Technical

Effect of Some Isothiocyanates on the Hydrogenation of Canola Oil

V. Abraham and **J.M. deMan**
Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1 Canada

Sulfur compounds were added to refined and bleached canola oil before hydrogenation in the form of allyl, heptyl and 2-phenethyl isothiocyanates, and the effects on hydrogenation rate, solid fat content and percentage *trans* fatty acids were determined. The poisoning effect was most pronounced with allyl isothiocyanate and least with phenethyl isothiocyanate. As the amount of added sulfur increased, the hydrogenation rate decreased. Of the three isothiocyanates used, allyl isothiocyanate caused formation of larger amounts of *trans* isomers. An increased sulfur level in the oil resulted in increased solid fat content and *trans* isomer level. Allyl isothiocyanate also caused formation of larger amounts of solid fat than other isothiocyanates at all levels of sulfur addition.

Metallic catalysts of group VIII are generally poisoned by molecules containing elements of groups VA and VIA. Poisoning has been considered a preferential adsorption effect dependent upon the formation of abnormally strong bonds between the catalyst and the adsorbed species (1). Sulfur poisoning has been an important industrial problem because it has prevented the catalytic conversion of many feedstocks that cannot be readily desulfurized. On the other hand, the controlled partial poisoning of the catalyst has been found useful in industrial processes and in scientific investigations. The negative influence of catalyst poisons during hydrogenation of vegetable oils in the presence of nickel catalysts has been studied in several investigations (2-9). These catalyst poisons may be constituents of natural oils or decomposition products or may be introduced during oil processing. Although most potential catalyst poisons are removed during refining, small quantities may remain in the oil prior to hydrogenation. These minute amounts have been shown to appreciably lower the effectiveness of hydrogenation catalysts.

Beckman (10) observed higher amounts of *trans* isomers when lower amounts of catalysts were used for hydrogenation of oils in the presence of sulfur. The nickel surface available to adsorb sulfur is small; consequently, the number of catalytic sites that can adsorb and dissociate hydrogen is reduced as poisoning takes place. Thus, the triglycerides have a high chance of being adsorbed on a sulfur-poisoned site and are eventually released in the *trans* isomer form. This phenomenon has been used by catalyst manufacturers and oil processors to obtain a product with a high *trans* content. The main purpose of this procedure is to obtain a hardened fat with a relatively high melting point at a high iodine value and a steep dilatometric curve, such as is required for hard base stock and cocoa butter extenders. Suzuki and Murase (11) reported that sulfur-containing amino acids deactivated the catalysts more than amino acids with no sulfur atom. From a series of experiments, Drozdowski et al. (12) concluded that allyl isothiocyanate (AITC) poisoned the nickel catalysts more than ethyl isothiocyanate, ethyl thiol or diethyl sulfide.

TABLE 1

Sulfur in Single Samples of Canola Oil as Determined by Ion Chromatography, Raney Nickel Method, and by GC

Sample	Ion chromatography (mg/kg)	Raney nickel (mg/kg)	Gas chromatography (mg/kg)
Crude	23.8	2.9	0.6
Refined	19.7	1.5	0.5
Refined and bleached	16.2	1.1	0.2

Each value represents the mean of eight determinations for Raney nickel and gas chromatography method (volatile sulfur) and five determinations for ion chromatography (total sulfur).

Sulfur contained in canola oil may occur in a variety of forms: volatile, thermolabile and nonvolatile organic compounds (13) and possibly inorganic forms such as sulfates and sulfides (6). Hougen and Daun (14) have studied the relationship of sulfur levels in crude canola oil and in refined and bleached oil as well as the effect of sulfur content on the hydrogenation of oil. Devinat et al. (13) found that poisoning is mainly caused by volatile compounds and to a lesser extent by thermolabile compounds. Volatile sulfur compounds in rapeseed oil have been identified by various researchers (15,16) and in canola oil by the present authors (17) using a gas chromatographic procedure.

The objective of this study was to identify and quantify the different volatile isothiocyanates in canola oil and to determine the relative catalyst poisoning ability of several of these sulfur compounds during hydrogenation using a nickel catalyst.

