TABLE III

Effect of Oil Concentration on Adsorption of Phosphorus on Silica[a]

Oil ppm P	Miscella % oil	Original P (mg/100 ml)	Adsorbed P (mg)
500	20	10.0	3.2
	40	20.0	5.0
1000	10	10.0	3.0
	20	20.0	5.1
	40	40.0	6.9

[a]1 g of silica reacted for 15 min with 100 ml miscella.

shows that the miscella containing less phosphorus exhibited a pattern (B) similar to the early portion of the isotherm. However, the adsorption pattern of the miscella containing 20 mg P differed widely (C). Although more absolute amounts of phosphorus were being removed from the miscella with increasing amounts of adsorbent, less phosphorus was adsorbed per gram of adsorbent. Thus, as the amount of adsorbent in the miscella increases, the adsorption capacity of a unit of adsorbent decreases. The reason for this behavior is not known. It does appear, however, that there are three isotherms, one for each level of adsorbent.

Effect of Concentration of Oil on Adsorption

Experiments were conducted to see if oil concentration influenced the adsorption of phosphorus. Table III shows how much phosphorus was adsorbed from oils containing 500 and 1000 ppm P. Although it takes two times the amount of the 500 ppm oil to achieve the same phosphorus level as with the 1000 ppm oil, there was no difference in the amount of phosphorus adsorbed based on P content up to 40% oil.

It was concluded that oil concentration in the miscella did not affect phosphorus adsorption below 40% oil. In our preliminary experiments, it was observed that phosphorus adsorption did not occur at around 45% oil. Also, concentrated levels of oil are difficult to pipette for proper sampling and analysis. Consequently, the conclusion by Gutfinger and Letan (3) on the poor adsorptive characteristics of silica for P may be incorrect because their adsorption experiment was conducted on pure oil instead of a dilute oil.

The observed adsorption isotherm pattern conceivably could result from competition by either IPA or triglyceride with phospholipids for sites on the silica. Data on changing the concentration of IPA (Fig. 1) or changing the concentration of oil (Table III) do not support the concept that either is competing with phosphorus for adsorption. Currently, we are studying the rates of P adsorption on silica for further insight into the observation that an equilibrium isotherm pattern exists and yet adsorption of the phosphorus is irreversible.

REFERENCES

1. Linters, L., and E. Handschumaker, JAOCS 27:260 (1950).
2. Lunde, G., L.H. Landmark and J. Gether, Ibid. 53:207 (1976).
3. Gutfinger, T., and A. Letan, Ibid. 55:856 (1978).
4. Beal, R.E., E.B. Lancaster and O.L. Brekke, Ibid. 33:619 (1956).
5. Freundlich, H. Colloid and Capillary Chemistry, translated by H.S. Hatfield from 3rd German edition. E.P. Dutton & Co., New York, 1922, 883 pages.
6. Bartlette, G.R., J. Biol. Chem. 234:466 (1959).
7. Brown, H.G., and H. Snyder, JAOCS 59:280 (1982).
8. Carroll, K.K., J. Lipid Res. 1:17 (1960).
9. Rich, A.D., JAOCS 31:374 (1954).
10. Brekke, O.L., in Handbook of Soy Oil Processing and Utilization, Erickson, D.R., E.H. Pryde, O.L. Brekke, T.L. Mounts and R.A. Falb, eds., ASA and AOCS (1980), pp. 17-88.

[Received June 5, 1984]

Polymorphism of Hydrogenated Canola Oil

AZZA NAGUIB-MOSTAFA and **JOHN M. deMAN**, Department of Food Science, University of Guelph, Guelph, Ont. Canada N1G 2W1

ABSTRACT

The polymorphism of hydrogenated Canola oil was investigated using X-ray diffraction. The effects of hydrogenation conditions (selective: 200 C; 48 kPa hydrogen pressure, and nonselective: 160 C; 303 kPa) and degree of unsaturation on the transformation $\beta' \rightarrow \beta$ are discussed. A densitometer was used to follow the changes in the relative density of the characteristic short spacings, in an attempt to present a semiquantitative measure of $\beta' \rightarrow \beta$ transformation during storage. The samples studied were selectively and nonselectively hydrogenated Canola oils of iodine values (IV) 70 and 60, respectively. Among the 4 samples, the selectively hydrogenated sample with IV 70 was the most stable and the nonselectively hydrogenated sample with IV 60 the least stable.

