# THE CHEMICAL PROCESSES ACCOMPANYING THE HYDROGENATION OF FATS

## III. GLYCERIDE ISOMERIZATION

A. I. Glushenkova and A. L. Markman

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It is known from literature sources that the hydrogenation process must be accompanied by glyceride isomerization i.e., by intra- or intermolecular transesterification of the glycerides. However, no experimental facts confirming this assumption have ever been given. In particular, B. N. Tyutyunnikov, in his monograph [1], writes: "Because of the high temperature of the fat and the influence of the catalyst on hydrogenation, the transesterification of the glycerides may take place with a change in their composition in accordance with the statistical distribution of the fatty acids present in the fat and those formed in the hydrogenation process. This question is complex and little studied and at the present time there is no reliable information on the intensity with which this process occurs."

We have resolved this question experimentally. The results of the experiments are given in the present paper (Tables 1-3).

It can be seen from a comparison of the figures of Tables 2 and 3 that the glycerides contained 30.3% of solid high-molecular-weight acids (P), and they are distributed in such a way that 37.31% is in the $\alpha,\alpha'$ positions and only 16.27% in the $\beta$ position; in agreement with this, of the unsaturated acids (O + L) there is 83.73% in the $\beta$ position and 62.69% in the $\alpha,\alpha'$ positions.

These values relate to a sample taken at zero time containing a small amount of hydrogenated fat added to the oil together with the catalyst. These figures, relating to the native oil and characterizing the distribution of the saturated and unsaturated acids between $\alpha,\alpha'$ and $\beta$ positions, once more confirm the predominant concentration of the unsaturated acids in the $\beta$ position.

If the central position in the triglyceride molecule is occupied by the acids of group P (16.27%), to the left of it there may be the acids P, O, or L in a ratio of 37.31 : 15.45 : 47.24. The amount of 16.27% (in the same ratio is distributed in the three subgroups as follows: PP = 16.27 × 0.3731 = 6.07; OP = 16.27 × 0.1545 = 2.51; LP = 16.27 × 0.4727 = 7.69.

TABLE 1. Fatty-acid Composition of the Initial Oil and the Hydrogenate, %

| Acid | Initial oil | | 1st sample after 0 min | | 2nd sample after 10 min | | 3rd sample after 30 min | |
|---|---|---|---|---|---|---|---|---|
| | I· No. 107,84 | | I No. 100,66. | | I No. 96,66 | | I No. 93,61 | |
| | triglycerides | monoglycerides | triglycerides | monoglycerides | triglycerides | monoglycerides | triglycerides | monoglycerides |
| $C_{10:0}$ | 0,13 | 0,65 | — | Traces | — | — | — | — |
| $C_{12:0}$ | 0,69 | 0,18 | — | | — | — | — | — |
| $C_{14:0}$ | 0,81 | 0,17 | 0,94 | 0,90 | 0,97 | 0,95 | 0,95 | 1,00 |
| $C_{16:0}$ | 22,77 | 2,62 | 24,38 | 11,67 | 24,35 | 31,18 | 24,91 | 20,31 |
| $C_{16:1}$ | 2,26 | 0,71 | Traces | 0,93 | Traces | Traces | Traces | Traces |
| $C_{18:0}$ | 2,19 | — | 4,98 | 3,70 | 4,48 | 8,38 | 4,90 | 6,14 |
| $C_{18:1}$ | 18,31 | 22,54 | 18,68 | 24,22 | 25,48 | 24,26 | 25,66 | 23,91 |
| $C_{18:2}$ | 53,44 | 73,13 | 51,02 | 58,58 | 44,71 | 33,82 | 43,58 | 32,02 |

