

Effect of the Presence of Sulfur During the Hydrogenation of Canola Oil

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ABSTRACT

Sulfur was added to refined and bleached canola oil before hydrogenation in the form of allyl isothiocyanate and the effects on hydrogenation rate and fatty acid composition were determined. The effect was more pronounced under selective conditions (200 C and 7 psi) than under nonselective conditions (160 C and 44 psi). Sulfur added at the level of 3 mg/kg under selective conditions stopped the hydrogenation at an iodine value (IV) of 81, with 5 mg/kg at IV 88. Under nonselective conditions, there was a decrease in reaction rate, but even with 10 mg/kg added S, the reaction could be made to reach IV 70. The amount of S bound to the commercial nickel catalyst was determined and in all cases was less than the amount that was bound to Raney nickel. Relatively more sulfur was bound at lower temperature (longer time) and higher pressure. Addition of 3 mg/kg of S or more resulted in considerably higher formation of *trans* isomers.

INTRODUCTION

Canola oil is obtained from rapeseed low in erucic acid and low in glucosinolates. By definition, canola oil has less than 5% erucic acid. This aim has been achieved in that canola oil available now has only ca. 1% erucic acid or less. The definition of glucosinolate content is expressed in terms of glucosinolate breakdown products in oil-free, moisture-free meal which should be less than 3 mg/g expressed as 3-

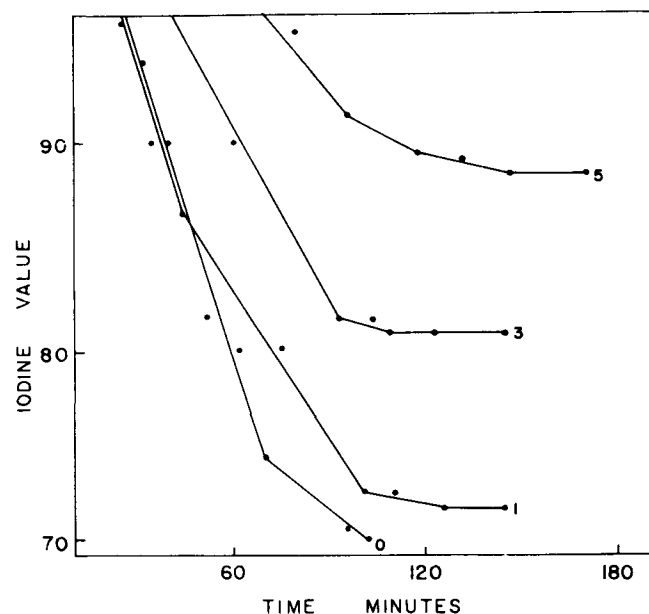


FIG. 1. Hydrogenation of canola oil under selective conditions with addition of 0, 1, 3 or 5 mg/kg sulfur in the form of allyl isothiocyanate.

butenyl isothiocyanate. The introduction of new cultivars with low glucosinolate content has resulted in reduced levels of sulfur-containing breakdown product in the oil. These breakdown products are mainly isothiocyanates, thiocyanates and sulfates (1). These may be further decomposed into oxazolidine-2-thione, hydrogen sulfide and several other sulfides. Many of these sulfur-containing compounds are powerful hydrogenation catalyst inhibitors. Although the level of glucosinolates has now been reduced to such an extent that hydrogenation does not present any special problems (2), there is a need further to reduce the level of these compounds in canola oil. In this study (2), it was shown that the reduction in sulfur content of an earlier variety, Zephyr, and a later one, Tower, amounted to ca. 3 mg/kg. Such minute differences apparently have important effects on the effectiveness of hydrogenation catalysts. One of the problems encountered in studying this phenomenon is that different methods of sulfur determination yield different results. The highest amounts of sulfur are found when combustion methods are used (2).

Devinat et al. (3) divided sulfur compounds in rapeseed oil into volatile, thermolabile and nonvolatile groups. They indicated that catalyst inhibition is mainly caused by the volatile and to a lesser extent by thermolabile compounds. They also reported that the relative proportions of these groups may differ from one sample of oil to another.

