Removal of Sulfur Compounds from Canola Oil

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The effect of a number of physical methods for the removal of sulfur compounds from canola oil was investigated. The methods tested included laboratory deodorization and use of catalyst and of bleaching earth. Nine temperature-time combinations were used for the deodorization. Bleaching earth had little effect on the removal of sulfur compounds from the oil. Other methods removed part of the sulfur. High temperature, longer time and high vacuum for deodorization facilitated the complete removal of volatile sulfur compounds. Treatment of oil with catalyst removed most of the volatile sulfur and part of the Raney nickel sulfur.

Sulfur compounds in canola oil have been implicated as hydrogenation catalyst poisons. It is believed that these are hydrolysis products of glucosinolates present in the canola seed. Damage to the seed or crushing for extraction purposes brings the enzyme in contact with the glucosinolates and results in hydrolysis. When the hydrolysis takes place during crushing, the soluble products enter the oil and are difficult to remove completely with conventional methods of refining and bleaching. The sulfur originating from glucosinolates poisons the hydrogenation catalysts (1), produces unpleasant odors during heating (2), causes possible damage to health (3) and adversely affects the processing of rapeseed (4).

The level of sulfur compounds in the new canola varieties has been lowered but not completely eliminated. Since the content of sulfur has been found to vary significantly among crushing plants, processing techniques may be a factor in controlling sulfur levels in oils (5). At present the sulfur level in refined oil is ca. 3-10 mg/kg. Such low levels apparently have an important effect on the effectiveness of hydrogenation catalysts. The catalyst inhibition is believed to be due mainly to volatile and, to a lesser extent, to thermolabile sulfur compounds. The relative proportion of these may differ from one sample of oil to another. Several authors (6-8) have identified a number of the sulfur compounds in rapeseed and canola oil.

For problem-free hydrogenation, sulfur compounds in the oil have to be removed. A pre-treatment of the oil to remove catalyst poisons was recommended by Ellis (9) and Battes (10).

Embong and Jelen (11) reported the effect of aqueous extraction on the sulfur content of rapeseed oil. Shahiti et al. (12) recommended an alcohol-ammonia treatment to reduce glucosinolates in high glucosinolate rapeseed and mustard seed. They also observed a higher rate of hydrogenation for such oils. Steam stripping at a high temperature and at low vacuum can effectively remove these compounds. This takes place during deodorization, which is the last major processing step in the refining of edible oils. This process removes volatile flavor components and establishes the characteristics most readily recognized by the consumer (13).

The effects of bleaching on sulfur removal have not been investigated. The purpose of the present work was to investigate the possibility of removing the sulfur compounds from canola oil using different physical methods. This work also deals with the sulfur content of oils laboratory-deodorized with nine time-temperature combinations.

MATERIALS AND METHODS

Degummed and refined canola oil samples were obtained from CSP Foods, Nipawin, Saskatchewan. Catalyst used was the American Oil Chemists' Society (AOCS) standard hydrogenation catalyst. Catalyst and AOCS standard bleaching earth were obtained from the American Oil Chemists' Society, Champaign, IL.

The laboratory deodorization of the oil was carried out in a four-l round-bottomed flask connected to a liquid nitrogen trap. Two kg of each of the oil samples were placed in the round-bottomed flask. Deaerated water was evaporated in a small tube heated by a heating mantle. The superheated steam entered the deodorizer flask and vigorously agitated the oil. Nine time-temperature combinations were selected for the experiment. The volatiles were removed from the oil by means of a mechanical vacuum pump. The oil was cooled in an atmosphere of nitrogen and subsequently analyzed for total sulfur by combustion/ion chromatography, volatile sulfur by GLC and Raney nickel sulfur (8,14).

One kg of oil was mixed with 10 g of catalyst in an atmosphere of nitrogen. The mixture was vigorously agitated at 185 C for one hr. The mixture was cooled and filtered and the oil analyzed for sulfur content.

The AOCS standard bleaching earth was mixed with the oil at a level of 40 g/kg oil. The mixture was agitated at 165 C for one hr and cooled. The oils were filtered and sulfur determination was done. The total sulfur in the oil was measured by the method of Abraham and deMan (14) using an ion chromatograph equipped with a conductivity detector. Five replicates were done on each sample, and the mean is reported as the total sulfur in the oil. A standard curve using sodium sulfate was used to calculate the sulfur content. Volatile sulfur was determined by a gas chromatographic procedure using a flame photometric detector (8). Raney nickel sulfur in the oil was measured by the method of Granatelli (15) as modified by Daun and Hougen (16). Four replicates of each sample were analyzed and the mean reported as the Raney nickel sulfur. All values are expressed as mg S/kg oil.

