Hydrogenation of Canola Oil as Affected by Chlorophyll

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Chlorophyll was added to refined and bleached canola oil before hydrogenation, and the effects on hydrogenation rate, fatty acid composition and the percentage *trans* isomers were determined. The hydrogenation rate was greatly slowed down by chlorophyll under selective (200 C and 48 kPa) and nonselective conditions (165 C and 303 kPa). Higher levels of chlorophyll reduced the reaction rate more than the lower levels under both conditions. Dropping points were slightly higher for the nonselectively hydrogenated samples than for the selectively hydrogenated ones. Addition of 1 mg/kg or more chlorophyll decreased the solid fat content under nonselective conditions. Addition of chlorophyll reduced the *trans* isomer content under nonselective conditions. Nonselective conditions also resulted in a greater decrease of 18:3 and faster production of 18:0 than selective conditions at all levels of chlorophyll addition.

Canola has become the most important oilseed crop in Canada; the oil is used for the production of margarines, shortenings and other fat products. Canola is the name reserved for rapeseed low in glucosinolates and erucic acid. The Canola varieties grown in Canada belong to summer rape (*Brassica napus*) and summer turnip rape (*Brassica campestris*) species, and account for about 45-50% of all deodorized fats and oils used in Canada. The presence of hydrogenation catalyst poisons may be responsible for less than ideal hydrogenation characteristics in some batches of the oil.

The inhibitory action of sulphur, phosphorus, free fatty acids, soaps and oxidation products has been investigated by Drozdowski (1). The green color in an immature seed is caused by the photosynthetic pigment chlorophyll (2). The main reason for the presence of chlorophyll in rapeseed is freezing before the seed has matured sufficiently. During extraction, a proportion of the chlorophyll will remain in oil and is very difficult to remove with conventional bleaching earth (3). Chlorophyll content is a measure of oil quality. Besides giving a product with undesirable color, chlorophyll has been implicated as a prooxidant in oxidative rancidity in oils (4). Crude oils with chlorophyll content greater than 20-30 mg/kg are difficult to refine. Oils with higher chlorophyll levels require special treatment during refining to obtain acceptable color values, free fatty acid content, oxidation values and flavor stability.

When present in canola seed, the green-colored chlorophyll is converted to russet-colored pheophytins during crushing. Both of these in the oil can be measured by using AOCS official method Cc 13d-55. Koritala (5) reported that addition of pheophytins reduced the hydrogenation rate of soybean oil. In this paper, the term chlorophyll is used to represent chlorophyll "a" and "b" and the respective pheophytins which absorb near 670 nm. This study deals with the relationship between chlorophyll content and the rate of hydrogena-

TABLE 1

Chlorophyll Content of Canola Oil Samples Obtained from Various Industrial Sources in Canada

Type of oil	Chlorophyll content mg/kg	s.d.
Physically refined oil		
1	2.12	0.0722
2	1.83	0.0285
3	0.0796	0.00533
4	0.0578	0.00384
5	0.0251	0.00342
6	0.0438	0.00399
Alkali refined and bleached oil		
1	0.0891	0.00543
2	0.0248	0.00531
3	0.0129	0.00781
4	0.0115	0.00482
Refined oil (unknown treatment)		
1	3.05	0.0291
2	2.79	0.0302
3	3.13	0.0288
4	2.40	0.0314
5	1.90	0.0183

Each value represents the mean of 10 determinations.

