

## 2,6-Diamino-2,6-dideoxy-D-mannose Dihydrochloride

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WE have been concerned with the synthesis of diamino-sugars in connection with structural studies on synthetic aminated polysaccharides,<sup>1</sup> and the synthesis of 3,6-diamino-3,6-dideoxy-D-altrose has been briefly reported.<sup>2</sup> The appearance of a paper<sup>3</sup> describing the synthesis of 2,6-diamino-2,6-dideoxy-D-mannose by a reaction sequence involving configurational inversion from a D-*altro*-precursor, prompts us to report our synthesis of this diamino-sugar by a route which sets out from a D-*manno*-precursor and involves no inversions at the secondary alcohol positions. A phenyl glycoside of 2-acetamido-2-deoxy-D-mannose was prepared by the fusion method,<sup>4</sup> and amination at C-6

was achieved by selective toluene-*p*-sulphonation, azide replacement, and reduction.

2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy- $\beta$ -D-mannopyranose<sup>5</sup> (I) was fused with phenol, containing toluene-*p*-sulphonic acid or a zinc chloride-acetic acid-acetic anhydride mixture, for 1.3 hr. at 120–125°, to give phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- $\alpha$ -D-mannopyranoside<sup>6</sup> (II), which crystallized (68%) from propan-2-ol, and had m.p. 192–193°,  $[\alpha]_D^{30} + 73.6^\circ$  (*c* 1, chloroform). Treatment of a methanolic solution of (II) with a catalytic amount of sodium methoxide gave phenyl 2-acetamido-2-deoxy- $\alpha$ -D-mannopyranoside<sup>6</sup> (III), which crystallized (85%) from ethanol-ether and

<sup>1</sup> M. L. Wolfrom, M. I. Taha, and D. Horton, *J. Org. Chem.*, 1963, **28**, 3553.

<sup>2</sup> M. L. Wolfrom, D. Horton, and Yen-Lung Hung, *Abstracts Papers Amer. Chem. Soc.*, 1964, **148**, 3D.

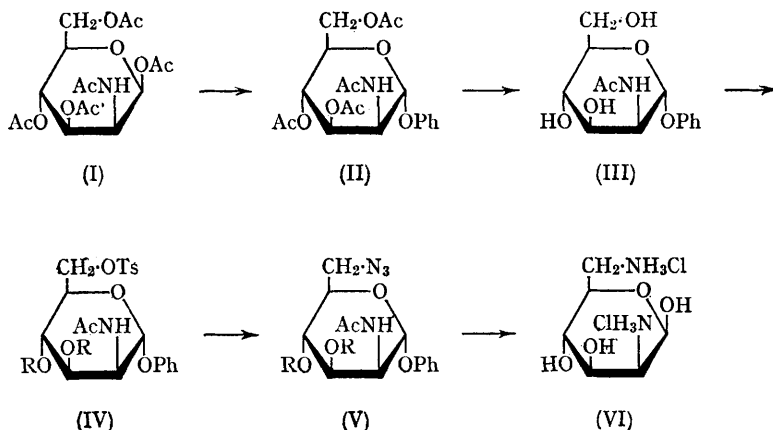
<sup>3</sup> W. Meyer zu Reckendorf, *Ber.*, 1965, **98**, 93.

<sup>4</sup> E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson, *J. Amer. Chem. Soc.*, 1942, **64**, 690; S. Fujise and K. Yokoyama, *J. Chem. Soc. Japan*, 1951, **72**, 728 (*Chem. Abs.*, 1952, **46**, 11116).

<sup>5</sup> A. N. O'Neill, *Canad. J. Chem.*, 1959, **37**, 1747.

<sup>6</sup> All new crystalline compounds gave satisfactory elemental analyses, were homogeneous by thin-layer chromatography on Silica Gel G (E. Merck, Darmstadt, Germany), and gave infrared spectra in agreement with the assigned structures.

had m.p. 94—98°,  $[\alpha]_D^{18} + 50.0^\circ$  ( $c$  1, ethanol). A solution of (III) in pyridine was treated with toluene-*p*-sulphonyl chloride (1.2 equiv.), to give phenyl 2-acetamido-2-deoxy-6-*O*-toluene-*p*-sulphonyl- $\alpha$ -D-mannopyranoside (IV; R=H) as a chromatographically homogeneous syrup (89%), characterized by acetylation with acetic anhydride-pyridine to the 3,4-diacetate (IV; R=Ac)



[77% ; based on (III)] (from propan-2-ol), m.p. 154°,  $[\alpha]_D^{18} + 102^\circ$  ( $c$  1, chloroform). The syrupy 6-toluene-*p*-sulphonyl derivative (IV; R=H) was heated with excess of sodium azide in aqueous acetone for 28 hr. at 100°, to give a syrupy product (yield quantitative), having azide absorption but no sulphonate absorption in the infrared spectrum, formulated as phenyl 2-acetamido-6-azido-2,6-

dideoxy- $\alpha$ -D-mannopyranoside (V; R=H). Acetylation of (V; R=H) with acetic anhydride-pyridine gave phenyl 2-acetamido-3,4-di-*O*-acetyl-6-azido-2,6-dideoxy- $\alpha$ -D-mannopyranoside (V; R=Ac) (57%) (from ether-petroleum), m.p. 144—145°,  $[\alpha]_D^{18} + 22.1^\circ$  ( $c$  1, ethanol). Reduction of either 6-azido-derivative (V; R=H or Ac) with hydrogen and palladium-charcoal gave products which no

longer showed azide absorption at 4.7—4.8  $\mu$ . Each product was hydrolyzed with 6*N*-hydrochloric acid for 1 hr. at 100°, to give crystalline 2,6-diamino-2,6-dideoxy- $\beta$ -D-mannose dihydrochloride (VI), m.p. 157° (decomp.),  $[\alpha]_D^{21} - 10.5 \rightarrow -1.0 \pm 0.5$  ( $c$  1, water).

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