RESULTS AND DISCUSSION

Deodorization of the oils was carried out in a laboratory deodorizer. This process is dependent on the following factors to assure the efficient removal of unde-

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sirable components: (i) vapor pressure of the components; (ii) intimacy of mixing steam with the oil; (iii) absolute pressure under which deodorization is carried out; (iv) temperature and duration of deodorization. For this experiment the temperatures selected were 150, 200 and 250 C, and deodorization times were 30, 60 and 90 min. The deodorized products were analyzed for total sulfur, Raney nickel sulfur and volatile sulfur. Table 1 shows the effect of different treatments on the sulfur levels in degummed and refined canola oils. It is evident from these results that more sulfur was removed from the oils with increasing deodorization time. Also, more sulfur was removed at the higher temperatures, and at these temperatures most of the volatile sulfur was removed in a relatively short time. Figure 1 shows the chromatograms of volatile sulfur compounds obtained from degummed, refined, laboratory bleached and laboratory deodorized oils. These indicate that volatile sulfur compounds were removed from the oil during each step in oil processing. The amounts of individual isothiocyanates are presented in Table 2. For degummed and refined oils, the minimum temperature for effective removal of the volatile sulfur compounds was 200 C. There are temperature limits to which edible fats may be raised without developing unwanted polymers (17). Therefore, a compromise must be considered between time and temperature. A deodorization temperature of 200 C and a period of 90 min appear to be optimal for the efficient removal of volatile sulfur compounds from canola oil.

Pretreatment of the oil with spent catalyst in order to remove catalyst poisons is a procedure well known in industry. Its application is particularly economical in dealing with oils in which the life of the catalyst is very short unless the poisons are removed. Metallic soaps and other impurities in oils, which act as catalyst poisons during hydrogenation, have been shown to be removed by treating the oil with 10% of Fuller's earth at 120 C for 20 min. For example, treating hardened oils in this manner markedly reduced their content of nickel or other mineral matter (18). Table 3 shows the effect of catalyst and bleaching earth on the sulfur contents of degummed and refined oils. The results from this experiment showed that the catalyst

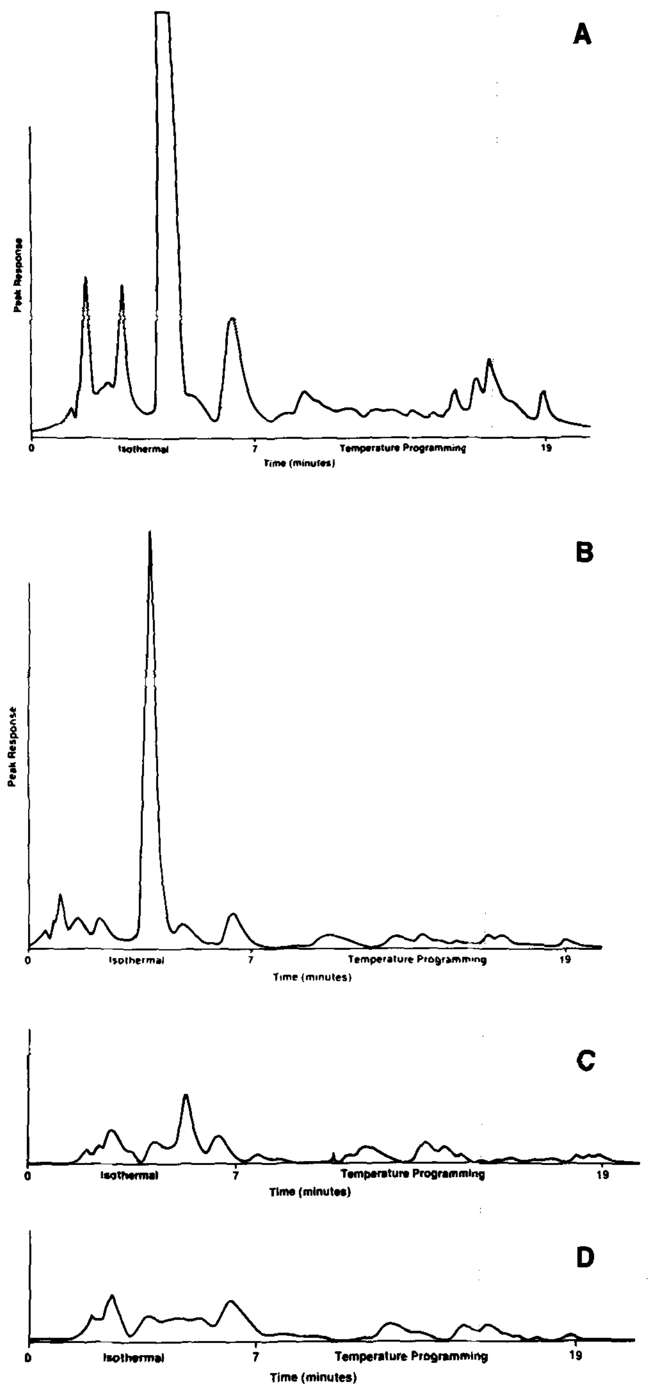

FIG. 1. Gas liquid chromatograms of volatile sulfur compounds on the FFAP column. From degummed canola oil (A); from refined canola oil (B); from laboratory bleached canola oil (C); from laboratory deodorized canola oil (D).

