New Process for the Production of Better-Quality Rapeseed Oil and Meal. I. Effect of Heat Treatments on Enzyme Destruction and Color of Rapeseed Oil[1]

K. E. EAPEN, N. W. TAPE and R. P. A. SIMS, Food Research Institute, Ottawa, Canada

Abstract

The thioglucosides (which are precursors of toxic principles) and the fibrous hulls of rapeseed are the two major factors which limit the utilization of rapeseed meal as a protein supplement in human foods. In commercial practice the enzyme responsible for the liberation of toxic principles from thioglucosides is destroyed by a dry-heat treatment, but no attempt is made to remove the thioglucosides or the fibrous matter from the meal. The new wet-heat method of processing to inactivate myrosinase also results in the production of an improved quality of oil. In this paper the advantages of a wet-heat treatment in processing rapeseed are discussed.

Introduction

AMONG THE EDIBLE vegetable oils, rapeseed ranks fifth in the total world production and is exceeded only by soybean, peanut, cottonseed, and sunflowerseed oils (1). Rapeseed, crushed in modern mills, yields approximately 40% oil and 50% meal; the remainder is moisture. The meal is used as a feedstuff although in some countries it is used mainly as a fertilizer.

Carefully prepared rapeseed meals are reported to contain protein approaching that of soybean meal in amino acid balance (2). The use of rapeseed meal as a protein supplement, even in live stock and poultry rations, has often resulted in adverse effects on growth and reproduction (3). Consequently rapeseed meal is only used when it is diluted with other meals. The adverse effects are mainly owing to the existence of thioglucosides, which liberate toxic isothiocyanates and oxazolidinethione upon enzymatic hydrolysis. Another factor detrimental to the use of rapeseed meal is its high fiber content (4). No attempt has been made to remove the fibrous hulls from the meal though various workers (5–13) have studied the procedures for the removal of thiocompounds of rapeseed and mustard seed meals. Of the various techniques studied hitherto, the dry-heat treatment to destroy the myrosinase and thereby to avoid the formation of toxic principles in the meal is at present used in rapeseed-processing plants. In present commercial practice, crushed rapeseed is cooked for 30 min without the addition of water at a temperature of 176–194F to inactivate the myrosinase (7). This operation leaves the thioglucosides intact in the meal and, if it is used for food purposes, the toxic principles can be liberated subsequently by the enzyme produced by certain bacteria, especially *E. coli* and *A. aerogenes* present in the gastrointestinal tract (3).

In this paper wet- and dry-heat treatments of rapeseeds are discussed with respect to their effectiveness in enzyme destruction and in the color of the oil.

[1] Contribution No. 70 of the Food Research Institute, Canada Department of Agriculture.

Materials and Methods

Preliminary studies indicated that the oil color is markedly affected by wet- or dry-heat treatment when the seed stock contains green seeds. Therefore, for the following studies, *Brassica campestris* (Echo variety) and *Brassica napus* (Tanka variety, containing 3% green seeds) rapeseeds were used. The moisture contents of the seeds were 5.2% and 6.0% respectively. After the various heat treatments the seeds were crushed and solvent-extracted with hexane to prepare oil and meal samples. The solvent-free oil samples were measured for red, yellow, and blue color units with the Lovibond Tintometer. The optical density at 550 μ was measured by using a Bausch and Lomb Spectronic 20 colorimeter.

The meal samples were shaken with a phosphate-citrate buffer of pH 7.0 for 2 hr, and the liberated volatile mustard oil collected in dichloromethane was estimated by the gas-liquid chromatography (GLC) method (14). An F&M gas-liquid chromatograph, fitted with a ¼-in. stainless steel column, packed with 20% FFAP on silanized Gas-Chrom W, 70–80 mesh (Chromatographic Specialties Ltd.) was used. The gas flow-rate was 60 ml/min, and the detector temperature was 230F. The amount of the mustard oil liberated per unit weight of seed was taken as an index of the residual enzyme in the seed.

Heat Treatments

1. *Dry Heat in Jacketed Pan.* Cracked *B. napus* seeds were stirred continuously in a jacketed pan for 30 min. The jacket temperature was maintained at 220F. At the end of the period the seed temperature was 181F. The heat-treated seeds were solvent-extracted, and the color of the solvent-free oil was measured. The residual meal was desolventized at room temperature, and the enzyme activity was estimated (Tables I and II).

