Degradation of Lipids and Glucosinolates in Dehulled Crambe Seed During Storage[1]

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ABSTRACT

Crambe as harvested contains seed accompanied by ca. one-third hull, a fraction of little commercial value that can be removed during processing. If the hull were removed before shipping, considerable transportation costs could be saved. Because little was known about the quality of crambe seed after dehulling and storage, decomposition of the glucosinolates in dehulled seed after storage was studied, as well as changes in color, free fatty acids, peroxide value, and ease of hydrogenation of the oil fraction. While not so stable as seed plus pericarp (hull), dehulled crambe seed can be stored for at least 3 months at temperatures up to 110 F at ambient moisture (6.3%). However, at 14% moisture, decomposition was significant after storage for 2 weeks at both ambient (77 F) and elevated (110 F) temperatures. Inactiviation of the endogenous enzyme after dehulling extends storage life to 3 months at either moisture level at ambient temperatures.

INTRODUCTION

Crambe abyssinica Hochst ex R.E. Fries, a member of the Cruciferae family, is botanically related to mustard, rape, and cabbage, and has been recommended as a new oilseed crop for the US. The primary interest in crambe is based on the high erucic acid content of its oil. Also, useful nitrogen derivatives can be prepared from erucic acid, which also is obtained from rapeseed. Erucamide, one such derivative, is gaining wide acceptance as an excellent slip and antiblocking agent for plastic films. A new polyamide (nylon 1313) having exceptionally low water absorption has been made from the cleavage products of erucic acid (1).

The plant grows ca. 3-4 ft tall, and the seeds (ca. 0.05 in.) are borne singly in pods (siliques) ca. 0.15 in. in diameter. As harvested, the seeds with pods average ca. 22-27 lb per bu. The hulls account for nearly one-third of the wt and ca. two-thirds of the volume. Dehulled seed averages ca. 39 lb per bu. If the hulls were removed before shipping, considerable savings in transportation cost could be realized. However, little is known about the quality of dehulled crambe seed during storage.

Crambe contains glucosinolates and thioglucosidase enzyme system, thioglucoside glucohydrolase, (EC 3.2.3.1) referred to as thioglucosides and myrosinase in the early literature. More than 90% of glucosinolates in crambe seed is *epi*-progoitrin, and VanEtten, et al., (2) demonstrated that hydrolysis by the endogenous enzyme breaks down the *epi*-progoitrin into glucose, sulfate ion, and, depending on conditions, into (R)-goitrin or 3 nitriles (Fig. 1). The work reported here was done to determine the extent to which such glucosinolate deterioration, as well as changes in the oil, takes place during seed storage.

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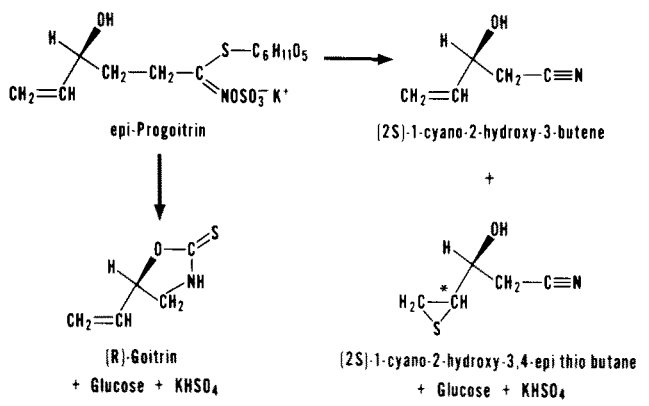

FIG. 1. Products from enzymatic hydrolysis of *epi*-progoitrin (2).

MATERIALS AND METHODS

Crambe seed used in this study was grown in Illinois in 1972. The seed was 'Prophet' variety, released by the Agricultural Experiment Station, Purdue University, Lafayette, Indiana. Whole pod contained 32.6% oil and 20.9% protein (N X 6.25) on a dry basis. Seed contained 42.6% oil and 28.7% protein, dry basis. The oil assayed 62.2% erucic acid. Defatted whole pod contained 4.7% glucosinolates, whereas, defatted dehulled seed contained 8.3 ± 0.5% glucosinolate.

