Sulfur Content of Rapeseed Oils[1]

J.K. DAUN and F.W. HOUGEN, Department of Plant Science, University of Manitoba, Winnipeg, Canada R3T 2N2

ABSTRACT

Sulfur contents in rapeseed oils were determined by reduction with Raney nickel, acidification, and titration of released H_2S with mercuric acetate. The sulfur contents decreased with successive steps of industrial processing, i.e., crude oil, 17-31 ppm S; degummed, 16 ppm; alkali refined, 4-9 ppm; bleached, 3-5 ppm; and deodorized, <1 ppm. Laboratory-extracted oil from sound seed contained no detectable sulfur, regardless of the glucosinolate content of the seed. Heating of the seed or addition of water to the seed prior to extraction increased the sulfur in the oil—less, however, for low-glucosinolate seed than for high-glucosinolate seed. Laboratory-extracted oils from green, frost-damaged, and bin-heated seed contained appreciable amounts of sulfur.

INTRODUCTION

Small amounts of sulfur occur in rapeseed oils (1), possibly as hydrolysis or degradation products of the glucosinolates contained in the seed. The sulfur in the oil has been implicated as being the cause of certain difficulties in hydrogenating the oil (2,3) and also as the cause of certain unpleasant odors of heated rapeseed oils (4). Published reports on the occurrence of sulfur in rapeseed oils have been scarce and somewhat contradictory (Table I); these reports refer to rapeseed grown and processed in Europe. The sulfur-containing compounds in rapeseed oil and meal have been reviewed by Göbel and Franzke (9). In the present work, a published method for determination of sulfur in rapeseed oil was evaluated and slightly modified. The method was used to determine the sulfur contents of oils from rapeseed grown and processed in Canada. A study was also made of the effect of various seed treatments and seed qualities on the amount of sulfur in the extracted oils.

EXPERIMENTAL PROCEDURES

Materials

Industrially extracted oils at different stages of processing were obtained from rapeseed varieties with high (normal) glucosinolate contents (*Brassica napus*, var. Oro, estimated 29 mg glucosinolates/g oil-free meal, and *B. campestris*, var. Echo, 21 mg/g, and Span, 19 mg/g). Oils were extracted in the laboratory from commercial seed samples of inferior quality (green, frost-damaged, and bin-heated seed of unknown varieties with high glucosinolate contents) and from sound seed samples with high and low glucosinolate contents (var. Oro, 29 mg/g meal, and plant breeder's line *B. napus* S69-2895, 3 mg/g).

Sulfur Analysis

Sulfur contents in rapeseed oils were determined by the method of Granatelli (10) with two modifications. The method is used routinely in the petroleum industry and has been shown to be applicable to rapeseed oil (7,11,12). The method involves desulfurization with Raney nickel, followed by evolution of hydrogen sulfide on addition of acid. The H_2S is trapped in NaOH solution and titrated with mercuric acetate with dithizone as indicator. The modifications included the use of a reflux condenser, inserted between the reduction flask and the gas trapping apparatus as recommended by Fensom et al. (13). This resulted in higher recoveries of sulfur, presumably because of reduced losses of volatile sulfur compounds during the reduction, before the distillation. Furthermore, the distilled gas was led through a glass tube ending in a bulb (2 cm diameter) with seven holes (3 mm diameter). The tube was inserted in a beaker containing the absorbing solution, with the bulb directly over a rapidly turning magnetic stirring bar (Teflon); this effectively broke up and dispersed the gas bubbles emerging from the tube and facilitated the titration of the solution.

Oil Extraction

Oils extracted in the laboratory were obtained by shaking the seed (5 g) with petroleum ether and steel balls in a steel tube according to Troëng (14). Stoppers of fluorosilicone rubber were used in the tubes to avoid contamination by sulfur from ordinary rubber stoppers.

RESULTS AND DISCUSSION

The Raney Nickel Method

The accuracy of the method was assessed by analyzing known sulfur compounds. Analyses of KCNS solutions gave 94% recovery of sulfur, with a standard deviation of 5. The presence of crude or refined rapeseed oil in these analyses did not appreciably influence the recovery of sulfur from the KCNS. Consequently, all analyses in the present study have been corrected for a 94% recovery of sulfur. Granatelli (10) reported an average recovery of 95%. It has been reported that tetravalent and hexavalent sulfur are not

[1]Contribution No. 403, Department of Plant Science, University of Manitoba.

TABLE I

Reported Sulfur Contents (ppm) of Processed Rapeseed Oils

Authors	Expelled	Extracted	Crude	Refined	Bleached	Deodorized
von Fellenberg (1)	25	31		13		
Kucera and Hejtmanek[a] (5)			500	50	250	5
Zeman and Zemanova[b] (6)	40	600				
Franzke et al. (7)			9-45	5 24	4-15	0.6-2
Kurucz and Perédi (8)			12-43	3-26	2-20	2-4

[a]Oil was bleached before refining.