MATERIALS AND METHODS

Canola oil samples were commercially produced crude, refined, and refined and bleached oils. Refined and bleached oil was used for hydrogenation, and the other oils were used for determination of sulfur. Allyl, heptyl and 2-phenethyl isothiocyanates were purchased from Eastman Kodak (Rochester, New York).

Volatile isothiocyanates were isolated and then analyzed by gas liquid chromatography (GLC) using a

TABLE 2

Concentration of Individual Isothiocyanates (Expressed as mg S/kg Oil) in Samples of Crude, Refined, and Refined and Bleached Oils As Determined by Gas Chromatography

	Sulfur content of isothiocyanates (mg/kg S)[a]									
Sample	1	2	3	4	5	6	7	8	9	Total mg/kg S
Crude	.02	.01	.04	.46	.06	—	.02	.02	.01	.6
Refined	.01	Tr	.04	.38	.06	—	.015	.015	.01	.5
Refined and bleached	.005	Tr	.02	.16	.03	—	.01	.01	.005	.2

[a]Identity of isothiocyanates (from ref. 17): 2, allyl isothiocyanate; 4, 3-butenyl isothiocyanate; 5, 4-pentenyl isothiocyanate; 9, phenethyl isothiocyanate; 6, heptyl isothiocyanate (internal standard, not present in oil); 1, 3, 7, 8 are unknown peaks.

flame photometric detector as described by Abraham and deMan (17).

Hydrogenation was carried out in a Parr Pressure Reactor apparatus using a 2-l bomb and a charge of 1-l oil. The American Oil Chemists' Society (AOCS) standard hydrogenation catalyst containing 25% nickel was used at a level of 0.2% by weight of oil. Hydrogenation conditions were temperature, 175 C; pressure, 137 kPa (20 psi); and agitation, 850 rpm. Three different sulfur compounds (allyl, heptyl and 2-phenethyl isothiocyanates) were added at three different levels (0, 5 and 10 mg S/kg oil) before hydrogenation; hydrogenation was continued until the oil reached an iodine value (IV) of 90. Samples were taken at 15-min intervals through the sampling valve to determine the hydrogenation rate. The reaction was stopped when all samples reached the same iodine value.

Iodine values were determined using the Wijs method (AOCS Cd 1-25). Fatty acid composition of the oils was determined by GLC of the methyl esters prepared by the method of Shehata et al. (18). The methyl esters were analyzed by the gas chromatographic procedure reported by Bansal and deMan (19). 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. Solid fat content was measured by nuclear magnetic resonance (20) using a Newport Analyzer MK3 with temperature-controlled magnet assembly. Total sulfur in the oil was determined by the ion chromatographic method reported earlier (21) using a Waters ion chromatograph equipped with a model 430 conductivity detector. Raney nickel sulfur was measured with the method reported by Granatelli (22).

RESULTS AND DISCUSSION

The canola industry usually relies on the use of the Raney nickel method to measure sulfur content. However, this method only measures a part of the total sulfur present. A combustion method followed by ion chromatography (21) has been proposed for the determination of total sulfur. Crude, refined, and refined and bleached oils were analyzed using the different methods; the results are presented in Table 1.

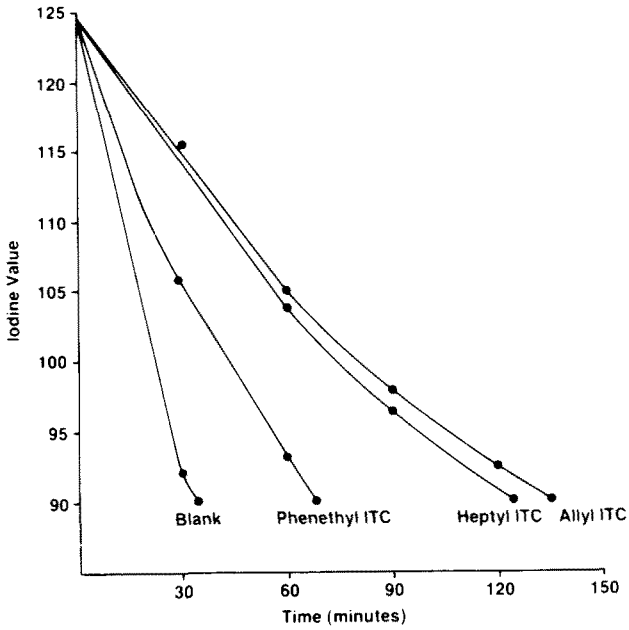

FIG. 1. Plot of iodine value (IV) vs time for the hydrogenation of canola oil in presence of 5 mg/kg S in the form of different isothiocyanates.