To ensure problem-free hydrogenation of canola oil, it is important that the effect of different groups of sulfur compounds be ascertained. This study deals with the effect of added isothiocyanate on the hydrogenation of canola oil.

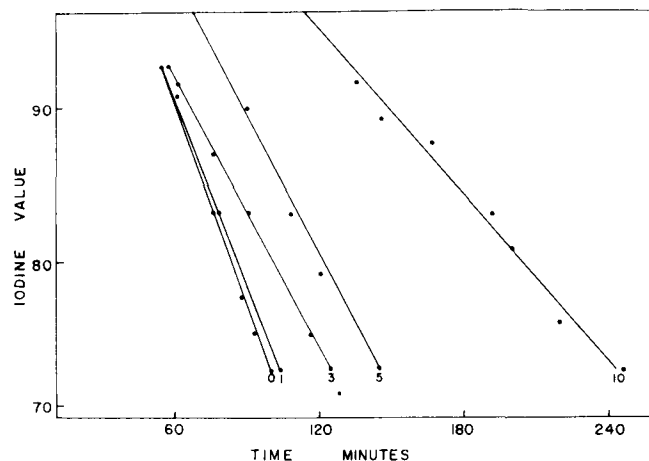


FIG. 2. Hydrogenation of canola oil under nonselective conditions with addition of 0, 1, 3, 5 or 10 mg/kg sulfur in the form of allyl isothiocyanate.

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TABLE I

Fatty Acid Composition (wt % as Methyl Esters) of Selectively Hydrogenated Canola Oil with Sulfur Added as Allyl Isothiocyanate (Expressed as mg S/kg oil)

FA	S (mg/kg)			
	0	1	3	5
16:0	5.0	5.2	4.9	5.4
18:0	4.8	3.2	4.2	5.5
18:1	74.2	76.8	70.7	80.0
18:2	11.2	11.3	15.0	6.7
18:3	2.8	1.8	2.9	1.1
20:0	1.1	0.7	1.0	0.6
20:1	1.4	1.0	1.3	1.1
IV	88.6	91.2	91.8	89.6
16:0	5.0	5.0	5.0	
18:0	6.1	4.9	4.4	
18:1	73.8	80.3	78.5	
18:2	10.2	6.3	7.1	
18:3	2.5	2.1	2.8	
20:0	0.8	0.7	1.0	
20:1	0.6	1.0	1.1	
IV	80.7	81.7	81.9	
16:0	4.9			
18:0	15.7			
18:1	69.9			
18:2	6.4			
18:3	0			
20:0	1.0			
20:1	2.1			
IV	71.6			

TABLE II

Fatty Acid Composition (wt % as Methyl Esters) of Non Selectively Hydrogenated Canola Oil with Sulfur Added as Allyl Isothiocyanate (Expressed as mg S/kg oil)

FA	S (mg/kg)				
	0	1	3	5	10
16:0	5.1	5.5	5.8	5.4	4.9
18:0	8.6	7.4	9.0	10.2	6.0
18:1	71.6	73.1	72.6	72.6	69.8
18:2	11.3	11.6	10.0	8.9	15.8
18:3	1.7	0.3	—	1.9	2.8
20:0	1.6	0.9	1.1	0.6	0.9
20:1	0.7	1.0	1.5	0.5	1.2
IV	88.7	89.3	89.3	87.1	91.9
16:0	5.3	5.3	5.7	5.5	5.3
18:0	10.8	10.3	8.0	9.6	8.8
18:1	66.7	73.4	72.0	72.4	68.3
18:2	13.2	9.8	10.6	8.6	13.1
18:3	1.7	0	0	2.3	2.8
20:0	1.2	1.0	1.4	1.0	1.0
20:1	1.0	1.1	2.2	0.6	1.0
IV	79.3	77.9	79.7	80.0	81.7
16:0	5.1	5.3	5.5	5.3	5.1
18:0	15.6	14.4	10.4	17.3	13.7
18:1	74.0	71.9	70.6	72.2	70.8
18:2	3.2	6.4	3.8	3.1	6.2
18:3	0.1	0	0	0	2.3
20:0	0.8	0.6	0.5	0.7	0.8
20:1	1.4	2.1	1.1	1.4	0.9
IV	69.5	70.6	70.6	68.2	72.1

MATERIALS AND METHODS

Refined and bleached canola oil was obtained from CSP Foods Ltd., Nipawin, Saskatchewan. The fatty acid composition of this oil has been reported by Bansal and deMan (4).

