Positional Isomers Formed During the Hydrogenation of Methyl Linoleate Under Various Conditions[1]

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THE MIGRATION of double bonds during the hydrogenation of unsaturated fatty acids and their derivatives has been the subject of a number of investigations during the last 40 or more years; though only within the last several years have suitable methods become available for determining quantitatively the extent of this migration. Boelhouwer *et al.* (4) determined the extent of this migration of the double bonds in methyl esters of several unsaturated fatty acids on hydrogenation at about 180°C. with a supported nickel catalyst. Later Knegtel *et al.* (9), using a more accurate method of analysis, determined the positions of the double bonds in progressively hydrogenated samples of methyl oleate. Allen and Kiess (1, 2) determined the extent of migration of double bonds in hydrogenated samples of oleic and linoleic acids and their methyl esters. The latter investigators used only one set of hydrogenation conditions for each sample except one; the two different temperatures were used for linoleic acid. Apparently the only investigation of the effect of the operating conditions on the migration of double bonds was conducted by Chahine *et al.* (5), using cottonseed oil.

The purpose of the present investigation was to obtain data on the shift of double bonds during the catalytic hydrogenation of methyl linoleate under conditions which have been in common use. In this investigation a single sample of methyl linoleate was used. The operating conditions varied with temperature, rate of hydrogen dispersion, type of catalyst, and catalyst concentration.

Experimental

Materials. The methyl linoleate was prepared from safflower oil obtained from the Chemurgy Division of the University of Nebraska. The oil had an iodine value of 144.0 and a free fatty acid content of 0.58% as oleic.

Mixed fatty acids were prepared from the oil by saponifying 2,000 g. in 3,000 ml. of a 50% ethanol-in-water solution containing a 10% excess of sodium hydroxide. After about 1 hr. at 75°C. the solution was diluted with 2,500 ml. of water and acidulated with dilute hydrochloric acid. The mixed fatty acids which separated were washed with water and dried.

Linoleic acid was separated from the mixed fatty acids of safflower oil by a modification of the urea complex precipitation method of Swern and Parker (11). Briefly the mixed acids were dissolved with 1.6 times their weight of urea in 4 volumes (based on the acids) of boiling absolute methanol. The hot solution was cooled slowly to room temperature and then stored over-night at 5–7°C. The following day the solution was filtered, and the linoleic acid was recovered from the filtrate. The yield was 525.1 g.

To obtain the methyl linoleate the linoleic acid was dissolved in 2,642 ml. of absolute methanol, 14.3 ml. of sulfuric acid were added, and the mixture was refluxed for 2 hrs. The methyl linoleate was extracted with petroleum ether, washed with water, dried, and stripped with nitrogen to remove the solvent. The methyl linoleate was fractionally distilled to obtain approximately 394 g. of finished product having an iodine value of 169.5 (theoretical, 172.4). This iodine value corresponds to a purity of 96.6%, assuming the impurity to be methyl oleate.

The nickel catalyst, obtained from the Girdler Company,[3] was of the supported type prepared by electrolytic precipitation and dry reduction. The hardened oil in which the catalyst was suspended was replaced with methyl linoleate just before each hydrogenation.

The sulfur-poisoned nickel catalyst was prepared by a procedure devised by Ziels and Schmidt (13). Five grams of sulfur and 500 g. of cottonseed oil were heated and mixed for 2 hrs. at 95°C., followed by another 2 hrs. of heating and mixing under nitrogen at 180°C. Nine grams of the sulfurated oil were mixed with 500 g. of fresh cottonseed oil and 25 g. of nickel. The mixture was hydrogenated to an iodine value of 86. The sulfur-poisoned catalyst then was removed by filtration and used to hydrogenate the methyl linoleate.

The other catalysts used were 10% palladium supported on carbon and platinum dioxide. Both were obtained from Baker and Company Inc.

