Effect of the Unsaturated Acyl Position in Triglycerides on the Hydrogenation Rate

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ABSTRACT AND SUMMARY

Linseed and cod liver oil triglycerides as well as the randomly rearranged triglycerides of soybean and rapeseed oils were subjected to partial hydrogenation in the presence of nickel or platinum catalyst. The hydrogenated triglycerides were subjected to enzymatic hydrolysis with pancreatic lipase in order to determine the changes of their structure. It follows from the data obtained that the position of an unsaturated acyl in a triglyceride affects its hydrogenation rate.

INTRODUCTION

The fatty acids in triglycerides are not randomly distributed among the individual positions. For example, 18-C unsaturated acids dominate in position 2 of vegetable oil triglycerides. The saturated acids and the long chain monoethylenic acids, e.g., erucic acid in rapeseed oil, occupy mainly the external positions. Considering the steric effect, it may be expected that the catalytic hydrogenation of unsaturated acyls should take place at different rates, depending on the position occupied in triglycerides. Studies on the mechanism of hydrogenation of the unsaturated fatty acids, especially in triglycerides, present many complex problems; therefore, few papers have dealt with this problem. All the published data (1-4), with the exception of one paper (5), suggest that there is no relation between the position of the unsaturated acyl group and its hydrogenation rate. On the other hand, some of these papers dealing with the identification of the triglyceride structure take it for granted that the fatty acids liberated by pancreatic lipase are representative for position 1,3. Our studies show the structural selectivity of lipase towards fatty acids (6).

EXPERIMENTAL PROCEDURES

Oils having a high content of certain polyenic acids, namely linseed oil (C18:3), soybean oil (C18:2), cod liver oil (C22:6, C20:5), and rapeseed oil were used in the studies. All oils except cod liver oil were fully refined under industrial conditions. Cod liver oil, owing to the possibility of transformations, was isolated from fresh stock and refined under laboratory conditions in the most preservative way.

As the interpretation of results obtained after the hydrogenation was difficult, soybean and rapeseed oils were first randomly rearranged in the presence of sodium methylate. The randomly rearranged raw oil was subjected to molecular distillation in order to separate free fatty acids and incomplete glycerides.

Hydrogenation was carried out in a glass, laboratory apparatus with continuous hydrogen flow under atmospheric pressure at 160 C. Vegetable oils were hydrogenated in the presence of two different nickel catalysts of the formate type, designated A and B. Catalyst A showed greater activity than catalyst B. For cod liver oil a platinum catalyst of the Adams type was used.

As we know from theoretical considerations, the concentration of hydrogen on the surface of catalyst has a decisive effect upon the mechanism of the hydrogenation reaction. Therefore, the speed of hydrogen flow was controlled as a variable parameter and its effect on the reaction rate was observed. Samples were collected for analysis during the process.

The composition of fatty acids in the individual triglyceride positions was determined by enzymatic hydrolysis with pancreatic lipase from Sigma Chemical Co. (St. Louis, MO) and Koch-Light Lab. (Colnbrook, Bucks, England). The enzyme was first purified by extraction with acetone and ethyl ether to remove lipids. The lipolysis of triglycerides was carried out by Brockerhoff's method (7), along with our own modifications. The reaction was stopped when the mixture contained 20% monoglyceride (MG). The glyceride structure was determined from the fatty acid compositions of the triglyceride (TG) before hydrolysis and of the MG isolated from the mixture after hydrolysis. The composition of fatty acids was determined by gas chromatography using a flame ionization detector (FID). Methyl esters of linseed, soybean, and rapeseed oils were separated on packed columns, 15% PEGA or DEGS on 80-100 mesh Chromosorb W, while capillary columns, 50 m long and 0.25 mm in diameter, coated with BDS, were used for cod liver oil.

RESULTS AND DISCUSSION

The first experiments were carried out with linseed oil, as its fatty acid composition is comparatively simple, and the distribution of linolenic acid between the individual positions is almost statistical (Table I). The hydrogenation was carried to two different final linolenic acid contents with the same catalyst. Owing to the uneven fatty acid distribution, the interpretation of results turned out to be difficult, especially for the C18:2 and C18:1 acids.