Hydrogenation was carried out in a Parr pressure reaction apparatus series 4500 using a 2 L bomb and a charge of 1 L oil. The catalyst used was Harshaw H32 (containing 25% nickel) at a level of 0.2% by weight of the oil. Hydrogenation conditions used were: selective, 200 C and hydrogen pressure of 48 kPa (7 psig); and nonselective, 160 C and hydrogen pressure 303 kPa (44 psig).

The sulfur was added to the oil in the reactor in the form of a stock solution containing 0.5 mg/g of allyl isothiocyanate (Eastman Kodak Co.) in canola oil. Hydrogenations were carried out to iodine values (IV) of 90, 80 and 70, and the partially hydrogenated oils were analyzed for iodine value, *trans* fatty acids, fatty acid composition, dropping point and solid fat content by using the methods described by El-Shattory et al. (2).

The sulfur content of the refined and bleached canola oil was determined by the Raney nickel method described by Franzke et al. (5). The sulfur was liberated from the catalyst with acid and the hydrogen sulfide reacted with N,N-dimethyl-*p*-phenylenediamine to form methylene blue which was determined colorimetrically at 665 nm.

To determine the amount of sulfur taken up by the catalyst under different conditions of hydrogenation, the

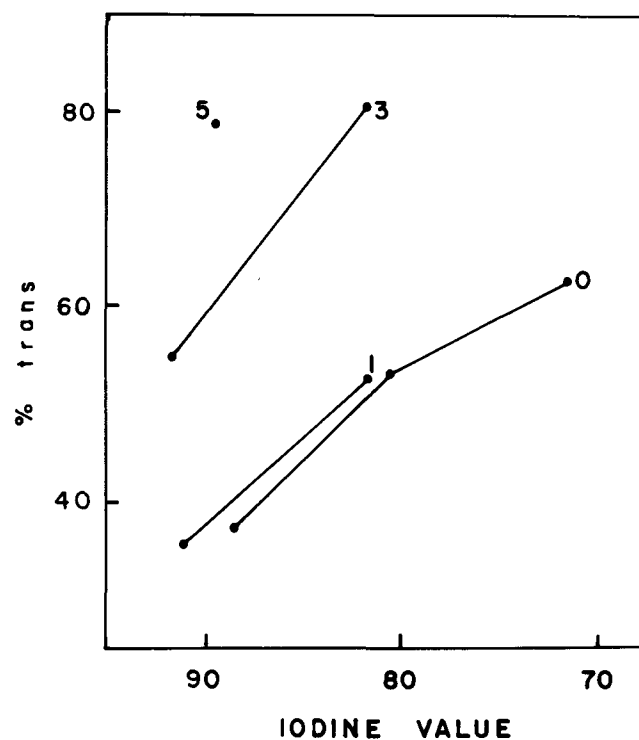


FIG. 3. Formation of *trans* fatty acids during selective hydrogenation of canola oil with addition of 0, 1, 3 or 5 mg/kg sulfur in the form of allyl isothiocyanate.

