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Note

Synthesis of methyl hexa-*O*-acetylacarviosin and the 6-acetoxy analogue*

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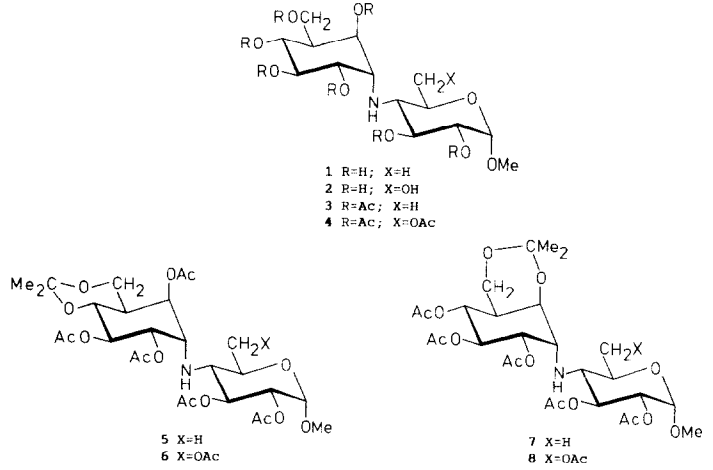
Methyl acarviosin[2], which is a core structure of acarbose and related pseudo-oligosaccharide inhibitors of alpha-amylase[3], was derived by methanolysis of oligostatins[4] via dehydration and possesses high inhibitory activity. We now describe the first syntheses of methyl acarviosin as the hexa-acetate **16** from methyl oligobiosaminide[5] (**1**) in a 6-step reaction, and of the 6-hydroxy analogue, the core structure of adiposin[6], as the hepta-acetate **17** from the corresponding 6′-hydroxy analogue (**2**).

Treatment of **1**, derived from the hepta-acetate[5] (**3**), with 2,2-dimethoxypropane in *N*,*N*-dimethylformamide in the presence of toluene-*p*-sulfonic acid at room temperature gave, after conventional acetylation of the products, the 4,7- (**5**, 51%) and 6,7-*O*-isopropylidene derivatives (**7**, 17%). Hydrolysis of **5** followed by isopropylid-



*Synthesis of Pseudo-oligosaccharide Glycosidase Inhibitors, Part VIII. For Part VII, see ref. 1.
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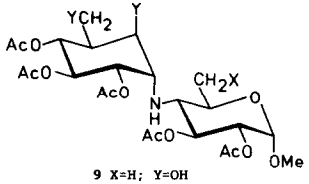
enation gave more **7** (total yield, 48%). Similarly, the isopropylidene derivatives **6** (54%) and **8** (13%) were prepared from **2** (obtained from the octa-acetate **4**).

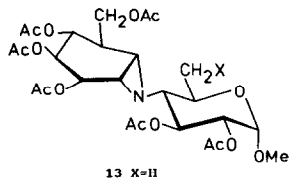
Removal of the isopropylidene group of **8** with aqueous 70% acetic acid gave the diol **9**. With sulfuryl chloride in pyridine at room temperature, **9** afforded 62% of the dichloride **10**, the structure of which was assigned on the basis of the ^{1}H-n.m.r. spectrum. Thus, the signal for H-6′ (δ 4.60, t, J 4 Hz) accorded with that (δ 5.17, J 3.6 Hz) of **3**[5]. 6′-Chlorination of **9** probably involved an intermediate aziridine formed by intramolecular attack of the 6′-chlorosulfonate by the imino function, which explains the retention of the configuration of C-6′. Similarly, the diol **11** (obtained from **8**) was chlorinated to give 60% of the dichloride **12**. Treatment of **10** with sodium acetate in *N*,*N*-dimethylformamide at 60° displaced the 7′-chloro substituent and gave the aziridine **13** by assistance of the imino group. Similar treatment of **12** afforded 10% of the olefin **17** and 17% of the aziridine **14**. Treatment of **13** with conc. hydrochloric acid in tetrahydrofuran gave 93% of the chloride **15**, which was converted into the olefin **16** (55%) by reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene in toluene at 120°; **13** was formed as a side-product.

Compounds **16** and **17** were identified by comparison with authentic samples.