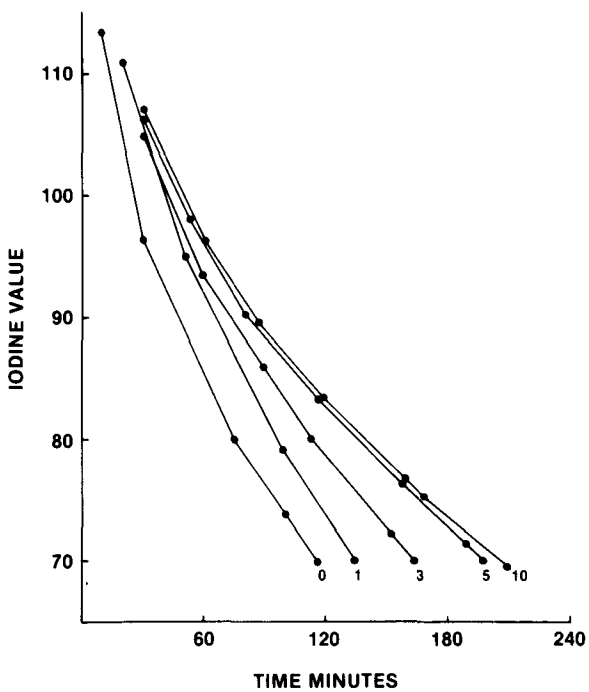

FIG. 1. Hydrogenation of canola oil under selective conditions with addition of 0, 1, 3, 5 and 10 mg/kg chlorophyll.

tion of canola oil.

MATERIALS AND METHODS

Canola oil samples were received from three different oil processing industries in Canada. Oil soluble chlorophyll was purchased from ICN Pharmaceuticals Inc., Plainview, New York. The chlorophyll content in the oils was determined using AOCS official method Cc 13d-55 with 50 mm Precision Optical Cells supplied by Fisher Scientific Co. Ltd., Toronto, Canada (14 386 346B 1EA). Spectrophotometric measurements were made on a Bausch and Lomb model 6917 Spectronic 70. Analytical grade carbon tetrachloride (redistilled) was used as blank.

Hydrogenation was carried out in a Parr pressure reactor apparatus, series 4500, using a 2 l bomb and a charge of 1 l oil. The American Oil Chemists' Society (AOCS) standard catalyst containing 25% nickel was used at a level of 0.2% by weight of the oil. Hydrogenation conditions used were: selective, 200 C and a hydrogen pressure of 48 kPa; and nonselective, 165 C and a hydrogen pressure of 303 kPa. The temperature was controlled ±1 with a Parr temperature controller, model 4821, and agitation at 850 rpm. Chlorophyll was added to the refined and bleached oil in the reactor in the form of a stock solution containing 60 mg/kg of chlorophyll in canola oil. Samples were taken during hydrogenation through the sampling valve at predetermined intervals. Hydrogenations were stopped at iodine values (IV) 90, 80 and 70, and the partially hydrogenated oils were analyzed for iodine value, *trans* fatty acids, dropping point, solid fat content and fatty acid composition.

Iodine values were determined by the Wijs method, AOCS Cd 1-25. Fatty acid composition of the oils was determined on the methyl esters prepared by the method of Shehata and deMan (6). The methyl esters were analyzed by gas liquid chromatography (GLC) using a Varian model 1400 instrument equipped with flame ionization detector (FID). Column length was 125 cm, diameter 2 mm, carrier gas flow 30 ml/min, and the column packing was 15% DEGS on Chromosorb RZ 60-80 mesh operated at 180 C. Total isolated *trans* fatty acid content was determined by infrared spectrometry, AOCS tentative method Cd 14-61, using a Beckman model IR 4230 infrared spectrophotometer. The solid fat content was measured by using the method of Mertens and deMan (7) by wide line nuclear magnetic resonance (NMR) using a Newport Analyzer Mk3 with temperature controlled magnet assembly. Measurements were taken at 0, 5,10, 20, 30 and 60 C. Dropping points of the hydrogenated fat were determined by a method reported by Mertens (8) using a Mettler FP 83 dropping point cell equipped with a Mettler FP 800 central processor.

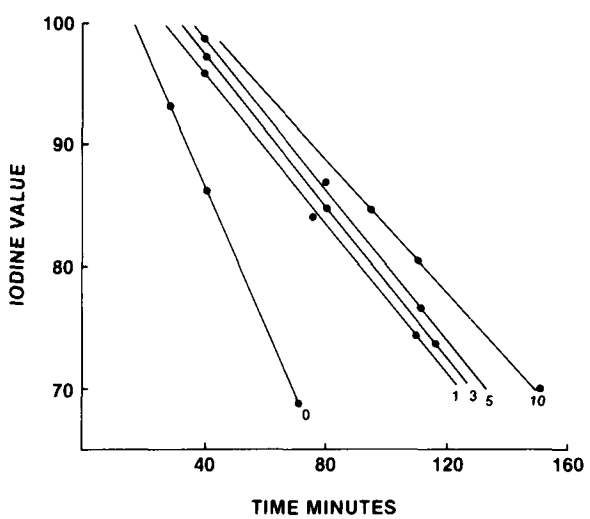

FIG. 2. Hydrogenation of canola oil under nonselective conditions with addition of 0, 1, 3, 5 and 10 mg/kg chlorophyll.