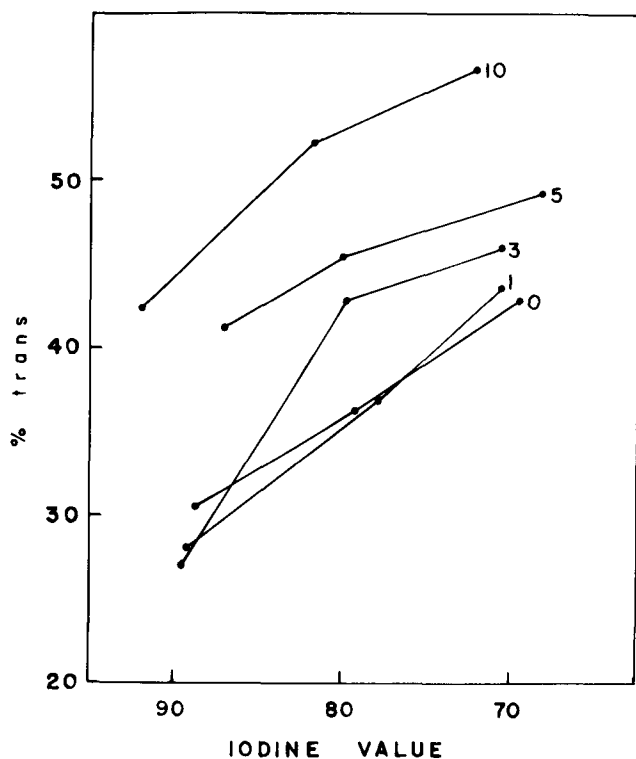


FIG. 4. Formation of *trans* fatty acids during nonselective hydrogenation of canola oil with addition of 0, 1, 3, 5 or 10 mg/kg sulfur in the form of allyl isothiocyanate.

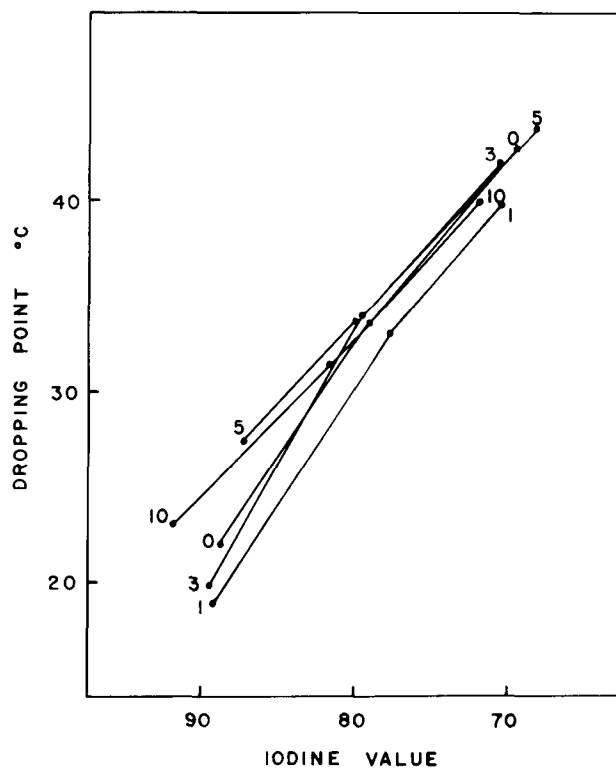


FIG. 6. Dropping points of canola oil during nonselective hydrogenation with addition of 0, 1, 3, 5 or 10 mg/kg sulfur in the form of allyl isothiocyanate.