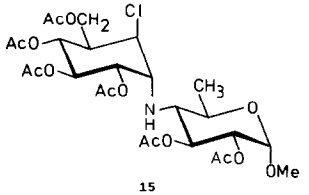
Introduction of unsaturation at the α-position of the hydroxyvalidamine portions of pseudo-disaccharides was effected in acceptable yield for **1** as has been carried out in diastereoselective fashion in the synthesis[7] of DL-validoxylamine A. The participation of the imino group seemed to be influenced by the adjacent *O*-protecting group. Thus, when the acetyl groups of **9** were replaced with benzyl, a complex mixture of products was formed by chlorination.



9 X=H; Y=OH
10 X=H; Y=Cl
11 X=OAc; Y=OH
12 X=OAc; Y=Cl



13 X=H
14 X=OAc



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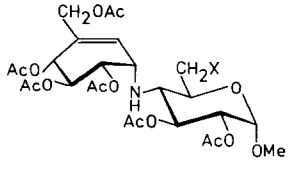

16 X=H
17 X=OAc

EXPERIMENTAL

General methods. — 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) or

D_2O (internal acetone) with a Jeol JNM GSX-270 FT (270 MHz) instrument. 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). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated at $< 50°$ under diminished pressure.

*Methyl 4,6-dideoxy-4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexylamino]-α-*D*-glucopyranoside* (**1**). — The hepta-acetate[1] **3** (66 mg, 0.10 mmol) was stirred with methanolic M sodium methoxide (0.2 mL) in methanol (2 mL) for 30 min at room temperature. Methanol (15 mL) was added and the solution was eluted from a column of Dowex 50W-X2 (H^+) resin (3 mL) with methanol→5% NH_4OH–methanol to give **1** (37 mg, ~100%), isolated as an amorphous powder, $[\alpha]_D^{24}$ +130° (*c* 0.8, methanol). ^{1}H-N.m.r. data (D_2O): δ 4.60 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.01 (t, 1 H, $J_{1',6'} = J_{5',6'}$ = 2.9 Hz, H-6'), 3.78 (dd, 1 H, $J_{1',2'}$ 4, $J_{2',3'}$ 11.2 Hz, H-2'), 3.25 (s, 3 H, OMe), 3.16 (dd, 1 H, H-1'), 2.24 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4), 1.80 (m, 1 H, H-5'), 1.16 (d, 1 H, $J_{5,6}$ 6.6 Hz, H-6).

*Methyl 4-deoxy-4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexylamino]-α-*D*-glucopyranoside* (**2**). — Treatment of the octa-acetate[1] **4** (83 mg, 0.12 mmol), as described above, gave **2** (40 mg, 91.7%), isolated as an amorphous powder, $[\alpha]_D^{24}$ +134° (*c* 0.7, methanol). ^{1}H-N.m.r. data (D_2O): δ 3.98 (t, 1 H, $J_{1',6'} = J_{5',7'}$ = 2.9 Hz, H-6'), 3.26 (s, 3 H, OMe), 3.21 (dd, 1 H, $J_{1',2'}$ 4 Hz, H-1'), 2.49 (t, 1 H, $J_{3,4} = J_{4,5}$ = 10.1 Hz, H-4), 1.80 (m, 1 H, H-5').