2. *Dry Heat in Hot-Air Oven.* Cracked *B. napus* seeds were kept for 30 min in a thin layer on an

TABLE I

Effect of Heat Treatments on Residual Enzyme Index

Variety	Treatments	Residual enzyme index
B. napus	30-min dry heat in jacketed pan at 220F	100
	30-min dry heat in hot-air oven at 220F	73
	5-min steam blanching	0
	10-min steam blanching	0
	15-min steam blanching	0
	30-min steam blanching	0
	1.5 min microwave heating	100
	3-min microwave heating	0
	0.5 min soaking in boiling water	73
	1-min soaking in boiling water	21
	1.5-min soaking in boiling water	0
	2-min soaking in boiling water	0
	3-min soaking in boiling water	0
B. campestris	0.5 min soaking in boiling water	75
	1-min soaking in boiling water	0
	1.5 min soaking in boiling water	0
	2-min soaking in boiling water	0
	3-min soaking in boiling water	0
B. napus	Not treated	100
B. campestris	Not treated	100

TABLE II

Effect of Heat Treatments on the Color of the Oil

Variety	Treatments	Optical density[a] at 550 mμ	Lovibond color at 2-inch depth		
			R	Y	B
B. napus	Dry heat in jacketed pan	0.136	6.0	30.0	0.0
	Dry heat in hot-air oven	0.119	6.0	30.0	0.0
	30-min steam blanching	0.420	7.0	37.0	6.0
	15-min steam blanching	0.444	8.0	36.0	6.5
	10-min steam blanching	0.444	7.5	36.0	4.5
	5-min steam blanching	0.356	6.0	36.0	4.5
	1.5-min microwave heating	0.367	7.0	39.0	3.0
	3-min microwave heating	1.347	9.9	30.0	9.0
	0.5-min in boiling water	0.173	5.6	37.0	0.0
	1-min in boiling water	0.221	5.0	35.0	1.1
	1.5-min in boiling water	0.177	4.0	37.0	1.6
	2-min in boiling water	0.251	5.0	37.0	4.5
	3-min in boiling water	0.221	4.5	37.0	4.5
B. campestris	0.5 min in boiling water	0.070	4.1	30.0	0.0
	1-min in boiling water	0.026	3.0	35.0	0.0
	1.5-min in boiling water	0.096	5.0	30.0	0.0
	2 min in boiling water	0.031	3.0	33.0	0.0
	3-min in boiling water	0.060	4.0	33.0	0.0
B. napus	Not treated	0.102	5.5	36.0	0.0
B. campestris	Not treated	0.017	3.0	30.0	0.0
B. napus	1.5 min in boiling 0.5% alkali	0.161	4.0	35.0	0.8
B. campestris	1.5 min in boiling 0.5% alkali	0.022	2.5	30.0	0.0
B. napus (free of green seeds)	2-min in boiling water	0.187	5.0	37.0	0.1

[a] 100% transmittance, adjusted with refined and bleached rapeseed oil.

aluminum tray in a hot-air oven maintained at 220F. The seed temperature at the end of the period was 194F. As in the previous case, the treated seeds were solvent-extracted, and the enzyme activity of the meal and the color of the oil were measured (Tables I and II).

3. *Steam-Blanching. B. napus* seeds were spread in a thin layer on a tray in a steam blancher. Dry steam was let in at atmospheric pressure. In separate experiments, after the seeds were kept in the blancher for 5, 10, 15, and 30 min, they were taken out, cracked, and solvent-extracted. The residual enzyme activity of the meal and the color of the extracted oil were measured (Tables I and II).

4. *Microwave Heating. B. napus* seeds, spread in a thin layer on a glass tray, were exposed 1.5 and 3 min to 2 KW of 2450 mc microwave irradiation. The seed temperature at the end of the period was 220F in the former case and 266F in the latter case. In both cases the treated seeds had a disagreeable, burnt odor. The seeds were cracked and solvent-extracted; the enzyme activity of the meal and the color of the oil were measured (Tables I and II).