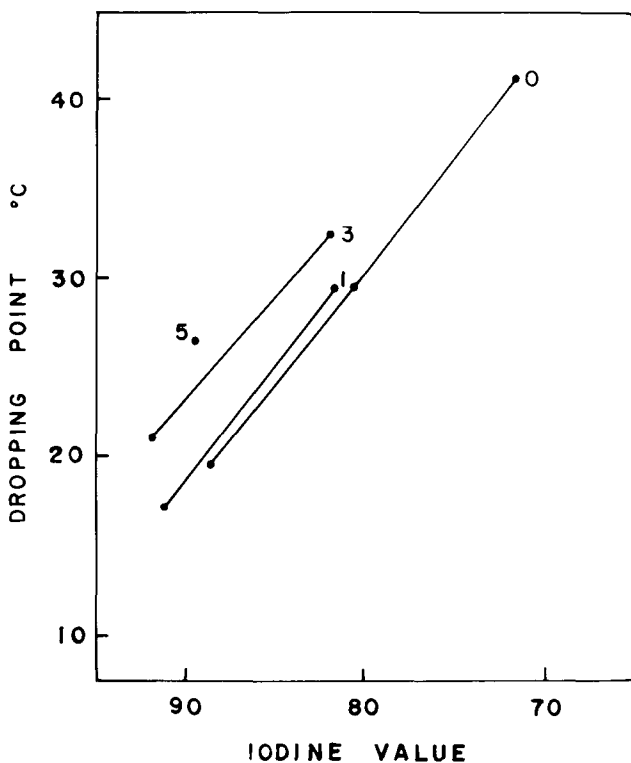


FIG. 5. Dropping points of canola oil during selective hydrogenation with addition of 0, 1, 3 or 5 mg/kg sulfur in the form of allyl isothiocyanate.

catalyst was filtered off at the end of each hydrogenation period and the amount of catalyst-bound sulfur determined by taking an aliquot of the catalyst and releasing the sulfur in the form of hydrogen sulfide with acid. The hydrogen sulfide was trapped in sodium hydroxide solution and the sulfur determined as in the Raney nickel method of Franzke et al. (5). The nickel content of the catalyst was measured by EDTA titration.

RESULTS AND DISCUSSION

Canola oil was hydrogenated under selective conditions with 0.2% catalyst and with addition of zero, 1, 3 and 5 mg/kg sulfur in the form of allyl isothiocyanate. The progress of the reactions is presented in Figure 1 as a plot of iodine value vs time. Even the lowest addition, 1 mg/kg, resulted in a definite poisoning effect, and this was even more pronounced at levels of 3 and 5 mg/kg sulfur. According to Mattil (6), the shape of these curves indicate catalyst poisoning or high temperature.

When the same experiment was repeated under nonselective conditions, the reaction was represented by straight lines (Fig. 2). There was virtually no effect of the addition of 1 mg/kg sulfur and increased levels of 3, 5 and 10 mg/kg sulfur resulted in prolonging the reaction but the straight lines indicate that first-order kinetics are maintained.

The fatty acid composition of the selectively and nonselectively hydrogenated oils are presented in Tables I and II respectively. The selectivity effect is most noticeable at $IV = 90$. The nonselective reaction resulted in greater re-

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TABLE III

Effect of the Addition of Allyl Isothiocyanate (Expressed as mg S/kg oil) on the Solid Fat Content of Selectively Hydrogenated Canola Oil

Added S (mg/kg)	IV	Solid fat (%)					
		0 C	5 C	10 C	15 C	20 C	25 C
0	71.6	75.9	73.1	65.5	55.1	45.9	38.0
0	80.7	42.0	37.7	27.9	17.7	9.7	3.5
0	88.6	14.9	13.1	6.8	3.2	0.8	0
1	81.7	38.4	34.1	24.5	14.9	7.4	1.8
1	91.2	9.1	8.6	3.3	0.6	0.6	0
3	81.9	64.7	60.9	51.3	38.1	25.0	12.7
3	91.8	20.0	17.2	9.4	2.9	0.3	0
5	89.6	50.9	46.5	35.8	21.4	9.6	1.1

TABLE IV

Effect of the Addition of Allyl Isothiocyanate (Expressed as mg S/kg oil) on the Solid Fat Content of Nonselectively Hydrogenated Canola Oil

Added S (mg/kg)	IV	Solid fat (%)					
		0 C	5 C	10 C	15 C	20 C	25 C
0	69.5	56.7	54.9	46.9	37.4	29.8	24.9
0	79.3	32.8	30.8	23.5	16.0	10.2	6.8
0	88.7	12.0	11.9	8.3	4.3	1.9	0.9
1	70.6	47.2	44.3	36.4	28.1	21.6	17.2
1	77.9	29.3	26.5	19.7	13.5	8.5	5.9
1	89.3	8.0	7.3	4.0	1.9	0.9	0
3	70.6	57.3	54.7	47.1	38.0	30.9	24.9
3	79.7	35.7	33.0	25.4	17.7	11.6	8.0
3	89.3	9.5	8.3	5.8	3.1	1.5	1.0
5	68.2	64.8	62.0	54.2	44.9	37.6	32.5
5	80.0	35.6	32.6	25.1	17.2	10.8	7.5
5	87.1	22.3	20.0	14.2	8.0	4.5	1.5
10	72.1	62.2	58.6	50.7	40.7	32.3	26.5
10	81.7	37.2	33.7	25.8	17.6	11.1	7.3
10	91.9	12.7	11.9	7.8	4.2	2.0	0.9

removal of 18:3 and faster production of 18:0. Under selective conditions, the addition of 10 mg S/kg resulted in complete inhibition of the reaction, whereas under nonselective conditions, the reaction was only slowed down.