*Methyl 2,3,2',3',6'-penta-*O*-acetyl-4,6-dideoxy-4',7'-*O*-isopropylidene-* (**5**) *and methyl 2,3,2',3',4'-penta-O-acetyl-4,6-dideoxy-6',7'-*O*-isopropylidene-4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexylamino]-α-*D*-glucopyranoside* (**7**). — To a solution of **1** (82 mg, 0.23 mmol) in *N*,*N*-dimethylformamide (3 mL) at 0° was added pyridinium toluene-*p*-sulfonate (76 mg, 0.30 mmol) and 2-methoxypropene (27 μL). The mixture was stirred for 18 h at room temperature, then neutralised with $NaHCO_3$, and concentrated, and the residue was acetylated with pyridine and acetic anhydride (each 1 mL) overnight at room temperature. Column chromatography (2:5 acetone–hexane) of the products (138 mg) gave, first, **5** (71 mg, 50.6%), isolated as an amorphous powder, $[\alpha]_D^{23}$ +79° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.28 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.5 Hz, H-3), 5.22 (dd, 1 H, $J_{2',3'}$ 10.6, $J_{3',4'}$ 8.8 Hz, H-3'), 5.13 (dd, 1 H, $J_{1',2'}$ 4.4 Hz, H-2'), 4.88 (t, 1 H, $J_{1',6'} = J_{5',6'}$ = 3.7 Hz, H-6'), 4.81 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.77 (dd, 1 H, H-2), 4.02 (dd, 1 H, $J_{4',5'}$ 11 Hz, H-4'), 3.80–3.70 (m, 2 H, H-7'), 3.61 (dq, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 6.2 Hz, H-5), 3.41 (dd, 1 H, H-1'), 3.38 (s, 3 H, OMe), 2.53 (q, 1 H, $J_{4,NH}$ 9.5 Hz, H-4), 2.42 (m, 1 H, H-5'), 2.13, 2.08, 2.03, and 1.94 (4 s, 3, 3, 6, and 3 H, 5 Ac), 1.42 and 1.36 (2 s, each 3 H, CMe_2), 1.35 (d, 3 H, H-6).

Anal. Calc. for $C_{27}H_{41}NO_{14}$: C, 53.73; H, 6.85; N, 2.32. Found: C, 53.05; H, 6.62; N, 2.23.

Eluted second was **7** (23 mg, 16.7%), isolated as an amorphous powder, $[\alpha]_D^{23}$ +83° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.57 (m, 1 H, H-4), 5.35–5.19 (m, 3 H, H-3,2', 3'), 4.86–4.79 (m, 2 H, H-1,2), 4.10 (t, 1 H, $J_{1',6'} = J_{5',6'}$ = 2.9 Hz, H-6'), 3.92 (dd, 1 H, $J_{5',7'}$ 2.2, $J_{7',7'}$ 12.5 Hz, H-7'), 3.78–3.60 (m, 2 H, H-5,7'), 3.39 (s, 3 H, OMe), 3.35

(t, 1 H, $J_{1',2'}$ 2.9 Hz, H-1'), 2.06, 2.05, 2.02, 2.00, and 1.99 (5 s, each 3 H, 5 Ac), 1.48 and 1.45 (2 s, each 3 H, CMe_2), 1.31 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6).

Anal. Found: C, 53.56; H, 6.55; N, 2.29.

4',7'-*O*-Isopropylidene derivative **5** and the other products obtained were treated with aq. 70% acetic acid, and then with methanolic sodium methoxide to give **1**, which was isopropylidenated to give **7**. Several conversions, finally, gave 44 mg (31.5%) of **7**.

Methyl 2,3,6,2',3',6'-hexa-O-*acetyl-4-deoxy-4',7'*-O-*isopropylidene-* (**6**) *and methyl 2,3,6,2',3',4'-hexa*-O-*acetyl-4-deoxy-6',7'*-O-*isopropylidene-4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexylamino]-α*-D-*glucopyranoside* (**8**). — A mixture of **2** (85 mg, 0.23 mmol), *N*,*N*-dimethylformamide (3 mL), pyridinium toluene-*p*-sulfonate (75 mg, 0.30 mmol), and 2-methoxypropene (26 μL) was stirred for 20 h at room temperature. The mixture was processed as in the preparation of **5** and **7**, and column chromatography (1:2 acetone–hexane) of the products (166 mg) gave, first, **6** (83 mg, 54%), isolated as a syrup, $[\alpha]_D^{26}$ +72° (*c* 1.4, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.34 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.9 Hz, H-3), 5.23–5.17 (m, 2 H, H-2',3'), 4.99 (t, 1 H, $J_{1',6'} = J_{5',6'}$ = 2.6 Hz, H-6'), 4.85 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.79 (dd, 1 H, H-2), 4.54 (dd, 1 H, $J_{5,6}$ 2.2, $J_{6,6}$ 12.1 Hz) and 4.33 (dd, 1 H, $J_{5,6}$ 3.3 Hz) (H-6), 3.99 (m, 1 H, H-4'), 3.69–3.65 (m, 3 H, H-5,7'), 3.40 (s, 3 H, OMe), 2.99 (q, 1 H, $J_{4,5} = J_{4,NH}$ = 9.9 Hz, H-4), 2.16, 2.14, 2.08, 2.04, 2.03, and 1.95 (6 s, each 3 H, 6 Ac), 1.40 and 1.35 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{29}H_{43}NO_{16}\cdot H_2O$: C, 51.25; H, 6.23; N, 2.06. Found: C, 51.31; H, 6.27; N, 2.10.