Hydrogenation Apparatus and Procedure. The hydrogenations were carried out in a glass vessel shaped like a test tube (28 mm. in diameter by 200 mm. long) and fitted at the upper end with a 29/42 standard taper joint. The outer part of the joint, which formed the head of the hydrogenation vessel, was fitted with hydrogen inlet and outlet tubes and a thermocouple well. The hydrogen inlet and thermocouple tubes extended to near the bottom of the hydrogenation vessel. The rate of gas dispersion was varied by the use of two types of hydrogen inlet tubes. One was equipped with a small, flat, fritted glass tip (high rate of dispersion) while the tip of the other was drawn down to a relatively small diameter (low rate of dispersion).

The sample was heated by use of an electric heating mantle. Temperature control to ± 1°C. was achieved by regulating the current to the mantle and raising the vessel partly out of or lowering it into the mantle.

Hydrogen was passed through the sample of methyl linoleate at a rate of approximately 425 ml. per minute. The unabsorbed hydrogen was recycled by means of a Sigma[3] pump and suitable connections and by-

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[3] It is not the policy of the Department to recommend or endorse a product of one firm over similar products manufactured by others.

TABLE I
Operational and Analytical Data on the Hydrogenation of Methyl Linoleate

Run No.	Hydrogenation conditions				Hydro. time, min.	Iodine value	*Trans* isomers, wt.%	Composition of dicarboxylic acids obtained on oxidation of acyl groups, mol. %								
	Temp., °C.	Catalyst		Hydrogen dispersion rate				C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
		Conc., %	Type													
1	170	0.2	Ni	High	41	80.5	37.1	4.7	8.6	6.9	15.8	20.2	14.8	14.6	9.4	5.0
2	200	0.2	Ni	High	38	79.1	40.3	5.6	7.9	10.8	12.0	19.0	14.6	12.9	11.0	6.1
3	170	0.4	Ni	High	36	81.0	39.0	8.2	9.5	10.5	10.6	26.3	11.2	9.7	10.6	3.4
4	170	0.2	Ni	Low	80	80.4	38.1	5.5	7.4	8.9	13.2	24.6	14.1	9.7	10.2	6.4
5	200	0.4	Ni	Low	60	80.1	45.0	5.6	9.0	11.4	15.2	24.9	12.6	8.7	6.1	6.5
6	170	0.1	Ni	High	44	80.9	35.0	4.9	9.6	10.6	15.2	20.4	13.4	13.5	7.4	5.1
7	140	0.2	Ni	High	79	79.2	26.2	6.6	9.7	10.6	18.9	14.3	7.6	10.6	17.1	4.6
8	110	0.2	Ni	High	244	81.4	32.4	0.0	3.4	6.9	29.4	14.1	15.5	23.9	3.6	3.4
9	170	0.2	Ni+S[a]	High	224	89.7	68.8	4.3	6.4	11.4	15.0	21.6	18.8	12.2	6.9	3.4
10	170	0.2	Pd	High	23	79.6	60.6	5.0	8.8	10.2	14.3	20.4	16.2	11.8	7.9	5.5
11	30	0.2	Pd	High	130	83.0	50.4	0.0	3.5	8.3	25.0	17.6	17.6	21.0	4.1	2.8
12[b]	30	0.2	Pd	High	22	77.8	57.2	0.0	3.4	8.8	24.0	19.5	16.8	19.4	5.1	3.0
13	170	0.2	Pt	High	36	74.2	53.4	3.7	6.9	11.5	15.0	16.6	17.6	14.4	9.0	5.4
Original methyl linoleate						169.5	0.0	......	......	4.7	95.3	......	......	......	......	......

[a] Nickel poisoned with sulfur.

[b] A 25-ml. solution of methyl linoleate and ethanol, 1:1 by wt., was hydrogenated. Catalyst concentration was calculated on a methyl linoleate basis.

pass lines. The rate of gas flow, measured by a rotometer, ensured good mixing of the oil and catalyst under all conditions. The amount of hydrogen absorbed was measured by the loss of volume in a small gas holder.