INTRODUCTION

As a result of selective breeding, most of the rapeseed grown in Canada now consists of cultivars which are low in erucic acid and glucosinolates. These cultivars and the oil produced from them are designated as Canola. Canola oil differs from high erucic acid rapeseed oil in that the erucic acid has been replaced mainly by oleic acid, thus raising the level of C18 acids to about 95%. This has affected the melting characteristics and polymorphic behavior of hydrogenated Canola oil. Hydrogenated low erucic acid rapeseed oil has been shown to exist mainly in the (β) modification (1). This results in the formation of large crystals, in the range of 5-25 μm, which may impart a grainy texture and cause products to be hard and brittle. A commonly used procedure to prevent the formation of β crystals is the addition of sorbitan esters (2,3). Recently (4), it has been suggested that diglycerides also may be useful in preventing β crystallization.

One of the factors which may influence polymorphic stability is the *trans* content of the hydrogenated oil. It is well known (5) that selective hydrogenation conditions favor the formation of high *trans* levels. In the present study, selectively and nonselectively hydrogenated Canola oils were examined for polymorphic stability by X-ray diffraction analysis.

MATERIALS AND METHODS

Commercially refined and bleached Canola oil was hydrogenated in a Parr Pressure Reaction Apparatus with a 2 l bomb and a charge of 1 kg oil. American Oil Chemists' Society standard catalyst was used at a level of 0.2% by weight of the oil. Selective conditions were 200 C and 48 kPa hydrogen pressure, and nonselective conditions were 160 C and 303 kPa hydrogen pressure. Hydrogenations were carried out to yield products with IV of 70 or 60. When hydrogenation was completed, the samples were filtered while still warm; this was followed by storage in tightly capped jars in a refrigerator at a temperature of 5 C. The samples were prepared for X-ray scanning by first melting the hydrogenated oil, followed by recrystallization at 15 C directly on the X-ray cell film (Spex Industries, Metuchen, New Jersey). The X-ray cells were stored at 15 C in a dessicator for the duration of the experiment. *Trans* isomer content was determined by infra-red spectrophotometry (AOCS method Cd 14-61) using a Beckman model 4300 infra-red spectrophotometer. Dropping points were determined with the Mettler FP 3 automatic dropping point apparatus (6) and solid fat by wide-line NMR using a Newport MK III quantity analyzer (7). Fatty acid composition was determined by gas liquid chromatography (GLC) of the methyl esters using a Varian 1400 gas chromatograph with a 2 m column packed with 20% DEGS on Chromosorb RZ 60-80 mesh operated at 185 C. X-ray diffraction patterns were obtained with a Diffractis 601 X-ray generator and Guinier camera model FR 552 of Enraf-Nonius, Delft, The Netherlands. The X-ray tube was a fine focus copper anode tube. The sample holder was modified so that cooling water from a thermostat bath could be circulated to maintain the sample at sub-ambient temperature. X-ray patterns were recorded at 15 C on Kodak Kodirex 35 mm unperforated film. The films, after development, were scanned with a Joyce-Loebl Chromoscan densitometer using a 2D filter and 10 x 0.1 mm aperture.

RESULTS AND DISCUSSION

Dropping points and *trans* fatty acid content of the 4 samples studied are presented in Table I. Among the 4 samples, the *trans* fatty acid content varied from 32.6% for the nonselectively hydrogenated sample with IV 60 to 51.5% for the selectively hydrogenated sample with IV 70. Solid fat content of the samples has been determined at 6 different temperatures, and the results are presented in Table II. The selectively hydrogenated samples (IV 70 and 60) had a higher solid fat content than the corresponding nonselectively hydrogenated samples. Similar results have been reported by Teasdale (8). Table III presents results of the fatty acid GLC analysis. The selectively hydrogenated samples (IV 70 and 60) had higher levels of 18:1 isomers and lower levels of stearic acid than the nonselectively hydrogenated samples.

Table IV summarizes the results obtained from the densitometer scanning of the X-ray diffraction pattern films of the short spacing area over a period of 60 days. These results show that there is a difference in the stability of selectively hydrogenated versus nonselectively hydrogenated samples with the same IV. The latter were less stable under the conditions of storage used. The following observations were made: The transition $\beta' \rightarrow \beta$ was detected using the densitometer after 6 days for the nonselectively hydrogenated sample with IV of 60. On the other hand, the selectively hydrogenated sample with IV of 60 showed this transition only after 60 days. The samples with IV 70 also differed in their stability. The nonselectively hydrogenated sample showed $\beta' \rightarrow \beta$ transition after 29 days. Under the same conditions, the selectively hydrogenated sample with the same IV was still stable in the β' modification after 60 days.