When samples were removed from experimental storage, they were dried overnight in a forced air dryer without heat. This step was taken to prevent oil-water emulsions in the high moisture samples during oil extraction. Samples were flaked on smooth flaking rolls before hexane extraction and desolventized by air drying overnight. The air dried, defatted meals were ground in a hammer mill. The oil was recovered from the hexane miscella by flash evaporation.

Total glucosinolates were determined on the air dried, defatted seed meals by measuring the glucose released by thioglucosidase. Goitrin was analyzed by a method similar to that of Appelqvist and Josefsson (3). Organic nitriles were determined by infrared (IR) analysis (4) or by gas liquid chromatrography (GLC) (5). Test for thioglucosidase activity was run by the method of VanEtten, et al., (6). Iodine value and free fatty acid analyses were conducted according to Official AOCS methods (7,8).

Oil fractions were refined by adding slightly in excess of the stoichiometric quantity of 10% sodium hydroxide solution to neutralize free fatty acids (FFA). After soapstock was centrifuged off, the oil was washed once with water, heated to 110 C, and dried under vacuum. Dried oil was slurried with 2% activated bleaching earth and filtered. The refined and bleached oil was hydrogenated for 4 hr at 175 C at 100 psig with 0.10% nickel catalyst.

EXPERIMENTAL PROCEDURE

For the high moisture samples, water content of crambe seed was increased from 7.8 to 14% by tempering the whole pod in a rolling baffled drum. This treatment kept breakage of the pod to a minimum. A second portion of the original whole pod was cracked on 6-in. corrugated cracking rolls set at a 0.025 in. clearance. At this setting a significant portion of the seed was broken and removed from the seed coat. Hulls then were removed by aspiration on a 0.1065-in.

round hole vibrating screen. Dehulled seed had a moisture content of 6.3%. Moisture was increased to 14% by spraying water on a portion of the dehulled seed while stirring in a Hobart mixer. Thioglucosidase was inactivated in a portion of the dehulled seed at 6.3% moisture by heating in a jacketed kettle to 185 F with indirect steam; water then was added to increase moisture to 10%, the temperature was held at 185 F for 15 min, followed by cooling and drying down to 6.3% moisture. A portion of the enzyme inactivated, dehulled seed was adjusted to 14% moisture as discussed previously.

Samples of whole pod, dehulled seed, and dehulled seed with enzyme inactivated at both ambient and 14% moisture were stored in wide mouth quart jars closed with screw cap lids. Storage was in a temperature controlled cabinet at 110 F and on shelves in the laboratory at 77 ± 3 F. At specified times, samples were removed from storage and hexane defatted. Analyses then were run on desolventized oil and meal samples.

RESULTS AND DISCUSSION

As harvested, crambe is generally low enough in moisture (6-8%) to present no particular spoilage problem in storage. However, the crop is harvested in the middle of the summer, and green debris, i.e., weeds, stems, and leaves high in moisture can cause serious problems unless they are removed in a seed cleaner before storage. The seed with pericarp used in our storage study had a moisture content of 7.8%; the seed, 6.3% moisture.

Because elevator operators usually accept grain for storage at 13% moisture, we deliberately added moisture to a 14% level to be just outside the limits of general acceptance. Our samples were sealed in closed containers so there was no loss of moisture during storage.

Decomposition of Glucosinolates

At ambient moisture (6.3-7.8%), no significant decomposition of glucosinolates was observed in any of the stored samples after storage for 26 weeks at 77 F or for 13 weeks at 110 F (Fig. 2). From a study of glucosinolate decomposition alone, it appeared that dehulled seed stored as well as whole pod at ambient moistures (6.3-7.8%). When the moisture was increased to 14%, decomposition of glucosinolates was considerably more rapid. At 77 F, dehulled seed deteriorated after only 2 weeks of storage. Whole pod under the same conditions was stable for 13 weeks, but deteriorated thereafter. Inactivation of the thioglucosidase enzyme system slowed the rate of decomposition in dehulled seed, but did not prevent it. Storage conditions of 14% moisture and 110 F were quite severe on all 3 kinds of samples, with decomposition occurring after only 4 weeks.

