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Note

Synthesis of two pseudo-sugar analogues of 2-amino-2-deoxy-α-D-glucopyranosyl α-D-mannopyranoside*

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Elucidation of the biological properties of pseudo-sugars may help to understand the roles that sugars play in biological systems. As part of a study[1] of the synthesis of biologically active pseudo-sugar derivatives, we have synthesised aminoglycoside antibiotics[2] composed partly of pseudo-sugars instead of true sugars.

2-Amino-2-deoxy-α-D-glucopyranosyl α-D-mannopyranoside[3], isolated from the fermentation broth of *Streptomyces virginiae* var. 4243-MTt$_1$, and related to the antibiotic trehalosamine[4], possesses a weak antimicrobial activity. Recently, neotrehalosadiamine[5] has been isolated from fermentation broths of *Bacillus pumilus* K169-B91, and comprises two 3-amino-3-deoxy-D-glucopyranose residues and an α,β-(1↔1) linkage. We now describe the syntheses and assay of biological activity of two pseudo-sugar analogues of trehalosamine and their respective diastereoisomers.

Condensation of DL-(1,2,4/3,5)-3,4-di-*O*-acetyl-5-bromomethyl-2-(toluene-*p*-sulfonamido)-1,3,4-cyclohexanetriol[6] (**4**) with 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide[7] (**5**) in boiling benzene in the presence of mercury(II) cyanide for 42 h gave 84% of a mixture of **6A** and **6B**. Treatment of the mixture with anhydrous sodium acetate in *N,N*-dimethylformamide at 80° gave 64% of a mixture of the 3′,4′,6′-triacetates **7A** and **7B**, which was *O*-deacylated with methanolic sodium methoxide and then acetylated. Chromatography then gave the heptaacetates **8A** (32%) and **8B** (30%). Reduction of **8A** and **8B** with sodium in liquid ammonia, followed by acetylation, gave the octa-*N,O*-acetyl derivatives **9A** (47%), $[\alpha]_D$ +53° (chloroform), and **9B** (42%), $[\alpha]_D$ −30° (chloroform). The ^{1}H-n.m.r. spectra of **9A** and **9B** contained signals at δ 4.89 (d, *J* 2 Hz) and 4.91 (bs),

*Synthesis of Pseudo-trehalosamine and Related pseudo-disaccharides, Part II. For Part I, see ref. 1.
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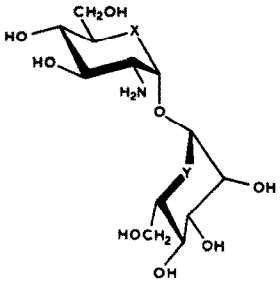
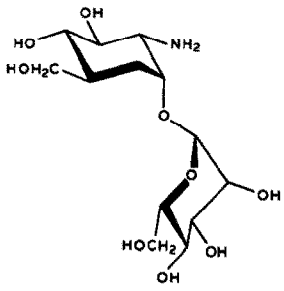


1 X = Y = O
2A X = CH_2, Y = O
3A X = O, Y = CH_2



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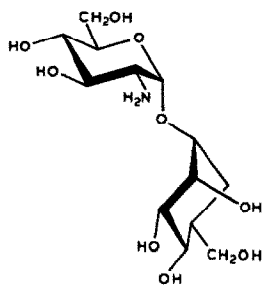

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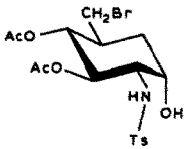
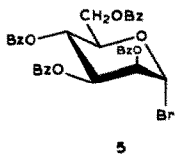


4 (racemate)



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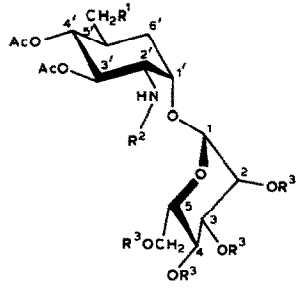


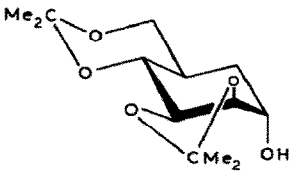
6A–9A

	R^1	R^2	R^3
6	Br	Ts	Bz
7	OAc	Ts	Bz
8	OAc	Ts	Ac
9	OAc	Ac	Ac

The formulae depict only the diastereoisomer (A series) corresponding to the natural compound.