All of the samples studied crystallized in the β'-form, which was evidenced by the short spacings at 4.2 Å and 3.8 Å. Figure 1 shows the β' modification X-ray diffraction

TABLE 1

Dropping Point and *Trans* Fatty Acid Content of Hydrogenated Canola Oil

Sample	*Trans* fatty acid (%)	Dropping point (C)
Selective IV 70	51.5	44.3
Selective IV 60	44.0	50.3
Nonselective IV 70	38.5	43.0
Nonselective IV 60	32.6	50.7

TABLE II

Solid Fat Content of Hydrogenated Canola Oil

Sample	Solid fat (%)					
	0 C	5 C	10 C	20 C	30 C	35 C
Selective IV 70	81.0	79.8	72.0	62.6	33.0	21.2
Selective IV 60	88.0	87.3	84.0	78.6	56.0	43.5
Nonselective IV 70	62.4	61.5	51.8	41.0	20.0	13.0
Nonselective IV 60	80.7	79.0	73.7	68.0	47.4	38.7

TABLE III

Fatty Acid Composition of Canola Oil and Hydrogenated Canola Oil.

Sample	Fatty acid wt %					
	16:0	18:0	18:1	18:2	18:3	20:1
Canola oil	3.9	1.3	58.7	22.8	11.5	0.8
Selective IV 70	4.2	18.0	71.7	2.4	0.9	1.2
Selective IV 60	4.0	28.9	63.6	1.0	1.2	0.8
Nonselective IV 70	4.2	18.8	69.8	4.1	1.7	1.2
Nonselective IV 60	4.2	31.8	60.3	2.0	tr	tr

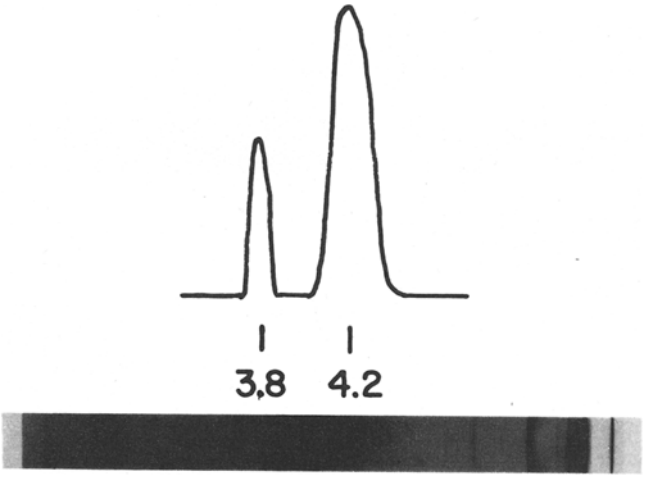

FIG. 1. X-ray diffraction pattern film with a scan of the short spacing area of hydrogenated Canola oil immediately after crystallization. The sharp line at the right on the film is the undiffracted beam. This pattern is representative of the β' modification.

TABLE IV

Short Spacings and Chain Packing of Hydrogenated Canola Oil During a Storage Period of 60 Days

Sample	Principal short spacings %			Chain packing	Storage time
	4.6 Å	4.2 Å	3.8 Å		
Selective IV 70	–	80 (d)	20	β'	
Nonselective IV 70	–	80 (d)	20	β'	
Selective IV 60	–	80 (d)	20	β'	0 hr
Nonselective IV 60	–	80 (d)	20	β'	
Selective IV 70	–	80 (d)	20	β'	
Nonselective IV 70		80 (d)	20	β'	
Selective IV 60		80 (d)	20	β'	6 days
Nonselective IV 60	8	59 (d)	33	$\beta' + \beta$	
Selective IV 70	–	80 (d)	20	β'	
Nonselective IV 70	10	66 (d)	24	$\beta' + \beta$	
Selective IV 60	–	80 (d)	20	β'	30 days
Nonselective IV 60	18	46 (d)	35	$\beta' + \beta$	
Selective IV 70	–	80 (d)	20	β'	
Nonselective IV 70	16	51 (d)	33	$\beta' + \beta$	
Selective IV 60	10	53 (d)	38	$\beta' + \beta$	60 days
Nonselective IV 60	26	36 (d)	38	$\beta' + \beta$	

(d) indicates a diffuse band.

