Selective Hydrogenation of Rapeseed Oils with Copper-Chromite Catalyst: Influence of Erucic Acid

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ABSTRACT

Rapeseed oils with different erucic acid contents have been hydrogenated in a "dead-end" type of laboratory reactor with Adkins-type copper-chromite catalyst. It was observed that, as is true with oleic acid, erucic acid is not hydrogenated by this catalyst, but it differs in that positional or geometrical isomerization does not occur. The presence of erucic acid does not change the mechanism of hydrogenation of rapeseed oils in a range of concentrations of this acid. On the other hand, it markedly influences the rate of reaction.

INTRODUCTION

Rapeseed oils contain about 8-12% of linolenic acid which shows the greatest susceptibility of all fatty acids of this raw material to autoxidation processes. In order to increase the oxidative stability of the oil, it is necessary to remove linolenic acid, and this may be done by selective hydrogenation. Problems arising during this process have been investigated in detail on model systems (1-6) and on soybean oil (7-12). Hydrogenation of rapeseed oils in the presence of a copper catalyst has been discussed only in a few publications (11-15).

Research presented in this paper is concerned with the kinetics and mechanism of selective hydrogenation of rapeseed oils with different erucic acid contents.

EXPERIMENTAL PROCEDURES

Materials

Rapeseed oils. High-erucic commercial oil was produced by the Fat Factory, Gen. W. Wróblewski, in Gdańsk; medium-erucic Wipol and low-erucic Janpol were extracted from seeds and then laboratory-refined. All 3 oils were characterized by approximately the same degree of refining. Sulfur content was about 1 μg/g; phosphorus, 5-8 μg/g; sodium, 1-3 μg/g; free fatty acids (FFA), 0.1% and the peroxide value (PV) was in the range of 0.6-1.0.

Methyl erucate was obtained by crystallizing the fatty acids of high-erucic rapeseed oil from an aqueous solution of acetone. The preparation contained 97% of methyl erucate. The rest contained the following acids: 0.3% 16:0, 0.5% 18:0, 0.1% 18:1, 1.1% 20:0, 0.6% 20:1 and 0.4% 22:0.

Catalysts. The hydrogenation catalyst used in these experiments was Cu-1106P (39% CuO; 43.5% Cr_2O_3; 10% BaO), distributed by Harshaw Chemie BV, Netherlands.

For comparison, an unsupported nickel catalyst containing 10.25% of Ni was used, which was obtained by decomposition of nickel formate from the Fat Factory in Gdańsk.

Methods

Hydrogenation. Kinetic studies were done in a "dead-end" type of laboratory reactor which gave a continuous recording of the volume of absorbed hydrogen. Hydrogenation was done under the following conditions: mass of oil, 50 g; temperature, 160-200 C (± 0.5 C); stirring rate, 2,700 rpm; hydrogen pressure, atmospheric; copper catalyst concentration, 0.5-3.0% catalyst; nickel catalyst concentration, 0.1% Ni. (These weights of catalyst are based on total copper catalyst weight and nickel catalyst as % nickel.)

The catalyst was introduced into the oil after stabilization of process conditions and after saturation of oil with hydrogen.

Activation of the copper catalyst, which is supplied by the producer in unreduced form, occurs simultaneously with the hydrogenation process. In order to calculate the amount of hydrogen added to the fatty acid double bonds (this quantity is called $A_{corrected}$), the following formula was used:

$$A_{corrected} = A_{total} - A_{catalyst\ reduction}\ (mL\ H_2/g\ oil),$$

where A_{total} = total amount of absorbed gas (mL H_2/g oil), and $A_{catalyst\ reduction}$ = amount of hydrogen used for catalyst reduction (mL H_2).