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TABLE 2. Amounts of Acids by Groups

| *P* |  | *O* |  | *L* |  |
|---|---|---|---|---|---|
| Triglycerides |  |  |  |  |  |
| $C_{14:0}$ | 0,94 | $C_{10:0}$ | 0 | $C_{18:0}$ | 51,02 |
| $C_{16:0}$ | 24,38 | $C_{12:0}$ | 0 | — | — |
| $C_{18:0}$ | 4,98 | $C_{16:1}$ | Trace | — | — |
|  |  | $C_{18:1}$ | 18,68 | — | — |
| Total | 30,30 |  | 18.68 |  | 51,02 |
| Monoglycerides |  |  |  |  |  |
| $C_{14:0}$ | 0,90 | $C_{16:1}$ | 0,93 | $C_{18:2}$ | 58,58 |
| $C_{16:0}$ | 11,67 | $C_{18:1}$ | 24,22 | — | — |
| $C_{18:0}$ | 3,70 | — | — | — | — |
| Total | 16,27 |  | 25,15 |  | 58,58 |

TABLE 3. Amounts of Acids in the $\alpha,\alpha'$ and the $\beta$ Positions

| Composition | Formula | *P* | *O* | *L* |
|---|---|---|---|---|
| Triglycerides | $a$ | 30,30 | 18,68 | 51,02 |
| Triglycerides × 3 | $3a$ | 90,90 | 36,04 | 153,06 |
| Monoglycerides | $b$ | 16,27 | 25,15 | 58,58 |
| Difference | $3a-b$ | 74,63 | 30,89 | 94,48 |
| $\alpha,\alpha'$-Diglycerides | $\frac{3a-b}{2}$ | 37,31 | 15,45 | 47,24 |

TABLE 4. Group Composition of the Glycerides

| Glycerides | Amts. of glycerides taking isomerism into account, % time from beginning of hydrogenation, min |  |  |
|---|---|---|---|
|  | 0 | 10 | 30 |
| GlSSS | 2,26 | 2,37 | 2,56 |
| GlSSU | 7,60 | 15,18 | 16,12 |
| GlSUS | 11,66 | 3,28 | 3,25 |
| GlSUU | 39,18 | 21,03 | 20,46 |
| GlUSU | 6,40 | 24,37 | 25,39 |
| GlUUU | 32,90 | 33,77 | 32,22 |

In each of these subgroups to the right of the central P there may again be either P or O or L, and again in a ratio of 37.31 : 15.45 : 47.24.

By distributing the precentage content of each of the subgroups in this ratio, we obtain the total glycerides, consisting of 18 types:

| Glycerides | % | Glycerides | % | Glycerides | % |
|---|---|---|---|---|---|
| PPP | 2.26 | OPL | 2,38 | OOO | 0,60 |
| PPO | 1.88 | LPL | 3.63 | OOL | 3,68 |
| PPL | 5.72 | POO | 2.90 | OLO | 1.40 |
| POP | 3.50 | POL | 8.86 | OLL | 8.54 |
| PLP | 8.16 | PLO | 6.76 | LOL | 5,61 |
| OPO | 0.39 | PLL | 20.66 | LLL | 13.07 |

The $C_{10:0}$ and $C_{12:0}$ acids are arbitrarily included in the unsaturated acids and, if the results of the position isomerism of the fatty-acid radicals are considered, six types of glycerides are found, while if these results are not taken into account four types are found.

The glyceride compositions of the hydrogenates taken 10 and 30 min after the beginning of hydrogenation were calculated similarly.

The iodine numbers of the three samples mentioned above were, respectively, 100.66, 99.66, and 93.61. These iodine numbers show that during the first 10, and even 30, min the addition of hydrogen takes place very slowly, while, as can be seen from Table 4, the migration of the fatty-acid radicals takes place extremely intensively. Under these conditions the content of trisaturated and also of triunsaturated glycerides remains almost unchanged during a half-hour (within the limits of error of the experiment); the amounts of disaturated-monounsaturated and monosaturated-diunsaturated glycerides also remain constant; within the limits of each of these two latter groups the ratio of the position isomers changes. Thus, in the $GlS_2U$ group the amount of GlSSU rises from 7.60% to 16.12% and GlSUS falls from 11.66 to 3.25%, while in the $GlSU_2$ group the amount of GlSUU falls from 39.18% to 20.46% and GlUSU rises from 6.40 to 25.39%.

