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Preliminary communication

The deamination of 2-amino-1,5-anhydro-2-deoxy-D-mannitol: hydride shift *versus* elimination

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The exploitation of the deamination of carbohydrate amines, for example in the selective degradation of complex carbohydrates[1], requires a thorough understanding of the mechanism of the reactions. Aminodeoxyaldopyranoses and their derivatives commonly undergo rearrangements that are strongly dependent on conformation, and we have recently presented evidence[2] for the participation of the anomeric hydroxyl group in the deamination of 2-amino-2-deoxy-D-mannopyranose, which gives D-glucopyranose as the main product. We now report on the deamination of 2-amino-1,5-anhydro-2-deoxy-D-mannitol (**1**).

The crystalline hydrochloride {m.p. 291–293° (dec.), $[\alpha]_D^{17}$ –40° (*c* 0.51, water)} of the amine **1**, prepared by hydrolysis of the tetra-O-acetyl derivative[3], when treated with sodium nitrite in M aqueous acetic acid, gave three main products and traces of others. Two of the main products were identified by g.l.c. and paper chromatography as 2-deoxy-D-*arabino*-hexose (**2**) and 1,5-anhydro-D-glucitol (**3**). These products were isolated crystalline in 8 and 6% yields, respectively, by preparative paper chromatography and were identified by comparison with authentic samples. The major product (isolated as a syrup in 68% yield by preparative paper chromatography) was a ketone (ν_{max} 1715 cm^{-1}) which gave a crystalline 2,4-dinitrophenylhydrazone ($C_{12}H_{14}N_4O_7$) and was identified as 1,5-anhydro-2-deoxy-D-*erythro*-hex-3-ulose by ^1H- and ^{13}C-n.m.r. spectroscopy. In the ^1H-spectrum, the most deshielded proton was H-4 (double doublet at τ 5.32, pyridine-d_5), which was axial, being strongly coupled to the neighbouring axial H-5 ($J_{4,5}$ 9.8 Hz) and long-range coupled to axial H-2 ($J_{2,4}$ 1.4 Hz). The highest field signals were multiplets (τ 7.21 and 7.58) due to the protons (H-2) α to the carbonyl group, these being coupled to both H-1 protons (τ 5.8 and 6.37). The ^{13}C noise and off-resonance decoupled spectra showed the carbonyl carbon (213.2 p.p.m., D_2O,TSP reference); three methylene carbons (69.6, 64.1, and 43.9), two of them attached to oxygen; and two methine carbons attached to oxygen (85.7 and 76.1). Minor signals due to the ketone hydrate were also present. 1,5-Anhydro-D-mannitol was tentatively identified as a minor product (< 1%) by g.l.c.

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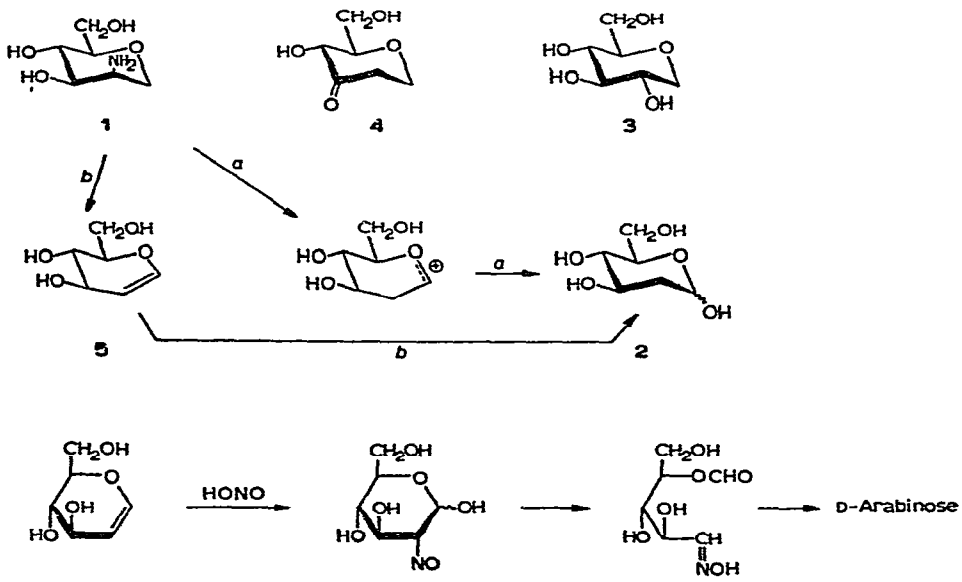
This deamination of **1** resembles that of methyl 2-amino-2-deoxy-α-D-manno-pyranoside[4] in that rearrangement of H-3 to give a 3-ulose occurs predominantly, in contrast to the deamination of 2-amino-2-deoxy-D-mannose[2]. The 3-ulose and 2-deoxy-D-*arabino*-hexose products could arise by either hydride-shift (route *a*) or elimination (route *b*) mechanisms, and these possibilities were differentiated for 2-deoxy-D-*arabino*-hexose by a control experiment. D-Glucal (**5**), the elimination product that could form 2-deoxy-D-*arabino*-hexose by acid-catalysed addition of water, was exposed to the conditions of deamination, and the neutralised solution was analysed (by paper chromatography and g.l.c.–m.s.) before and after deionisation with Amberlite MB3 ion-exchange resin. Before the resin treatment, the solution contained mainly glucal, arabinose, and an unidentified compound; after deionisation, when there was much less glucal, the main components were arabinose, 2-deoxy-*arabino*-hexose, and an unidentified compound of low retention time on g.l.c. The mixture of deamination products from **1** contained only a trace of arabinose and thus the 2-deoxy-D-*arabino*-hexose was formed in the deamination *via* a hydride shift.

Enol ethers are known to react with nitrite in weakly acid solution[5], and a possible route for the formation of D-arabinose from D-glucal is shown in Scheme 1. Oximes are converted into the parent carbonyl compounds by nitrous acid[6], and the formic ester presumably hydrolyses under the conditions used. Small-scale experiments had shown that the composition of the deamination product mixture from **1** is qualitatively unchanged by deionisation, and quantitative g.l.c. measurements gave, for the 3-ulose (**4**), 1,5-anhydro-D-glucitol (**3**), and 2-deoxy-D-*arabino*-hexose (**2**), molar ratios of 10.1 : 1.0 : 1.1 and



Scheme 1

8.0 : 1.0 : 1.0 before and after deionisation, respectively. Thus, deionisation causes a significant, differential loss of the reducing components.

Thus, when enol ethers are possible or actual products of deamination reactions, control experiments should be carried out to determine their stability to the conditions of reaction.

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