The progress of catalyst reduction was observed during the so-called stimulated hydrogenation reaction, in which the completely hardened soybean oil was used as the fatty raw material. Reaction rate constants (k) were calculated from the following formula:

$$k = -\frac{2.303}{t} \cdot 1g \frac{\tau\nu_0}{\tau\nu_t},$$

where t = time of hydrogenation, $\tau\nu_0$ = initial iodine value of the oil, and $\tau\nu_t$ = final iodine value of the oil.

Fatty acids. Fatty acid (FA) composition was determined by gas liquid chromatographic (GLC) separation of their methyl esters. A Jeol chromatograph with a flame ionization detector was used. A 2-m steel column (3 mm id) was filled with 10% EGSS-Y on Chromosorb W. The content of conjugated dienes in hydrogenated oil samples and the content of 18:2 and 18:3 acids, after the transformation of these acids into conjugated dienes and trienes by alkali isomerization, were determined spectrophotometrically by AOCS Official Method Cd 7-58. Total isolated *trans* double bond content of the methyl esters was calculated from infrared (IR) absorption at 10.36 and 8.6 μm (16).

The double bond distribution of methyl erucate after hydrogenation was determined by oxidative ozonolysis followed by GLC analysis of mono- and dicarboxylic esters.

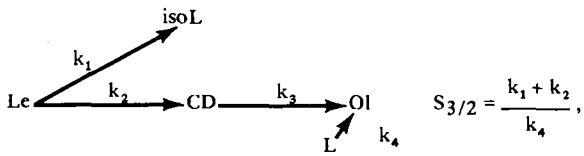
Lipase hydrolysis. This hydrolysis was done with hog pancreatic lipase by Brockerhoff's method (17) with Drozdowski's (18) modifications.

The fatty acid composition in positions 1 and 3 was calculated according to the formula:

$$\%\ FA\ in\ pos.\ 1,3 = \frac{3TG - MG}{2},$$

where TG = % of the particular fatty acid in the original triglyceride and MG = % of the particular fatty acid in the monoglyceride formed.

Calculation of linolenate selectivity ($S_{3/2}$). Relative rate constants and linolenate selectivity were determined (19) by a digital computer ICL 29-03, according to the following scheme:



$$S_{3/2} = \frac{k_1 + k_2}{k_4},$$

where Le = linolenic acid, L = linoleic acid, isoL = isolinoleic acid (nonconjugatable diene), CD = conjugated diene, Ol = oleic acid, and k = reaction rate constant.

By this method, coefficient $S_{3/2}$ can be accurately calculated (20).

RESULTS AND DISCUSSION

The fatty acid content and positional distribution of fatty acids in the glycerides of rapeseed oils were determined and the results are presented in Table I.

The influence of temperature and catalyst concentration on the progress of hydrogenation of rapeseed oils with different erucic acid content was studied. Because the process was done at atmospheric pressure, high temperature (200 C) and high Cu-1106P catalyst concentrations (0.5-3%) were required. Figure 1 represents selected kinetic curves of oil hydrogenation and the catalyst reduction curve. The curves show changes in total hydrogen absorption (A_{total}) with time. In the rest of the work, $A_{corrected}$ was used.

Influence of reaction temperature (catalyst conc.=const) and catalyst concentration (temperature=const) on the hydrogenation rate in the presence of the Cu 1106P catalyst is shown in Figure 2. The reaction rates for medium- and low-erucic oils increased proportionately with catalyst concentration. However, with the high-erucic variety, doubling the catalyst concentration more than doubles reaction rates. This phenomenon suggests catalyst poisoning, although the catalyst poisoning should behave similarly for any oil because of similar levels of typical inhibitors (S, Na, P, FFA).

Detailed analysis of the FA composition during hydrogenation in the presence of a copper catalyst showed that changes are observed only in the C_{18} acids. This is logical and readily understandable because, in rapeseed oils, the polyene acids are the only acids having that chain length.

