The Synthesis of 6-*O*-α-D-Xylopyranosyl-D-mannopyranose using the Nonparticipating Chlorosulphate Group

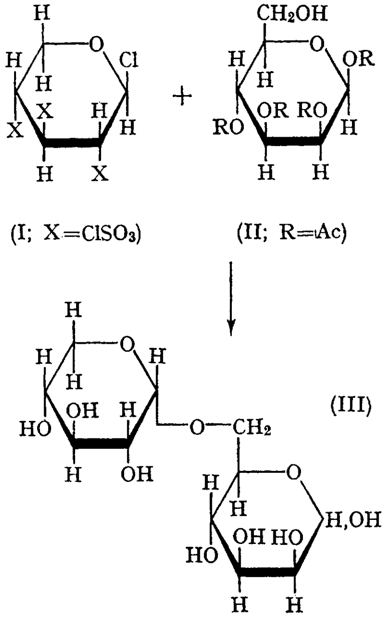
By H. J. JENNINGS

(*Division of Biosciences, National Research Council of Canada, Ottawa, Ontario*)

THE Koenigs–Knorr syntheses of both α- and β-1,2-*cis*-linked disaccharides, using nonparticipating groups at C-2 of the halogenose moieties, have been reported.[1,2] The syntheses of the modified halogenoses require multistep procedures.[1,2] We now report the synthesis of 6-*O*-α-D-xylopyranosyl-D-mannopyranose (III) using β-D-xylopyranosyl chloride 2,3,4-trichlorosulphate (I), a chlorosulphated halogenose produced in a one-step synthesis, and 1,2,3,4-tetra-*O*-acetyl-β-D-mannopyranose[3] (II). Low-temperature (—20°) isolation of the products of the reaction of D-xylose with sulphuryl chloride[4] gave a crystalline mass, which when recrystallized from chloroform–light petroleum (b.p. 30—60°) gave crystalline (I) (40%, m.p. 84°, $[\alpha]_D$ —91°; *c* 1·06 in chloroform).

Compounds (I) and (II) (in the molar ratio 2 : 1 respectively) were dissolved in chloroform and shaken for 16 hr. with silver carbonate, Drierite, and a catalytic quantity of silver perchlorate.[1] Preferential removal of the chlorosulphate groups was achieved using sodium iodide[5] and the removal of the acetoxy-groups (sodium methoxide) resulted in the precipitation of the sodium complex of (III). The eluate material following deionization with Amberlite I.R. 120 (H^+) was chromatographically pure (III), obtained as a hygroscopic amorphous glass (35%, $[\alpha]_D$ +95·7°; *c* 1·14 in water). That (III) was uncontaminated by its β-linked analogue was proved by the independent synthesis of 6-*O*-β-D-xylopyranosyl-D-mannopyranose by the method of Bredereck.[6] Both disaccharides were clearly resolved by paper chromatography.

That both disaccharides were α- and β-linked analogues was ascertained on the following evidence. The acid hydrolysis of both disaccharides gave xylose and mannose (paper chromatography), and the acid hydrolysis of their reduced (sodium borohydride) products gave xylose as the only detectable reducing sugar (paper chromatography). Also methylation and subsequent hydrolysis of both disaccharides gave 2,3,4-tri-*O*-methylxylopyranose (1 part) and 2,3,4-tri-*O*-methylmannopyranose (1 part) as determined by t.l.c. and g.l.c. All new compounds gave elemental analyses consistent with their structures.



(I; X=$ClSO_3$)

(II; R=Ac)

(III)

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