Free glucose, a product of enzymatic hydrolysis of *epi*-progoitrin, was found in significant quantities in the dehulled seed after only 2 weeks storage at 14% moisture. The rate of glucose formation approximated the rate of decomposition of glucosinolates (Fig. 3). Similar quantities of free glucose were found in the dehulled, enzyme inactivated samples stored at 14% moisture. However, in the enzyme inactivated seed stored at the same temperature and moisture conditions, free glucose appeared at about the same rate, but glucosinolate decomposition was minimal (Fig. 3). This glucose appeared to be formed from something other than the glucosinolate in the seed. Goitrin formation was inhibited in the enzyme inactivated seed, whereas, nitrile formation was the same in each case (Fig. 3).

Change in Oil Characteristics During Storage

Free fatty acids. At ambient moisture (6.3-7.8%) there was no significant increase in FFA in the oil fraction from any of the crambe seed samples stored at 77 F for 26 weeks or at 110 F for 13 weeks. These results were similar to

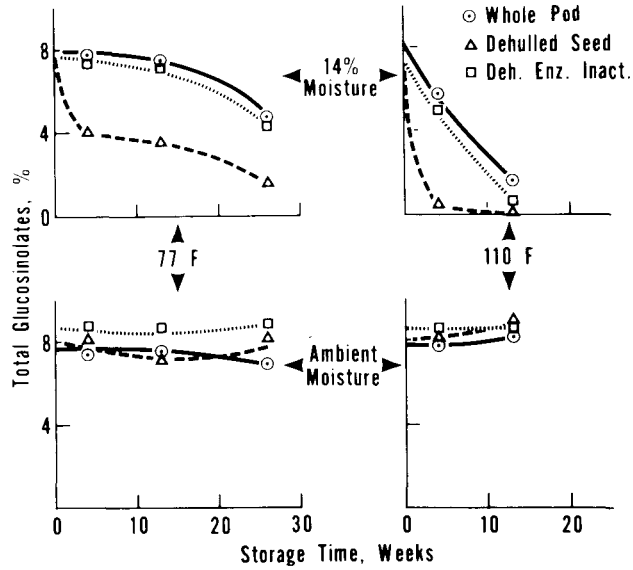

FIG. 2. Decomposition of glucosinolates in crambe seed during storage.

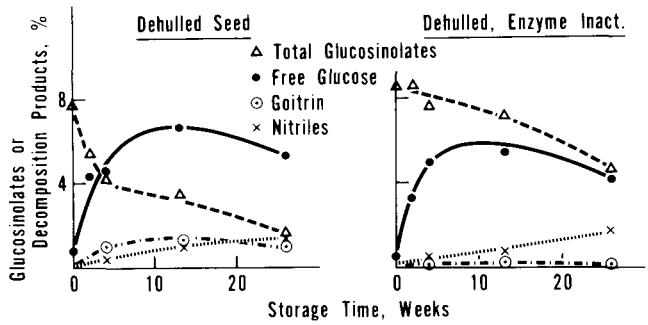

FIG. 3. Decomposition products of crambe seed stored at 14% moisture and 77 F.

those of Tookey and Wolff (9) who found no active lipase in crushed seeds stored at 5-7% moisture at room temperature. At 14% moisture and 77 F, FFA in the whole pod remained fairly constant for 26 weeks, whereas, both dehulled samples showed some increase in FFA after 4 weeks (Fig. 4). Dehulled seed showed an increasing amount of FFA as storage time increased, whereas, dehulled, enzyme inactivated samples leveled off after a slight increase (Fig. 4). This suggested that the first slight increase in FFA, which was common to both samples, was not enzyme related, and the second increase was.

