

DI- AND POLYAMINO SUGARS, XIV¹⁾
SYNTHESIS OF 2.3.4.6-TETRA-AMINO-2.3.4.6-TETRADEOXY-D-GLUCOSE

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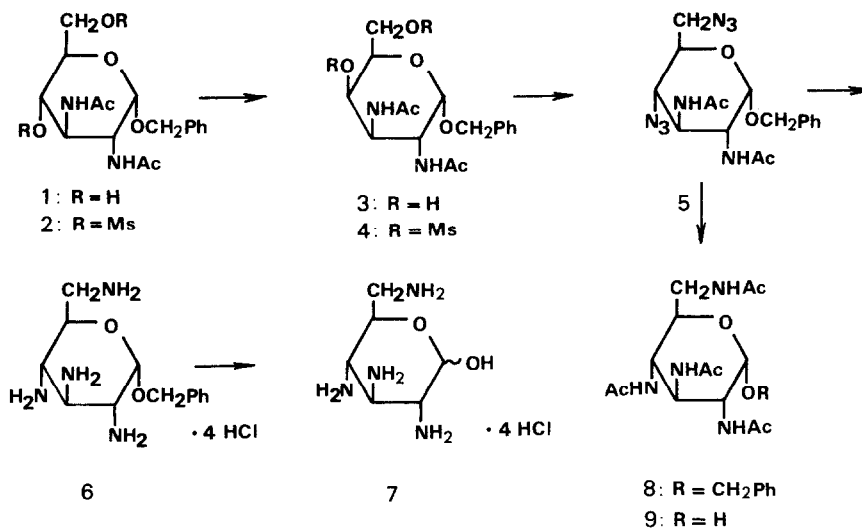
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Free amino sugars containing more than two amino groups in the molecule have not yet been described. Recently we disclosed the synthesis of crystalline 2.3.4.6-tetra-amino-2.3.4.6-tetradexy-D-galactose tetrahydrochloride¹⁾. A similar route led to the preparation of the title compound.

Inversion of configuration at C-4 in a derivative of 2.3-diamino-2.3-dideoxy-D-glucose (1)²⁾ can be effected by sodium acetate in methoxyethanol³⁾. The resulting galacto derivative 3⁴⁾ is dimesylated to give 4 [yield 97 %; m. p. 234-235°; $[\alpha]_D$: +159° (c=1; DMSO)] which smoothly reacts with sodium azide in DMSO (100°) to give the diazide 5 [yield 89 %; m. p. 248-249°; $[\alpha]_D$: +223° (c=1; DMSO)]. Catalytic hydrogenation (Pd/C in methanol), saponification (sodium hydroxide, 20 hrs. reflux), and neutralization with HCl yields the extremely hygroscopic glycoside 6 which, after hydrogenation (Pd/C in water) gives the free sugar 7 [hygroscopic powder; yield 63 %; m. p. ~166° (dec.); $[\alpha]_D$: +8.0° → +10.0° (c=1; water)]. In spite of its noncrystallinity 7 appears to be almost pure on TLC (cellulose, t.-BuOH/acetic acid/water 2:2:3 or pyridine/ethyl acetate/water/acetic acid 5:5:3:1, ninhydrin). Solutions of 7 in water decompose with discoloration.

Hydrogenation of 5 followed by acetylation (acetic anhydride in methanol) gives 8 [yield 92 %; m. p. 351-352°; $[\alpha]_D$: +135° (c=0.5; DMSO)] which, on



hydrogenation in water yields 2,3,4,6-tetra-acetamido-2,3,4,6-tetra-deoxy- α -D-glucose (9) [79 %; m. p. 273-274°; $[\alpha]_D^{20}$: +55° \rightarrow +33.5° (c=1; water)].

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