Crambe Seed Processing: Filtration-Extraction on a Bench Scale [1]

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Abstract

Crambe abyssinica is a potential source of erucic fatty acid and of good quality protein, provided satisfactory methods for processing the seed can be developed. Among the oil recovery methods currently under study is that of filtration-extraction, a direct solvent process for high-oil content seeds. Good oil recovery at satisfactory filtration rates was accomplished by a series of processing steps including dehulling, flaking, cooking, drying, crisping and extracting with hexane.

When the conventional cook procedure was modified to incorporate an enzyme-conversion step, significant improvement in rat feeding tests was obtained without loss in subsequent extraction efficiency. The recovered oils from the non-conversion cooks were refined and bleached by conventional procedures to oils of light color. The oil product from the conversion cook apparently contained sulfur compounds, even after refining and bleaching, whose removal will require special treatment as yet undeveloped in order to produce a hydrogenatable oil.

Introduction

Crambe abyssinica is being studied by USDA scientists to determine its potential as a new oilseed crop for the United States (2,3,7,8). Agronomic characteristics of this seed are favorable, and the plant lends itself to harvesting by conventional combining. The prime value of crambe lies in the unusual composition of its oil whose fatty acids are approximately 53–59% erucic. The degummed, refined, triglyceride oil itself has recently been shown to have value as a mold release and is in demand for the continuous casting of steel.

The residue meal obtained after oil extraction has a high protein content, and its amino-acid analysis suggests that it could be converted to a nutritious animal feed. The feeding value of this meal is complicated, however, by the presence of undesirable compounds known as thioglucosides. The major thioglucoside in crambe was recently identified by Daxenbichler et al. (3) of this Laboratory as (R)-2-hydroxy-3-butenyl glucosinolate. Natural enzymes in the meal break down this thioglucoside readily under proper moisture and temperature conditions as illustrated in Figure 1. The cyclic product, an optical isomer of the goitrogenic compound *l*-5-vinyl-oxazolidone-2-thione (thiooxazolidone) found in rapeseed, is believed responsible for the goitrogenicity of untreated crambe meal, which has been observed in rat and chick feeding tests but not in the feeding of ruminants.

The present studies were underaken to determine conditions for preparing crambe seed for extraction and the effects of enzyme conversion upon the quality of recovered oil and meal.

Since filtration-extraction is a method suitable for removing oil from high-oil content seeds, it was explored in some detail for application to crambe. The preparatory cook step of this method is particularly suitable for incorporation of enzyme conversion of thioglucosides as was demonstrated previously with mustard seed (6). Such a conversion step with other oilseeds has resulted in significant improvement in the feeding value of meals. By variations in the temperature and moisture levels during cooking, either enzyme-converted or thioglucoside-intact meals were produced for evaluation.

Experimental

Materials, Methods, and Equipment

Crambe abyssinica seed was furnished through a planting program of the ARS Crops Research Division, USDA. The major lot of seed used was grown in Texas in 1961. After dehulling and defatting the seed, the thioglucoside content was 12.4% (moisture-free basis). The hull content of hull-intact seeds was 23%. Filtrol bleaching earth, an activated bentonite clay produced by Filtrol Corp., and Hyflo Super-Cel filter aid, a product of Johns-Manville Corp., were used in the lipid-refining step. The Rufert nickel catalyst employed in hydrogenation was a flake preparation produced by the Rufert Chemical Division containing 24.4% nickel.

Thioglucoside content was determined by the sulfate method (5) with the molecular weight of (R)-2-hydroxy-3-butenyl glucosinolate (MW 411) as the basis of calculation. Thiooxazolidone yield was determined by Wetter's procedure (9) modified by replacing the pH 4.0 buffer with a pH 5.8 buffer. Residual oil content was obtained by pentane-hexane extraction for 6 hr followed by drying the sample overnight at 175F before weighing. The degree to which refined bleached oils could be hydrogenated was determined from the IV of samples subjected to a standard hydrogenation procedure. Conditions for this hydrogenation were: 0.1% nickel catalyst, 347F, 100 psig hydrogen pressure, 4-hr reaction time.

