EFFECT OF AMMONIATION ON THE QUALITY OF SOLVENT-EXTRACTED RAPESEED PRODUCTS

F. Shahidi

Department of Biochemistry
Memorial University of Newfoundland, St. John's, NF, Canada, A1B 3X9

INTRODUCTION

The production of rapeseed as of 1987 ranks third in the world, and in this respect is expanding faster than any other oilseed crop (Shahidi, 1990). The traditional varieties of rapeseed contain some 20-60% erucic acid in the oil and up to 6% glucosinolates in their defatted meal. While presence of erucic acid compromised the nutritional value of oil, goitrogenic products of glucosinolates limited the feeding quality of the meal. Through genetic alterations, however, low erucic acid (<2% in the oil), low glucosinolate (≤30 μmol/g meal) cultivars, known as double-low, or canola, have been produced. Although canola oil has been accredited a GRAS (Generally Recognized As Safe) status by the United States Food and Drug Administration since 1985, the meal is still not suitable for unrestricted use in animal feeds.

Glucosinolates in view of their goitrogenic breakdown products are perhaps the most important limiting factors in canola and rapeseed. However, presence of other antinutrients such as phytic acid, phenolics, high fibre content (hull) and possibly flatulence-causing sugars introduce their own complications. Thus, efforts have been underway for upgrading the proteinaceous meal so that its unrestricted use in animal feeds and possibly human foods be achieved (Afzalpurkar et al., 1974; Jones and Holme, 1979; Maheshwari et al., 1981; Fenwick et al., 1986).

Recently, ammoniation of Brassica seeds has been pursued by many researchers (Kirk et al., 1966; Keith and Bell, 1983; McGregor et al., 1983; Schlingmann and von Rymon-Lipinski, 1982). Among these, Schlingmann and co-workers (Schlingmann and Vertesy, 1978; Schlingmann and von Rymon-Lipinski, 1980, 1982) made use of methanol-ammonia to enhance oil extraction from single-cell proteins and vegetable oilseeds, including rapeseed. Later on, in line with Schlingmann's findings, a two-phase solvent extraction system consisting of alcohol-ammonia and hexane was patented (Rubin et al., 1984).

In this paper, advantages and disadvantages of methanolic ammoniation of rapeseed with respect to the removal of antinutrients from meals and quality of the oil so obtained will be presented.

THE ALCOHOL-AMMONIA/HEXANE EXTRACTION OF RAPESEED

Removal of antinutrients from rapeseed by genetic, microbiological, chemical, physical and enzymatic methods has been attempted. Procedures using combinations of two or more of the above methods such as extraction by diffusion or by alcoholic ammoniation have also been developed. Schematic representation of the two-phase solvent extraction system for rapeseed/canola is shown in Figure 1. The yield and quality of the oil and meal so obtained was investigated. In general, 88-97% of the oil was extracted from canola and rapeseed as a result of this process. However, the recovery of meal was only 87-91%. Dissolution of low-molecular-weight polar compounds and their removal by the ammoniated alcohol was responsible for this observation.

QUALITY OF THE OIL

The oil obtained from canola and rapeseed after extraction via a two-phase solvent extraction system, described above, had a low content of both free-fatty acids and phosphorus (Table 1). Removal of free fatty acids and phospholipids by the polar phase was responsible for this observation. However, low levels of sulphur and non-sulphurous glucosinolate breakdown products such as nitriles, especially for high glucosinolate rapeseed cultivars of Midas and Hu You 9, (Shahidi and Naczk, 1990) were detected in the extracted oil (Table 1).

QUALITY OF THE MEAL

Removal of low-molecular-weight polar matters from meals resulted in enhancement of protein content in the final products by approximately 10% The increased concentration of proteins in the meal is considered as advantageous. The polar constituents which were specifically monitored in this process included glucosinolates and/or their degradation products, phenolic compounds and low-molecular-weight sugars.

