Reactivity of Fatty Acids in the Different Positions of the Triglycerides during Hydrogenation of Canola Oil

Tie Fan[1], **L. deMan** and **J.M. deMan***
Department of Food Science, University of Guelph, Guelph, Ont., Canada N1G 2W1

Canola oil was hydrogenated under selective and nonselective conditions. After various hydrogenation times, the triglycerides were hydrolyzed by pancreatic lipase and the monoglycerides separated by TLC. Triglycerides and monoglycerides were analyzed for fatty acid composition and *trans* isomer content. The reaction rate in the 2- and 1,3-positions of the glycerides was identical and of first order kinetics. Since the 2-position of the canola oil contained higher levels of 18:2 acids, the rate of change was greater than in the 1,3-positions. There were indications of a slightly lower rate of *trans* formation in the 2-position during nonselective hydrogenation. Linoleate selectivities for the 2- and 1,3-positions were determined.

During the hydrogenation of vegetable oils, hydrogen is added to the double bonds of the fatty acid moieties of the triglycerides. Much information is available about the progress of the reaction in terms of changes in the fatty acid moieties. Much less is known about the relative effect of hydrogenation on the fatty acids in the 1,3- and 2-positions of the triglycerides. Mattson and Volpenhein (1) investigated the composition of fatty acids in the different positions of randomly rearranged soybean oil and concluded that the position of a fatty acid in the triglyceride molecule does not influence its rate of hydrogenation. Similar results were obtained by Suzuki and Murase (2), who analyzed randomized and non-randomized soybean oil after hydrogenation and concluded that *trans* isomerization is not affected by acyl position, and there is no acyl migration during hydrogenation. Several aspects of the effect of hydrogenation of canola oil have been examined previously, including the formation of *trans*-isomers, trisaturated glycerides and physical properties (3-6). In this study, changes in fatty acid composition and *trans*-isomers in the 2- and 1,3-positions of the glycerides during the hydrogenation of canola oil were investigated.

MATERIALS AND METHODS

The oil used was commercially refined and bleached canola oil. The sulfur content of the oil as determined by the Raney nickel method (7) was 2.3 mg/kg, and the volatile sulfur content as determined by the method of Abraham and deMan (8) was 0.28 mg/kg. Hydrogenation was carried out in a Parr pressure reaction apparatus, Series 4500 with 2-l capacity. The charge of oil was 1 kg. Hydrogenation procedure was followed as outlined in AOCS Tz 1a-78(9) with 0.2% nickel catalyst (AOCS standard, 25% Ni) and agitation speed of 600 rpm. Selective conditions were: temperature 200 C and hydrogen pressure 48 kPa (7 psi); nonselective conditions 165 C and 303 kPa (44 psi) (6). The extent of hydrogenation was controlled by refractometer, and iodine values were calculated from the fatty acid composition. The fatty acid composition was determined by gas liquid chromatography (GLC) of the methyl esters on a 150-cm packed column of 10% SP2330 on Chromosorb W/AW 100-120 mesh. Column temperature was 185 C and nitrogen flow rate 15 ml/min. *Trans* isomers were measured by infrared spectrophotometry (AOCS Cd 14-61) (9) using a Beckman 4230 spectrophotometer and NaCl cells of 1 mm pathlength.

Methyl elaidate and mono elaidin standards were obtained from Sigma Chemical Co., St. Louis, Missouri. Preparation of 2-monoglycerides was done using the IUPAC method (10). Pancreatic lipase was obtained from Sigma Chemical Co., St. Louis, Missouri. When the melting point of the fat to be analyzed was over 45 C, an addition of 0.3 ml hexane was made before hydrolysis. The 2-monoglycerides were separated from the reaction mixture by thin layer chromatography (TLC) on KSF silica gel plates of 250 μm thickness (Whatman Chemical Separation Inc., Clifton, New Jersey). The developing solvent was hexane-ethyl ether-formic acid (70:30:1). The 2-monoglyceride bands were scraped off the plates, extracted with ethyl ether and analyzed for fatty acid composition and *trans* content.