TABLE I

Composition of Fatty Acids and Positional Distribution of Fatty Acids in Triglycerides of Tested Rapeseed Oils

Rapeseed variety	Position	Fatty acids (%)										
		16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	20:2	22:0	22:1
High-erucic	1, 2 and 3 (TG)	3.1	0.2	1.0	13.1	13.3	7.8	0.6	9.4	0.1	0.2	51.2
	2 (MG)	1.1	0.5	1.3	30.1	35.0	23.2	–	2.0	0.1	0.1	6.6
	1, 3	4.1	0.1	0.8	4.6	2.5	0.1	0.9	13.1	0.1	0.2	73.5
"Wipol"	1, 2 and 3 (TG)	3.7	0.3	1.0	37.5	14.6	7.1	–	17.2	–	–	18.6
	2 (MG)	–	–	–	47.0	34.1	18.9	–	–	–	–	–
	1, 3	5.5	0.5	1.5	32.8	4.8	1.2	–	25.8	–	–	27.9
"Janpol"	1, 2 and 3 (TG)	4.5	0.4	1.0	67.5	19.8	6.8	–	tr	–	–	tr
	2 (MG)	–	–	–	54.3	32.4	13.3	–	–	–	–	–
	1, 3	6.8	0.6	1.5	74.1	13.5	3.5	–	–	–	–	–

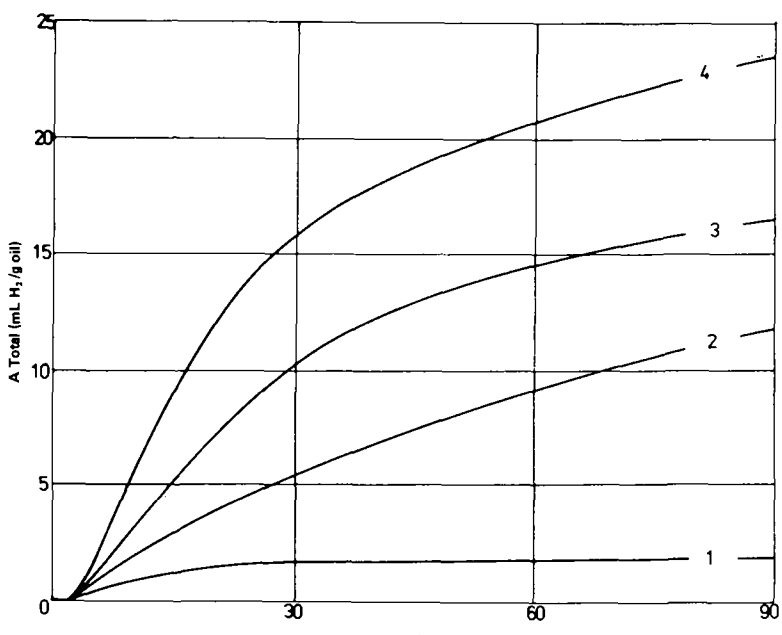


FIG. 1. Kinetic curves of the Cu 1106P catalyst reduction (curve 1) and of rapeseed oil hydrogenation: high-erucic (curve 2), medium-erucic (curve 3) and low-erucic (curve 4). Reaction temperature: 200 C. catalyst concentration: 1.5%.