5. *Wet-heat Treatment.* In different experiments *B. napus* and *B. campestris* seeds were enclosed in cloth bags and soaked in boiling water for the following periods: 0.5, 1, 1.5, 2, and 3 min. At the end of the period they were quickly cooled by soaking in cold water and divided into two portions. One portion was dried, flaked and defatted; the residual enzyme index was determined. The other portion was passed through a vertical plate grinder along with a stream of water. This wet-grinding procedure squeezed out the meats from the fibrous hulls which had been loosened by the previous wet-heat treatment. These decorticated seeds, along with the hulls, were then extracted with water to remove the thioglucosides (14) and dried; the hulls and meats were separated by air classification. The meats fraction was solvent-extracted, and the color of the oil was measured. In a separate experiment *B. napus* and *B. campestris* seeds were soaked for 1.5 min in boiling 0.5% alkali (NaOH) solution to take advantage of the bleaching and neutralizing effect of the alkali on oil and were processed further as described for hot-water treated seeds. The enzyme activity of the resultant meal and the color of the oil were measured (Tables I and II).

Comparison of Treatments

The following samples were collected from two large rapeseed-processing plants (xs) and (xa), where the dry-heat treatment is used, whole rapeseeds before processing and crushed seeds after the dry-heat treatment. The whole rapeseeds from the two plants were processed by the wet-heat treatment method by using 0.5% alakli solution as described above (Table III, No. 2 and 4). The alkali solution was found to be effective in yielding a comparatively lighter-colored

TABLE III

Comparison Between Commercial Dry-Heat Treated and Wet-Heat Treated Rapeseed

Method of processing	Residual enzyme index	Fines formed on solvent extraction cc/100 g flakes	Lovibond color at 2-inch depth			Optical density at 550 μ	Free fatty acid content %
			R	Y	B		
No. 1 rapeseed meats from Plant (xs), processed by dry-heat treatment	0	4.1	6.0	39.0	3.0	0.232	0.50
No. 2 rapeseed (from the same seed stock above) from Plant (xs), processed by wet-heat treatment	0	1.8	2.7	30.0	0.0	0.102	0.15
No. 3 rapeseed meats from Plant (xs), processed by dry-heat treatment	0	3.8	7.3	39.0	3.0	0.292	0.70
No. 4 rapeseed (from the same seed stock above) from Plant (xa), processed by wet-heat treatment	0	1.75	3.0	30.0	0.0	0.086	0.15

oil (Table II) irrespective of the presence of green seeds.

The meats fraction, produced by the wet-heat treatment, was flaked and mixed with solvent for 30 min. The slurry was filtered over a 60-mesh screen to form a bed of 1-in. thickness, and the miscella was refiltered over the bed as in filtration extraction. Finally the bed was washed with fresh solvent. The total miscella was collected, and the fines were allowed to settle overnight; the volume of the sedimented fines was determined. The oil was recovered from the clear miscella, and the color and free fatty acid content were measured.

The operation was repeated with cracked and cooked seed collected from the production line of the commercial plants (Table III, No. 1 and 2). The residual enzyme index of the different samples, color and free fatty acid content of the crude oil samples, and the volume of the fines formed on solvent extraction in each case are presented in Table III.

Results and Discussion

Dry-heat treatment proved unsatisfactory from the dual standpoint of myrosinase inactivation and oil color. The heating of the cracked seeds for 30 min in the jacketed pan, with a jacket temperature at 220F, did not destroy myrosinase, as shown by the residual index of 100 (Table I), indicating that the myrosinase is practically 100% active for the complete hydrolysis of all the glucosides in the seed. Dry-heat treatment for 30 min in the hot-air oven at 220F reduced the enzyme index to 73.0. No blue unit indicating dark color was developed in the oil (Table II) even when the seed stock subjected to the heat treatment contained 3% green seeds. This would indicate that, although dry-heat treatments do not darken the oil, they fail to destroy the enzyme completely.

Although microwave heating for 1.5 min was not effective in destroying the enzyme, a 3-min exposure destroyed the enzyme completely. However microwave heating for as short a period as 1.5 min reduced the quality of the oil as well as the meal, as indicated by the high blue unit and optical density of the oil and the burnt smell of the meal.

