

Diastereomeric 1-Cyano-2(*S*)-hydroxy-3,4-epithiobutanes from *epi*-Progoitrin of Crambe Seed

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AUTOLYSIS of defatted seed meal from *Crambe abyssinica* Hochst ex R. E. Fries yields a mixture of nitriles derived from the *epi*-progoitrin^{1,2} (I) present. One of the nitriles, identified as (II),¹ was first obtained as a product when purified *epi*-progoitrin was enzymatically hydrolyzed at acidic pH in the absence of other meal solids.³ We now report the separation from autolyzed meal of additional nitriles (IIIa) and (IIIb) and their structural characterization. Both these episulphide-containing nitriles have the (*S*)-configuration at the chiral centre containing the hydroxyl group, but the configuration at the second chiral centre has not been determined. To our knowledge, isolation of episulphides from natural products has not been reported, and (IIIa) and (IIIb) are previously unknown.

The mixture of nitriles was obtained from an

aqueous acetone extract of autolyzed Crambe meal. That part of the nitrile mixture which redissolved in water was chromatographed on Sephadex G-10, with water as a developing solvent. Components (II), (IIIa), and (IIIb) were eluted in that order, at an average weight ratio of 1:1:1.8. The average total weight recovery from the column was 79%. Isomers (IIIa) and (IIIb), obtained as clear oils, were stored below 0° under nitrogen to retard polymerization. Both compounds gave satisfactory elemental analyses (C, H, N, and S).

Low-temperature acetylation of the hydroxyl group in each of the three compounds, with acetic anhydride and pyridine, gave liquids in yields of 70–90% of theory. Elemental analyses and molecular weights agreed with those required for a monoacetate.

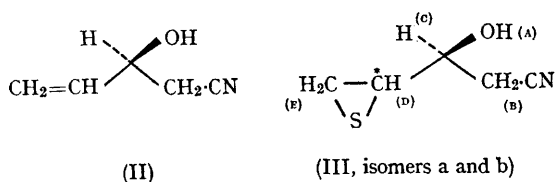
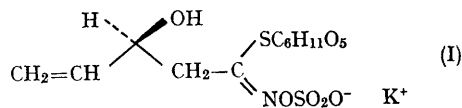
Isolated (IIIa) and its acetate gave λ_{\max}

(EtOH) 254—255 $m\mu$ and isolated (IIIb) and its acetate, λ_{\max} (EtOH) 256—257 $m\mu$. All four displayed the low absorptivity typical of episulphides.⁴ Infrared spectra of (II), (IIIa), and (IIIb) from films between KBr discs were grossly similar, except that (II) showed a strong doublet due to the vinyl group absorption at 900—1000 cm^{-1} ; (IIIa) and (IIIb) showed, respectively, peaks at 640 and 620 cm^{-1} , which were assigned to C-S stretching vibrations.

The n.m.r. spectra for (IIIa) and (IIIb) supported the suggested structures. The peaks for the protons designated in the formula shown for (III) are as follows: (IIIa) proton(s) A, δ 2.9 (broad); B, doublet centred δ 2.7; C, quartet centred near δ 4.0; D, multiplet centred δ 3.25; and E, three closely spaced doublets with the middle doublet centred near δ 2.45. (IIIb) proton(s) A, under C; B, doublet centred δ 2.75; C, quartet centred δ 3.7; D, multiplet centred δ 3.1; and E, three closely spaced doublets with the middle doublet centred near δ 2.45.

Desulphurization of the acetyl derivatives of (IIIa) and (IIIb) with triphenylphosphine, an expected reaction of episulphides,⁵ gave the acetyl derivative of (II) in isolated yields of 47 and 37%, respectively. The desulphurized product from each episulphide was identical with the acetate of (II) by thin-layer and gas-liquid chromatography

and in i.r. and n.m.r. spectra, and optical rotatory dispersion curves.



The formation of (IIIa) and (IIIb) suggests either an alternative or a secondary reaction course not previously recognized in the breakdown of mustard thioglucosides. Since two isomeric episulphides are formed rather than a single stereochemical isomer, we suggest that they may be derived by a nonenzymatically-catalyzed step from intermediate precursors available after initial enzymatic hydrolysis of *epi*-progoitrin.

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⁴ R. E. Davis, *J. Org. Chem.*, 1958, **23**, 216.

⁵ R. E. Davis, *J. Org. Chem.*, 1958, **23**, 1767.