RESULTS AND DISCUSSION

Chlorophyll content of 15 different canola oil samples was measured using the AOCS official method, and the results are presented in Table 1. Most of the physically

TABLE 2

Fatty Acid Composition (wt % as Methyl Esters), Dropping Point and *trans* Isomer Content of Selectively Hydrogenated Canola Oil with Added Chlorophyll[a]

	Chlorophyll mg/kg				
Fatty acid	0	1	2	5	10
16:0	4.4	4.5	4.3	4.3	4.2
16:1	0.2	0.2	0.3	0.3	0.3
18:0	8.9	8.0	9.0	7.9	9.9
18:1	78.5	73.6	78.1	77.3	75.6
18:2	6.3	6.7	7.1	7.5	7.9
18:3	1.7	1.6	1.4	1.3	1.4
Iodine value	89.8	90.0	90.5	90.3	89.0
trans isomer (%)	34.6	36.6	36.8	36.4	37.4
Dropping point (° C)	27.7	27.8	27.3	26.8	29.4
16:0	4.4	4.3	4.3	4.2	4.3
16:1	0.3	0.2	0.3	0.3	0.1
18:0	18.6	19.7	17.1	16.4	17.6
18:1	74.5	71.7	71.8	71.1	71.6
18:2	1.0	1.1	4.1	4.6	4.6
18:3	1.2	1.2	1.1	1.2	1.1
Iodine value	80.1	78.7	80.3	80.5	79.8
trans isomer (%)	42.5	42.3	42.1	44.1	42.4
Dropping point (° C)	38.8	40.7	38.2	37.6	38.6
16:0	4.5	4.4	4.4	4.4	4.3
16:1	0.2	0.2	0.2	0.2	0.3
18:0	31.3	30.3	27.8	29.4	30.2
18:1	61.5	62.3	63.2	63.7	62.3
18:2	0.2	0.4	0.4	0.9	0.9
18:3	0.9	1.0	1.0	1.1	1.2
Iodine value	69.3	69.8	70.1	68.6	69.8
trans isomer (%)	45.4	45.3	43.6	44.8	43.2
Dropping point (° C)	47.4	47.1	46.7	46.4	47.0

[a]Expressed as mg chlorophyll/kg oil.

TABLE 3

Fatty Acid Composition (wt % as Methyl Esters), Dropping Point and *trans* Isomer Content of Nonselectively Hydrogenated Canola Oil with Added Chlorophyll[a]

	Chlorophyll mg/kg				
Fatty acid	0	1	3	5	10
16:0	4.2	4.3	4.3	4.3	4.4
16:1	0.4	0.3	0.3	0.2	0.2
18:0	9.5	10.3	10.7	11.5	11.2
18:1	75.9	75.5	75.1	74.0	73.8
18:2	7.1	7.2	7.2	7.5	9.2
18:3	1.3	1.2	1.1	1.0	0.8
Iodine value	89.5	89.6	88.9	89.3	90.1
trans isomer (%)	33.1	30.8	30.3	30.1	30.0
Dropping point (° C)	28.2	29.6	29.7	31.0	30.1
16:0	4.3	4.4	4.4	4.4	4.3
16:1	0.3	0.2	0.2	0.2	0.2
18:0	20.8	19.7	20.3	21.1	19.6
18:1	72.4	72.7	68.6	67.7	68.9
18:2	0.3	0.5	4.9	5.0	5.9
18:3	1.1	1.0	0.8	0.8	0.6
Iodine value	79.8	78.9	79.6	79.0	80.2
trans isomer (%)	39.6	35.6	35.6	34.9	34.2
Dropping point (° C)	41.6	40.7	40.6	41.3	39.4
16:0	4.3	4.4	4.4	4.4	4.3
16:1	0.1	0.1	0.1	0.1	0.2
18:0	31.9	30.4	32.0	30.8	30.2
18:1	61.0	62.4	62.3	62.4	63.3
18:2	Tr	0.1	0.2	0.2	0.2
18:3	1.1	0.9	0.8	0.8	0.5
Iodine value	68.8	70.1	69.1	69.6	69.6
trans isomer (%)	40.4	37.6	37.1	35.0	34.0
Dropping point (° C)	48.6	47.8	47.5	47.8	47.7

