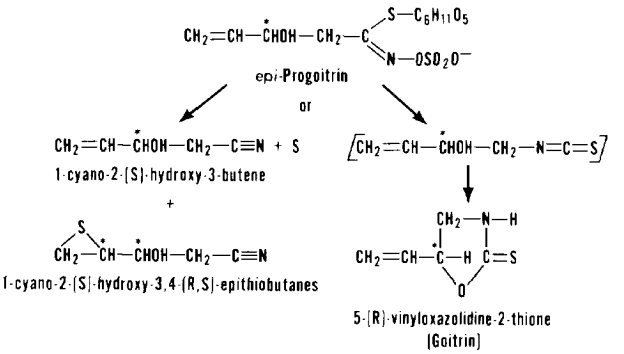
CHEMISTRY AND BIOLOGICAL EFFECTS OF THE MAJOR GLUCOSINOLATE IN *Crambe abyssinica*, A POTENTIAL OILSEED CROP

By Cecil H. Van Etten

Northern Regional Research Center
Federal Research
Science and Education Administration
U.S. Department of Agriculture
Peoria, Illinois 61604, U.S.A.

Crambe abyssinica Hochst ex R. E. Fries of the Cruciferae family contains erucic acid as 50 to 60% of the seed oil. Because erucic acid is valuable to industry as a raw material, the U.S. Department of Agriculture has been interested in developing the plant as a new crop. This report is a brief review of the thioglucosidase hydrolytic products from epi-progoitrin, the major glucosinolate in crambe; of the biological effects of compounds formed from the glucosinolate; and of the current status of crambe as a farm crop.

Epi-progoitrin (Scheme 1) is an optical isomer of progoitrin (2-



hydroxy-3-butenylglucosinolate), which is found in many crucifers of commerce (Daxenbichler *et al.* 1965). Knowledge concerning nitrile formation from epi-progoitrin and other natural glucosinolates is important in relation to the methods of preparation and processing of all crucifer crops for food as well as for feed.

Organic nitriles instead of isothiocyanates were reported in the early literature but their significance was not fully recognized (Challenger 1959). Enzymatic hydrolysis to form 3-indolyl acetonitriles from glucobrassicins was demonstrated by Gmelin and Virtanen in 1961; phenylacetonitrile from benzylglucosinolate in *Lepidium* species was reported by Virtanen and Saarivirta in 1962. Daxenbichler *et al.* (1968) found that organic nitriles were formed from epi-progoitrin instead of the expected (R)-5-vinyloxazolidine-2-thione (Scheme 1). The optical isomers of these nitriles from progoitrin of *Brassica napus* seed were identified by Daxenbichler *et al.* (1967). In plant parts in which the glucosinolates may hydrolyze to give either nitriles or isothiocyanates, nitrile formation predominates when the fresh untreated material is crushed at low temperature in the presence of small amounts of water. The episulfide-containing nitriles are derived from glucosinolates containing unsaturation at the terminal carbon of the aglucon. The formation of such nitriles from crambe is dependent upon a

labile protein isolated from crambe seed (Tookey 1973). This protein is not active except in the presence of thioglucosidase. By extension of this work to rapeseed (Daxenbichler et al. 1967) and to other crucifer crops, it has been shown that formation of nitriles is very common. The glucosinolates in edible cabbage form organic nitriles on autolysis (Daxenbichler et al. 1977). The more volatile nitriles from cabbage, cauliflower, and broccoli have been reported by Cole (1976), Buttery et al. (1976), and Kirk and Macdonald (1974).

A critical examination of the early literature on the feeding of Brassica to animals shows many cases of poor growth and pathological change that could not be related to goitrogens such as goitrin or thiocyanate ion (Greer 1950). When fed to rats, autolyzed crambe seed meal or a nitrile-containing fraction from it caused poor growth and pathology in the liver and kidney, as compared with better growth but enlarged thyroids when the animals were fed equivalent amounts of goitrin (Tookey et al. 1965, VanEtten et al. 1969a). Similar results were found by feeding autolyzed rapeseed meals or the nitrile fraction from them (Srivastava et al. 1975, Josefsson 1975). Acute oral toxicity of the nitriles to mice was 160-240 mg/kg compared with 1260-1415 mg/kg for goitrin (VanEtten et al. 1969b). In view of these findings, it is essential to know the amount and kind of aglucon hydrolytic products as well as glucosinolates that are in processed meals used for animal feeding.

The glucosinolates have been extracted with water from whole crambe seed (VanEtten et al. 1969c) and from the defatted seed meal (Baker et al. 1977). By either method, from 20 to 25% of the meal solids were lost. The extracted meal from both methods of preparation gave excellent protein efficiency ratios in tests with rats.

Ruminants appear to be less subject to toxic effects from glucosinolates than are monogastric animals. To establish maximum feeding levels for beef cattle, prepressed solvent-extracted crambe seed meals were evaluated for practical use as part of the finishing ration. These meals (including the hull) contained no thioglucosidase activity, up to 0.1% goitrin, 1.5% 1-cyano-2-hydroxy-3-butene, and 3.7% epi-progoitrin, all calculated as the glucosinolate. In four feeding experiments over 3 years' time, it was found that such seed meals could be fed with satisfactory gains in 150-180 day finishing trials with beef cattle at as high as 8% of the ration (Perry et al. 1974). At the end of these experiments, tests for aglucon products in body tissues were made on selected animals and on animals fed dehulled crambe meal as 10% of the ration for 14 to 30 days. The meals fed for a short term contained up to 0.5% goitrin, 3.8% 1-cyano-2-hydroxy-3-butene, and 8.6% epi-progoitrin, expressed as the glucosinolate. The body fat, muscle, kidney, and liver of the animals contained no epi-progoitrin, organic nitriles, or goitrin by tests sensitive to 1 ppm (VanEtten et al. 1977).