Completeness of enzyme conversion was indicated by a paper chromatographic technique. The chromatogram was prepared from aqueous extracts of crambe meal by descending technique employing the top layer of an *n*-butanol:ethanol:water mixture in volume ratio 4:1:4 as developing solvent. The extract was prepared in the following manner: a 10-g sample of converting meal was added to 250 ml of boiling distilled water and held 5 min for enzyme deactivation. The slurry was filtered and the cake reextracted 3 times in 50 ml of hot water. All extracts were combined and the solution was made up to 500 ml. The chromatographic paper was spotted

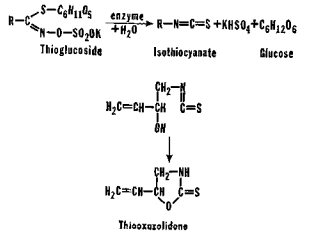

FIG. 1. Enzymatic hydrolysis of crambe thioglucoside.

[1] *Presented in part at AOCS Meeting, New Orleans, 1964.*
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with a 10-μl sample of the extract and developed overnight. The thioglucoside was made visible by dipping the dried chromatogram in a solution of saturated silver nitrate in acetone, followed by aqueous sodium hydroxide in ethanol. The thioglucoside appeared as a dark spot near R_f 0.1. Complete conversion was indicated when no thioglucoside was visible on the chromatogram. The IV determination and all other analyses were according to AOCS standard methods (1).

The cracking rolls were 6 in. in diameter with 10 corrugations per inch. Dehulling equipment consisted of a vibrating screen (0.093 in. perforated) with aspiration hoods at the point of introduction of the cracked seed and over the tails fraction leaving under the screen. A pneumatic system returned "overs" material from the screen to the cracking rolls. A fiber drum turned by a roller mill was used to temper the dehulled grits. The flaking rolls were single stand of 12 in. diameter and smooth-faced. Converting, steaming and cooking steps were conducted in the cooker described by Mustakas et al. (6). This unit was a 5-gal jacketed stainless-steel vessel equipped with a meshing rod agitation system, a spray nozzle and a steam sparging coil. The unit was also used as the slurry tank for filtration-extraction. The 16-in. diameter funnel with 60-mesh screen and 5-gal receiver tank described by Mustakas et al. (6) was used in evaluating filtration-extraction characteristics of the cooked meals.

Procedure

A flowsheet of the test procedures is shown in Figure 2. The cracked, dehulled meats containing 4–5% moisture were tempered to 6–7% and flaked in two passes at roll clearances of 0.003-in. and 0.001-in., respectively. When enzymatic conversion was incorporated in the cooking step, the flakes were moistened with water to 30% and mixed continuously during moisture addition. After mixing for about 5 min, the flakes were heated to 130F and held for 15–75 min to accomplish enzymatic conversion of the thioglucosides. The meal was then heated rapidly to 212F by means of live steam and 30 psig jacket steam. Steaming was continued for 30 min and the meal dried for 30 min with jacket steam alone. After discharging, the hot meal was allowed to cool and "crisp" before rerolling through smooth rolls and extracting. When enzymatic conversion of crambe thioglucosides was not desired in the cooking procedure, the meal was heated to 180F before moisture addition. Moisture was added to 12% and the meal dried for 30 min before discharging and crisping.

Filtration-extraction of the rerolled material was carried out according to Graci's procedure (4). The crisped meal was slurried 60 min in a miscella initially containing 10% oil in hexane and charged to the extraction funnel. Three washes containing 5, 1 and 0% oil in hexane were then added successively to the cake. All washes and initial slurry liquors were added at a 1.3:1 solvent:meal ratio. A crambe oil recovered from thioglucoside-intact meal and free of catalyst deactivator was used for makeup miscella. The spent cake was air-dried to remove solvent.