These results enable us to determine whether the transesterification process has the nature of an intermolecular or an intramolecular reaction. With any intermolecular exchange of radicals the amounts of $GlS_3$, $GlS_2U$, $GlSU_2$, and $GlU_3$ must vary, and only with intramolecular exchange will these four components be constant. Single-acid glycerides remain the same with any intramolecular transfer of acyl groups while two-acid glycerides undergo transformations; however, their sum remains unchanged. This shows that the glyceride isomerization of fats accompanying the hydrogenation process takes place as an intramolecular reaction.

In addition, we have calculated the amounts of saturated and unsaturated radicals in the glycerides in the $\alpha,\alpha'$ and the $\beta$ positions. In the first 10 min the ratio of the number of S acyls in the $\alpha,\alpha'$ positions to the number of the same acyls in the $\beta$ position changed from 4.59 to 1.13 (decreased by a factor of 4); the same ratio for the U acyls rose from 1.5 to 2.63 (by a factor of 1.75). In the next 20 min, these ratios decreased by a factor of only 1.04 for the S acyls and increased by a factor of 1.03 for the U acyls; i.e., the position was almost stabilized; the migration process had approximated to a state of dynamic equilibrium.

If the isomerization of the glycerides led to a redistribution of the acyl groups according to the laws of probability, the process would give rise to a ratio of the S radicals in the $\alpha,\alpha'$ and the $\beta$ positions of 2 and to the same ratio of U radicals. Nevertheless, as can be calculated from the figures in Table 1, under the conditions of our experiment this ratio tends to 1 for the S radicals and to 2.75 for the U radicals. The reason for this departure from the probability law of distribution still remains unclear.

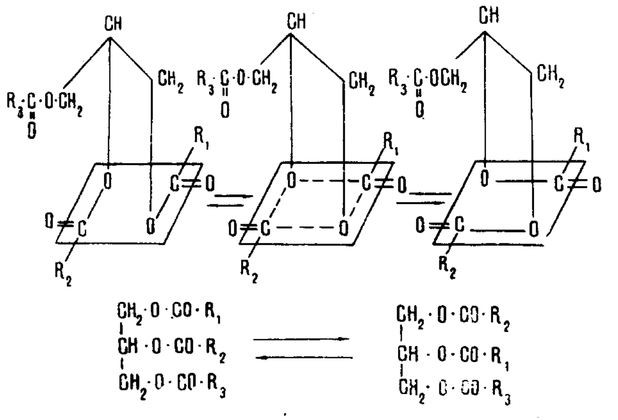

Fig. 1. Scheme of glyceride isomerization.

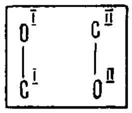

Fig. 2. Index group of the process of glyceride isomerization.

We obtained similar results in the experiments performed with the same disperse Ni − Cu catalyst at 80 and 100°C, with Al − Ni − Cu and Al − Ni − Cu − Cr alloy catalysts at 120°C and also with a palladium catalyst on a support. In all cases, the same intramolecular glyceride isomerization was found. However, any fact increasing the intensity of the hydrogenation process (the temperature and the activity and amount of catalyst) makes it difficult to follow the course of isomerization; nevertheless, the general tendency of the accompanying processes that was found at 120°C is also observed at 150°C and at 180°C during the first 5-10 min of the reaction.

We shall explain the mechanism of glyceride isomerization, like the processes of geometrical and position isomerization [5], on the basis of A. A. Balandin's multiplet theory [6]. It can be seen from the scheme (Fig. 1) why the transesterification reaction takes place as an intramolecular reaction. However, intermolecular transesterification, as well, is not excluded although it appears considerably less probable because of the conditions of steric hindrance.

To calculate the energy relationships we started from the sequence of processes taking place within the limits of the index group (Fig. 2): the cleavage of the $C^{I}-O^{I}$ and $C^{II}-O^{II}$ $\sigma$ bonds and the creation of new $C^{I}-O^{II}$ and $C^{II}-O^{I}$ bonds. From this it is quite natural that the sum of the energies of the bonds cleaved is equal to the sum of the energies of the newly formed bonds; the same applies to the sum of the energies of the adsorption bonds.