attributable to the α-anomeric protons. Formation of the α-glycoside may also be expected by the reaction conditions employed. The absolute configurations of **9A** and **9B** were assigned on the basis that a dextrorotatory contribution of the pseudo-2-amino-2-deoxy-D-glucose moiety was predicted. Hydrazinolysis of **9A** and **9B** and purification of the products on Dowex 50W-X2 (H^+) resin afforded the pseudo-disaccharides **2A** and **2B**, respectively.

The di-*O*-isopropylidene derivative[8] (**10**) of pseudo-α-DL-mannopyranose with 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranosyl bromide[9] (**11**) were condensed in dichloromethane in the presence of silver carbonate and silver perchlorate at room temperature for 2 h, followed by treatment of the products with aqueous 80% acetic acid to remove the isopropylidene groups and then reacetylation. Fractionation of the products on silica gel afforded the α-glycosides **12A** (12%) and **12B** (17%), and the β-glycosides **14A** (26%) and **14B** (12%). The ^{1}H-n.m.r. spectra of **12A** and **12B** contained signals for anomeric protons at δ 5.14 (d, *J* 3.6 Hz) and 5.28 (d, *J* 3.8 Hz) indicative of the α-glycosides. The anomeric protons of **14A** and **14B** resonated at δ 4.81 (d, *J* 8.4 Hz) and 4.62



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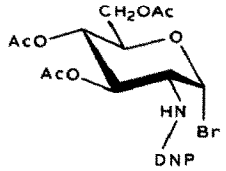

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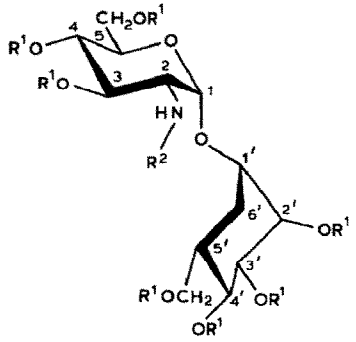
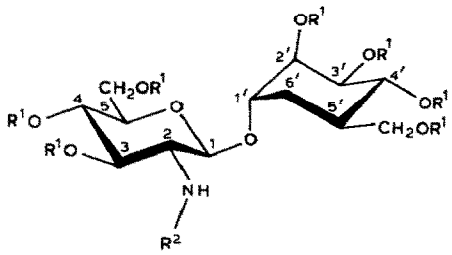


12A – 13A



14A – 16A

		R^1	R^2
12	14	Ac	DNP
13	15	Ac	Ac
16		H	H

(d, *J* 6 Hz), respectively, suggesting the presence of β-glycoside linkages. *N*-Deprotection of **12A** and **12B** with Amberlite IRA-400 (HO^-) resin in aqueous acetone at room temperature gave, after acetylation, the octa-*N*,*O*-acetyl derivatives **13A** (76%), $[\alpha]_D$ +64° (chloroform), and **13B** (83%), $[\alpha]_D$ +44° (chloroform). Similarly, **14A** and **14B** were converted into the respective octa-*N*,*O*-acetyl derivatives **15A** (77%), $[\alpha]_D$ −9° (chloroform), and **15B** (83%), $[\alpha]_D$ −19° (chloroform). Considering the $[\alpha]_D$ value [+29° (water)] of α-D-mannose, rather small contributions of the pseudo-α-D-mannose moieties to the $[\alpha]_D$ values of the pseudo-disaccharides may be predicted. Therefore, the structures of **13A** and **15A** were tentatively assigned to the diastereoisomers containing pseudo-α-D-mannose residues. Compounds **13A, 13B, 15A**, and **15B** were converted into the respective pseudo-disaccharides **3A, 3B, 16A**, and **16B**.

The pseudo-disaccharides **2A, 2B, 3A, 3B, 16A**, and **16B** possessed almost no activity against *Klebsiella pneumoniae* No. 126, *Staphylococcus aureus* 209P, and *Bacillus subtilis* PC1-219 as shown by a dilution assay method[10].