Eluted second was **8** (20 mg, 13.4%), isolated as an amorphous powder, $[\alpha]_D^{26}$ +79° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.55 (m, 1 H, H-4'), 5.37 (tt, 1 H, $J_{2,3} = J_{3,4}$ = 9.9, *J* 1.5 Hz, H-3), 5.28–5.26 (m, 2 H, H-2',3'), 4.88–4.83 (m, 2 H, H-1, 2), 4.43 (dd, 1 H, $J_{5,6}$ 2.2, $J_{6,6}$ 11.9 Hz) and 4.33 (dd, 1 H, $J_{5,6}$ 3.3 Hz) (H-6), 4.07 (t, 1 H, $J_{1',6'} = J_{5',6'}$ = 2.8 Hz, H-6'), 3.86 (dd, 1 H, $J_{5',7'}$ 2.2 $J_{7',7'}$ 12.5 Hz) and 3.63 (d, 1 H, $J_{5',7'}$ 0 Hz) (H-7'), 3.69 (ddd, 1 H, $J_{4,5}$ 9.9 Hz, H-5), 3.41 (s, 1 H, OMe), 3.38 (t, 1 H, $J_{1',2'}$ 2.8 Hz, H-1'), 2.90 (q, 1 H, $J_{4,NH}$ 9.9 Hz, H-4), 2.17, 2.06, 2.05, 2.02, 2.00, and 1.99 (6 s, each 3 H, 6 Ac), 1.47 and 1.44 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{29}H_{37}NO_{16}$: C, 52.64; H, 6.09; N, 2.12. Found: C, 52.43; H, 6.23; N, 2.09.

Recycling, as described above, finally gave 55 mg (36.2%) of **8**.

Methyl 2,3,2',3',4'-penta-O-*acetyl-4-[(1S)-(1,2,4/3,5,6)-6-chloro-5-chloromethyl-2,3,4-trihydroxycyclohexylamino]-4,6-dideoxy-α*-D-*glucopyranoside* (**10**). — Compound **7** (44 mg, 0.073 mmol) was heated in aqueous 70% acetic acid (4 mL) for 30 min at 55° and the solution was concentrated to give the diol **9** (43 mg). To a solution of **9** in pyridine (2 mL) at −20° was added sulfuryl chloride (24 μL, 0.29 mmol), and the mixture was stirred for 52 h at room temperature, then poured into ice–water (5 mL), and extracted with chloroform (10 mL × 3). The combined extracts were concentrated and the syrupy residue (45 mg) was eluted from a column of silica gel with 1:5 acetone–toluene to give **10** (24 mg, 62.4%), isolated as a syrup, $[\alpha]_D^{22}$ +89° (*c* 1.2, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.48 (dd, 1 H, $J_{1',2'}$ 4, $J_{2',3'}$ 10.3 Hz, H-2'),

5.36–5.28 (m, 1 H, H-3), 5.31 (dd, 1 H, $J_{3',4'}$ 9.2 Hz, H-3'), 5.14 (dd, 1 H, $J_{4',5'}$ 11 Hz, H-4'), 4.83–4.77 (m, 2 H, H-1,2), 4.60 (t, 1 H, $J_{1',6'} = J_{5',6'} = 4$ Hz, H-6'), 3.80 (t, 1 H, H-1'), 3.67 (t, 1 H, $J_{5',7'} = J_{7',7'} = 11$ Hz) and 3.55 (dd, 1 H, $J_{5',7'}$ 4 Hz) (H-7'), 3.69–3.59 (m, 1 H, H-5), 3.39 (s, 3 H, OMe), 2.87 (tt, 1 H, H-5'), 2.52 (q, 1 H, $J_{3,4} = J_{4,5} = J_{4,NH} = 10$ Hz, H-4), 2.08, 2.05, 2.04, 2.00, and 1.99 (5 s, each 3 H, 5 Ac), 1.36 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6).