TABLE 1

Effect of Laboratory Deodorization on the Total, Raney Nickel and Volatile Sulfur Content of Degummed Refined Canola Oil

Temperature, °C	Time (min)	Total sulfur mg/kg	Raney nickel sulfur mg/kg	Volatile sulfur mg/kg
Treatment of degummed oil				
150	30	9.5	0.86	0.07
150	60	8.5	0.80	0.07
150	90	8.4	0.65	0.04
200	30	9.0	0.78	0.03
200	60	5.5	0.78	0.03
200	90	4.5	0.45	0.02
250	30	9.0	0.68	0.02
250	60	5.0	0.45	0.02
250	90	4.5	0.40	0.02
Treatment of refined oil				
150	30	6.0	0.78	0.03
150	60	5.4	0.78	0.03
150	90	5.0	0.64	0.02
200	30	5.6	0.63	0.02
200	60	5.4	0.45	0.02
200	90	4.4	0.45	0.02
250	30	4.9	0.40	0.02
250	90	3.9	0.40	0.02

TABLE 2

Calculated Amounts of Individual Isothiocyanates (expressed as mg S/kg oil) in Degummed and Refined Canola Oil Before and After Different Treatments

			Individual isothiocyanates (mg/kg S.)									
			1	2	3	4	5	6	7	8	9	Total (mg/kg S)
Degummed oil			0.07	0.01	0.06	0.18	0.05	0.02	0.01	0.005	0.02	0.45
Deodorization	Temp, °C	Time (min)										
	150	30	0.01	—	0.02	0.02	—	—	0.005	0.005	0.005	0.065
	150	60	0.01	—	0.02	0.02	—	—	0.005	0.005	0.005	0.065
	150	90	—	—	0.01	0.01	—	—	0.005	0.005	0.005	0.035
	200	30	—	—	0.01	0.01	—	—	0.002	0.002	—	0.024
	200	60	—	—	0.01	0.01	—	—	0.002	0.002	—	0.024
	200	90	—	—	0.01	0.01	—	—	—	0.002	—	0.022
	250	30	—	—	0.01	0.01	—	—	0.001	0.002	—	0.023
	250	60	—	—	0.01	0.01	—	—	0.001	0.001	—	0.022
	250	90	—	—	0.01	0.01	—	—	0.001	0.001	—	0.022
Bleaching			—	—	0.01	0.04	—	—	0.001	0.001	0.001	0.053
Catalyst treatment			—	—	0.01	0.02	—	—	0.001	0.001	0.001	0.033
Refined oil			0.01	0.005	0.04	0.10	0.03	0.005	—	0.01	.01	.21
Deodorization	Temp, °C	Time (min)										
	150	30	0.005	—	0.005	0.01	0.005	—	—	—	0.005	0.03
	150	60	0.005	—	0.005	0.01	0.005	—	—	—	0.005	0.03
	150	90	—	—	0.005	0.01	0.004	—	—	—	0.001	0.02
	200	30	0.001	—	0.004	0.01	0.004	—	—	—	0.001	0.02
	200	60	—	—	0.005	0.01	0.004	—	—	—	0.001	0.02
	200	90	—	—	0.005	0.01	0.004	—	—	—	0.001	0.02
	250	30	0.001	—	0.004	0.01	0.004	—	—	—	0.001	0.02
	250	60	—	—	0.005	0.01	0.004	—	—	—	0.001	0.02
	250	90	—	—	0.005	0.01	0.004	—	—	—	0.001	0.02
Bleaching			0.005	0.002	0.009	0.03	0.008	0.00	—	—	0.004	0.06
Catalyst treatment			0.001	0.001	0.008	0.02	0.007	0.00	—	—	0.002	0.04

was very effective in removing various forms of sulfur. Pretreatment of the degummed oil with catalyst removed 24% of total sulfur, 58% of Raney nickel sulfur and about 90% of volatile sulfur. The same treatment removed 29% of total sulfur, 37% of Raney nickel sulfur and 79% of volatile sulfur from refined oils. About 22% of the total sulfur was removed from both oils by the treatment with bleaching earth. Raney nickel sulfur was increased in both oils by this method. It appears that some of the total sulfur was changed into a form that reacts with Raney nickel. Because the identity of these sulfur compounds is unknown, it is impossible to provide an explanation for this phenomenon. The removal of volatile sulfur was about 85% effective in both cases. Because the volatile sulfur compounds have been implicated as the major catalyst poisons (19), this removal rate should result in a considerably lower catalyst poisoning activity in the oil.

TABLE 3

Effect of Different Treatments on the Total, Raney Nickel and Volatile Sulfur Content of Degummed and Refined Canola Oils

Sample	Total sulfur mg/kg	Raney nickel sulfur mg/kg	Volatile sulfur mg/kg
Degummed oil	10.5	2.16	0.45
Degummed oil, catalyst treated	8.0	0.90	0.03
Degummed oil, bleached	8.2	3.15	0.06
Refined oil	7.0	1.21	0.21
Refined oil, catalyst treated	5.0	0.76	0.04
Refined oil, bleached	5.5	2.80	0.06

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