EXPERIMENTAL

General methods. — Melting points were determined with a MEL-TEMP

capillary melting-point apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-4 polarimeter. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with Varian EM-390 (90 MHz) and Jeol FX-200 (200 MHz) instruments. T.l.c. was performed on Silica Gel 60 GF (Merck) with detection by charring with sulfuric acid. Column chromatography was conducted on Wakogel C-300 (300 mesh, Wako Co., Osaka). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated at <50° under diminished pressure.

[(1S)-(1,2,4/3,5)-3,4-Diacetoxy-5-bromomethyl-2-(toluene-p-*sulfonamido)-1-cyclohexyl] 2,3,4,6-tetra*-O-*benzoyl-α*-D-*mannopyranoside* (**6A**) *and its (1*R*) diastereoisomer* (**6B**). — A mixture of DL-3,4-di-*O*-acetyl-(1,2,4/3,5)-5-bromomethyl-2-(toluene-*p*-sulfonamido)-1,3,4-cyclohexanetriol[6] (**4**; 100 mg, 0.21 mmol), mercury(II) cyanide (100 mg, 0.40 mmol), powdered Drierite (170 mg), and benzene (10 mL) was boiled until ~7 mL of the solvent had distilled. The mixture was cooled, 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide[7] (**5**; 276 mg, 0.42 mmol) was added, the mixture was boiled under reflux for 42 h, and more **5** (140 mg, 0.21 mmol) was added after 22 h. The cooled mixture was neutralised with triethylamine, an insoluble material was removed, the filtrate was concentrated, and the yellow syrupy residue (613 mg) was eluted from a column of silica gel (30 g) with 1:8 2-butanone–toluene to give a mixture (186 mg, 84%) of **6A** and **6B** as an amorphous powder. ^{1}H-N.m.r. data (90 MHz): δ 8.25–6.92 (m, 48 H, aromatic protons), 2.35 and 2.25 (2 s, each 3 H, 2 Ts Me), 2.02, 1.88, 1.83, and 1.68 (4 s, each 3 H, 4 OAc).

Anal. Calc. for $C_{52}H_{50}BrNO_{16}S$: C, 59.09; H, 4.77; N, 1.33. Found: C, 58.73; H, 4.74; N, 1.27.

[(1S)-(1,2,4/3,5)-3,4-Diacetoxy-5-acetoxymethyl-2-(toluene-p-*sulfonamido)-1-cyclohexyl] 2,3,4,6-tetra*-O-*benzoyl-α*-D-*mannopyranoside* (**7A**) *and its (1*R*) diastereoisomer* (**7B**). — The foregoing mixture (50 mg, 0.05 mmol) of **6A** and **6B** was heated with anhydrous sodium acetate (26 mg, 0.20 mmol) in *N,N*-dimethylformamide (2 mL) for 15 h at 80°. The mixture was cooled, filtered, and concentrated. The syrupy product (49 mg) was eluted from a column of silica gel (1.5 g) with 1:7 2-butanone–toluene to give a mixture (32 mg, 64%) of **7A** and **7B** as an amorphous powder. ^{1}H-N.m.r. data (90 MHz): δ 8.25–7.03 (m, 48 H, aromatic protons), 2.39 and 2.28 (2 s, each 3 H, 2 Ts Me), 2.06, 2.03, 1.99, 1.90, 1.88, and 1.68 (6 s, each 3 H, 6 OAc).

Anal. Calc. for $C_{54}H_{53}NO_{18}S$: C, 62.60; H, 5.16; N, 1.35. Found: C, 62.35; H, 5.06; N, 1.11.

[(1S)-(1,2,4/3,5)-3,4-Dihydroxy-5-hydroxymethyl-2-(toluene-p-*sulfonamido)-1-cyclohexyl] α*-D-*mannopyranoside hepta-acetate* (**8A**) *and its (1*R*) diastereoisomer* (**8B**). — The foregoing mixture (464 mg, 0.45 mmol) of **7A** and **7B** was stirred with methanolic M sodium methoxide (1.8 mL) in methanol (18 mL) for 2 h at room temperature. The mixture was neutralised with Dowex 50W-X2 (H^+) resin (1.8 mL) and concentrated, and the resulting syrup (267 mg) was treated conventionally with acetic anhydride (3 mL) and pyridine (3 mL) overnight at room temperature.