Steam blanching of the seeds for different periods from 5 to 30 min were all effective in completely destroying the enzyme, as indicated by the zero enzyme index. However steam blanching of the *B. napus* seeds resulted in a dark-colored oil with a blue value ranging from 4.5 to 6.5.

Immersion of the seed in boiling water was effective in inactivating myrosinase and produced a lighter-colored oil. When *B. napus* seeds were soaked in boiling water, the myrosinase was completely destroyed in 1.5 min whereas the enzyme in *B. campestris* seeds was destroyed in 1.0 min.

Rapeseed stock with 3% green seeds generally yields dark-colored oil in commercial plants. The color of the oil in *B. napus* seeds containing 3% green seeds was found to darken as the treatment time in boiling water was increased from 1.5 to 3 min. However similar seeds, soaked in boiling 0.5% NaOH solution, yielded oil of a comparatively lower blue reading. In the case of *B. campestris* seeds which were free of green seeds, prolonged boiling in water, up to 3 min, did not affect the color of the oil. When seed stock with 3% green seeds was extracted without heat treatment, light-colored oil resulted (Table II). The data in Tables I and II show the importance of a short, controlled heat-treatment for the production of light-colored oil and enzyme-inactivated meal especially when green seeds are present.

The data in Table III show that the commercial dry-heat treatment results in the production of dark-colored oil although it is as effective as the wet-heat treatment in myrosinase destruction. It can also be observed that wet-heat treatment results in the formation of a comparatively smaller volume of fines in the miscella. Another advantage of wet-heat treatment is that the crude oil extracted from wet-heat treated seeds is light-colored with low free fatty acid content compared with the crude oil produced from the same seed stock of rapeseed which was processed by the conventional dry-heat treatment.

Besides yielding a better quality of oil, wet-heat treatment also results in a better quality of meal, richer in protein (15), because it facilitates the removal of the fibrous hulls, an operation difficult to carry out in the conventional process. Investigations on thioglucosides removal and the nutritional evaluation of the dehulled, detoxified rapeseed meal, produced by the new process, are underway.

ACKNOWLEDGMENT

G. Brunton and G. Johnson carried out some of the speed-processing operations.

REFERENCES

1. Downey, R. K., Canada Department of Agriculture, Publication 1257 (1965).
2. Clandinin, D. R., and W. E. Tajcnar, Poultry Sci. *39*, 291–293 (1961).
3. Bell, J. M., and R. J. Belzile, "Goitrogenic Properties," Review, Canada Department of Agriculture, Publication No. 1257, 33–47 (1965).
4. Wetter, L. R. "The Chemical Composition of Rapeseed Meal," Review, Canada Department of Agriculture, Publication No. 1257, 22–33 (1965).
5. Belzile, R. J., and J. M. Bell, unpublished data (1963).
6. Belzile, R. J., J. M. Bell and L. R. Wetter, Can. J. Animal Sci. *43*, 169–173 (1963).
7. Youngs, C. G., "Processing of Rapeseed Meal," Review, Canada Department of Agriculture, Publication No. 1257, 15–22 (1965).
8. Goering, K. J. (Oil Seed Products Inc.), U.S. Patent 2,987,399 (1961).
9. Mustakas, G. C., L. D. Kirk and E. L. Griffin Jr., JAOCS *39*, 372–377 (1962).
10. Goering, K. J. (Oil Seed Products Inc.), U.S. Patent 3,044,876 (1962).
11. Mustakas, G. C., E. D. Griffin Jr., E. A. Gastrock, E. L. D'Aquin, E. L. Keating and E. L. Patton, Biotechnol. Bioeng. *5*, 27–39 (1963).
12. Mustakas, G. C., and L. D. Kirk (United States Department of Agriculture), U.S. Patent 3,106,469 (1963).
13. Mustakas, G. C., L. D. Kirk, V. E. Sohns and E. L. Griffin Jr., JAOCS *42*(1), 33–37 (1965).
14. Youngs, C. G. (Prairie Regional Laboratory, Saskatoon), personal communication.
15. Eapen, K. E., N. W. Tape and R. P. A. Sims, in preparation.

[Received October 30, 1967]