In a typical run 25 g. of methyl linoleate and the desired amount of catalyst were placed in the hydrogenation vessel. The entire system was flushed with hydrogen. Then the sample was heated to the operating temperature, and the flow of gas was started. When the predetermined amount of gas had been removed from the holder, the flow of gas was stopped; the sample was cooled to about room temperature and filtered to remove the catalyst. Each sample was stored under hydrogen in a refrigerator until analyzed.

Methods of Analysis. The analytical techniques employed to determine the positions of the double bonds have been described previously (5) and will be summarized only. A 2-g. portion of each hydrogenated sample was refluxed for 1 hr. with a 10% excess of alcoholic potassium hydroxide. Then the ethanol was evaporated under nitrogen, keeping the volume constant by the addition of water. The ethanol-free soap solution was acidulated, the fatty acids were extracted with ethyl ether and washed with water, and the ether was removed.

A 1-g. portion of each fatty acid sample was dissolved in 35 ml. of ethyl acetate, cooled to −5°C., and ozonized, using 6–7% ozone in oxygen, until the reaction was complete as judged by the effect of the spent gas on a potassium iodide solution. Then 10 ml. of 30% hydrogen peroxide were added to the ozonides, the mixture was refluxed for 1 hr., and the solvent was removed by evaporation under nitrogen. The residual mixture of mono- and dibasic acids was dissolved in 100 ml. of a 5% tert-amyl alcohol-in-chloroform solution, and 5-ml. portions were analyzed on each of two types of chromatographic columns, using modifications of techniques described by Higuchi *et al.* (8) and Corcoran (6).

The percentages of C_6 through C_{10} dibasic acids were determined with a column of silicic acid mixed with a citrate buffer (25 g. of acid plus 18.75 ml. of 1 *M* citrate of pH 5.40). Percentages of C_{11} through C_{14} dibasic acids were determined by using a column of a special silicic acid mixed with a glycine buffer (25 g. of acid plus 16.5 ml. of 2 *M* glycine of pH 8.50). Both columns were eluted with chloroform and solutions of butanol in chloroform as indicated in the typical titration curves shown in Figures 1 and 2. The volume of each of the several eluants used was 100 ml. except that the volume of the last eluant in each series was 200 ml.

Iodine values and linoleate contents were determined by using the methods of the American Oil Chemists' Society (3).

Trans isomers were determined by a modification (7) of the infrared spectrophotometric method of Swern *et al.* (10).

Results and Discussion

General Considerations. Subsequent to the laboratory work on the preparation of the methyl linoleate it was found (5) that even the mild conditions of saponification mentioned above cause some shifting of the double bonds of linoleic acid. Apparently the double bonds in both the 9 and 12 positions are involved. The small percentages of double bonds found in other than the 9 position (Table I) are believed to have been formed by a shift during saponification of the safflower oil. In analyzing the methyl linoleate for the positions of the double bonds, the customary order of first saponifying and then ozonizing was reversed so as not to cause a shift of positions during the actual analysis. This precaution was found unnecessary with half-hydrogenated methyl linoleate.

Tests conducted in the course of a related investigation (5) indicated that the conditions of ozonization employed did not produce a detectable shift in the double bonds of linoleic, oleic, and iso-oleic acids.

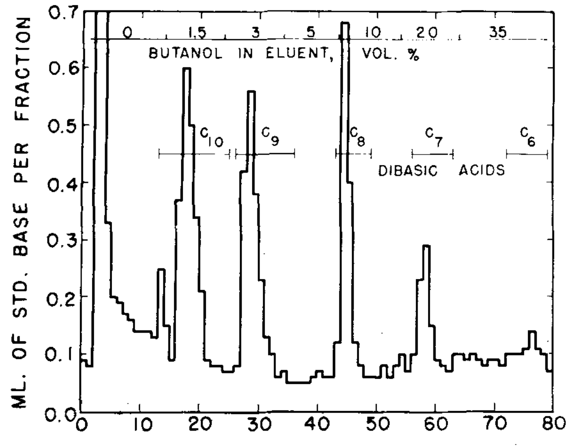

FIG. 1. Titration curve, citrate column, for mixture of mono- and dibasic acids derived from end-product of Run 9.