RESULTS AND DISCUSSION

The reaction rate of the oils during hydrogenation is measured by plotting the iodine value or logarithm of iodine value against time. In a semilogarithmic plot a straight line is indicative of first order kinetics (8). Because the iodine value of the 2-monoglycerides was determined as well as that of the oil, the iodine value of the fatty acids in the 1,3-positions could be calculated. Figure 1 is a semilogarithmic plot of iodine value vs time of selectively hydrogenated canola oil and the fatty acids

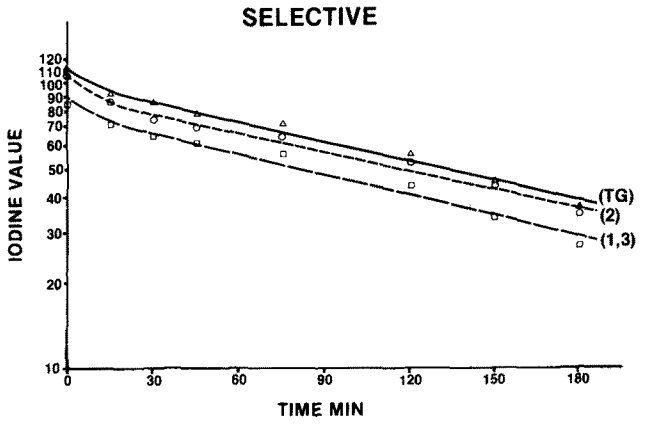

FIG. 1. Selective hydrogenation of canola oil. Semilogarithmic plot of iodine value vs time for triglycerides (TG), 2-position in the glycerides (2) and 1,3-positions in the glycerides (1,3).

[1]Permanent address, Cereal and Oil Chemistry Institute, Ministry of Commerce, Beijing, People's Republic of China.
*To whom correspondence should be addressed.

in 2- and 1,3-positions. There is a slight curvature in the curves at the early part of the hydrogenation; this usually is associated with high temperature and selective hydrogenation (11). A similar plot for nonselective hydrogenation (Fig. 2) yields straight lines for the oil and the 2- and 1,3-positions. Because the lines are essentially parallel these results indicate that the reaction rate of fatty acids in the different positions in the triglycerides is equal during both selective and nonselective hydrogenation. The calculations of iodine value in the 2- and 1,3-positions are based on mono- and diglyceride compositions, respectively; this is why the triglyceride iodine value is higher than those of either 2- or 1,3-positions. The fatty acid composition of canola oil and of the partial glycerides is listed in Table 1. As has been shown previously (12), the fatty acids present in the 2-position consist virtually completely of only three acids, oleic, linoleic and linolenic. The linoleic acid level in the 2-positon is almost twice that of the 1,3-positions. A small amount of *trans* isomers was found in the oil, possibly the result of processing conditions; all of the *trans* isomers were in the 1,3-positions.

The change in fatty acid composition of the triglycerides, the 2-position and the 1,3-positions as a function of decreasing iodine value during hydrogenation is given in Figure 3 for selective conditions and in Figure 4 for nonselective conditions. Results shown are for 18:0, 18:1 and 18:2 only. The 18:3 content was

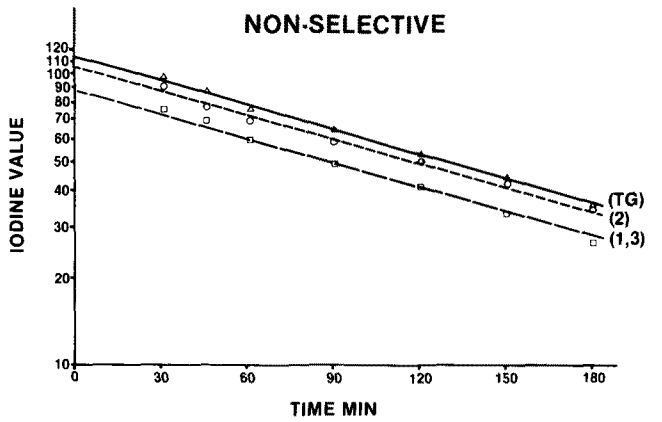

FIG. 2. Nonselective hydrogenation of Canola oil. Semilogarithmic plot of iodine value vs time for triglycerides (TG), 2-position of the glycerides (2) and 1,3-positions of the glycerides (1,3).

