5-Amino-5,6-dideoxy-L-idose

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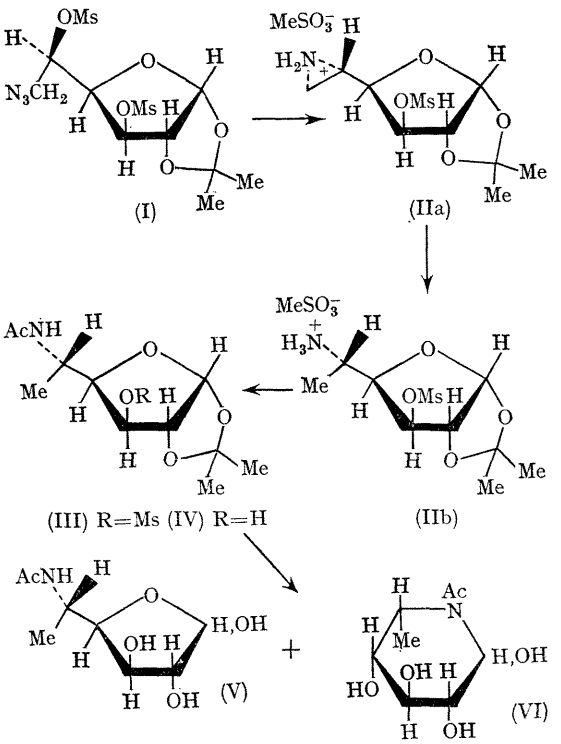
Summary The title compound, which exists predominantly in the furanose rather than the piperidinose form, has been synthesised by two routes, one involving the reduction of a 6-azido-5-*O*-mesyl derivative *via* the 5,6,-epimine which was not isolated.

CURRENT interest[1,2] in 5-amino- and 5,6-epimino-sugars as potential antibiotics and chemotherapeutic agents prompts us to record a synthesis of 5-acetamido-5,6-dideoxy-L-idose.



Treatment of 6-azido-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose with methanesulphonyl chloride, gave the 3,5-bismethanesulphonate (I),[3] m.p. 99—100°. Reduction of this azido-sulphonate (I) with hydrazine–Raney nickel yielded the methanesulphonic acid salt of 5-amino-5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-mesyl-β-L-idofuranose (IIb), m.p. 200—201,° $[\alpha]_D$ — 14° (*c* 1, water) rather than the expected epimine (IIa). Conversion into the free base and acetylation gave 5-acetamido-5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-mesyl-β-L-idofuranose (III), m.p. 133—135°, $[\alpha]_D$ —48° (*c* 2, chloroform). The structure of (III), deduced from the i.r. spectrum (amide I, amide II, and NH stretching but no OH stretching bands), and the n.m.r. spectrum (doublet of 3 protons at τ 8·75), was confirmed by an independent synthesis from 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose. Thus mesylation of the latter, followed by selective azide replacement gave 5-azido-5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-mesyl-β-L-idofuranose, and subsequent reduction and acetylation gave the 5-acetamido-5,6-dideoxy-derivative (III). The mechanism of the hydrazine–Raney nickel reaction no doubt involved the formation of a 5,6-epimine (IIa) followed by reductive ring-opening which would be predicted to open stereospecifically to give (IIb). Removal of the 3-*O*-mesyl group from (III) with sodium ethoxide, followed by acid hydrolysis of the isopropylidene group gave 5-acetamido-5,6-dideoxy-L-idose as a mixture of the furanose (V) and piperidinose (VI) forms. Separation by column chromatography gave the predominant furanose form as crystals {m.p. 162—165°; $[\alpha]_D$ −17° (*c* 0·5, water)} and the piperidinose form as a syrup {$[\alpha]_D$ +10·5° (approx.) (*c* 0·8, methanol)}. The structures were deduced from their i.r. spectra, the furanose (V) showing amide I and amide II bands and the piperidinose (VI) showing an amide I but no amide II band. The isomers were stable in neutral solution, but acid or alkaline conditions caused equilibration and the formation of other products.

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[3] D. Buss, Ph.D. Thesis, Bristol University, 1964.