References

Baker, E. C., Mustakas, G. C., Gumbmann, M. R., Gould, D. H., Biological Evaluation of Crambe Meals Detoxified by Water Extraction on a Continuous Filter, J. Am. Oil Chem. Soc. 54, 392-396 (1977).

Buttery, R. G., Guadagni, D. G., Ling, L. C., Seifort, R. M., Lipton, W., Additional Volatile Components of Cabbage, Broccoli, and Cauliflower, J. Agric. Food Chem. 24, 829-832 (1976).

Challenger, F., The Natural Mustard Oil Glucosides and the Related Isothiocyanates and Nitriles, pp. 115-161, In "Aspects of the Organic Chemistry of Sulfur," Butterworth Scientific Publications, London (1959).

e, R. S., Isothiocyanates, Nitriles and Thiocyanates as Products of Autolysis of Glucosinolates in Cruciferae, Phytochemistry 15, 759-762 (1976).
enbichler, M. E., VanEtten, C. H., Wolff, I. A., A New Thioglucoside (R)-2-Hydroxy-3-Butenylglucosinolate(sic) from Crambe abyssinca Seed, Biochemistry 4, 318-323 (1965).
enbichler, M. E., VanEtten, C. H., Wolff, I. A., Diastereomeric Episulfides from epi-Progoitrin Upon Autolysis of Crambe Seed Meal, Phytochemistry 7, 989-996 (1968).
enbichler, M. E., VanEtten, C. H., Tallent, W. H., Wolff, I. A., Rapeseed Meal Autolysis. Formation of Diastereomeric (2R)-1-Cyano-2-Hydroxy-3,4-Epithiobutanes from Progoitrin, Can. J. Chem. 45, 1971-1974 (1967).
enbichler, M. E., VanEtten, C. H., Spencer, G. F., Glucosinolates and Derived Products in Cruciferous Vegetables. Identification of Organic Nitriles from Cabbage, J. Agric. Food Chem. 25, 121-124 (1977).
lin, R., Virtanen, A. I., Glucobrassicin der Precursor von SCN, 3-Indolylacetonitril und Ascorbigen in Brassica oleraceae Species, Am. Acad. Sci. Fennicae A II Chemica No 107, 1-25 (1961).
er, M. A., Nutrition and Goiter, Physiol. Rev. 30, 513-548 (1950).
efsson, E., Influence of Glucosinolates and High Molecular Factors on the Nutritional Value of Low Glucosinolate Rapeseed Meal, J. Sci. Food Agric. 26, 1299-1310 (1975).
k, F. T. O., Macdonald, C. G., 1-Cyano-3,4-epithiobutane: A Major Product of Glucosinolate Hydrolysis in Seeds from Certain Varieties of Brassica campestris, Phytochemistry 13, 2611-2615 (1974).
ry, T. W., Beeson, W. M., Tallent, W. H., Mohler, M. T., Levels of Protein and Crambe for Steers, J. Anim. Sci. 39, 248 (1974) (abstract).
vastava, V. K., Philbrich, D. J., Hill, D. C., Response of Rats and Chicks to Rapeseed Meal Subjected to Different Enzymatic Treatments, Can. J. Anim. Sci. 55, 331-335 (1975).
key, H. L., VanEtten, C. H., Peters, J. E., Wolff, I. A., Evaluation of Enzyme-modified, Solvent-extracted Crambe Seed Meal by Chemical Analysis and Rat Feeding, Cereal Chem. 42, 507-514 (1965).
key, H. L., Crambe Thioglucoside Glucohydrolase (EC 3.2.3.1): Separation of a Protein Required for Epithiobutane Formation, Can. J. Biochem. 51, 1654-1660 (1973).
Etten, C. H., Daxenbichler, M. E., Schroeder, W., Princen, L. H., Perry, T. W., Tests for epi-Progoitrin, Derived Nitriles and Goitrin in Body Tissues from Cattle Fed Crambe Meal, Can. J. Anim. Sci. 57, 75-80 (1977).
Etten, C. H., Gagne, W. E., Robbins, D. J., Booth, A. N., Daxenbichler, M. E., Wolff, I. A., Biological Evaluation of Crambe Seed Meals and Derived Products by Rat Feeding, Cereal Chem. 46, 145-155 (1969a).
Etten, C. H., Daxenbichler, M. E., Wolff, I. A., Natural Glucosinolates (Thioglucosides) in Foods and Feeds, J. Agric. Food Chem. 17, 483-491 (1969b).
Etten, C. H., Daxenbichler, M. E., Wolff, I. A., Removal of Glucosinolates from Cruciferous Oilseeds by Aqueous Extraction of Intact Seeds, Abstr. AGFD 53, 158th National Meeting of the American Chemical Society, New York, September 1969c.
tanen, A. I., Saarivirta, M., The Formation of Benzyl Nitrile, Benzyl Isothiocyanate and Benzyl Thiocyanate in the Crushed Seeds of Lepidium sativum, S. Kemistilehti B. 35, 248 (1962).