Volatile sulfur was only a small fraction of the Raney nickel sulfur or the total sulfur. Individual isothiocyanates were identified and measured by the gas chromatographic technique reported earlier (17). Table 2 shows the results obtained for individual sulfur compounds in crude, refined, and refined and bleached oils. It was found that more than 60% of the sulfur in canola oil was present in the form of 3-butenyl isothiocyanate.

The effect of added sulfur compounds on the rate of hydrogenation was illustrated by the plots of IV vs time. Hydrogenation rates decreased following the addition of 5 mg/kg S in the form of allyl, heptyl and phenethyl isothiocyanates (Fig. 1). The shapes of these curves illustrate catalyst poisoning (23), and the patterns suggest first order kinetics. The highest catalyst poisoning was observed for AITC and the least for 2-phenethyl isothiocyanate. Similar results were obtained when 10 mg/kg S was added to the oil before hydrogenation (Fig. 2). To reach the same IV, samples

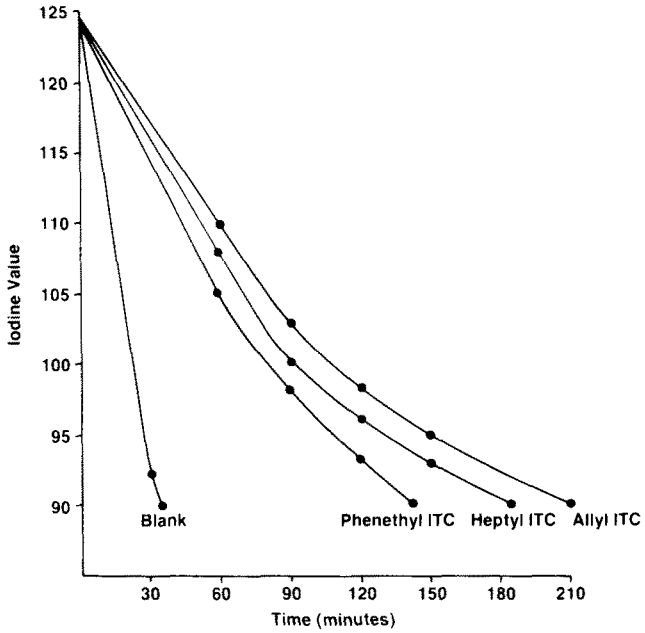

FIG. 2. Plot of iodine value (IV) vs time for the hydrogenation of canola oil in presence of 10 mg/kg S in the form of different isothiocyanates.

containing allyl, heptyl and phenethyl isothiocyanate took 210, 185 and 143 min, respectively, compared to 34 min taken by the sample with no added sulfur compounds (Table 3). This illustrates that an increase in sulfur content in the oil decreases the hydrogenation rate, and different isothiocyanates slowed the reaction to a different extent with the same amount of added sulfur. This observation suggests that not only the amount of sulfur but also the type of sulfur compound is important in catalyst poisoning. Small organic radicals attached to isothiocyanates have high poisoning ability compared to those containing large radicals.

The fatty acid composition of the original and hydrogenated oils is presented in Table 4. The lowest level of 18:0 was obtained for oil with 10 mg/kg S added as AITC and the highest in the hydrogenated reference oil; the oil containing phenethyl isothiocyanate was intermediate. The differences in the level of 18:0 may be due to the lower activity caused by the presence of sulfur compounds. Hydrogenation of oil with higher levels of added sulfur compounds was so effectively retarded that the level of 18:0 remained low. Table 5 lists the solid fat content of the hydrogenated oils. Higher levels of sulfur produced larger amounts of solid fat in all hydrogenations. Here again, AITC addition resulted in the highest and phenethyl isothiocyanate the lowest amounts of solid fat at all levels of sulfur addition.