TABLE 1

Fatty Acid Composition and *trans* Isomer Content of Canola Oil, the 2-Position and the 1,3-Positions in the Glycerides

Fatty acid %	Canola oil	2-Position	1,3-Positions
16:0	3.9	0.1	5.8
16:1	0.2	0	0.3
18:0	1.7	0	2.5
18:1	63.3	59.6	65.1
18:2	20.2	30.2	15.2
18:3	8.2	10.1	7.3
Σ 18	93.4	99.9	90.2
20:0	0.4	0	0.6
20:1	1.5	0	2.3
22:0	0.2	0	0.3
22:1	0.5	0	0.7
trans	3.9	0	5.9

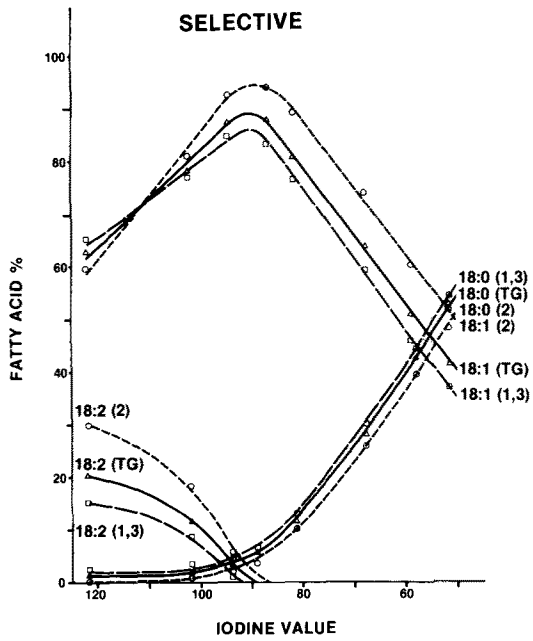

FIG. 3. Change in fatty acid composition during selective hydrogenation of canola oil. Triglycerides (TG), 2-position of the glycerides (2) and 1,3-positions of the glycerides (1,3).

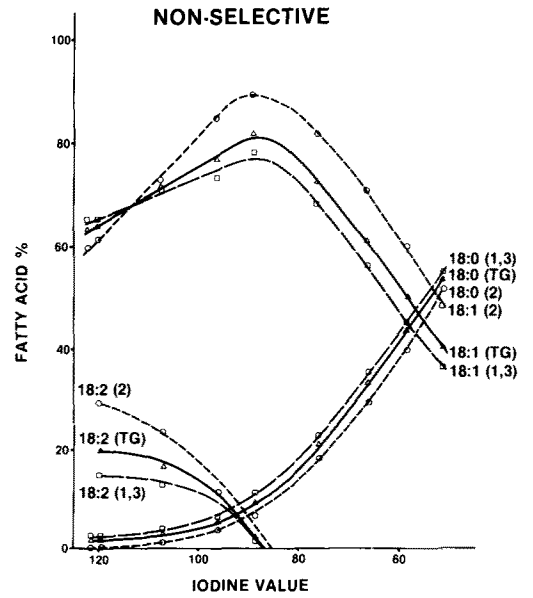

FIG. 4. Change in fatty acid composition during nonselective hydrogenation of canola oil. Triglycerides (TG), 2-position of the glycerides (2) and 1,3-positions of the glycerides (1,3).

reduced to zero at an iodine value of approximately 100. The 18:2 content decreased at a similar rate in the triglycerides and the 2- and 1,3-positions and approached zero at approximately 90 iodine value. The formation of 18:1 took place at a higher rate in the 2-position than in the 1,3-positions. However, it should be remembered that the initial level of 18:2 and 18:3 in the 2-position is considerably higher than in the 1,3-positions. Fatty acid changes during selective and nonselective hydrogenation were similar.

Changes in *trans*-isomer content during selective and non-selective hydrogenation are shown in Figures 5 and 6, respectively. There was essentially no difference in the rate of *trans* formation in the 2-position during selective hydrogenation when compared with those of the triglycerides and the 1,3-positions. However, when it is considered that the 2-position has higher unsaturation this might actually be considered to indicate a slightly lower rate of *trans* formation in the 2-position. During nonselective hydrogenation (Fig. 6) there is evidence of an increase rate of *trans* formation in the 2-position.