Combined miscella from filtration-extraction was desolventized in a rising film glass evaporator to produce the crude oil. Degumming-refining was accomplished by adding to the oil at room temperature sufficient sodium hydroxide to neutralize free fatty acids (plus an excess equivalent in weight to 0.2% of the oil weight), holding for 30 min, heating to 150F and centrifuging. The decanted oil was water-washed at 180F with agitation for 30 min and centrifuged. The recovered oil was vacuum-dried at 155F and bleached by adding bleaching clay (equivalent to 5% of the charge weight), heating to 215F for 30 min and filtering. Filter aid (5% of charge weight) was added to the hot oil to promote filtration.

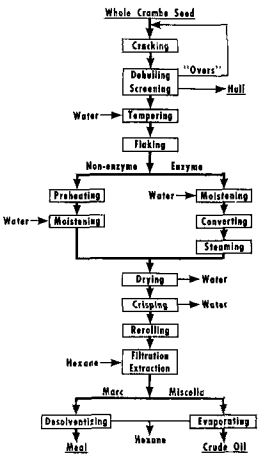

FIG. 2. Flowsheet of processing crambe seed by filtration-extraction.

Results and Discussion

Flake Preparation

Crambe seed consists of an outer pericarp or hull loosely surrounding an inner seed coat and kernel. Since a coarse crack was employed, almost all the dark inner seed coat remained with the kernel. The size distribution of whole and dehulled seed is shown in Table I. Pertinent analyses for whole seed, kernels, hulls and defatted meal appear in Table II. The hulls, constituting about 23 weight per cent of the seed, are high in fiber and low in oil and protein. Dehulling before solvent extraction not only reduces tonnage to the extraction, but is necessary where a high-protein, low-fiber meal is desirable, as in the feeding of chicks and swine. Although the material prepared for these studies was cracked at 0.035-in. roll clearance, later studies have shown that essentially whole dehulled seed can be produced at a roll clearance of 0.060 in.

Flaking the dehulled grits through smooth rolls gave considerable fine material, which contributed to a "gumming" problem on adding moisture during the enzymatic conversion. Tempering the grits to 7% moisture content, before flaking, eliminated this problem. At temper levels of 9% and higher, the flakes began to mat together and adhere to the roll. This matting on the roll scraper bars formed sheets of flakes resembling crepe paper. The optimum moisture level would probably vary somewhat with the oil content of the seed used; however, the range of 6–7% is belived most suitable.

TABLE I

Size Distribution of Whole and Dehulled Crambe Seed

Mesh size	Per cent retained	
	Whole seed	Dehulled seed
6	1.2	0.0
7	50.0	0.0
8	45.3	0.0
10	3.3	39.4
12	0.0	54.1
14	0.0	6.1
Pan	0.2	0.4

TABLE II

Analyses of Crambe Seed and Seed Fractions[a]

Constituent	Per cent of each constituent in:			
	Whole seed	Kernels	Hulls	Meal
Moisture	4.8	3.7	8.8	7.0
Oil	34.0	44.0	1.6	1.0
Protein (N × 6.25)	18.9	27.0	5.4	45.9
Crude fiber	13.6	3.0	41.2	8.3
Ash	1.5	3.7	7.7	8.2
Nitrogen-free extract	27.2	18.6	35.3	29.6

[a] The fractions were separated by a combination of screening, aspirating and manual sorting.