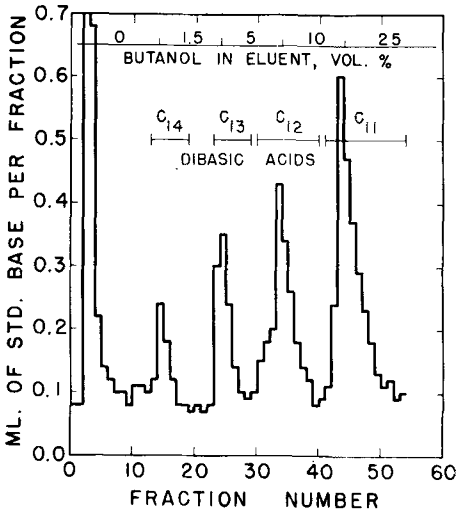

Fig. 2. Titration curve, glycine column, for mixture of mono- and dibasic acids derived from end-product of Run 9.

An effort was made in each of the hydrogenation runs to reduce the iodine value to about 80. At this level practically all of the linoleate had disappeared, which was confirmed by actual measurements, and the hydrogenation of the monoenes had just begun. In all except two instances the iodine values recorded in Table I are within 3 units of 80 and most are within 1 unit. In one instance the iodine value of the hydrogenated product was 89.7. This product contained 3.5% linoleate.

Each hydrogenation was essentially a zero-order reaction, that is, the decrease in iodine value was directly proportional to the reaction time. However the factors responsible for this reaction order varied. In some runs it was determined by the rate of solution of hydrogen in the oil while in others reactivity of the catalyst or the temperature was the controlling factor.

Concerning the mole percentages of the different dibasic acids produced on oxidizing the double bonds, each determined value is estimated to be accurate to within 2 or 3 percentage units. In calculating the mole percentages, the titrations for each peak (Figures 1 and 2) were corrected by substracting the blank titration. The titrations between peaks were disregarded. The total acidity found by this procedure was nearly always about equal to the total acidity of the mixed fatty and dibasic acids put on the column. On eluting a column, the fatty acids always emerged first and formed the first peak on the titration curve. The full height of the fatty acid peak is not shown in either Figure 1 or 2.

Temperature Effects. Within the usual range of temperatures (140–200°C.) used in the commercial hydrogenation of oils, the general effect of varying the temperature has been well established. Increasing the temperature increases the selectivity, that is, it increases the tendency of the linoleic acid group to hydrogenate in preference to the oleic acid group. Also increasing the temperature increases the rate of formation of *trans* isomers. In the current investigation most of the data on temperature effect obtained with the nickel catalyst (Runs 1, 2, 7, and 8, Table I) and the data obtained with the palladium catalyst (Runs 10 and 11, Table I) conform with the observation regarding *trans* isomers. Selectivity data were, of course, not obtained.

The pattern of distribution of the double bonds in the samples hydrogenated at 170 and 200°C., Runs 1 and 2, respectively, is obviously quite similar when represented graphically, Figure 3. The concentration of the double bonds is greatest at the 10 position and decreases more or less uniformly as the distance from this position increases. The pattern indicates that a large amount of positional isomerization occurred during Runs 1 and 2, which conforms with the pattern found on the half-reduction of the linoleic acid group in cottonseed oil with the same catalyst (5).

When the temperature of the hydrogenations with the nickel catalysts was reduced to 140 and 110°C., Runs 7 and 8, respectively, substantially *different* patterns emerged, Figure 3. In both of these the greatest concentration of the double bonds was found in the 9 position. In the run at 110°C. more than 50% of the residual double bonds apparently were in their original positions. It is not known at this time why the hydrogenation at 140°C. shifted a relatively large proportion of double bonds to the 13 position. Neither of the products obtained at 140 and 110°C. contained unhydrogenated methyl linoleate.