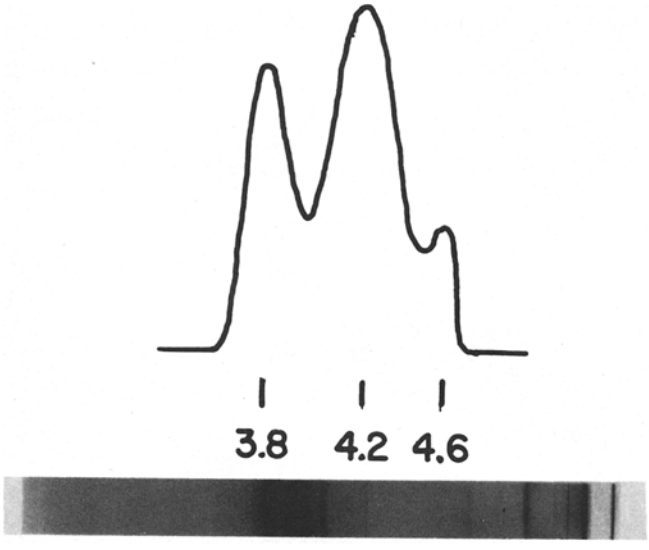

FIG. 2. X-ray diffraction pattern film with a scan of the short spacing area of nonselectively hydrogenated Canola oil with IV 60 after 6 days' storage.

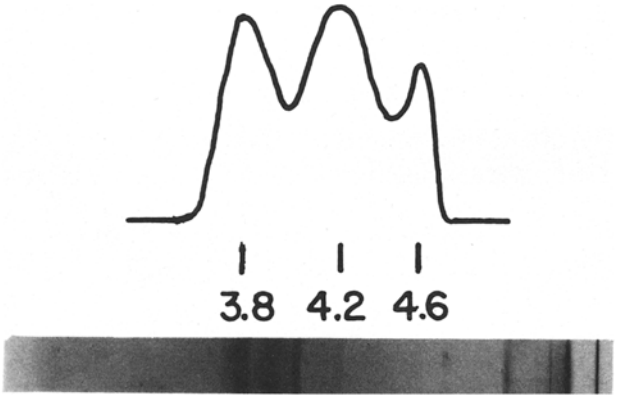

FIG. 3. X-ray diffraction pattern film with a scan of the short spacing area of nonselectively hydrogenated Canola oil with IV 60 after 30 days' storage.

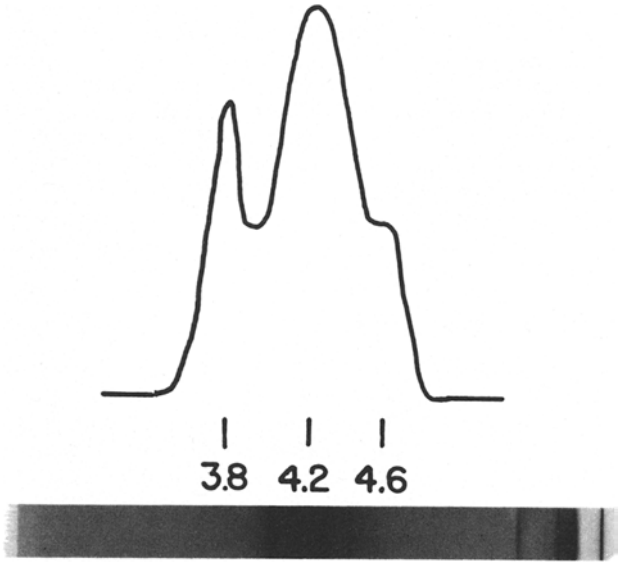

FIG. 4. X-ray diffraction pattern film with a scan of the short spacing area of nonselectively hydrogenated Canola oil with IV 70 after 30 days' storage.

pattern together with a scan of the short spacing area of all the samples immediately after crystallization. The sharp line at the right on the film is caused by the undiffracted beam. Figure 2 shows the X-ray diffraction pattern together with a scan of the short spacing area of the nonselectively hydrogenated sample with IV 60 after 6 days. The start of $\beta' \rightarrow \beta$ transformation is evident by the presence of a band at 4.6 Å, which is the strong characteristic short spacing of β modification. Figure 3 represents the X-ray diffraction pattern and scan of the same sample after 30 days. Figure 4 represents the X-ray diffraction pattern and scan of the nonselectively hydrogenated sample with IV 70 showing the presence of β' and β modification. Figure 5 shows the X-ray diffraction pattern and scan of the selectively hydrogenated sample with IV 60 after 60 days. Figure 6 represents the β modification of the nonselectively hydrogenated sample with IV 60 after 120 days.

