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A NEW APPROACH TO THE SYNTHESIS OF CYANOGENIC GLYCOSIDES

The synthesis of
O-(tetra-O-acetyl-D-glucopyranosyl)-DL-4-benzoyloxymandelonitrile

Helmer Kofod and Reynir Eyjólfsson,
Chemical laboratory B, Royal Danish School of Pharmacy,
Copenhagen, Denmark.

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Laboratory syntheses of several naturally occurring "cyanogenic" glycosides have been reported (1-4). They all utilize the appropriate hydroxycarboxylic acid ethyl ester as the starting material, which, upon condensation with an acetobromosaccharide, is converted into the corresponding amide. This in turn is dehydrated to the desired nitrile. The overall procedure normally consists of at least four steps.

In the present communication we report a somewhat simpler method which seems to be generally applicable for cyanohydrin-glycosides. It involves the direct condensation of a cyanohydrine with an aceto-bromosaccharide in nitromethane, mercuric cyanide being used as a catalyst. An analogous method has been successfully employed for the synthesis of some simple alcohol glycosides (5) but has not so far to our knowledge been tried for the present type of compound.

An equimolar mixture of carefully dried 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide, prepared according to (6), mercuric cyanide and DL-4-benzoyloxy-benzaldehyde-cyanohydrin in absolute nitromethane was shaken mechanically at room temperature for 24 h.

After removal of the solvent, as well as mercuric salt and hydrogen cyanide, the reaction mixture was chromatographed on silica gel using benzene/methanol (99,75/0,25 v/v) as irrigating solvent. The separation procedure gave 5.9 % yield of a substance which contained some solvent of crystallization (abs. ethanol). Its melting interval was 90 to 110° C. No effort was made to obtain high yields.

The experimental details will be described elsewhere.

Found (dried substance): C 59.80; H 5.20; N 2.13 %. Calc. for $C_{29}H_{29}O_{12}N$: C 59.68; H 5.01; N 2.40 %.

The IR-spectrum (dried substance in KBr-pellet) showed bands at 3100 and 2980 (*w.*) (C-H), 1750 (*s.*)(acetyl), 1600 and 1510 (*m.*) (aromatic ring), 1460 and 1370 (*m.*) (aliph. C-H), 1280-1200 and 1050 (*s.*) (C-O-C) and 705 cm^{-1} (*m.*) (monosubst. phenyl).

The NMR-data of the substance (60 mg dissolved in 250 µl of $CDCl_3$) fits satisfactorily to those reported for dhurrin pentaacetate and taxiphyllin pentaacetate (7).

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After this manuscript was submitted for publication a lecture-abstract came to our knowledge, describing the preparation of linamarin by a similar method (R.C.Clapp, F.H.Bisset, R.A.Coburn, and L.Long,jr. Abstract Book, 4th. Internat.Symp. on the Chem of Nat. Prod. Stockholm 1966 p.40).