The products (281 mg) were fractionated by a column of silica gel (28 g) with 1:1 ethyl acetate–hexane to give, first, **8B** (106 mg, 30%), isolated as an amorphous powder, $[\alpha]_D^{25}$ −25° (*c* 1, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 7.75 and 7.27 (2 d, each 2 H, *J* 8.7 Hz, aromatic protons), 5.85 (d, 1 H, $J_{2',NH}$ 9 Hz, NH), 3.68–3.23 (m, 1 H, H-2'), 2.40 (s, 3 H, Ts Me), 2.18, 2.04, 2.01, 2.00, and 1.67 (5 s, 3, 6, 6, 3, and 3 H, 7 OAc).

Anal. Calc. for $C_{34}H_{45}NO_{18}S$: C, 51.84; H, 5.76; N, 1.78. Found: C, 52.02; H, 5.83; N, 1.60.

Eluted second was **8A** (111 mg, 32%), isolated as an amorphous powder, $[\alpha]_D^{23}$ +61° (*c* 1.1, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 7.71 and 7.25 (2 d, each 2 H, *J* 8.7 Hz, aromatic protons), 5.75 (d, 1 H, $J_{2',NH}$ 9 Hz, NH), 3.66–3.31 (m, 1 H, H-2'), 2.41 (s, 3 H, Ts Me), 2.18, 2.11, 2.10, 2.05, 1.99, 1.98, and 1.62 (7 s, each 3 H, 7 OAc).

Anal. Found: C, 52.13; H, 5.88; N, 1.55.

[*(1S)-(1,2,4/3,5)-2-Acetamido-3,4-dihydroxy-5-hydroxymethyl-1-cyclohexyl*] *α*-D-*mannopyranoside hepta-acetate* (**9A**) *and its (1R) diastereoisomer* (**9B**). — To liquid ammonia (~20 mL) containing sodium (~90 mg) was added a solution of **8A** (111 mg, 0.14 mmol) in tetrahydrofuran (2.5 mL), and the mixture was stirred for 5 h at −78°. Ammonium chloride (130 mg) was added, the ammonia was evaporated, and the residue was acetylated in the usual way. The resulting brown syrup (131 mg), which was eluted from a column of silica gel (6.6 g) with 1:10 ethanol–toluene, gave **9A** (45 mg, 47%), isolated as a syrup, $[\alpha]_D^{23}$ +53° (*c* 2, chloroform). ^{1}H-N.m.r. data (200 MHz): δ 6.70 (d, 1 H, $J_{2',NH}$ 9 Hz, NH), 5.42 (dd, 1 H, $J_{2,3}$ 3.6, $J_{3,4}$ 10 Hz, H-3), 5.25 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.15 (dd, 1 H, $J_{1,2}$ 2 Hz, H-2), 5.15 and 5.06 (2 t, each 1 H, $J_{2',3'} = J_{3',4'} = J_{4',5'} = 9.6$ Hz, H-3',4'), 4.89 (d, 1 H, H-1), 2.16, 2.10, 2.08, 2.07, 2.06, 2.03, and 1.96 (7 s, 3, 3, 3, 3, 3, 6, and 3 H, NAc and 7 OAc).

Anal. Calc. for $C_{29}H_{41}NO_{17} \cdot 0.5\ H_2O$: C, 50.88; H, 6.18; N, 2.05. Found: C, 51.13; H, 5.99; N, 2.09.

Similarly, **8B** (106 mg, 0.13 mmol) was converted into syrupy **9B** (38 mg, 42%), $[\alpha]_D^{23}$ −30° (*c* 1.5, chloroform). ^{1}H-N.m.r. data (200 MHz): δ 6.35 (d, 1 H, $J_{2',NH}$ 8.6 Hz, NH), 5.36–5.20 (m, 3 H, H-2,3,4), 5.15 and 5.06 (2 t, each 1 H, $J_{2',3'} = J_{3',4'} = J_{4',5'} = 9.6$ Hz, H-3',4'), 4.91 (bs, 1 H, H-1), 2.12, 2.08, 2.05, 2.04, 2.03, 2.02, and 1.99 (7 s, 3, 6, 3, 3, 3, 3, and 3 H, NAc and 7 OAc).