The formation of *trans* isomers has been expressed in terms of specific isomerization index (SII) (13). The SII is defined as the number of *trans* double bonds formed per unit of iodine value decrease. A plot of SII vs iodine value for selective hydrogenation (Fig. 7) shows similar changes for the triglycerides and the 2- and 1,3-positions, with a somewhat higher SII evident for the 1,3-position at lower iodine values, which confirms the suggestion made above that there may be a slightly

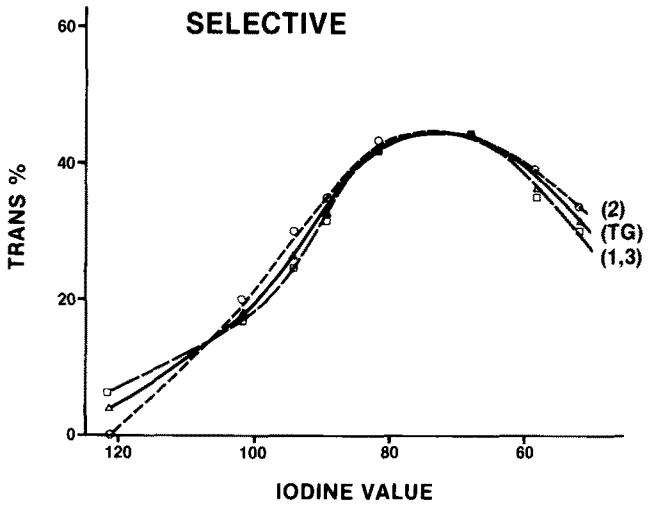

FIG. 5. Formation of *trans* isomers during selective hydrogenation of canola oil in the triglycerides (2) and 1,3-positions of the glycerides (1,3).

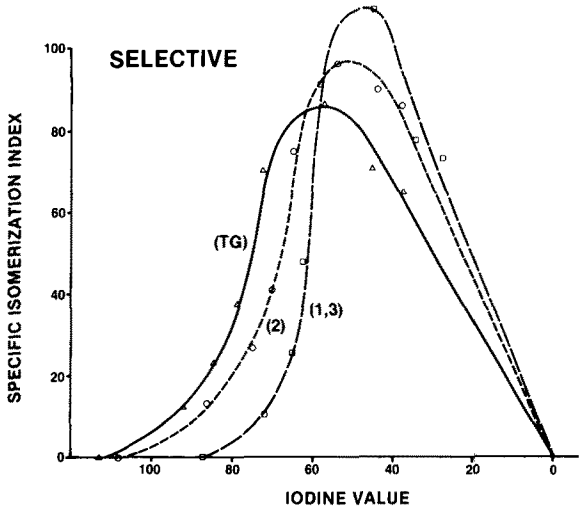

FIG. 7. Specific isomerization index during selective hydrogenation of canola oil in the triglycerides (TG), 2-position of the glycerides (2) and 1,3-positions of the glycerides (1,3).

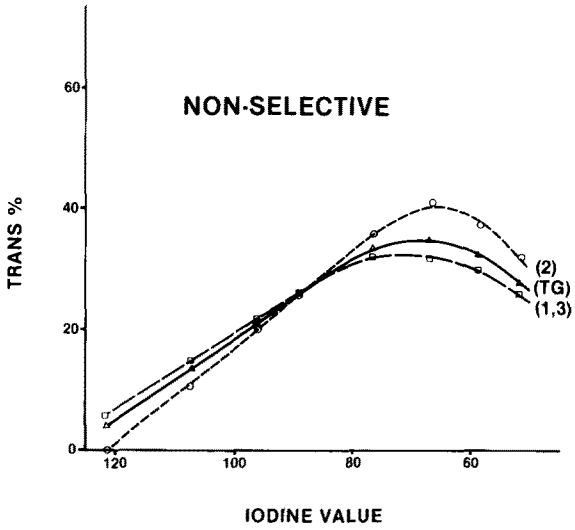

FIG. 6. Formation of *trans* isomers during nonselective hydrogenation of canola oil in the triglycerides (TG), 2-position of the glycerides (2) and 1,3-positions of the glycerides (1,3).