Table I gives examples of the analyses for two samples of partly hydrogenated linseed oil. The data of column 5 refer to the fatty acid composition of the hardened triglycerides. The relative loss of the acid in position 1,3 (column 9) or 2 (column 13) was calculated according to the formula: column 9 = column 8/column 7 x 100 or column 13 = column 12/column 11 x 100, where column 8 = column 7 - column 6, or column 12 = column 11 - column 10. Columns 7 and 11 defined as the initial levels need some explanations. The calculations for C18:3 acid are self-evident; the initial level in positions 1 and 3 (column 7) and position 2 (column 11) were the same as the concentrations in positions 1 and 3 and position 2 of the initial triglycerides (columns 3 and 4). The problem becomes more complex when acids C18:2 and C18:1 are considered. According to the concept of consecutive reactions, the initial level of C18:2 in positions 1 and 3 (column 7) consists of the value of column 3 augmented by the absolute loss of C18:3 acid (column 8). The same procedure was applied to determine the initial value for oleic acid, using the value for the absolute loss of C18:2. Initial values for the fatty acids in position 2 are calculated in the same manner.

Value A (column 14) expressed by the formula: A = column 9/column 13, compares the reactivity of the acid in positions 1 and 3 with the reactivity of the acid in position 2.

The results of the initial studies, contained in Table I,

TABLE I

Hydrogenation of Unsaturated Acyls in Positions 1,3 and 2 of Linseed Oil Triglyceride

	Initial oil			Hydrogenated oil								
		Position			Position 1,3				Position 2			
Acid	TG_o	1,3	2	TG_h	Final comp.	Initial level	Absolute loss	Relative loss %	Final comp.	Initial level	Absolute loss	Relative loss %	A
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample 1													
18:0	5.0	7.3	0.4	7.4	10.3	---	---	---	1.6	---	---	---	---
18:1	19.4	17.4	23.4	26.8	24.9	27.9	3.0	10.8	30.6	31.8	0.8	2.5	4.3
18:2	15.9	13.3	21.1	18.9	16.3	26.8	10.5	39.2	24.1	32.5	8.4	25.8	1.5
18:3	59.7	62.0	55.1	46.9	48.5	62.0	13.5	21.8	43.7	55.1	11.4	20.6	1.1
Sample 2													
18:0	5.0	7.3	0.4	8.1	11.2	---	---	---	2.0	---	---	---	---
18:1	19.4	17.4	23.4	29.4	27.7	31.6	3.9	12.3	32.8	34.4	1.6	4.7	2.6
18:2	15.9	13.3	21.1	21.2	18.9	33.1	14.2	43.0	25.7	36.7	11.0	30.0	1.4
18:3	59.7	62.0	55.1	41.3	42.2	62.0	19.8	31.9	39.5	55.1	15.6	28.3	1.1

TABLE II

Percentage Distribution of C20:5 and C22:6 Acids Between the External and Internal Triglyceride Positions of Natural and Partly Hydrogenated Cod Liver Oil

Acid	Position	Natural oil	Hydrogenated oil	
			Sample 1	Sample 2
20:5	1,3	63.9	57.0	54.7
	2	36.1	43.0	45.3
22:6	1,3	37.2	25.4	6.9
	2	62.8	74.6	93.1

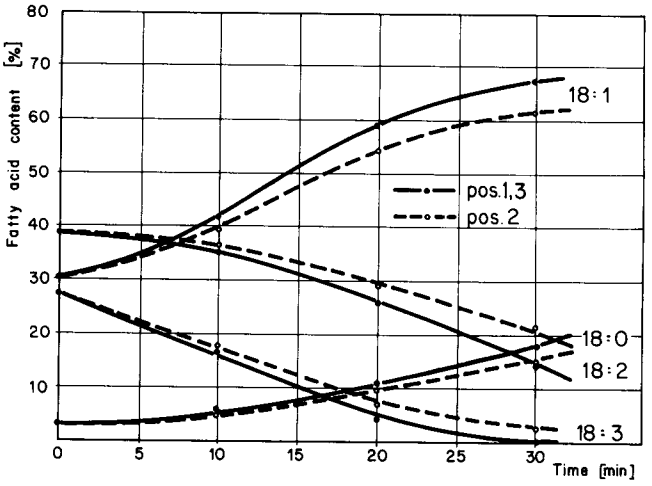

FIG. 1. Percentage changes of 18-C acids content in the acids of 1,3 and 2 triglyceride positions for the randomized rapeseed oil as a function of hydrogenation time. Catalyst A; hydrogen flow rate 0.5 l./min.

indicate that the hydrogenation rate for the unsaturated acyls is a function of their position in triglycerides.