[a]Expressed as mg chlorophyll/kg oil.

refined oils had higher chlorophyll content than alkali refined and bleached oils. Refined and bleached oil was hydrogenated under selective and nonselective conditions with 0.05% nickel and with 0, 1, 3, 5 and 10 mg/kg chlorophyll. A plot of iodine value vs time under selective conditions with different levels of chlorophyll is shown in Figure 1. The shape of these curves indicates catalyst poisoning (9). Under nonselective conditions, although higher levels of chlorophyll prolonged the reaction, poisoning was not as marked as under selective conditions. Figure 2 illustrates the zero order kinetics prevailing under nonselective conditions. Addition of 1 mg/kg or more chlorophyll greatly increased the time to reach IV 70. Fatty acid composition, *trans* isomer content and dropping points of the selectively and nonselectively hydrogenated oils are presented in Tables 2 and 3, respectively. Higher levels of chlorophyll provided higher amounts of 18:2 under both conditions.

TABLE 4

Effect of the Addition of Chlorophyll[a] on the Solid Fat Content of Selectively Hydrogenated Canola Oil

Added Chlorophyll mg/kg	Solid fat (%)				
	IV	5 C	10 C	20 C	30 C
0	89.8	31.5	24.5	11.4	3.8
1	90.0	30.3	23.1	10.4	0.8
3	90.5	29.0	22.2	10.0	2.9
5	90.3	30.5	23.8	12.7	5.3
10	89.0	34.1	26.4	15.0	6.2
0	80.1	58.5	52.2	38.3	18.2
1	78.7	65.1	60.0	46.1	24.4
3	80.3	58.1	49.5	36.1	18.3
5	80.5	55.8	48.7	35.0	16.2
10	79.8	59.7	52.8	39.0	18.4
0	69.3	79.9	76.0	68.8	50.3
1	69.8	79.9	76.0	68.7	48.9
3	70.1	78.3	72.9	64.8	44.9
5	68.6	76.5	74.6	64.6	43.7
10	69.8	78.4	74.8	68.7	49.1

[a]Expressed as mg chlorophyll/kg oil.

TABLE 5

Effect of the Addition of Chlorophyll[a] on the Solid Fat Content of Nonselectively Hydrogenated Canola Oil

Added Chlorophyll mg/kg	Solid fat %				
	IV	5 C	10 C	20 C	30 C
0	89.5	23.9	19.8	7.9	4.1
1	89.6	25.7	20.1	12.1	6.9
3	88.9	24.8	18.8	10.2	5.5
5	89.3	26.9	21.8	12.0	6.5
10	90.1	24.2	20.5	11.9	5.5
0	79.8	57.8	51.8	40.5	22.7
1	78.9	51.1	43.8	33.7	18.1
3	79.6	52.1	45.7	34.5	17.7
5	79.0	54.2	47.8	36.8	20.7
10	80.2	49.1	43.8	33.2	18.3
0	68.8	75.9	73.5	65.2	48.6
1	70.1	71.6	68.6	59.8	41.4
3	69.1	73.7	69.9	63.7	45.3
5	69.6	71.8	68.0	60.3	42.1
10	69.6	71.8	67.4	60.3	40.0

[a]Expressed as mg chlorophyll/kg oil.

The solid fat contents of the partially hydrogenated oils are listed in Tables 4 and 5 for selective and nonselective conditions, respectively. With increased levels of added chlorophyll, solid fat levels were generally lower under both conditions.