[b]Calculated from results for isothiocyanates and oxazolidinethione.

TABLE II

Sulfur Content (ppm) of Industrially Processed Oils[a]

Oil sample	Seed variety		
	Oro	Echo	Span
Expelled[b]	19	21	25
Extracted[b]	57	10	33
Crude	31	18[c]	27[c]
Degummed	16		
Refined	7	4	9
Bleached	5	3	4
Deodorized	1	1	1

[a]Means of two or more analyses.

[b]Prepress solvent-extraction method.

[c]Calculated from results for expelled and extracted oils.

reduced by Raney nickel (15). In this study, dimethyl sulfoxide (tetravalent sulfur) gave good recovery (88%), while methyl methane sulfonate (hexavalent) gave only 7% recovery. The precision of the method was assessed by analyzing three or more replicate samples of rapeseed oils containing 19, 31, and 57 ppm sulfur. The relative standard deviations for the three samples were 8%, 3%, and 4%, respectively.

Effect of Oil Processing

Rapeseed oils at different stages of industrial processing and refining were analyzed for sulfur content (Table II). The analytical results were similar to those of von Fellenberg (1), Franzke et al. (7), and Kurucz and Perédi (8).

The prepress expelled oils tended to have lower sulfur contents than the subsequently extracted oil fractions. This can probably be explained by an association of sulfur compounds with gum and colored material which are extracted from the seed preferentially with the extracted oils. The extracted oil of the variety Oro contained the largest amount of sulfur (57 ppm) and also, by visual insepction, the most gum. A gum fraction amounting to 6% of the total oil was separated from this oil by centrifugation. The gum fraction contained 385 ppm sulfur, while the remaining oil contained only 33 ppm sulfur. Similar observations were made by von Fellenberg (1) and André et al. (16), who noted that the sulfur in rapeseed oil seemed to be concentrated preferentially in the nonsaponifiable portion of the oil. Norris (17) noted that the phosphatide and nonsaponifiable portions of oils are extracted mostly during the last stage of the extraction process. This was substantiated by the observation that refining losses from the last 1% of oil extracted may be as high as 80% (17). It may thus be worthwhile for processors to consider using a slightly lower efficiency of extraction in order to provide an oil of superior quality with lower contents of gum and sulfur.

The crude oil is the combined expelled and solvent-extracted oils. A number of crude oils not listed in Table II were also analyzed. The sulfur contents of these oils again appeared to be related to the color and gum content of the oils. Some crude oils, which had a light color and appeared to contain no gum, contained only 5 ppm sulfur.

Degumming and alkali refining removed a substantial proportion of the sulfur from the oils. The refined oils still contained 4-9 ppm sulfur, however, which might be considered a somewhat high level if the oil is to be hydrogenated. Bleaching with activated clays further reduced the sulfur contents to 3-5 ppm. Bleaching with deactivated nickel catalysts has been reported to completely remove sulfur from oils as well as to reduce the oil color as efficiently as with conventional bleaching clays (17). Finally, deodorization reduced the sulfur content of the oils to <1 ppm.

Effect of Hydrogenation

Hydrogenation of a refined oil reduced its sulfur content from 8 ppm to <1 ppm. This almost complete loss of sulfur could be accounted for by a large increase in sulfur content of the nickel hydrogenation catalyst, i.e., from 520 ppm in the fresh catalyst to 6400 ppm in the spent catalyst. The large sulfur content of the spent catalyst would render it inefficient and uneconomical for reuse. Refined rapeseed oils to be hydrogenated might with advantage first be deodorized, or bleached with deactivated (spent) nickel catalyst, in order to substantially reduce the sulfur content of the oil.

Effect of Seed Condition

The effects of moisture content, glucosinolate content, heat treatment, and inferior quality of the seed upon the sulfur content of the extracted oil were studied. In these experiments, laboratory-extracted rather than industrial oils were used.

The effects of different moisture contents were evaluated by adding various amounts of water to replicate samples of seed prior to oil extraction. For the high-glucosinolate seed, there was a gradual increase in the sulfur content of the oil with increasing amounts of water added to the seed (Table III). For the low-glucosinolate seed, there was a smaller increase of sulfur in the oil; for the three samples analyzed, however, this increase did not vary

TABLE III

Effect of Seed Moisture, Heat, and Glucosinolate Content on the Sulfur Content of the Oil

Heating time for the seed (hr at 118 C)	Water added to the seed (%)[a]	Sulfur in oil (ppm)	
		High-glucosinolate seed[b]	Low-glucosinolate seed[c]
0	0	0	0
0	2	8	
0	4	16	12
0	5		10
0	6	58	
0	8		11
0	10	88	
0	19	467	
12	0	16	0
144	0	84	
12	5	50	
12	10	37	
12	14	41	

[a]As % by seed wt in addition to the original moisture contents of 5% and 4% for the high- and low-glucosinolate seed, respectively.