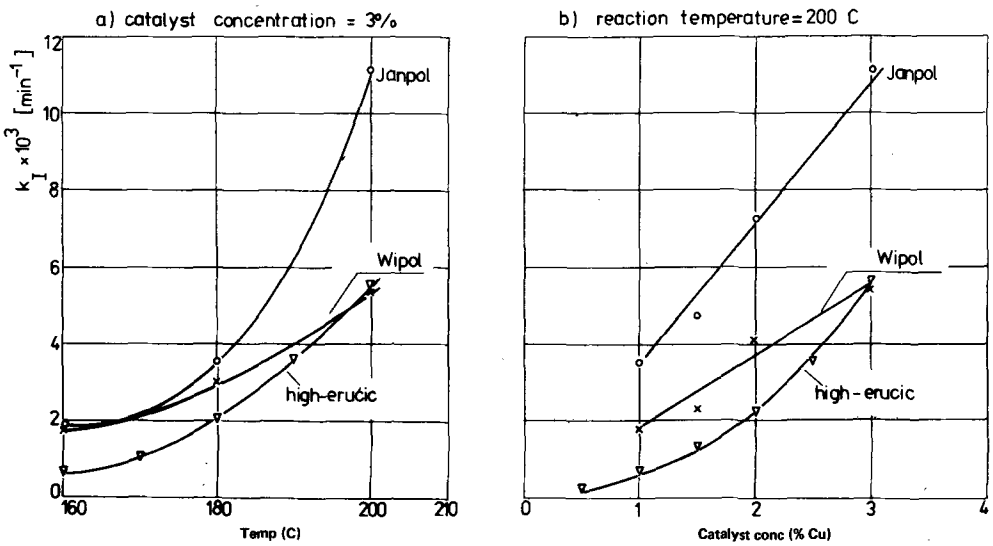


FIG. 2. Comparison of hydrogenation rate for different rapeseed oils in the presence of the Cu 1106P catalyst, as a function of temperature (a) and catalyst concentration (b).

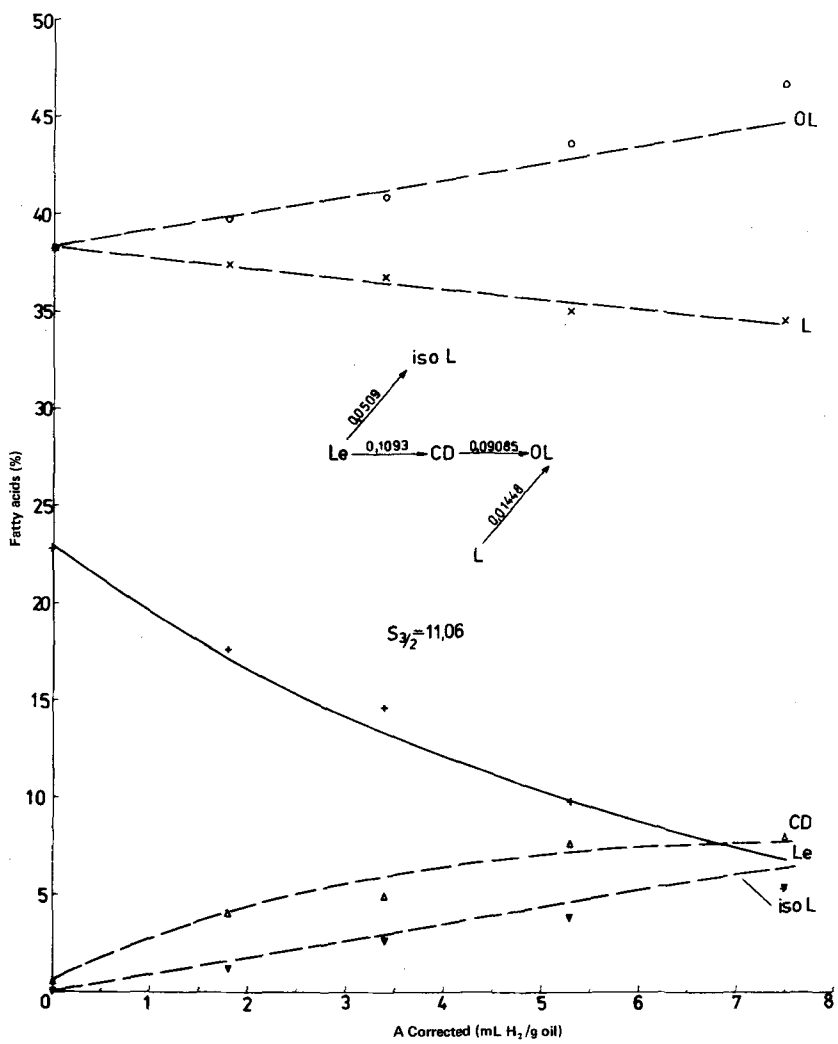


FIG. 3. Change in fatty acid composition during hydrogenation of the high-erucic oil with copper catalyst. Curves drawn by computer when experimental values best fit computer simulation according to reaction scheme are shown in inset. Le—linolenate; L—linoleate; CD—conjugated diene; isoL—nonconjugatable diene; Ol—oleate. $\sum_{n=0}^{n=3} 18{:}n = 100\%$.