For similar iodine values, lower dropping points were obtained for most of the samples when higher levels of

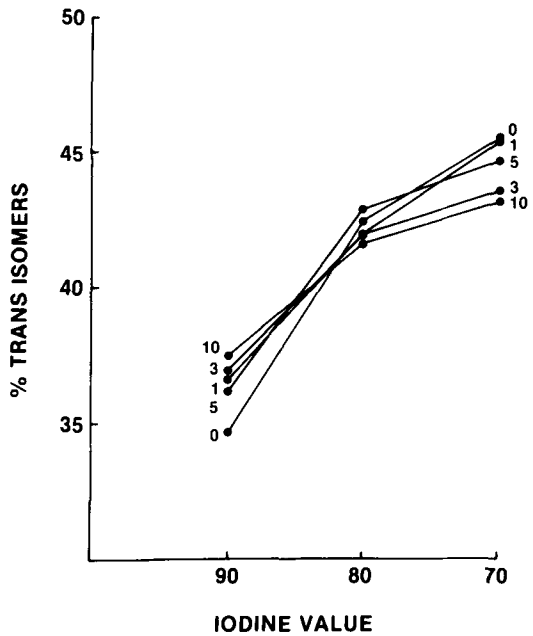

FIG. 3. Percentage of *trans* isomers formed during selective hydrogenation of canola oil with addition of 0, 1, 3, 5 and 10 mg/kg chlorophyll.

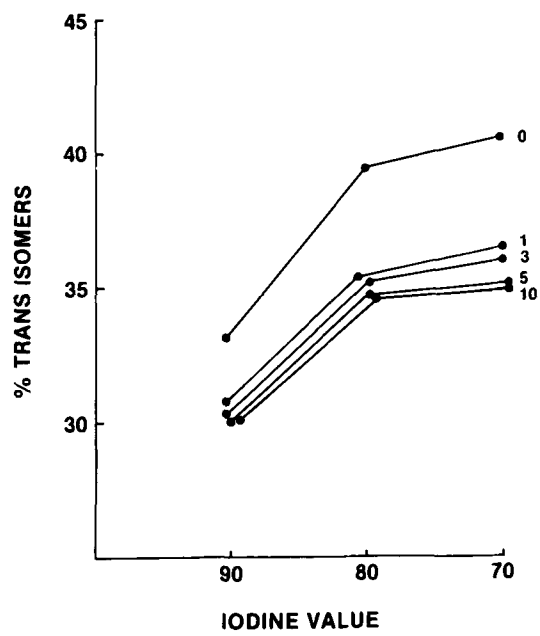

FIG. 4. Percentage of *trans* isomers formed during nonselective hydrogenation of canola oil with addition of 0, 1, 3, 5 and 10 mg/kg chlorophyll.

chlorophyll were added. This effect was more pronounced under nonselective conditions. The percentage of *trans* isomers formed is shown in Figures 3 and 4. Under nonselective conditions, the levels of *trans* isomers were lower with higher levels of added chlorophyll. Similar results were observed by Beckman (3) during vegetable oil hydrogenation in the presence of phosphorus. The reason for this occurrence may be that chlorophyll resides at the pore entrance of the catalyst and prevents the exit of the triglycerides which are already in the pore. The result is higher saturation in triglycerides. Due to high concentration of hydrogen at the nickel surface and the low availability of multiple bonds to be hydrogenated, the *trans* isomer content is reduced. This was found to be true especially under nonselective conditions where high hydrogen pressure was maintained. This also explains the larger amounts of 18:0 under nonselective conditions. It is known that addition of sulfur increases the production of *trans* isomers (10). This is in contrast to the effect observed with chlorophyll.

This study revealed the capability of chlorophylls and/or their decomposition products to reduce the rate of hydrogenation of canola oil. Strong catalyst poisons like sulfur are attached to the nickel surface by electron donation to the vacant d-orbitals (11), whereas chlorophylls are strongly adsorbed at the entrance of the pores at the nickel surface. The inhibiting effect of chlorophyll on hydrogenation is most likely caused by the physical blocking of the active centers of the catalyst.

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