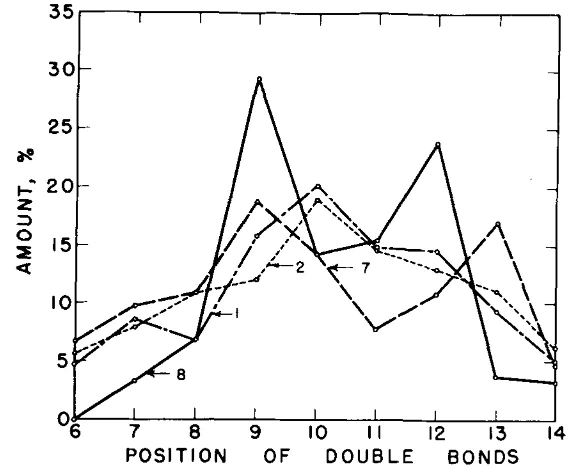

Fig. 3. Distribution of double bonds at different hydrogenation temperatures: 110°C., 8; 140°C., 7; 170°C., 1; and 200°C., 2. Curve numbers refer to run numbers in Table I.

The temperature effect on the shift of double bonds when palladium was used as a catalyst, Runs 10 and 11, Table I, was similar to that observed with nickel but not as great. Decreasing the temperature of the reduction with palladium by 140° produced less of an increase of double bonds in the 9 position than did a decrease of 60° in the temperature of the reduction with nickel.

On the basis of the data obtained it should be possible to devise a hydrogenation with the nickel catalyst such that practically no shift in double bonds and no formation of *trans* isomers occurs. However this possibility has not yet been investigated because of a lack of suitable equipment.

Catalyst Concentration. The effect of the concentration of nickel catalyst on the distribution of double bonds (Runs 1, 3, and 6) is shown in Figure 4. The distribution patterns for these three runs are quite similar; the only noteworthy difference is a somewhat higher concentration of double bonds at the 10 posi-

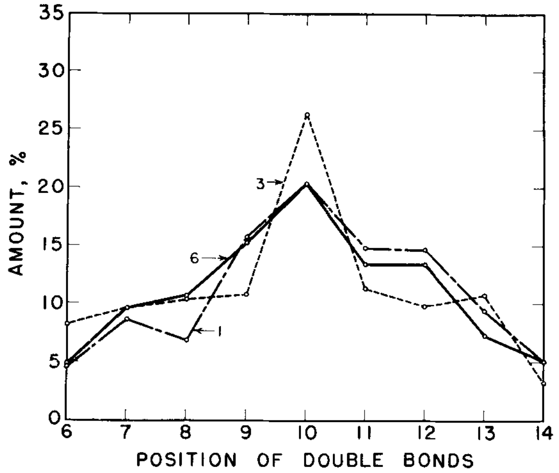

FIG. 4. Distribution of double bonds at different concentrations of nickel catalyst: 0.1%, 6; 0.2%, 1; and 0.4%, 3. Curve numbers refer to run numbers in Table I.

tion for the run with the highest amount of nickel. In each instance the highest concentration of double bonds was found at the 10 position; and the concentration decreased as the distance from the 10 position increased, producing a more or less symmetrical distribution curve.

The hydrogenations represented in Figure 4 were zero-order reactions probably because the over-all rate was limited by the rate of solution of hydrogen in the methyl esters. The over-all rate did increase with an increase in catalyst concentration, and, as might be expected, an increase in catalyst concentration increased the proportion of *trans* isomers.