Anal. Calc. for $C_{24}H_{35}Cl_2NO_{12}$: C, 48.01; H, 5.88; N, 2.33. Found: C, 48.25; H, 6.33; N, 1.95.

*Methyl 2,3,6,2',3',4'-hexa-*O*-acetyl-4-[(1*S*)-(1,2,4/3,5,6)-6-chloro-5-chloromethyl-2,3,4-trihydroxycyclohexylamino]-4-deoxy-α-*D*-glucopyranoside* (**12**). — Compound **8** (55 mg, 0.083 mmol) was heated in aqueous 70% acetic acid (2 mL) for 30 min at 55° and the solution was concentrated. The resulting diol **11** (53 mg) was stirred with sulfuryl chloride (27 μL, 0.33 mmol) in pyridine (2 mL), and the mixture was processed as described in the preparation of **10**. Column chromatography (1:5 acetone–toluene) of the resulting syrup (52 mg) gave **12** (29 mg), isolated as a crude syrup. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.49 (dd, 1 H, $J_{1',2'}$ 4.4, $J_{2',3'}$ 10.6 Hz, H-2'), 5.36 (t, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3), 5.28 (dd, 1 H, $J_{3',4'}$ 9.5 Hz, H-3'), 5.13 (dd, 1 H, $J_{4',5'}$ 10.6 Hz, H-4'), 4.86–4.79 (m, 2 H, H-1,2), 4.60 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,6}$ 11.7 Hz) and 4.17 (dd, 1 H, $J_{5,6}$ 4.2 Hz) (H-6), 4.58 (dd, 1 H, $J_{1',6'}$ 3.7, $J_{5',6'}$ 2.9 Hz, H-6'), 3.83 (dd, 1 H, H-1'), 3.70 (ddd, 1 H, $J_{4,5}$ 9.9 Hz, H-5), 3.64 (dd, 1 H, $J_{5',7'}$ 10.6, $J_{7',7'}$ 11 Hz) and 3.55 (dd, 1 H, $J_{5',7'}$ 4.4 Hz) (H-7'), 3.41 (s, 1 H, OMe), 2.97 (q, 1 H, H-4), 2.72 (dddd, 1 H, H-5'), 2.12, 2.09, 2.05, 2.01, and 1.99 (5 s, 3, 3, 6, 3, and 3 H, 6 Ac).

*Methyl 2,3,2',3',4',7'-hexa-*O*-acetyl-4,6-dideoxy-4-[(1*S*)-(1,2,4,6/3,5)-2,3,4-trihydroxy-5-hydroxymethyl-1,6-cyclohexylenamino]-α-*D*-glucopyranoside* (**13**). — Compound **10** (23 mg, 0.037 mmol) was heated with sodium acetate (19 mg, 0.22 mmol) in *N*,*N*-dimethylformamide (1 mL) for 40 h at 60° and the mixture was concentrated, filtered, and concentrated further to give **13** (22 mg, 99.5%) as an amorphous powder, $[\alpha]_D^{23}$ +89° (*c* 1.1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.46 (t, 1 H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 5.25 (dd, 1 H, $J_{1',2'}$ 3.5, $J_{2',3'}$ 9.2 Hz, H-2'), 5.14 (dd, 1 H, $J_{3',4'}$ 10.3 Hz, H-3'), 4.85 (t, 1 H, $J_{4',5'}$ 10.3 Hz, H-4'), 4.76 (dd, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.73 (d, 1 H, H-1), 4.16 (dd, 1 H, $J_{5',7'}$ 3.6, $J_{7',7'}$ 11.5 Hz, H-7'), 4.13–4.00 (m, 2 H, H-5,7'), 3.42 (s, 3 H, OMe), 2.66 (dd, 1 H, $J_{1',6'}$ 6.5 Hz, H-1'), 2.38 (ddd, 1 H, $J_{5',6'}$ 0 Hz, H-5'), 2.08, 2.07, 2.04, 2.00, 1.96, and 1.94 (6 s, each 3 H, 6 Ac), 1.74 (d, 1 H, H-6'), 1.36 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6).