The percentages of *trans* fatty acids in the partially hydrogenated oils are presented in Figure 3. Increased levels of added sulfur in the oil resulted in higher levels of *trans* fatty acids. It has been reported (24) that sulfur-impregnated nickel catalysts result in higher amounts of isomerization at the expense of lower activity. Among the isothiocyanates, AITC produced more *trans* fatty acids than other isothiocyanates at all levels of added sulfur.

From the results presented it is evident that different isothiocyanates differ in their capacities to poison hydrogenation catalysts. Presumably the size of

TABLE 3

Effect of Different Volatile Sulfur Compounds on the Rate of Hydrogenation of Canola Oil

Sulfur compound	Added sulfur (mg/kg)	Iodine value	Time to reach IV (min)
— — —	—	89.2	34
Allyl isothiocyanate	5	89.6	135
	10	90.9	210
Heptyl isothiocyanate	5	90.8	130
	10	90.7	185
Phenethyl isothiocyanate	5	91.0	68
	10	90.7	143

TABLE 4

Fatty Acid Composition of Original Oil and Hydrogenated Canola Oil With and Without Added Sulfur (Expressed as mg A/kg Oil)

Compound	Added sulfur (mg/kg)	Iodine value	Fatty acid (wt% as methyl esters) 16:0	18:0	18:1	18:2	18:3
— — —	0[a]	125.0	3.9	1.8	60.3	23.9	9.6
— — —	0[b]	89.2	3.9	13.5	69.6	11.1	1.3
Allyl	5	89.6	3.9	10.5	70.4	13.3	1.3
isothiocyanate	10	90.9	3.8	8.2	70.4	16.2	0.8
Heptyl	5	90.8	4.0	11.8	75.9	6.3	1.4
isothiocyanate	10	90.7	4.0	11.1	77.2	5.9	1.4
Phenethyl	5	91.0	4.0	11.9	77.2	4.8	1.6
isothiocyanate	10	90.7	4.0	11.3	75.3	7.9	1.0

[a]Original oil.
[b]Original oil hydrogenated to iodine value 89.2.

TABLE 5

Effect of Addition of Isothiocyanates (Expressed as mg S/kg oil) on the Solid Fat Content of Hydrogenated Canola Oil (Iodine Value = 90)

Sulfur compound	Added sulfur (mg/kg)	Solid fat (%)					
		0 C	5 C	10 C	15 C	20 C	25 C
— — —	0	32.1	30.5	22.5	14.1	10.5	7.5
Allyl	5	46.4	41.9	33.6	20.9	16.1	11.0
isothiocyanate	10	49.4	45.0	36.3	23.6	17.7	11.1
Heptyl	5	40.9	36.2	28.2	17.0	13.0	8.7
isothiocyanate	10	42.0	38.3	28.6	18.5	13.8	10.8
Phenethyl	5	31.4	29.0	20.4	12.6	8.2	4.7
isothiocyanate	10	38.1	34.6	23.9	14.8	10.7	7.1

the molecule has some effect on how effectively the sulfur combines with the active sites on the catalyst. To improve the ease of hydrogenation of the oil, removal of volatile sulfur compounds and possibly of nonvolatile sulfur compounds remains the major objective.

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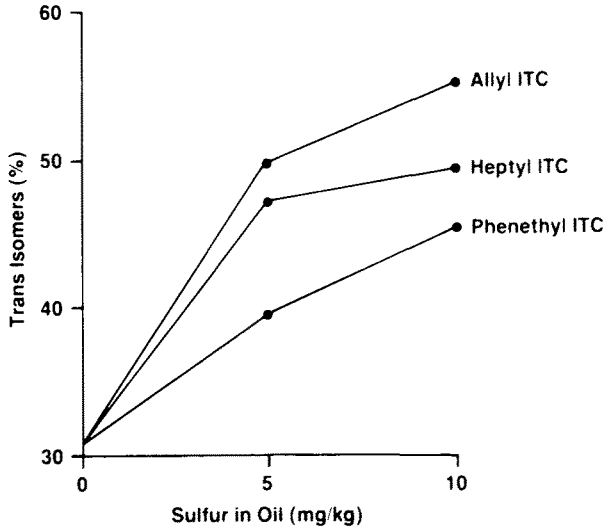

FIG. 3. Plot of *trans* isomers (%) vs sulfur concentration in oil (mg S/kg oil) during the hydrogenation of canola oil.

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