GLUCOSINOLATES AND THEIR AGLYCONE PRODUCTS

The effective removal of glucosinolates by alcohol-ammonia solutions was achieved only when methanol was used. Removal of glucosinolates by MeOH-NH_3-H_2O/Hexane extraction ranged from 81.3 to 96.5% for both low and high glucosinolate rapeseed cultivars (Table 2), as determined by standard chromatographic procedures (Shahidi and Gabon, 1989).

An examination of the polar phase indicated that most glucosinolates were extracted, in the intact form. However, a close scrutiny of the data indicated the presence of some glucosinolates' degradation products. Small amounts of aglycone products were also present in the oil and meal fractions (Shahidi *et al.*, 1990a). The concentrations of the aglycone breakdown products in the meal and oil from Midas and Hu You 9 rapeseed cultivars were higher than those in selected canola cultivars (Table 3).

Presence of aglycones in the oil and meal has a detrimental effect on their quality. We have found that some of these degradation compounds can be removed by further processing of the oil, although the same is not true for all. Toxicity of nitriles is much higher than those of oxazolidinethiones and in this respect the crude products so obtained may be less desirable. However, at concentrations present, they do not exceed the acceptable nutritional/toxicological limits. The recovered solvents also showed the presence of some volatile aglycone products. Repeated use of the solvents would increase the concentration of these aglycones and thus adversely affects the economics of the process.

PHENOLIC COMPOUNDS

Phenolic compounds are present in a much higher concentration in rapeseed as compared with other oilseed crops. In rapeseed, they occur as phenolic acids in the free, esterified and insoluble-bound forms and also as condensed tannins (Kozlowska *et al.*, 1990). The major phenolic acid present in canola and rapeseed meals was sinapic acid and it was present predominantly in the esterified form. Methanolic ammoniation of canola and rapeseed removed 46.2-68.7% of the total phenolics from the free and 79.8-91.3% of those from the esterified fractions (Table

4). The content of insoluble-bound phenolics remained unchanged (Naczk and Shahidi, 1989).

Condensed tannins in canola and rapeseed are present at concentrations of up to 3% in the defatted meals (Clandinin and Heard, 1968). Our own work has shown that tannins, reported as catechin equivalents, are present in quantities ranging from 426 to 772 mg/100 g meal (Shahidi and Naczk, 1989). Methanolic ammoniation of the seeds/meals resulted in the removal of tannins from 70.1 to 96.2%. The effect of reduced phenolics content in the resultant meals was reflected in their sensory properties as they had generally a light-beige colour and were bland in taste.

LOW-MOLECULAR-WEIGHT SUGARS

The soluble sugars constitute a relatively low proportion of canola and rapeseed. Sucrose was the major soluble sugar present and raffinose, stachyose, fructose and glucose were present in smaller amounts.

Due to the undesirable effects of raffinose and stachyose, a number of processes have been developed for their removal from oilseeds and legumes, especially from soybean meal. Enzymatic degradation, soaking, germination, autolysis were amongst the methods examined. Partial removal of flatulence-causing sugars from rapeseed was an added advantage of the two-phase solvent extraction system (Shahidi et al., 1990b) (Table 5).

OTHER ANTINUTRIENTS

Phytates and indigestible fibres are known to adversely affect the quality of rapeseed meal. Phytates in rapeseed meals are present in concentrations of 2.0-5.0% and are responsible for reducing the bioavailability of minerals, mainly zinc. Indigestible fibres also reduce the feed utilization of rapeseed meals in monogastric animals.

Separation of phytates from rapeseed may be achieved by dissolution of proteins at pH 11, or preferably pH 7 in the presence of sodium hexametaphosphate (Thompson, 1990). Removal of insoluble matters and precipitation of proteins at their isolectric pH affords protein isolates with a very low phytate content. Preparation of low-phytate protein isolates by membrane-based techniques has also been achieved (Rubin et al., 1990).

Separation of hulls from rapeseed may be achieved by including an initial dehulling step in the process. Removal of hulls by a density gradient procedure during wet processing may also be achieved. Methanolic ammoniation did not remove any of the indigestible hulls or phytates from rapeseed meals.