For selected tests (3% cat., 200 C) computer best-fit graphs of theoretical curves to experimental data for each C_{18} acid (Figs. 3, 4 and 5) are presented.

Table II represents the content of geometrical isomers formed during hydrogenation in the presence of a copper catalyst and, for comparison, in the presence of nickel catalyst, at the same temperature and pressure, but at different catalyst concentrations.

It was observed that, similar to other monoenic acids, during hydrogenation of rapeseed oil with high and medium contents of erucic acid and also in model tests performed with the methyl ester of the erucic acid, this acid is not reduced in the presence of a copper catalyst (in the range of tested reaction conditions). However, this does not exclude geometrical and positional isomerization which does occur, e.g., in the case of oleic acid (21). In order to observe if this isomerization does occur, hydrogenation of methyl erucate in the presence of 3% Cu 1106P catalyst and at 200 C was done. During the hydrogenation, the formation of geometrical and positional isomers was practically not observed. After 4 hr of reaction, the *trans* isomer content was below 0.5%. It is supposed that such behavior of erucic acid is caused by the structure of its molecule (length of the hydrocarbon chain and position of the double bond).

The results obtained indicate that, for a raw material such as rapeseed oil, selective hydrogenation in the presence of a copper catalyst is an effective method of elimination of linolenic acid. The value of linolenate selectivity ($S_{3/2}$) is between 8 and 11 (Figs. 3-5). During hydrogenation, an increase in stearic acid was not observed, and the quantity of *trans* isomers formed was about 2-2.5 times smaller than in the processes carried out with Ni to the same degree of hydrogenation (Table II), which is important from a nutritional viewpoint.

The presence of erucic acid in rapeseed oils has no influence in macroscale on the direction of polyenic acid transformation. However, it has a rather marked influence on the reaction kinetics. It was observed that, independent of temperature and catalyst concentration, the sequence of reaction rates is (Fig. 2): high-erucic rapeseed>medium-erucic rapeseed≥low-erucic rapeseed. (A similar phenomenon was also observed for the nickel catalyst.)

Taking into account the fact that these 3 oil types were refined to the same degree, the observed differences may be

