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Note

Oxidative deamination of aminodeoxy sugars

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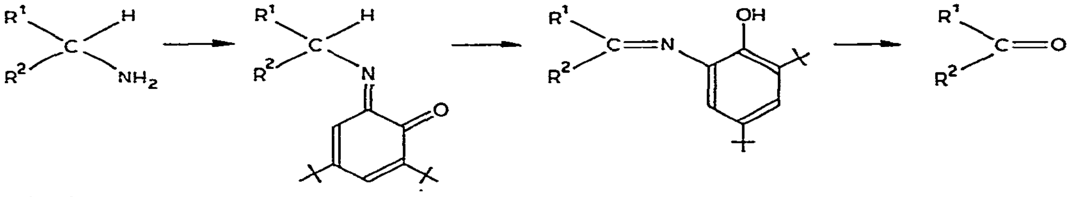
Oxidative deamination of primary amines may be useful in carbohydrate chemistry, both for preparative purposes and for specific degradations in structural studies. Corey and Achiwa[1] have devised a method that involves reaction of the amine with a sterically hindered quinone to yield an imine, which is rearranged into an isomeric imine during the reaction, followed by mild hydrolysis with acid to give the ketone, as indicated below. The method has been used for the synthesis of 1-deoxy-D-fructose[2].



R^1, R^2 = alkyl

We now report on the oxidative deamination of methyl 2-amino-2-deoxy-β-D-glucopyranoside (**1**), the corresponding α-glucoside (**2**), and methyl 3-amino-3-deoxy-β-D-allofuranoside[3,4] (**3**) by this method. The labile hexosiduloses formed were not isolated, but were reduced to a mixture of the two corresponding hexosides and hydrolysed, and the sugars were analysed by g.l.c. as their alditol acetates[5]. The results, summarised in Table I, demonstrate that the imines can be prepared in ~50% yield and that the hexosiduloses are formed in about the same yields. The overall yield of the reactions was 5–10% higher if the isolation of the imine was omitted and the reaction mixture was directly subjected to hydrolysis. The somewhat lower yield of imine from **2** could be attributed to steric hindrance from the axial methoxyl group at C-1.

An imine could also be prepared from 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allose[6] (**4**), but it was not possible to effect hydrolysis to the ulose without simultaneous removal of isopropylidene groups and decomposition (*cf.* Ref. 7).

TABLE I

PROPERTIES AND YIELDS OF PRODUCTS FROM OXIDATIVE DEAMINATION OF AMINODEOXY SUGARS

Starting compound	*Imine*[a] *Yield (%)*	*M.p.*[b] *(degrees)*	$[\alpha]_{589}^{22}$ *(degrees)*[c]	*Hexosidulose Yield (%)*
1	50	177–178	−67	65
2	35	158–160	+32	55
3	52	—	−33	45
4	55	—	+44	—

[a]All compounds gave ^{1}H-n.m.r. spectra in accordance with the proposed structures. [b]Melting points are corrected. [c]All rotations were recorded for solutions (*c* 0.5) in chloroform.

EXPERIMENTAL

General method. — A solution of the aminodeoxyhexoside (40 mg) and 3,5-di-*tert*-butyl-1,2-benzoquinone[8] (40 mg) in methanol (4 ml) was kept under nitrogen in a sealed vial for 1 h at room temperature and then heated for 15 min on a steam bath. The solvent was evaporated, and the residue was fractionated by chromatography on a column (2.5 × 20 cm) of silica gel (Merck) with ethyl acetate. The imines from **1** and **2** crystallised and were recrystallised from chloroform–light petroleum. *Anal.* Calc. for $C_{21}H_{33}NO_6$: C, 63.79; H, 8.35; N, 3.54. Found (imine from **1**): C, 63.61; H, 8.29; N, 3.44; (imine from **2**): C, 63.84; H, 8.28; N, 3.46.

For hydrolysis to the hexosidulose, a mixture of each pyranosidic imine (5 mg) and Dowex-50(H$^+$) resin (150 mg) in methanol–water (3:1, 2 ml) was kept at room temperature. D-Arabinose (1 mg) was added as the internal standard. After 8 h, the resin was filtered off, sodium borohydride (15 mg) was added, and the solution was kept for 1 h at room temperature and then worked-up as usual. The product was hydrolysed in 0.25M sulfuric acid at 100° overnight, neutralised with barium carbonate, reduced with sodium borohydride, acetylated, and analysed by g.l.c.[5] on an OV-225 column at 190°.

The furanosidic imine (5 mg) derived from **3** was hydrolysed at room temperature in methanol–water (3:1, 2 ml) adjusted to pH 2.5 with oxalic acid. After 48 h, the mixture was neutralised with calcium carbonate and worked-up as described above.

ACKNOWLEDGMENTS

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