear in one of three geometrical forms. For example, if hydrogen adds to the 9 position in linoleic acid and hydrogen is then removed, there can be formed the original *cis*-9,*cis*-12, the *trans*-9,*cis*-12, and the two conjugated isomers, *cis*-10,*cis*-12, and *trans*-10, *cis*-12. When the other end of the original pentadiene system goes through this reaction sequence, the bonds at the 12 and 11 positions may be converted to the *trans* forms in the same way.

Reference to the table shows more *trans*-12 than *trans*-9 in both samples. This is probably due to the greater reactivity of the 12 bond. Since this bond is hydrogenated faster than the 9 bond, it seems reasonable that the rate of isomerization might also be greater.

The presence of larger percentages of *trans*-10 and -11 than of *trans*-9 and -12 is due to the formation of *trans*-10 and -11 isomers in two ways. In the first place, half hydrogenation-dehydrogenation forms not only the two *cis,cis* conjugated dienes, 9,11 and 10,12, but also the two conjugated dienes in which the double bonds that have migrated are *trans*, i.e., *cis*-9, *trans*-11, and *trans*-10,*cis*-12. In the second place, it has been shown (2) that in the hydrogenation of a conjugated diene (which results in the formation of equal amounts of 3 monoenes) the 1,4 addition forms a *trans* bond. For example, hydrogenation of a *cis*-9, *cis*-11 diene produces the three monoenes *cis*-9, *trans*-10, and *cis*-11, and hydrogenation of a *cis*-10,*cis*-12 diene forms *cis*-10, *trans*-11, and *cis*-12 monoenes. Combinations of these reactions must lead to larger amounts of *trans*-10 and -11. The larger percentage of *trans*-10 than of -11 may be explained by the greater reactivity of the 12 bond, which results in the formation of larger amounts of 9,11 diene and therefore more *trans*-10 monoene.

Summary

The isomerization that takes place during the catalytic hydrogenation of linoleic acid and methyl linoleate produces *cis* and *trans* 9, 10, 11, and 12 monoenes. The double bond at the 12 position appears to hydrogenate slightly faster than that in the 9 position. More octadecenoic acids with double bonds at the 10 or 11 positions are produced during a selective (high temperature, low pressure) hydrogenation than during a non-selective process.

Although the degree of selectivity of the hydrogenation is determined by the amount of isomerization of the original pentadiene system to a conjugated diene, only part of the methylene-interrupted diene goes through this type of isomerization even during a highly selective hydrogenation.

The half hydrogenation-dehydrogenation reaction mechanism is applied to explain the simultaneous positional and geometrical isomerizations.

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