Anal. Calc. for $C_{26}H_{38}NO_{14}$: C, 53.15; H, 6.35; N, 2.38. Found: C, 53.04; H, 6.35; N, 2.09.

*Methyl 2,3,6,2',3',4',7'-hepta-*O*-acetyl-4-deoxy-4-[(1*S*)-(1,2,4,6/3,5)-2,3,4-trihydroxy-5-hydroxymethyl-1,6-cyclohexylenamino]-α-*D*-glucopyranoside* (**14**) *and methyl 2,3,6,4',5',6',7'-hepta-*O*-acetyl-4-deoxy-4-[(1*S*)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenylamino]-α-*D*-glucopyranoside* (**17**). — Compound **12** (29 mg) was heated with sodium acetate (22 mg, 0.26 mmol) in *N*,*N*-dimethylformamide (1 mL) for 60 h at 60° and the mixture was concentrated. Column chromatography (1:5 acetone–toluene) of the residue (30 mg) gave, first, **17** (5.3 mg, 9.8% from **8**), isolated as an amorphous powder, $[\alpha]_D^{24}$ +139° (*c* 0.2, chloroform); lit.[2] $[\alpha]_D^{20}$ +130° (*c* 0.96, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.91 (d, 1 H, $J_{1',2'}$ 5.1 Hz, H-2'), 5.58–5.50 (m, 2

H, H-4′,5′), 5.25 (tt, 1 H, $J_{2,3} = J_{3,4} = 9.9$, J 1.8 Hz, H-3), 4.87–4.73 (m, 3 H, H-1,2,6′), 4.58 and 4.29 (2 d, each, 1 H, $J_{7',7'}$ 12.8 Hz, H-7′), 4.33 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,6}$ 12.1 Hz) and 4.14 (dd, 1 H, $J_{5,6}$ 4.6 Hz) (H-6), 3.66–3.57 (m, 2 H, H-5,1′), 3.32 (s, 3 H, OMe), 2.74 (q, 1 H, $J_{4,5} = J_{4,NH} = 9.9$ Hz, H-4), 2.04, 2.035, 2.00, 1.98, 1.96, and 1.95 (6 s, 3, 3, 6, 3, 3, and 3 H, 7 Ac). The ^{1}H-n.m.r. spectrum (90 MHz, $CDCl_3$) was superimposable on that reported[2] for an authentic sample.

Anal. Cal. for $C_{28}H_{39}NO_{16}$: C, 52.09; H, 6.09; N, 2.17. Found: C, 52.50; H, 6.08; N, 1.78.

Eluted second was **14** (9.2 mg, 17.1% from **8**) isolated as an amorphous powder, $[\alpha]_D^{25}$ +88° (*c* 0.4, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.49 (tt, 1 H, $J_{2,3} = J_{3,4}$ 9.5, J 1.8 Hz, H-3), 5.22 (dd, 1 H, $J_{1',2'}$ 3.3, $J_{2',3'}$ 9.2, H-2′), 5.14 (dd, 1 H, $J_{3',4'}$ 10.3 Hz, H-3′), 4.89 (t, 1 H, $J_{4',5'}$ 10.3 Hz, H-4′), 4.81 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.78 (dd, 1 H, H-2), 4.57 (dd, 1 H, $J_{5,6}$ 1.8, $J_{6,6}$ 12.1 Hz) and 4.20 (dd, 1 H, $J_{5,6}$ 4.6 Hz) (H-6), 4.22 (dd, 1 H, $J_{5',7'}$ 3.1 $J_{7',7'}$ 11.7 Hz) and 3.98 (dd, 1 H, $J_{5',7'}$ 5.5 Hz) (H-7′) (4.12 (ddd, 1 H, $J_{4,5}$ 9.5 Hz, H-5), 3.44 (s, 3 H, OMe), 2.72 (dd, 1 H, $J_{1',6'}$ 6.2 Hz, H-1′), 2.33 (m, 1 H, H-5′), 2.18 (t, 1 H, H-4), 2.14, 2.09, 2.08, 2.05, 2.00, 1.96, and 1.95 (7 s, each 3 H, 7 Ac), 1.75 (d, 1 H, $J_{5',6'}$ 0 Hz, H-6′).