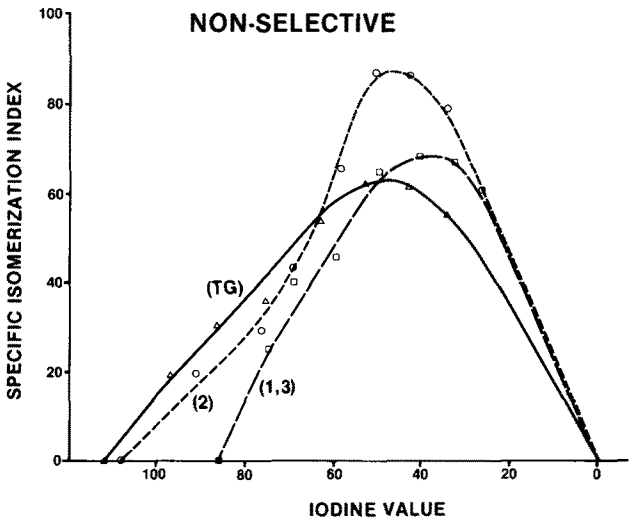

FIG. 8. Specific isomerization index during nonselective hydrogenation of canola oil in the triglycerides (TG), 2-position of the glycerides (2) and 1,3-positions of the glycerides (1,3).

TABLE 2

Linoleate Selectivity of Canola Oil, the 2-Position and the 1,3-Positions in the Glycerides

Hydrogenation conditions	Hydrogenation time (min)	Iodine value of oil	Linoleate Selectivity		
			Canola oil	2-Position	1,3-Positions
Selective	15	101.6	69.6	126.4	59.4
	30	93.7	238.4	92.1	152.5
Non-selective	15	119.5	7.4	10.7	—
	30	106.9	19.8	26.8	17.4
	45	95.7	20.1	28.3	14.7

lower rate of *trans* formation in the 2-position during selective hydrogenation. The data for nonselective hydrogenation (Fig. 8) show a higher SII for the 2-position at lower iodine values.

Linoleate selectivities were calculated from the fatty acid data by using the AOCS computer program, Recommended Practice Tz 1b-79(9). The results obtained for the oil, the 2-positions and the 1,3-positions are listed in Table 2. Under selective conditions the linoleate selectivity at 15 min was higher in the 2-position than in the 1,3-positions; this was reversed at 30 to 75 min and remained virtually the same thereafter. Under nonselective conditions the selectivity was higher at the 2-position during the first 45 min and remained virtually identical thereafter.

It is difficult to compare the selectivities of the 2- and 1,3-positions because of the different degrees of unsaturation in these positions.

The data in Table 2 demonstrate the difference in selectivities between selective and nonselective hydrogenation conditions.

The results obtained in this study indicate that the reaction rates of the 2- and 1,3-positions of canola oil triglycerides are identical. This is in accordance with findings of Suzuki and Murase (2), who found no difference in the rate and selectivities of the 2-position of soybean oil compared with the 1,3-position. Other workers have found differences in reaction rates at the 2-position. Drozdowski (14) studied linseed and cod liver oil and found that unsaturated fatty acids in the 1,3-positions are hydrogenated faster than those in the 2-position. Kaimal and Lakshminarayana (15), using cottonseed, sesame, soybean and safflower oils, found preferential hydrogenation of linoleic acid present in the 1,3-positions over that in the 2-position. Results obtained for *trans*-isomer formation in this study show only a slightly lower *trans* level in the 2-position of selectively hydrogenated canola oil and essentially no difference in nonselectively hydrogenated canola oil. This is in accordance with the results obtained by Suzuki and Murase (2) with soybean oil. However, Strocchi (16) found a preferential *trans* isomer formation at the 2-position of hydrogenated corn oil.

Fatty acids in the 2-position appear more reactive because of their higher degree of unsaturation, not because of their position in the triglyceride molecule.

ACKNOWLEDGMENT

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