

(S)-3-Hydroxypent-4-enethionamide: A New Reaction Product of a Natural Thioglucoside

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FOUR conversion products have so far been identified from the action of endogenous enzyme(s) on *epi*-progoitrin (I), the major thioglucoside of seed from *Crambe abyssinica* Hochst ex R. E. Fries. These are (*R*)-5-vinyloxazolidine-2-thione¹ (*R*-goitrin) and three compounds which contain a nitrile group.^{2,3} We have discovered that ferrous ion without enzyme attacks (I) to produce a

mixture of (*S*)-1-cyano-2-hydroxybut-3-ene (II) and a new compound, (*S*)-3-hydroxypent-4-enethionamide (III), in the approximate ratio of 1 to 4.

This reaction was carried out in water containing the thioglucoside (I), to which was added six to eight molar equivalents of a soluble ferrous salt. The mixture was covered with nitrogen and 16 hr. later the products were isolated by ether extraction

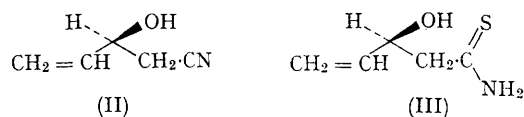
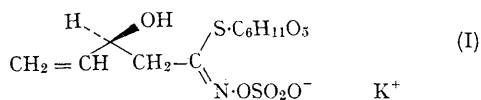
and separated by chromatography on alumina. Unsaturated nitrile (II) was eluted with chloroform and the thionamide (III) with methanol-chloroform (5:95). Identical products resulted either from purified *epi*-progoitrin or from defatted crambe seed meal in which the native enzyme had been inactivated. Both ferrous sulphate and ferrous ammonium sulphate produced the same mixture; hence, the amido-group did not derive from an external source of ammonium ions.

Isolated compound (III) had m.p. 56.5–57° and showed λ_{\max} (EtOH) 330, 267 $m\mu$ ($\log \epsilon$ 1.73, 4.05) in common with simpler thionamides.⁴ Infrared spectra in chloroform showed a strong amide II band at 1605 cm^{-1} , –OH and –NH stretching bands between 3190 and 3680 cm^{-1} , and a vinyl group absorption at 900–1000 cm^{-1} . The n.m.r. spectrum resembled that of the nitrile (II) and supported the open-chain structure. Elemental analysis and molecular weight also were in agreement with the thionamide formulation.

The addition of an aqueous solution of the thionamide (III) to one equivalent of N/10-silver nitrate produced quantitative conversion to the unsaturated nitrile (II) together with precipitation of silver sulphide. Isolated (II) from this reaction was identical with (II) obtained directly from (I)

by enzymic conversion. The i.r. spectrum, mobility on thin-layer chromatography, and the optical rotatory dispersion curve² were compared. Complete agreement was observed, including sign and magnitude of the optical rotation. The ready transformation of (III) to the nitrile (II) supports the thionamide structure and the optical data establish configuration at the chiral centre.

Although the transformation of natural thioglucosides to insoluble silver salts of the corresponding aglycone is well known, chemical degradation comparable to enzymic conversion under equally mild conditions has not, to our knowledge, been reported previously.



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¹ M. E. Daxenbichler, C. H. VanEtten, and I. A. Wolff, *Biochemistry*, 1965, **4**, 318.

² M. E. Daxenbichler, C. H. VanEtten, and I. A. Wolff, *Biochemistry*, 1966, **5**, 692.

³ M. E. Daxenbichler, C. H. VanEtten, and I. A. Wolff, *Chem. Comm.*, 1966, 526.

⁴ M. J. Janssen, *Rec. Trav. chim.*, 1960, **79**, 454.