Among the 4 samples studied, the selectively hydro-

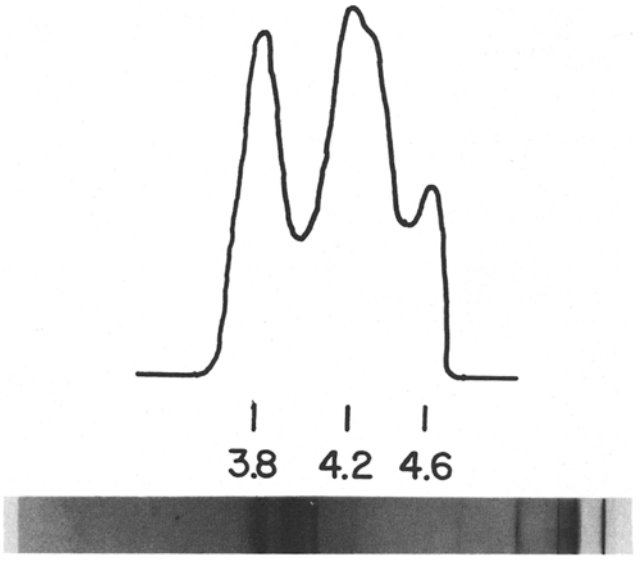

FIG. 5. X-ray diffraction pattern film with a scan of the short spacing area of selectively hydrogenated Canola oil with IV 60 after 60 days' storage.

genated sample with IV 70 was the most stable, and the nonselectively hydrogenated sample with IV 60 was the least stable. The sample exhibiting maximum stability was the one with the highest *trans* fatty acid content (51.5%), and the least stable sample was the one having the lowest *trans* fatty acid content (32.6%). The order of decreasing stability coincides with the order of decreasing the *trans* fatty acid content. This points to the fact that *trans* fatty acid level might be a determining factor in the rate at which the polymorphic transition occurs. The stabilizing effect of a high *trans* fatty acid content might be explained on the basis of perturbing the crystal lattice, thus preventing rearrangement to the β modification.

These results indicate that conditions of hydrogenation and factors inherent in the fat should be considered during the preparation of hydrogenated oil products. The densitometer provided a semiquantitative method for following polymorphic transitions occurring during fat storage.

ACKNOWLEDGMENT

The Natural Sciences and Engineering Research Council of Canada and the Ontario Ministry of Agriculture and Food provided financial support. B. Blackman provided technical assistance.

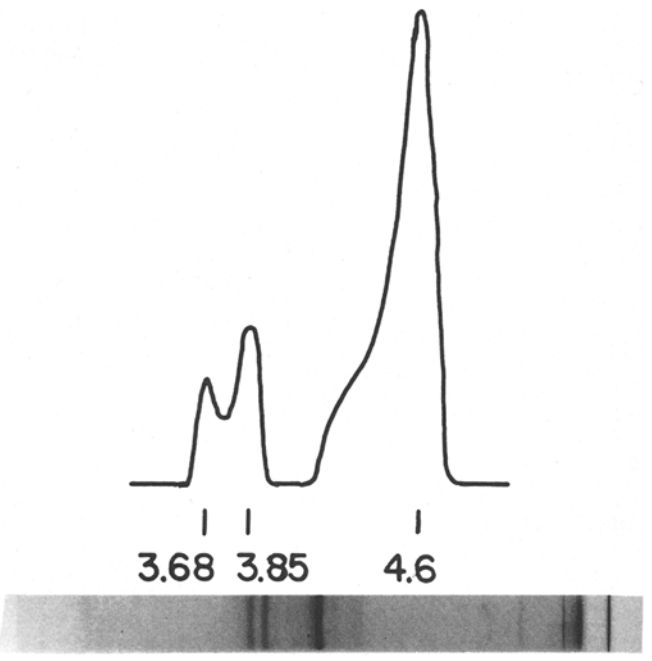

FIG. 6. X-ray diffraction pattern film with a scan of the short spacing area of nonselectively hydrogenated Canola oil with IV 60. The pattern is representative of the β modification.

REFERENCES

1. Weinberg, B., Can. Inst. Food Sci. Technol. J. 5:A57 (1972).
2. Hernqvist, L., Proc. 10th Scandinavian Symp. on Lipids, Nyborg, Denmark, (1979) p. 224.
3. Lee, S. M.Sc. Thesis, University of Guelph (1982).
4. Hernqvist, L., B. Herslöf, K. Larsson and O. Podloha, J. Sci. Food Agric. 32:1197 (1981).
5. Bansal, J.D., and J.M. deMan, J. Food Sci. 47(4):1338 (1981).
6. Mertens, W.G., and J.M. deMan, JAOCS 49:366 (1972).
7. Mertens, W.G., and J.M. deMan, Can. Inst. Food Sci. Technol. J. 5:77 (1972).
8. Teasdale, B.F. Paper presented to the 12th International Grain Industry Course, Canadian International Grains Institute, Winnipeg, Manitoba (1979).

[Received November 21, 1983]