[b,c]Oil from seed of high and low glucosinolate content, respectively (Oro and S69-2895).

appreciably with the amount of water added to the seed. The additional sulfur in the oils with increasing seed moisture presumably may be ascribed to oil-soluble hydrolysis products from the glucosinolates in the seed.

The effect of heat was assessed by heating replicate samples of seed at 118 C for 12 and 144 hr prior to oil extraction (Table III). Contrary to expectation, heat treatments (of high-glucosinolate seed) resulted in increasing amounts of sulfur in the oil. The prolonged heating of these samples may have partially pyrolyzed the glucosinolates to yield oil-soluble compounds. In the one test carried out with low-glucosinolate seed, heat treatment did not produce any sulfur in the oil.

Three seed samples were given the combined treatment of heat and subsequent addition of water. The extracted oils contained increased amounts of sulfur but less than the sum for the two treatments independently (Table III).

Laboratory extraction of seed with no prior moisture or heat treatment yielded oils that were free of sulfur, regardless of the glucosinolate content of the seed (Table III). This extraction method thus produced oils of a higher quality than the industrially extracted crude oils which had sulfur contents of 5-31 ppm.

Finally, commercial rapeseed of inferior quality, designated as green, frozen, and bin-heated, were examined. These samples, with no prior heat treatment or addition of water, were extracted in the laboratory to yield oils of appreciable sulfur contents (Table IV). This was in marked contrast to the high-quality seed (Oro), which under the same extraction conditions produced a sulfur-free oil (Table III).

In summary, the factors that should favor the production of low sulfur content in rapeseed oil are the use of sound seed with low glucosinolate content and low moisture content, a minimal amount of water and heat in the extraction process, and a slightly low extraction yield.

TABLE IV

Sulfur Content of Oil from Seed of Inferior Quality[a]

Seed quality	Sulfur in oil (ppm)
75% Green	50
40% Frost-damaged	18
Bin-heated	8

[a]Unknown commercial varieties of normal (high) glucosinolate contents.

ACKNOWLEDGMENTS

The authors are highly indebted to the late Dr. Bernd Weinberg of the Canada Department of Industry, Trade, and Commerce for his untiring interest and support in this work. Oil and seed samples were supplied by I. Levi, Grain Research Laboratory, Canadian Grain Commission, Winnipeg; B.R. Stefansson; and Canadian rapeseed processors. The work was supported by the Canada Department of Industry, Trade, and Commerce; the Rapeseed Association of Canada; and the National Research Council of Canada.

REFERENCES

1. von Fellenberg, T., Mitt. Lebensm. Hyg. 36:355 (1945); C.A. 40:36248.
2. Babuchowski, K., and A. Rutkowski, Seifen Öle Fette Wachse 95:27 (1969).
3. Babuchowski, K., and A. Rutkowski, Ibid. 95:381 (1969).
4. Moser, H.A., C.D. Evans, G. Mustakas, and J.C. Cowan, JAOCS 42:811 (1965).
5. Kucera, Z., and M. Hejtmanek, Prum. Potravin 8:199 (1957); C.A. 51:12511c.
6. Zeman, I., and D. Zemanova, Tluszcze Jadalne 11:111 (1967).
7. Franzke, C., R. Göbel, and E. Holstein, Nährung 16:867 (1972); C.A. 79:4019s.
8. Kurucz, E., and J. Perédi, Proc. 4th Int. Rapeseed Conf., Giessen, Germany, Deutsche Gesellschaft für Fettwissenschaft, Münster, June 1974, p. 363.
9. Göbel, R., and C. Franzke, Lebensm. Ind. 22:30 (1975); C.A. 83:7236d.
10. Granatelli, L., Anal. Chem. 31:434 (1959).
11. Baltes, J., Fette Seifen Anstrichm. 69:67 (1967).
12. Babuchowski, K., and R. Zadernowski, Tluszcze Jadalne 14:140 (1970).
13. Fensom, A., N. Roberts, and G.M.S. Duff, Analyst 96:186 (1971).
14. Troëng, S., JAOCS 32:124 (1955).
15. Wronski, M., and E. Bald, Chem. Anal. (Warsaw) 14:173 (1969); C.A. 70:120902n.
16. André, E., M. Carbouères, and M. Maille, C.R. Acad. Sci. (Paris) 236:1819 (1953); C.A. 48:6716b.
17. Norris, F.A., in "Bailey's Industrial Oil and Fat Products," Edited by D. Swern, Interscience Publishers, New York, NY, 1964, pp. 637-710.

[Received September 2, 1975]