The calculations were based on the following indices:

$$Q_{C-O} = 85.5;\quad Q_{C-Ni} = 14.0;\quad Q_{O-Ni} = 48.5 \text{ kcal} \quad [7].$$

Hence, the energy of formation of the complex assumes the form

$$E' = -2Q_{C-O} + (2Q_{C-Nt} + 2Q_{O-Ni}) = -46 \text{ kcal}.$$

The energy of the decomposition of the complex E″ = 46 kcal, and the heat effect of the reaction U = O.

The sum of the energies of the reacting bonds

$$S = 4Q_{C-O} = 4 \cdot 85.5 = 342 \text{ kcal};$$

and the adsorption potential of the catalyst

$$q = 2Q_{C-Ni} + 2Q_{O-Ni} = 125 \text{ kcal}.$$

The condition expressed by the equation

$$\left| q - \frac{S}{2} \right| \leqslant \frac{U}{2}$$

is not observed here:

$$\left| 125 - \frac{342}{2} \right| > 0.$$

The energy threshold E′ = 46 kcal. However, in view of the fact that the redistribution of the bonds in the complex takes place not only after their cleavage but also as a result of their weakening, the true activation energy [8] can be written as

$$E = A - \gamma E = 11{,}5 - 0{,}25 \cdot 46 = 0$$

Thus, the reaction proves to be completely justified from the energy aspect.

## EXPERIMENTAL

Cottonseed oil was hydrogenated at 120°C in the presence of a disperse nickel–copper catalyst (1:1) prepared by precipitation from a solution of an equimolecular mixture of the sulfates of these metals with sodium carbonate and subsequent reduction of the carbonates in oil at 200°C. The amount of catalyst used was 0.2% of combined metals on the weight of the oil undergoing hydrogenation. Since a small amount of hydrogenated oil with an iodine number close to zero, formed in the process of reducing the carbonates, was introduced into the hydrogenation flask together with the metals, this mixture, similar in composition to the oil, but with a somewhat higher amount of saturated fatty acids, was regarded as the initial material. Thus, the first sample of oil was taken at the beginning of hydrogenation, and then samples of the hydrogenates were taken 10 and 30 min after the beginning of hydrogenation. All three samples, after transesterification and conversion into the methyl esters, were analyzed by gas-liquid chromatography to determine their fatty-acid composition.

We subjected a part of each of the three samples taken to enzymatic hydrolysis, using for this purpose the lipase of the pancreatic gland of large-horned cattle [2, 3]. Since in this case hydrolysis took place with the splitting out from the glycerides of the acyls in the $\alpha,\alpha'$ positions, the main hydrolysis products consisted of the $\beta$-monoglycerides. Their transesterification once again gave fatty acid methyl esters.

To simplify the calculations, the acids present in the glycerides were divided into three groups (see Table 2).

Palmitic Acids (P). These include the solid acids (under the living conditions of the plant during the period of the oil-forming process): myristic, palmitic, and stearic. The name "palmitic" is used arbitrarily from the name of the main component of this mixture of acids.

Oleic Acids (O). These acids include, in addition to oleic acid itself and palmitoleic acid, the low-molecular-weight saturated acids present in cottonseed oil in extremely small amounts. Under the growth conditions of the cotton plant (dry subtropical zone) these acids are liquid and behave similarly to oleic acid.

Linoleic Acid (L). This includes only linoleic acid itself (L).

Then, by Coleman's method [4] the percentages of the acids P, O, and L in the $\alpha,\alpha'$ positions in the glycerides of the samples that we took were determined (see Table 3).

## SUMMARY

It has been established that the catalytic hydrogenation of a fat is accompanied by its glyceride isomerization (transesterification), which is particularly pronounced in the initial stage of the process. Transesterification takes place as an intramolecular reaction.

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