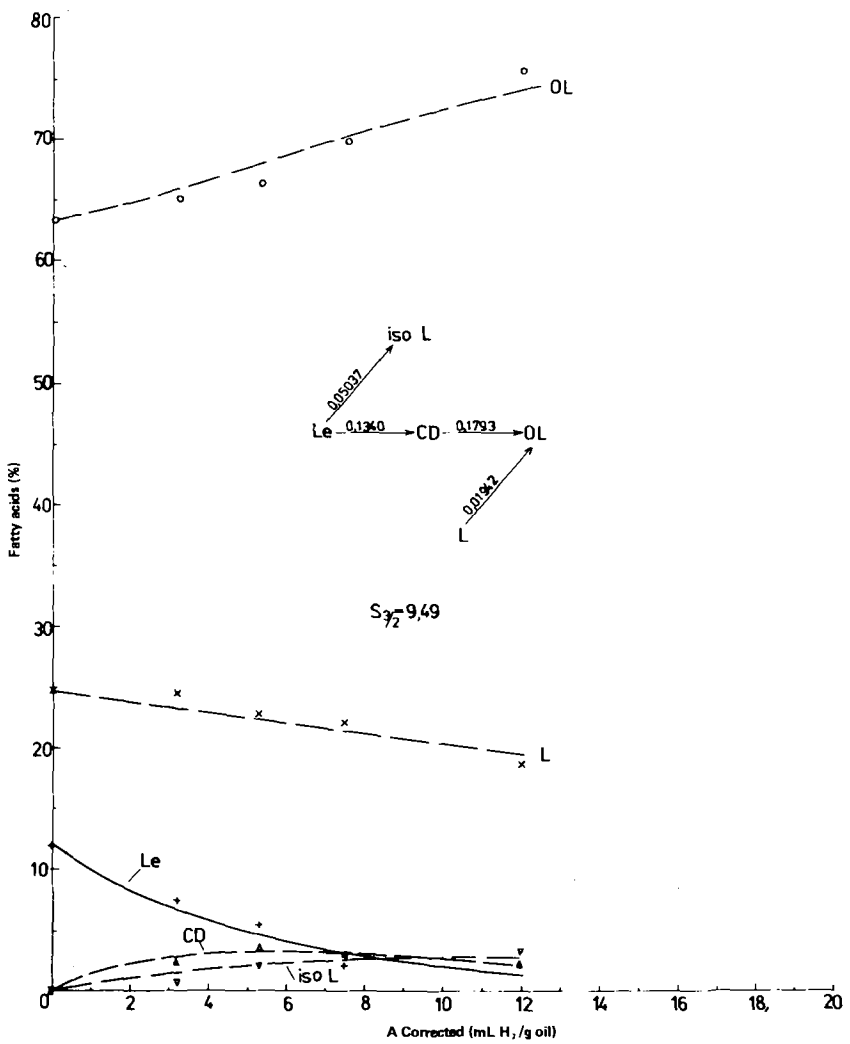


FIG. 4. Change in fatty acid composition during hydrogenation of the medium-erucic oil with copper catalyst. Curves drawn by computer when experimental values best fit computer simulation according to reaction scheme are shown in inset. Le—linolenate; L—linoleate; CD—conjugated diene; isoL—nonconjugatable diene; Ol—oleate. $\sum_{n=0}^{n=3} 18{:}n = 100\%$.