Hydrogen Dispersion. Ordinarily in the hydrogenation reaction the formation of *trans* isomers increases as the rate of dispersion of hydrogen in the liquid phase decreases. While this trend holds for Runs 1 and 4, the increase in *trans* isomers found on decreasing the rate of hydrogen dispersion was very small. The distribution patterns for the double bonds, Figure 5, also are similar except that the concentration of double bonds at the 10 position was somewhat greater for the hydrogenation carried out at the lower rate of hydrogen dispersion. A probable explanation of the similarity of distribution patterns is that in both hydrogenations the rate of solution of hydrogen in the methyl esters was the rate-setting factor and that, in effect, the concentration of hydrogen in the methyl esters was relatively low and practically equal for both hydrogenations.

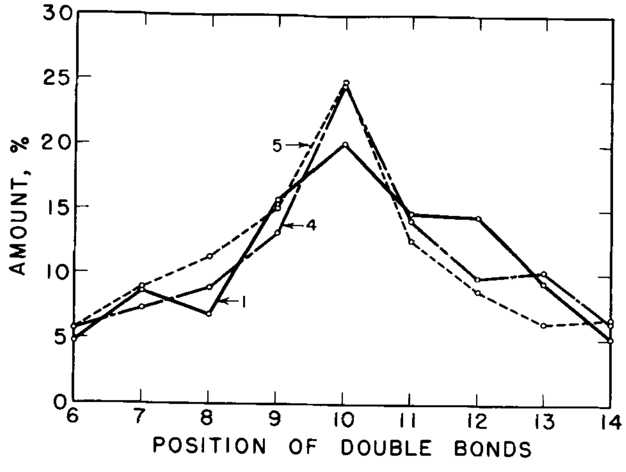

FIG. 5. Distribution of double bonds at different rates of hydrogen dispersion: high rate, 1; low rate, 4; and low rate plus an increase in temperature and catalyst concentration, 5. Curve numbers refer to run numbers in Table I.

In one hydrogenation, Run 5, an attempt was made to accentuate the effect of a low rate of hydrogen dispersion by simultaneously increasing the catalyst concentration and the temperature. When compared with Run 4, it increased the content of *trans* isomers slightly but left the pattern of double bond distribution practically unchanged.

In Run 12 the rate of hydrogen dispersion was increased over that in Run 11 by carrying out the hydrogenation in an ethanol solution. The total volume of liquid phase and other operating conditions were the same in both runs. The use of ethanol increased the hydrogenation rate about six-fold but had little effect on the amount of *trans* isomers and even less effect on the distribution of the double bonds. It must be recognized, of course, that the ethanol may have increased the rate of reaction by doing more than merely facilitating the transfer of hydrogen into the liquid phase.

Type of Catalyst. Palladium is inherently a more active catalyst than is platinum, which in turn is more active than is nickel. Twigg and Rideal (12) have correlated these relative activities with the lattice distances of the three metals. Using known atomic distances and the tetrahedral angle 109° 28′, it was shown that $-C=C-$ could be chemisorbed without deformation when the lattice distance for the metal was 2.73 Å. The distances for palladium, platinum, and nickel are 2.74, 2.76, and 2.47 Å, respectively.

It is generally recognized that palladium and platinum are not as selective as is nickel. Presumably in hydrogenations with nickel the proportion of desorptions of catalyst-hydrogen-double bond complexes without reduction of the double bond is relatively large. In other words, a nickel catalyst might be expected to produce more isomers than would either a palladium or platinum catalyst.

The data in Table I (Runs 1, 9, 10, and 13) and Figure 6 do not bear out this expectation. The palladium and platinum catalysts produced far greater proportions of *trans* isomers than did the nickel catalyst. The palladium catalyst produced nearly as great a portion of *trans* isomers as did the nickel catalyst poisoned with sulfur. All four types of catalyst, when used under identical operating conditions, produced hydrogenated methyl esters in which the positional distribution of double bonds was remarkably alike.