CONCLUSIONS

The alcoholic ammoniation of rapeseed has many advantages and some disadvantages. While a reduction in the content of glucosinolates, phenolic acids, tannins and flatulence-causing sugars is considered as desirable, presence of some glucosinolate degradation products in the resultant meal and oil cannot be overlooked. Caution must particularly be practiced when dealing with traditional rapeseed cultivars with a high glucosinolate content.

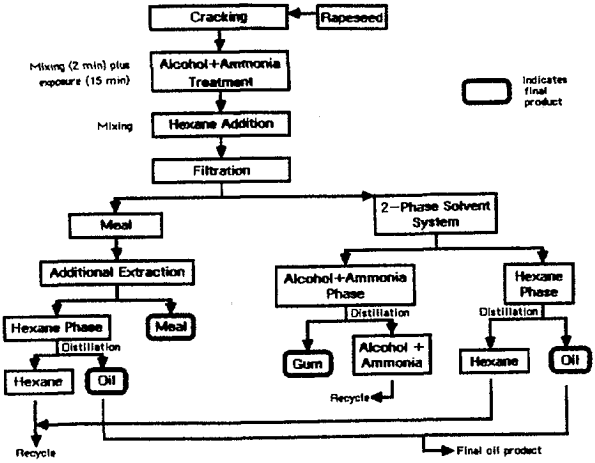

Figure 1. Flowsheet for Alcohol-ammonia/Hexane extraction of rapeseed.

Table 1. Crude oil extracted from canola and rapeseed with $MeOH-NH_3-H_2O$/Hexane.

Constituent (Content)	Canola[a]	Rapeseed[b]
Free fatty acids (%)	0.23-0.26	0.19-0.27
Phosphorus (ppm)	78.1-87.4	69.6-83.2
Sulphur (ppm)	1.56-1.86	3.22-8.12
Nitriles[c] (µmol/100 g)	1.1-1.5	2.9-6.3

[a]Altex canola. [b]Midas and Hu You 9 rapeseed. [c]Including hydroxy- and epithio-nitriles.

Table 2. Removal (%) of glucosinolates from canola and rapeseed with $MeOH-NH_3-H_2O$/Hexane.

Glucosinolate Side Chain	Canola[a]	Rapeseed[b]
3-Butenyl	90.9-91.8	90.0-96.5
4-Pentenyl	91.3-100.0	91.6-96.1
2-Hydroxy-3-butenyl	86.5-89.5	88.2-95.5
2-Hydroxy-4-pentenyl	50.0-90.9	88.4-96.0
Total	85.7-91.3	89.0-94.8

[a]Altex canola. [b]Midas and Hu You 9 rapeseed.

Table 3. Breakdown products of glucosinolates in the oil and meal of $MeOH-NH_3-H_2O$/hexane extracted seeds (µmol/100 g).

Compound	Meal		Oil	
	Canola[a]	Rapeseed[b]	Canola[a]	Rapeseed[b]
Desulphoglucosinolates	0.4-0.5	1.8-2.3	0	0
Isothiocyanates	0.4-0.6	0.8-1.1	0	0
Oxazolidinethiones	0	0	0.6-0.9	1.2-1.3
Nitriles	1.2-1.8	5.6-9.9	1.1-1.5	5.1-8.4

[a]Altex canola. [b]Midas and Hu You 9 rapeseed.

Table 4. Removal (%) of phenolic acids and tannins by MeOH-NH_3-H_2O from rapeseed and canola.

Meal	Phenolic Acids		Tannins
	Free	Esterified	
Canola[a]	44.8-57.0	81.0-84.5	70.1-84.9
Rapeseed[b]	32.2-68.7	79.8-91.3	79.3-96.2

[a]Range for canola cultivars of Altex, Regent, Tower and Triton.
[b]Range for rapeseed cultivars of Midas and Hu You 9.

Table 5. Removal (%) of soluble and flatulence-causing sugars from rapeseed by MeOH-NH_3-H_2O treatment.

Sugar	Canola[a]	Rapeseed[b]
Sucrose	77.3	86.0-89.0
Raffinose	88.7	77.8-88.6
Stachyose	34.4	58.0-64.6
Total	67.8	81.2-82.2

[a]Triton canola. [b]Midas and Hu You 9 rapeseed.

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