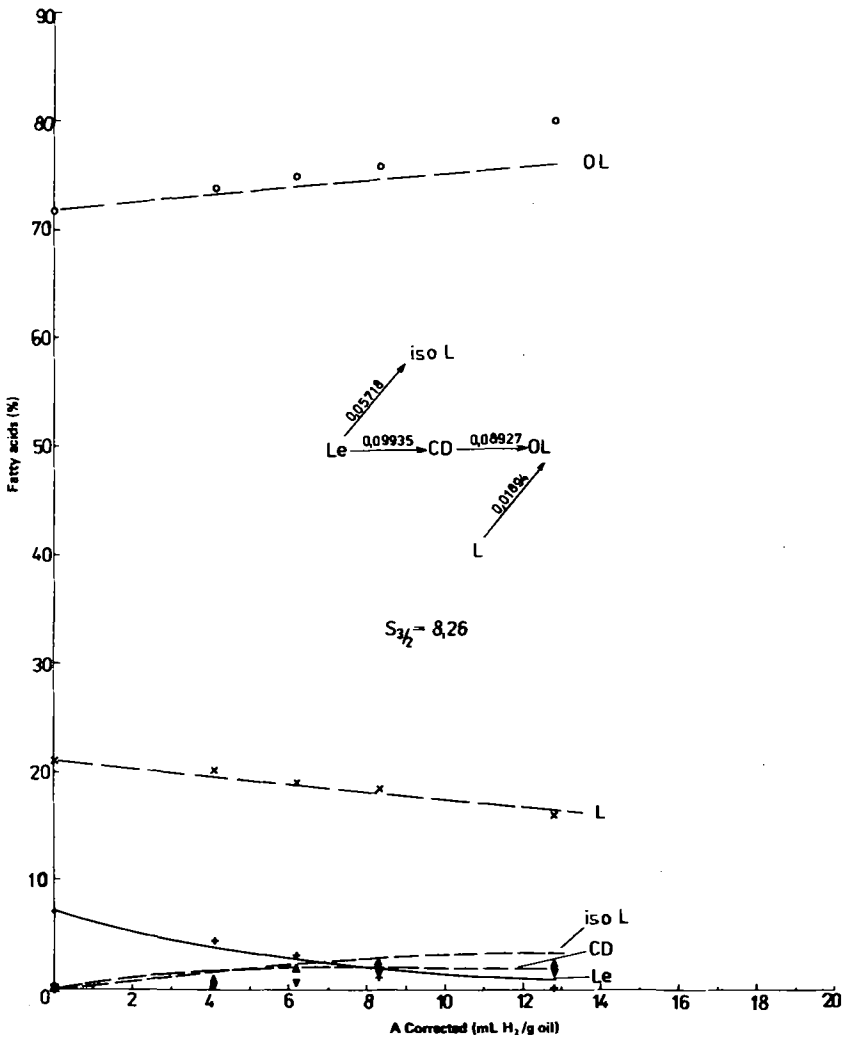


FIG. 5. Change in fatty acid composition during hydrogenation of the low-erucic oil with copper catalyst. Curves drawn by computer when experimental values best fit computer simulation according to reaction scheme are shown in inset. Le—linolenate; L—linoleate; CD—conjugated diene; isoL—nonconjugatable diene; Ol—oleate. $\sum_{n=0}^{n=3} 18{:}n = 100\%$.

TABLE II

***Trans* Isomer and 18:3 Acid Content in Rapeseed Oil Hydrogenated in the Presence of the Cu 1106P Catalyst (3% cat., 200 C) and for Comparison in the Presence of a Nickel Catalyst (0.05% Ni, 200 C)**

Rapeseed oil	$A_{cor.}$ (mL H_2/g oil)	18:3 (%)	*Trans* (%)
	Copper-chromite catalyst		
High-erucic	0	7.8	0.0
	3.4	5.0	tr
	7.5	1.8	3.5
	12.0	0.0	5.2
	20.5	0.0	9.2
"Wipol"	0	7.1	0.0
	3.2	4.4	0.0
	7.5	1.2	2.7
	12.0	0.1	5.4
	21.5	0.0	13.0
"Janpol"	0	6.8	0.0
	4.1	4.2	0.0
	8.3	1.2	3.1
	12.8	0.1	5.0
	21.7	0.0	11.5
	Nickel catalyst		
High-erucic	4.9	5.8	6.5
	11.7	3.6	10.8
	22.5	0.0	28.8

attributed to the presence of large amounts of erucic acids, i.e., 51.2 and 18.6% (Table I) in high- and medium-erucic oils, respectively, which nearly exclusively occupies the external positions in triglyceride molecules (Table I). This acid, though it does not undergo any transformations during the hydrogenation process, can, by its presence, slow the process as the result of the so-called steric effect. Also, the position occupied by the linolenic acid in triglyceride molecules of each of the oils is of some significance. In the high-erucic oil, practically all of the 18:3 acid is in the internal positions, whereas in low-erucic oil, only 65% of this acid is in position 2. During selective hydrogenation, this acid first is reduced and, as it was proven (22), fatty acids in external positions are hydrogenated more quickly than the same acids in internal positions, this fact should be reflected in the hydrogenation reaction rate. In effect, both of these factors—positional selectivity and the presence of large amounts of erucic acid—may combine to produce the observed experimental results in which the rate of high-erucic rapeseed oil selective hydrogenation is lower.

The tested rapeseed oils, after the elimination of linolenic acid by selective hydrogenation, and after separation of the metal, showed several times higher oxidative stability than the initial raw material and retained the liquid state at ambient temperatures.

ACKNOWLEDGMENTS

Supported in part by research grants from the Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Poland.

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[Received July 17, 1981]