Anal. Found: C, 51.59; H, 5.83; N, 2.09.

Methyl 2,3,2′,3′,4′,7′-hexa-O-*acetyl-4-[(1S)-(1,2,4/3,5,6)-6*-dideoxy-*chloro-2,3,4-trihydroxy-5-(hydroxymethyl)cyclohexylamino]-4,6*-dideoxy-α-D-*glucopyranoside* (**15**). — Compound **13** (22 mg, 0.037 mmol) was stirred with conc. hydrochloric acid (20 μL) in tetrahydrofuran (2 mL) for 30 min at 0°. After neutralisation with $NaHCO_3$, the mixture was concentrated. Column chromatography (1:5 acetone–toluene) of the residue (23 mg) gave **15** (22 mg, 92.9%), isolated as an amorphous powder, $[\alpha]_D^{25}$ +85° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.48 (dd, 1 H, $J_{1',2'}$ 4, $J_{2',3'}$ 10.3 Hz, H-2′), 5.31 (ddd, 1 H, $J_{2,3}$ 11, $J_{3,4}$ 9.9, J 1.5 Hz, H-3), 5.30 (t, 1 H, $J_{3',4'} = J_{4',5'} = 9.5$ Hz, H-4′), 5.20 (dd, 1 H, H-3′), 4.83–4.77 (m, 2 H, H-1,2), 4.36 (t, 1 H, $J_{1',6'} = J_{5',6'} = 3.3$ Hz, H-6′), 4.22 (dd, $J_{5',7'}$ 4.8, $J_{7',7'}$ 11 Hz) and 4.13 (dd, 1 H, $J_{5',7'}$ 9.5 Hz) (H-7′), 3.75 (dd, 1 H, H-1′), 3.64 (dq, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 6.2 Hz, H-5), 3.40 (s, 3 H, OMe), 2.92 (tdd, 1 H, H-5′), 2.48 (q, 1 H, $J_{4,NH}$ 9.9 Hz, H-4), 2.08, 2.06, 2.043, 2.04, 1.99, and 1.988 (6 s, each 3 H, Ac), 1.31 (d, 3 H, H-6).

Anal. Calc. for $C_{26}H_{38}ClNO_{14}$: C, 50.04; H, 6.14; N, 2.24. Found: C, 49.83; H, 5.99; N, 1.58.

Methyl 2,3,4′,5′,6′,7′-hexa-O-*acetyl-4,6-dideoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenylamino]-α-D-glucopyranoside* (**16**). — A mixture of **15** (21 mg, 0.033 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (10 μL, 0.065 mmol), and toluene (1 mL) was heated at 120° for 6 h, then concentrated. Column chromatography (1:7 acetone–toluene) of the residue gave, first, **16** (11 mg, 55.4%), isolated as an amorphous powder, $[\alpha]_D^{24}$ +106° (*c* 0.5, chloroform); lit.[3] $[\alpha]_D^{20}$ +57.2° (chloroform); lit.[4] $[\alpha]_D^{20}$ +97° (ethanol). ^{1}H-N.m.r. data ($CDCl_3$): δ 6.00 (d, 1 H, $J_{1',2'}$ 5.5 Hz, H-2′), 5.67–5.60 (m, 2 H, H-4′,5′), 5.27 (t, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3), 4.97–4.91 (m, 1 H, H-6′), 4.85–4.80 (m, 2 H, H-1,2), 4.67 and 4.38 (2 d, each 1 H, $J_{7',7'}$ 13 Hz, H-7′), 3.74 (dd, 1 H, $J_{1',6'}$ 4.4 Hz, H-1′), 3.60 (dq, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 6.2 Hz, H-5), 2.43 (t, 1 H, H-4), 2.11, 2.07, 2.06, 2.04, and 2.02 (5 s, 3, 3, 3, 3, and 6 H, 6 Ac), 1.25 (d, 3 H, H-6).

Anal. Calc. for $C_{26}H_{38}NO_{14}$: C, 53.15; H, 6.35; N, 2.38. Found: C, 53.20; H, 6.32; N, 2.22.

Eluted second was **14** (4.6 mg, 23.6%), isolated as an amorphous powder.

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