At 14% moisture and elevated temperature (110 F) significant quantities of fatty acid formed in the oil fraction of both whole pod and dehulled seed; however, inactivation of the enzyme system in dehulled seed inhibited the formation of FFA (Fig. 4). No mold growth was observed on any of the samples.

Hydrogenation of oil from stored seed. From an analysis of the data involved with glucosinolate decomposition and FFA formation, apparently dehulled seed can be stored at ambient (6.8%) moisture and temperature (77 F) for 26 weeks. However, when we included the iodine values (IV) from hydrogenated oil from a sample stored for 26 weeks, we suspected a slight release of sulfur into the oil which poisoned the nickel hydrogenation catalyst, as evidenced by the higher IV (Fig. 5). At the higher moisture (14%) only the enzyme inactivated samples resisted sulfur release into the oil. These samples showed only a slight increase in IV compared to whole pod and enzyme active dehulled seed (Fig. 5).

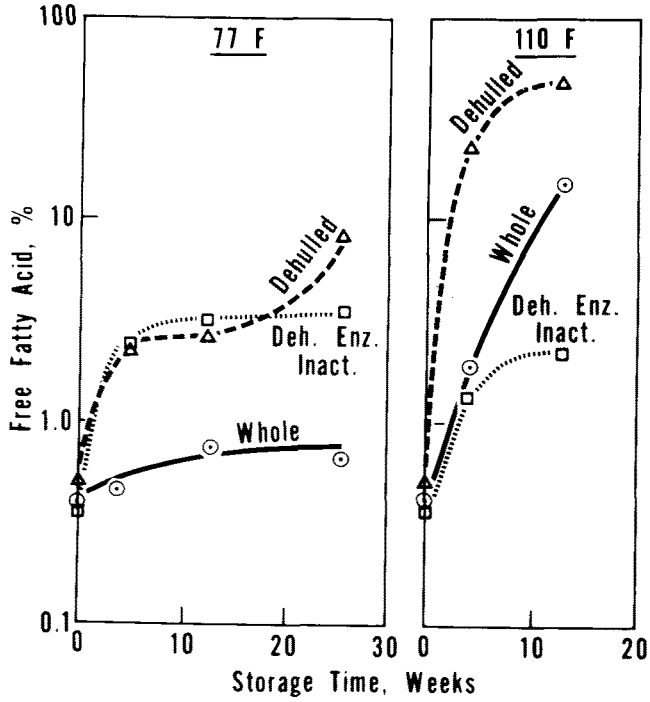

FIG. 4. Free fatty acid formation in crambe oil from seed during storage at 14% moisture.

Peroxide value of oils. This assay proved of little value in following deterioration of oil fractions during storage. The changes in peroxide value were not consistent with the degree of deterioration of stored samples. Dehulled seed at 14% moisture deteriorated severely, yet there was no increase in peroxide value.

Photometric color of oils. This assay was not a good indicator of seed deterioration. A significant color change was noted only once, and that was for dehulled seed after 4 weeks storage at 14% moisture and 110 F, the conditions under which deterioration was most severe.

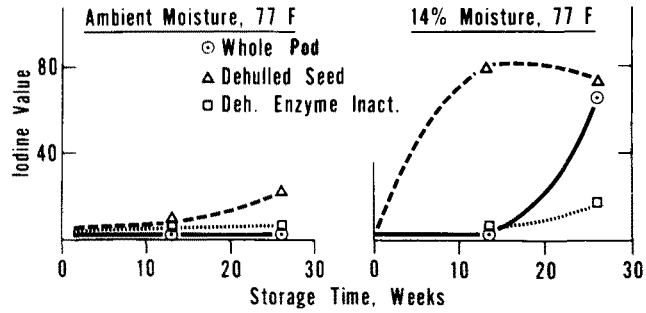

FIG. 5. Iodine value of hydrogenated crambe oil from stored seed.

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