The most complex problem was encountered during the studies of cod liver oil hydrogenation. This was owing to the uneven distribution of the fatty acids between the individual positions of the glyceride, as well as to the very complex, still not well understood, mechanism of hydrogenation. The addition of hydrogen to double bonds, mainly of C20:5 and C22:6 polyenic acids, gives rise to new, formerly absent acids, taking into account only the degree of unsaturation at a given chain length while omitting all other transformations. Therefore, the problem was limited to studies of only two acids – C20:5 and C22:6. These acids have the highest degree of unsaturation at a given chain length. The comparison of the absolute loss of these acids in the individual triglyceride positions defines their reactivity in these positions. Similarly as for linseed oil, two samples of partly hydrogenated oil (platinum catalyst) were analyzed. The reaction was stopped when ca. 50% of clupanodonic acid was reduced. Table II represents the percentage distribution of C20:5 and C22:6 acids between the individual positions in triglycerides (TG). In both cases we can clearly observe that the contribution of the above-mentioned acids in position 2 of the partly hydrogenated triglycerides increases in relation to the same position in the initial triglycerides. This denotes that these acids are less reactive in the internal position.

In order to simplify the interpretation of results, soybean and rapeseed oils were randomly rearranged before hydrogenation. This process was particularly important for rapeseed oil as the 18-C polyenic acids that mainly undergo transformations during hydrogenation are localized almost totally in position 2 in the natural oil. Figures 1 to 5 represent the transformations of 18-C acids as a function of

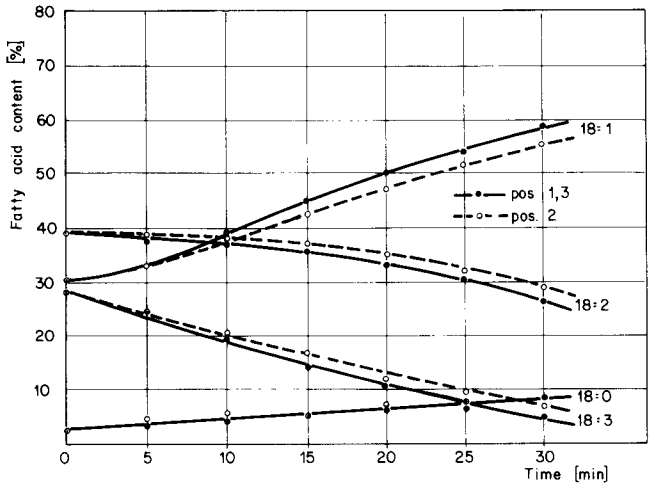

FIG. 2. Percentage changes of 18-C acids content in the acids of 1,3 and 2 triglyceride positions for randomized rapeseed oil as a function of hydrogenation time. Catalyst B; hydrogen flow rate 0.5 l./min.

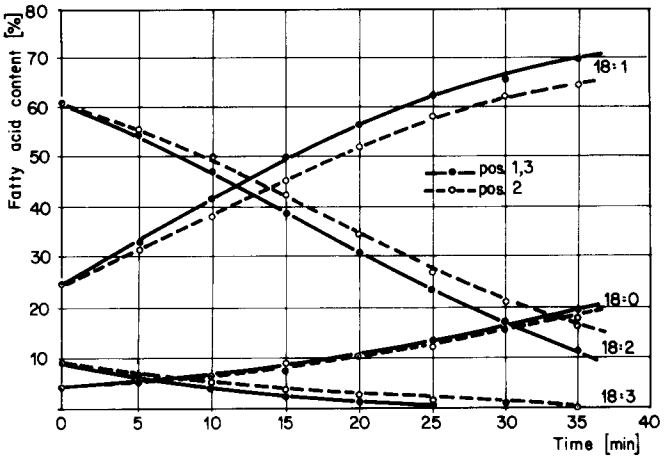

FIG. 3. Percentage changes of 18-C acids content in the acids of 1,3 and 2 triglyceride positions for randomized soybean oil as a function of hydrogenation time. Catalyst B; hydrogen flow rate 1.5 l./min.

