Note

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

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(Received June 13th, 1989; accepted for publication, August 16th, 1989)

Methyl acarviosin², which is a core structure of acarbose and related pseudooligosaccharide inhibitors of alpha-amylase³, was derived by methanolysis of oligostatins⁴ via dehydration and possesses high inhibitory activity. We now describe the first syntheses of methyl acarviosin as the hexa-acetate **16** from methyl oligobiosaminide⁵ (1) in a 6-step reaction, and of the 6-hydroxy analogue, the core structure of adiposin⁶, as the hepta-acetate **17** from the corresponding 6'-hydroxy analogue (**2**).

Treatment of 1, derived from the hepta-acetate⁵ (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 ¹H-n.m.r. spectrum. Thus, the signal for H-6' (δ 4.60, t, J4 Hz) accorded with that (δ 5.17, J3.6 Hz) of 3⁵. 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 *a*-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 synthesis⁷ 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.



EXPERIMENTAL

General methods. — Optical rotations were measured with a Jasco DIP-4 polarimeter. ¹H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me₄Si) 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 $< 50^\circ$ under diminished pressure.

Methyl 4,6-dideoxy-4-[(1S)-(1,2,4/3,5,6)-2,3,4,6-tetrahydroxy-5-(hydroxymethyl)cyclohexylamino]-a-D-glucopyranoside (1). — The hepta-acetate¹ 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% NH₄OH-methanol to give 1 (37 mg, ~100%), isolated as an amorphous powder, $[a]_p^{24}$ +130° (c 0.8, methanol). ¹H-N.m.r. data (D₂O): 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]-a-D-glucopyranoside (2). — Treatment of the octa-acetate¹ 4 (83 mg, 0.12 mmol), as described above, gave 2 (40 mg, 91.7%), isolated as an amorphous powder, $[a]_{D}^{24} + 134^{\circ}$ (c 0.7, methanol). ¹H-N.m.r. data (D₂O): 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]-a-D-alucopyranoside (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 μ L). The mixture was stirred for 18 h at room temperature, then neutralised with NaHCO₃, 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, $[a]_{p}^{23} + 79^{\circ}$ (c 1, chloroform). ¹H-N.m.r. data (CDCl₃): 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, J₄₅ 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, CMe₂), 1.35 (d, 3 H, H-6).

Anal. Calc. for C₂₇H₄₁NO₁₄: 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, $[a]_{D}^{23}$ +83° (*c* 1, chloroform). ¹H-N.m.r. data (CDCl₃): 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, CMe₂), 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]-a-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 μ L) 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, $[a]_{0^{26}}^{2^{6}} + 72^{\circ}$ (c 1.4, chloroform). ¹H-N.m.r. data (CDCl₃): 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 $C_{29}H_{43}NO_{16}$ · 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, $[a]_{D}^{26}$ + 79° (*c* 1, chloroform). ¹H-N.m.r. data (CDCl₃): 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 C₂₉H₃₇NO₁₆: 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-a-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 μ L, 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, $[a]_{D}^{22} + 89^{\circ}$ (c 1.2, chloroform). ¹H-N.m.r. data (CDCl₃): 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 C₂₄H₃₅Cl₂NO₁₂: 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-[(1S)-(1,2,4/3,5,6)-6-*chloro-5-chloromethyl-2,3,4-trihydroxycyclohexylamino]-4-deoxy-a-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 \muL, 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. ¹H-N.m.r. data (CDCl₃): \delta 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-[(1S)-(1,2,4,6/3,5)-2,3,4-trihydroxy-5-hydroxymethyl-1,6-cyclohexylenamino]-a-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, $[a]_{D}^{23} + 89°$ (*c* 1.1, chloroform). ¹H-N.m.r. data (CDCl₃): 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 C₂₆H₃₈NO₁₄: 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-[(1S)-(1,2,4,6/3,5)-2,3,4-trihydroxy-5-hydroxymethyl-1,6-cyclohexylenamino]-a-D-glucopyranoside (14) and methyl 2,3,6,4',5',6',7'-hepta-O-acetyl-4-deoxy-4-[(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenylamino]-a-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, $[a]_{p}^{24}$ +139° (c 0.2, chloroform); lit.² $[a]_{p}^{20}$ +130° (c 0.96, chloroform). ¹H-N.m.r. data (CDCl₃): 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, J₅₆ 2.6, J₆₆ 12.1 Hz) and 4.14 (dd, 1 H, J₅₆ 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 ¹H-n.m.r. spectrum (90 MHz, CDCl₃) was superimposable on that reported² for an authentic sample.

Anal. Cal. for C₂₈H₃₉NO₁₆: 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, $[a]_{p}^{25} + 88^{\circ}$ (c 0.4, chloroform). ¹H-N.m.r. data (CDCl₃): 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-dideoxcy-chloro-2, 3,4-trihydroxy-5-(hydroxymethyl)cyclohexylamino]-4,6-dideoxy-a-D-glucopyranoside (15). — Compound 13 (22 mg, 0.037 mmol) was stirred with conc. hydrochloric acid (20 μ L) in tetrahydrofuran (2 mL) for 30 min at 0°. After neutralisation with NaHCO₃, 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, $[a]_{p}^{25} + 85^{\circ}$ (c 1, chloroform). ¹H-N.m.r. data (CDCl₃): 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 C₂₆H₃₈ClNO₁₄: 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-f(1S)-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenylamino]-a-D-glucopyranoside (16). — A mixture of 15 (21 mg, 0.033 mmol), 1.8-diazabicyclo[5.4.0]undec-7-ene ($10 \mu L$, 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, $[a]_{p}^{24} + 106^{\circ}$ (c 0.5, chloroform); lit.³ $[a]_{p}^{20} + 57.2^{\circ}$ (chloroform); lit.⁴ $[a]_{p}^{20} + 97^{\circ}$ (ethanol). ¹H-N.m.r. data (CDCl₃): 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 C₂₆H₃₈NO₁₄: 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.

ACKNOWLEDGMENTS

We thank Mr. Hisao Arita for the elemental analyses. This work was partially supported by a grant of the Asahi Glass Foundation for the contribution to industrial technology.

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