The amount of *trans* isomers formed under selective conditions is shown in Figure 3. There was virtually no difference between zero and 1 mg S/kg, but very high *trans* levels were obtained when 3 or 5 mg S/kg oil were added. The 5 mg S/kg addition gave a *trans* content of 78.9% at iodine value of 89.6 and the 3 mg S/kg addition resulted in a *trans* level of 80.4% at iodine value of 87.9. The *trans* levels obtained under nonselective conditions were lower as indicated in Figure 4. Again, addition of 1 mg S/kg oil had virtually no effect on *trans* content but levels of 3, 5 and 10 mg S/kg raised the *trans* levels considerably, although not to the same extent as under selective conditions.

The dropping points of the hydrogenated oils are shown in Figures 5 and 6. For similar iodine values, higher dropping points were obtained when the amount of added sulfur increased, reflecting the effect of the higher *trans* levels. The solid fat content of the hydrogenated oils are listed in

Tables III and IV for selective and nonselective conditions, respectively. The selectively hydrogenated oils had higher solid fat levels with increasing levels of sulfur addition as a result of the higher *trans* contents.

These results indicate that added sulfur in the form of allyl isothiocyanate has an important effect on canola oil hydrogenation and that this effect is greatly influenced by reaction temperature and hydrogen pressure. The canola oil used in these experiments contained 4.3 mg S/kg as determined by the Raney nickel method. The amount of sulfur absorbed by the catalyst under different hydrogenation conditions was measured. The spent catalyst was filtered off and analyzed for nickel and sulfur content. Since the amounts of catalyst and oil were known, it was possible to calculate the amount of sulfur retained by the catalyst, assuming that the sulfur content of the oil as determined by the Raney nickel method represents 100%. Hydrogenations were carried out at 140, 160 and 200 C and hydrogen pressures of 48 and 303 kPa. The results of these experiments are listed in Table V. The percentage of sulfur retained by the catalyst was greatly influenced by hydrogenation

TABLE V

Effect of Hydrogenation Conditions on Sulfur Absorption by Catalyst
(Assuming 100% = Sulfur Content in the Canola Oil of 4.3 mg S/kg)

Temp (C)	Press (kPa)	Time (min)	IV	Δ IV/min	% S in catalyst
200	40	15	95.0	1.60	24.1
200	48	30	81.0	1.27	38.5
200	48	45	70.0	1.09	42.9
200	48	60	60.0	0.98	44.9
200	303	15	69.5	3.30	52.8
160	303	15	97.5	1.43	70.2
160	303	30	78.0	1.37	73.9
160	303	45	69.0	1.11	77.1
160	303	60	64.0	0.92	80.2
140	303	60	90.0	0.48	58.6
140	303	90	70.1	0.54	83.2

tion conditions. It appears that the percentage of sulfur absorbed by the catalyst increases with decreasing temperature and increasing pressure. This means that less sulfur is taken up from the oil under selective conditions than under nonselective conditions. This is in accordance with earlier experiments (2), of measuring sulfur in oil by using normal nickel hydrogenation catalyst instead of Raney nickel. Nonselective conditions always result in higher sulfur levels. These results were unexpected since added sulfur had a greater catalyst poisoning effect under selective conditions. It is generally assumed that sulfur exerts its poisoning effect by irreversibly attaching itself to the active sites of the catalyst (6). If this were the case, the highest sulfur uptake by the catalyst should occur under selective conditions. The opposite effect was observed in this study. Further research is in progress to clarify this apparent contradiction.

ACKNOWLEDGMENT

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