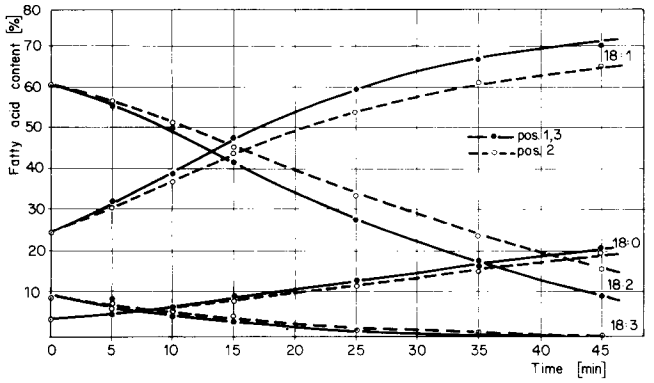

FIG. 4. Percentage changes of 18-C acids content in the acids of 1,3 and 2 triglyceride positions for randomized soybean oil as a function of hydrogenation time. Catalyst B; hydrogen flow rate 1.0 l./min.

hydrogenation time for these oils.

The slower decrease of C18:2 and C18:3 acid concentration in position 2 than in positions 1 and 3 with increasing reaction time may be explained by their higher hydrogenation rates in the external positions. The proof of

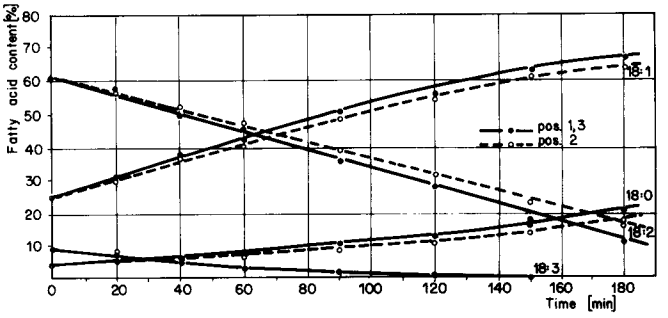

FIG. 5. Percentage changes of 18-C acids content in the acids of 1,3 and 2 triglyceride positions for randomized soybean oil as a function of hydrogenation time. Catalyst B; hydrogen flow rate <0.5/min.

TABLE III

Percentage Distribution of 18-C Acyls Between the External and Internal Triglyceride Positions as a Function of Hydrogenation Time for Randomized Rapeseed Oil (Fig. 1)

Acid	Position	Hydrogenation time (min) 0	10	20	30
18:0	1,3	64.0	65.5	69.3	70.3
	2	36.0	34.5	30.7	29.7
18:1	1,3	67.0	67.7	68.5	68.6
	2	33.0	32.3	31.5	31.4
18:2	1,3	66.5	66.0	63.8	57.6
	2	33.5	34.0	36.2	42.4
18:3	1,3	68.0	66.3	55.8	33.6
	2	32.0	33.7	44.2	66.4

TABLE IV

Percentage Distribution of 18-C Acyls Between the External and Internal Triglyceride Positions as a Function of Hydrogenation Time for Randomized Soybean Oil (Fig. 3)

Acid	Position	Hydrogenation time (min) 0	7.5	15	25	35
18:0	1,3	64.4	66.1	66.5	67.2	68.1
	2	35.6	33.9	33.5	32.8	31.9
18:1	1,3	65.7	68.1	68.7	68.0	68.0
	2	34.3	31.9	31.3	32.0	32.0
18:2	1,3	67.2	65.8	64.7	63.5	58.3
	2	32.8	34.2	35.3	36.5	41.7
18:3	1,3	67.0	65.5	61.7	52.4	---
	2	33.0	34.5	38.3	47.6	---

it is also the reverse situation for C18:1 and C18:0 acids. The greater increase of stearic acid in positions 1 and 3 than in position 2 denotes the higher hydrogenation rate of oleic acid in the external positions. Similarly, the higher hydrogenation rate of polyunsaturated acids in positions 1 and 3 causes the greater accumulation of C18:1 in those positions.

The absolute value of the difference in concentration of a given acid in both positions increases as a function of time. This difference, however, is not too great if the acid content in the initial system is not too high. The difference becomes considerable if it refers to the content of a given acid in any position, especially in the terminal stage of the process and for the acids whose concentrations decrease with time. The nature of these changes may be clearly seen in Tables III and IV. Here we can observe a great increase of polyunsaturated acid contribution in position 2. The minor changes of C18:1 are due to the fact that the greater decrease of this acid in positions 1 and 3 is compensated for by its greater increase in those positions as a consequence

of polyunsatured acid hydrogenations.

The aim of our studies was to demonstrate whether the unsaturated acyl position in triglycerides has any effect on the reaction course. Proving it, we are aware that the reaction conditions should influence this phenomenon. Our further studies in this field are being continued.

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