Anal. Found: C, 51.10; H, 6.04; N, 1.85.

[*(1S)-(1,2,4/3,5)-2-Amino-3,4-dihydroxy-5-hydroxymethyl-1-cyclohexyl*] *α*-D-*mannopyranoside* (**2A**) *and its (1R) diastereoisomer* (**2B**). — Compound **9A** (39 mg, 0.06 mmol) was heated with aqueous 80% hydrazine hydrate (1 mL) for 0.5 h at 70° and then the mixture was concentrated. The product (42 mg) was eluted from a column of Dowex 50W-X2 (H^+) resin (4.2 mL) with methanol to give **2A** (11 mg, 58%), isolated as an amorphous powder, $[\alpha]_D^{23}$ +65° (*c* 0.3, methanol).

Similarly, **9B** (31 mg, 0.05 mmol) was converted into **2B** (9.2 mg, 58%) as an amorphous powder, $[\alpha]_D^{23}$ −68° (*c* 0.3, methanol).

These compounds were subjected, without further purification, to a microbial assay[10].

[(1S)-(1,4/2,3,5)-2,3,4-Trihydroxy-5-hydroxymethyl-1-cyclohexyl] 2-deoxy-2-(2,4-dinitrophenylamino)-α- (**12A**) *and -β-*D*-glucopyranoside hepta-acetate* (**14A**), *and the respective (1*R*) diastereoisomers* **12B** *and* **14B**. — A mixture of (1*RS*, 2*RS*,7*RS*,9*SR*,10*RS*)-4,4,12,12-tetramethyl-3,5,11,13-tetraoxatricyclo[8.3.0.$0^{2,7}$]-tridecan-9-ol[8] (**10**; 100 mg, 0.34 mmol), powdered Drierite (400 mg), 2,4,6-trimethylpyridine (0.11 mL), and dichloromethane (6 mL) was stirred for 1 h at room temperature. Silver carbonate (107 mg, 0.39 mmol), silver perchlorate (81 mg, 0.39 mmol), and a solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranosyl bromide[9] (**11**; 621 mg, 1.16 mmol) in dichloromethane (4 mL) were added in turn, and the mixture was stirred for 2 h, then neutralised with triethylamine, filtered, and concentrated. The resulting yellow syrup (904 mg) was fractionated of a column of silica gel (45 g) with 1:8 2-butanone–toluene to give a syrupy mixture (292 mg) of four components.

The syrup was heated in aqueous 80% acetic acid (12 mL) for 1 h at 80°, and the product was acetylated conventionally. The resulting yellow syrup (399 mg) was fractionated on a column of silica gel (34 g) with 1:4 2-butanone–toluene to give, first, **14A** (81 mg, 26%) and then a mixture (145 mg) of **12A**, **12B**, and **14B**, isolated as a yellow amorphous powder. The mixture was further fractionated on a column of silica gel (7.3 g) with 1:3 ethyl acetate–chloroform to give **12A** (36 mg, 12%), **12B** (53 mg, 17%), and **14B** (36 mg, 12%), isolated as a yellow amorphous powder.

Compound **12A** had $[\alpha]_D^{25}$ +10° (*c* 1.3, chloroform). ^{1}H-N.m.r. data (200 MHz): δ 9.13 (d, 1 H, $J_{3,5}$ 3 Hz, H-3 of DNP), 8.85 (d, 1 H, $J_{2,NH}$ 8.8 Hz, NH), 8.30 (dd, 1 H, $J_{5,6}$ 9.8 Hz, H-5 of DNP), 7.24 (d, 1 H, H-6 of DNP), 5.52 (t, 1 H, $J_{1',2'} = J_{2',3'} = 3.6$ Hz, H-2'), 5.44 and 5.32 (2 t, each 1 H, $J_{2,3} = J_{3,4} = J_{4,5} = 10$ Hz, H-3,4), 5.28 (t, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4'), 5.17 (dd, 1 H, H-3'), 5.14 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 3.83 (q, 1 H, $J_{1',6'a} = J_{1',6'e} = 3.6$ Hz, H-1'), 2.16, 2.13, 2.09, 2.01, and 1.83 (5 s, 3, 9, 3, 3, and 3, 7 OAc).