Cooking Conditions

An important step in the application of filtration-extraction to crambe is the cooking procedure that prepares the flakes for removal of oil. *Crambe abyssinica* like other members of the Cruciferae family contains thioglucosides which, under favorable conditions of heat and moisture, are readily broken down by natural enzymes to undesirable products. A process was developed (6) in which the thioglucoside sinigrin of oriental mustard was enzymatically converted to a volatile product which could be steam distilled in the cooking process. This step produced a meal of good feeding value; however, for crambe the bulk of the conversion products are nonvolatile. Since it was desired to produce both converted and unconverted test meals, cooking conditions were determined to either promote or inhibit such conversion. When enzyme conversion was desired, the conditions approximated those used in the conversion of oriental mustard; namely, moisture was added to the flakes to 30% and then the flakes were heated to 130F and held at this temperature to promote thioglucoside hydrolysis. The conversion period was varied from 15–75 min although in previous work with oriental mustard complete thioglucoside conversion was realized in 15 min. Optimum conditions for conversion of the major thioglucoside of crambe (R)-2-hydroxy-3-butenyl glucosinolate were difficult to determine. The cyclic conversion product reported by other workers at this Laboratory (8) was not formed in substantial yield under these moisture conditions so that simple measurements of thiooxazolidone yield did not show completeness of conversion. Paper chromatograms, however, did indicate complete thioglucoside breakdown after 15 min of conversion.

Filtration-Extraction

When enzyme conversion was employed, the flakes were discharged from the cooker at an initial temperature of 217–220F and a moisture content of 17–20%. As the flakes cooled and lost moisture, they became noticeably gritty, a typical observation of the "crisping" step. As crisping progressed, the solids hardened and formed an incompressible cake bed through which solvent readily flowed during filtration-extraction. This effect is demonstrated by the data in Table III for crisping periods of ½ hr and 2½ hr. The extended crisping time noticeably improved the filtration rate although it did not affect extraction efficiency. Passing the crisped meal through smooth rolls before extraction greatly improved extraction efficiency. This process, known as "rerolling," improved extraction efficiency at the sacrifice of filtration rate as demonstrated by progressively severe rerolling conditions (see Table III).

TABLE III

Effect of Crisping Time and Rerolling Conditions on Filtration Rate and Extraction Efficiency in Processing Crambe

Crisping time hr	Reroll conditions[a]	Slurry time, min	Filtration rate, lb/hr/ft²	Residual oil, % mfb
½	No reroll	30	1,350	9.2
2½	No reroll	30	4,030	9.0
2½	1 Pass at 0.002-in. roll clearance	30	2,890	6.3
2½	1 Pass at zero-roll clearance	30	2,330	3.2
2½	3 Passes at zero-roll clearance	30	1,680	3.0
2½	3 Passes at zero-roll clearance	60	1,350	1.5

[a] Reroll moisture 6.5–8.0%.

The moisture content at which the meal was rerolled affected filtration rate. A moisture level of 6–9% under severe reroll conditions of three passes at zero-roll clearance gives a filtration rate of 1,500–2,000 lb/hr/ft² considered sufficiently rapid for practical extraction.

To achieve residual lipid levels in the range of 1–2%, it was necessary to extend the slurry period from 30–60 min (Table III). A solvent-to-meal ratio of 1.3:1 was used in all the studies reported here. Based on previous experience in the filtration-extraction of oriental mustard, it was felt that this ratio was optimum.

Evaluation of Products

Lipid

The recovered crude lipids from cooks with and without an enzyme-conversion step contained 2.6% and 1.5% free fatty acids, respectively, indicating some action of lipase enzyme during conversion.

Hydrogenation of the refined-bleached lipid recovered from a cook where enzyme-conversion was not used produced a hard white wax of 1.2 residual IV. When enzyme-conversion was incorporated in the cook step, the recovered lipid was only partially hydrogenated (IV 36.6). This rather high IV of the conversion-cook lipid after 4 hr of hydrogenation indicated the presence of sulfur-containing hydrolysis products which deactivated the nickel catalyst used. Although conventional refining-bleaching procedures did not remove this deactivator, it is conceivable that variations in technique might be found to accomplish this removal at reasonable cost.

Meal

Preliminary feeding studies have been conducted with small animals. Converted meals showed marked improvement over thioglucoside-intact meals when fed to rats and chicks but feeding results were not comparable to those obtained with soybean meal. Further studies are in process to produce a good feed meal by a method compatible with filtration-extraction.

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[Received October 8, 1965]