A possible explanation of this similarity is the great difference in the observed hydrogenation rates. For example, the rate for palladium was about 10 times that for the sulfur-poisoned nickel. These differences in rate might have influenced significantly the concentration of hydrogen in the liquid phase and thereby influenced the selectivity. Thus the faster hydrogenations would have been carried out under more selective conditions. However the remarkable similarity in the distribution patterns of the double bonds found in the four hydrogenations suggests that other factors are also involved.

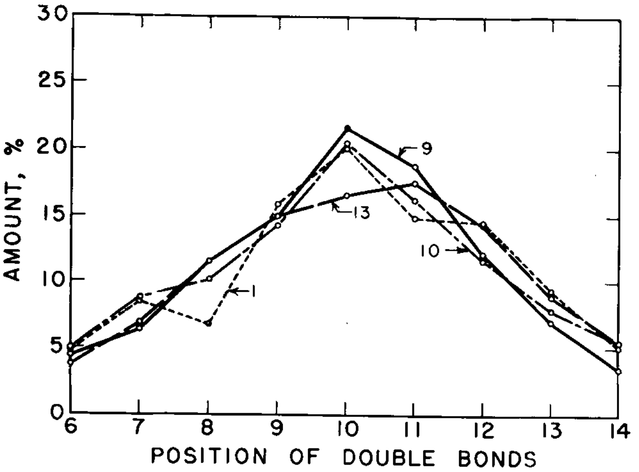

FIG. 6. Distribution of double bonds produced by different hydrogenation catalysts: nickel, 1; sulfur-poisoned nickel, 9; palladium, 10; and platinum, 13. Curve numbers refer to run numbers in Table I.

Summary

Methyl linoleate was hydrogenated to an iodine value of about 80 under various operating conditions. The temperature, rate of hydrogen dispersion, catalyst concentration, and type of catalyst were varied. The several hydrogenation products were analyzed for content of *trans* isomers and the positions of the residual double bonds.

The pattern of distribution of the double bonds was similar in most of the hydrogenations. The greatest concentration of double bonds was found in the 10 position, and the concentrations in the other positions decreased as the distance from the 10 position increased. The distribution curve tended to be symmetrical, that is, approximately the same number of double bonds was found on each side of the 10 position. Operating conditions which normally tend to increase selectivity and the formation of *trans* isomers also tended to increase the concentration of double bonds at the 10 position.

Greatly lowering the temperature of hydrogenation produced a different pattern of distribution of the double bonds. With nickel catalyst at 110°C. the greatest concentrations of residual double bonds were found at the 9 and 12 positions. More than 50% of the total double bonds were in these positions.

The several hydrogenation catalysts (nickel, sulfur-poisoned nickel, platinum, and palladium) produced the same pattern of distribution of double bonds when used under identical conditions. Also the platinum and palladium produced much higher proportions of *trans* isomers than did the nickel.

Acknowledgment

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Evaluating Refined Cottonseed Oils in Storage

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THIS PROJECT is of value to the vegetable oils industry and to the Government in any marketing operation involving the storage of large quantities of fats and oils, particularly cottonseed oil. It can indicate economies in the type and grade of oil best suited for storage and in the methods used as to size and condition of tanks and their location. Improvements can be indicated in the management of tank farm operations and of fats and oils inventories.

Industry rarely stores oil for its own use beyond the season's requirements in view of the lack of knowledge as to possible deterioration. During the early 1950's however the Government stored cottonseed oil up to two years. Experience with these stocks showed deterioration, with a corresponding decrease in market value when stored in commercial field tanks available at that time.

If oils can be stored for longer periods than is now practiced in industry without change of quality or value, a more orderly and efficient marketing operation would be possible. Furthermore a better knowledge as to the storage of oils will contribute much to the production of oils of better quality and value.

Little information on the subject is available from industry, and the judgment of the members of industry does not agree well on the basis of problems which have been presented. This has required that a controlled storage experiment be set up to obtain the data needed to arrive at the economic considerations involved.

The cost and impracticability of using commercial field tanks for the work suggested the use of 50–55

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