Anal. Calc. for $C_{33}H_{41}N_3O_{20}$: C, 49.56; H, 5.17; N, 5.25. Found: C, 49.51; H, 5.25; N, 4.52.

Compound **12B** had $[\alpha]_D^{26}$ −9° (*c* 1.9, chloroform). ^{1}H-N.m.r. data (200 MHz): δ 9.14 (d, 1 H, $J_{3,5}$ 3 Hz, H-3 of DNP), 8.84 (d, 1 H, $J_{2,NH}$ 8.8 Hz, NH), 8.30 (dd, 1 H, $J_{5,6}$ 9.8 Hz, H-5 of DNP), 7.16 (d, 1 H, H-6 of DNP), 5.48, 5.28, and 5.24 (3 t, each 1 H, $J_{2,3} = J_{3,4} = J_{4,5} = J_{3',4'} = J_{4',5'} = 10.2$ Hz, H-3,4,4'), 5.40 (t, 1 H, $J_{1',2'} = J_{2',3'} = 3.8$ Hz, H-2'), 5.28 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.07 (dd, 1 H, H-3'), 2.13, 2.12, 2.08, 1.88, and 1.86 (5 s, 9, 3, 3, 3, and 3 H, 7 OAc).

Anal. Found: C, 49.53; H, 5.26; N, 4.86.

Compound **14A** had $[\alpha]_D^{26}$ −56° (*c* 2, chloroform). ^{1}H-N.m.r. data (200 MHz): δ 9.13 (d, 1 H, $J_{3,5}$ 3 Hz, H-3 of DNP), 8.75 (d, 1 H, $J_{2,NH}$ 9.8 Hz, NH), 8.30 (dd, 1 H, $J_{5,6}$ 9.8 Hz, H-5 of DNP), 7.10 (d, 1 H, H-6 of DNP), 5.64 and 5.04 (2 t, each 1 H, $J_{2,3} = J_{3,4} = J_{4,5} = 10.2$ Hz, H-3,4), 5.25 (t, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz,

H-4'), 5.17 (t, 1 H, $J_{1',2'} = J_{2',3'} = 3.8$ Hz, H-2'), 4.81 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 2.14, 2.12, 2.08, 2.07, 2.03, 1.88, and 1.84 (7 s, each 3 H, 7 OAc).

Anal. Found: C, 49.74; H, 5.26; N, 4.60.

Compound **14B** had $[\alpha]_D^{25}$ −103° (*c* 1, chloroform). ^{1}H-N.m.r. data (200 MHz): δ 9.12 (d, 1 H, $J_{3,5}$ 3 Hz, H-3 of DNP), 8.64 (d, 1 H, $J_{2,NH}$ 9.6 Hz, NH), 8.42 (dd, 1 H, $J_{5,6}$ 9.8 Hz, H-5 of DNP), 7.39 (d, 1 H, H-6 of DNP), 5.38 (t, 1 H, $J_{1',2'} = J_{2',3'} = 2.8$ Hz, H-2'), 5.38 and 5.01 (2 t, each 1 H, $J_{2,3} = J_{3,4} = J_{4,5} = 7.8$ Hz, H-3,4), 5.24 (t, 1 H, $J_{3',4'} = J_{4',5'} = 7$ Hz, H-4'), 4.94 (dd, 1 H, H-3'), 4.62 (d, 1 H, $J_{1,2}$ 6 Hz, H-1), 2.15, 2.11, 2.08, 2.05, 2.00, 1.99, and 1.92 (7 s, each 3 H, 7 OAc).

Anal. Found: C, 49.74; H, 5.28; N, 4.65.

[(1S)-(1,4/2,3,5)-2,3,4-Trihydroxy-5-hydroxymethyl-1-cyclohexyl] 2-acetamido-2-deoxy-α- (**13A**) *and -β-*D*-glucopyranoside hepta-acetate* (**15A**), *and the respective (1R) diastereoisomer* **13B** *and* **15B**. — A mixture of **12A** (26 mg, 0.03 mmol), methanol (4 mL), acetone (2.5 mL), water (1.5 mL), and Amberlite IRA-400 (HO^-) resin (4 mL) was stirred for 24 h at room temperature. The product was acetylated conventionally to give a syrup (22 mg), which was eluted from a column of silica gel (1.2 g) with 4:5 2-butanone–toluene to give **13A** (17 mg, 76%), isolated as an amorphous powder.

Similarly, **12B** (47 mg, 0.06 mmol), **14A** (41 mg, 0.05 mmol), and **14B** (28 mg, 0.04 mmol) were converted, respectively, into **13B** (32 mg, 78%), isolated as an amorphous powder, **15A** (27 mg, 77%), and **15B** (20 mg, 83%).

Compound **13A** had $[\alpha]_D^{26}$ +64° (*c* 0.9, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 6.22 (d, 1 H, $J_{2,NH}$ 8.4 Hz, NH), 2.11, 2.06, 2.04, 1.96, and 1.93 (5 s, 3, 9, 6, 3, and 3 H, NAc and 7 OAc).

Anal. Calc. for $C_{29}H_{41}NO_{17} \cdot H_2O$: C, 50.21; H, 6.25; N, 2.02. Found: C, 50.46; H, 5.98; N, 1.74.

Compound **13B** had $[\alpha]_D^{26}$ +44° (*c* 1.6, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 6.05 (d, 1 H, $J_{2,NH}$ 9 Hz, NH), 5.00 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 2.10, 2.08, 2.03, and 1.98 (4 s, 3, 9, 9, and 3 H, NAc and 7 OAc).

Anal. Calc. for $C_{29}H_{41}NO_{17} \cdot 0.5\ H_2O$: C, 50.88; H, 6.18; N, 2.05. Found: C, 50.63; H, 5.93; N, 1.58.

Compound **15A** had m.p. 199–200° (from ethanol), $[\alpha]_D^{26}$ −8.7° (*c* 1, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 6.09 (d, 1 H, $J_{2,NH}$ 8.7 Hz, NH), 5.38 (t, 1 H, $J_{2',3'} = J_{3',4'} = 3.6$ Hz, H-2'), 4.70 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 2.10, 2.06, 2.04, 2.00, 1.97, and 1.94 (6 s, 3, 3, 3, 9, 3, and 3 H, NAc and 7 OAc).

Anal. Found: C, 51.13; H, 5.97; N, 1.83.

Compound **15B** had m.p. 185° (dec., from ethanol), $[\alpha]_D^{26}$ −19° (*c* 0.8, chloroform). ^{1}H-N.m.r. data (90 MHz): δ 6.00 (d, 1 H, $J_{2,NH}$ 8.7 Hz, NH), 2.08, 2.06, 2.04, 2.03, 2.02, 1.92, and 1.09 (7 s, 3, 3, 3, 3, 6, 3, and 3 H, NAc and 7 OAc).

Anal. Found: C, 50.82; H, 6.04; N, 1.72.

[(1S)-(1,4/2,3,5)-2,3,4-Trihydroxy-5-hydroxymethyl-1-cyclohexyl] 2-amino-2-deoxy-α- (**3A**) *and -β-*D*-glucopyranoside* (**16A**), *and the respective (1R) diastereoisomers* **3B** *and* **16B**. — Compounds **13A** (15 mg, 0.04 mmol), **13B** (31 mg,

0.09 mmol), **15A** (15 mg, 0.04 mmol), and **15B** (14 mg, 0.04 mmol) were converted, as described in the preparation of **2A**, into **3A** (6.7 mg, 90%), $[\alpha]_D^{22}$ +92° (*c* 0.3, methanol), **3B** (11 mg, 68%), $[\alpha]_D^{23}$ +64° (*c* 0.5, methanol), **16A** (4.8 mg, 63%), $[\alpha]_D^{23}$ −31° (*c* 0.2, methanol), and **16B** (5.6 mg, 82%), $[\alpha]_D^{22}$ −46° (*c* 0.3, methanol), respectively, as an amorphous powder.

Without further purification, these compounds were subjected to a microbial assay.

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