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## Note

# Synthesis of *N*-[(1*R*)-(1,5/4,6)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenyl] derivatives of 4'-amino-4'-deoxy- and 4'-amino-4',6'-dideoxycellobiose*

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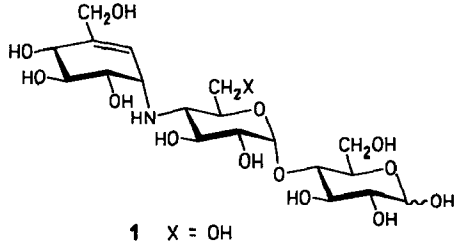
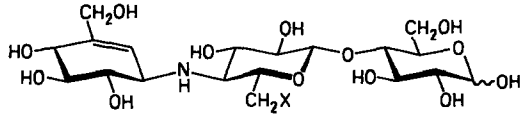
Recently, there has been much interest in the structure–activity relationship of pseudo-oligosaccharide inhibitors of glucosidase[2]. We have synthesised some stereoisomers of the pseudo-disaccharide acarviosin[3] in this context. We now describe a synthesis of the acetylated derivatives of the title pseudo-trisaccharides (**3** and **4**), the cellotriose-type analogues of adiposin-1[4] (**1**) and amylostatin XG[5] (**2**). Although the building blocks of **3** and **4** are similar to those of **1** and **2**, respectively, they are attached by a (1→4)-β-D-glucosidic linkage and therefore are expected to be inhibitors of cellulase.

The synthesis involved a regioselective coupling reaction of 4'-amino-4'-



**1** X = OH
**2** X = H



**3** X = OH
**4** X = H

*Synthesis of Pseudo-oligosaccharide Glycosidase Inhibitors, Part V. For Part IV, see ref. 1.
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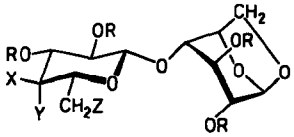
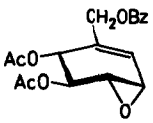
deoxy and 4′-amino-4′,6′-dideoxy derivatives (**9** and **13**) of β-cellobiose with racemic cyclohexadiene monoepoxide[6] (**15a,b**).

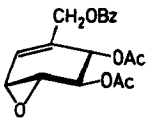
2,3,2′,3′-Tetra-*O*-acetyl-1,6-anhydro-β-lactose[7] (**5**) was benzoylated selectively at room temperature, and the product, which was not isolated, was treated with methanesulfonyl chloride to give the 4′-mesylate **6** (71% from **5**). Treatment of **6** with an excess of sodium azide in *N,N*-dimethylformamide at 100° gave 68% of the crystalline azide **7**, treatment of which with methanolic M sodium methoxide (→**8**) followed by hydrogenation gave **9** in good yield. The $^1$H-n.m.r. spectrum of the hexa-*N,O*-acetyl derivative (**10**) of **9** contained signals at δ 5.05 (t, *J* 10.5 Hz) and 4.82 (d, *J* 7.5 Hz) due to H-3′ and H-1′, respectively, indicating that inversion of the configuration at C-4′ of **6** had occurred.

When **8** was treated with *N*-iodosuccinimide and triphenylphosphine in *N,N*-dimethylformamide at 50°, 76% of the syrupy iodide **11** was obtained, which was converted into the tetra-acetate **12**, the $^1$H-n.m.r. spectrum of which supported the structure assigned. Hydrogenation of **11** in the presence of pyridine gave **13** in quantitative yield; **13** was characterised as the penta-*N,O*-acetyl derivative **14**, the $^1$H-n.m.r. spectrum of which contained a signal at δ 1.25 (d, *J* 6 Hz) ascribable to Me-5′.




**15a**




**15b**

| | R | X | Y | Z |
|---|---|---|---|---|
| **5** | Ac | H | OH | OH |
| **6** | Ac | H | OMs | OBz |
| **7** | Ac | $N_3$ | H | OBz |
| **8** | H | $N_3$ | H | OH |
| **9** | H | $NH_2$ | H | OH |
| **10** | Ac | NHAc | H | OAc |
| **11** | H | $N_3$ | H | I |
| **12** | Ac | $N_3$ | H | I |
| **13** | H | $NH_2$ | H | H |
| **14** | Ac | NHAc | H | H |

Condensation of **9** with DL-(1,2,4/3)-3,4-di-*O*-acetyl-1,2-anhydro-5-benzoyloxymethyl-5-cyclohexene-1,2,3,4-tetrol[6] (**15a,b**) in *N,N*-dimethylformamide and 2-propanol at 55° for 6 days followed by acetylation of the products and column chromatography on silica gel gave 19% of a mixture of diastereoisomers of **16a,b**. Deacylation with methanolic sodium methoxide and fractionation of the hydroxy compounds on Dowex 1-X2 ($HO^-$) resin gave two crystalline compounds, which were converted into the nona-acetates **18a** (7%), $[\alpha]_D$ −66° (chloroform), and **18b** (7%), $[\alpha]_D$ +24° (chloroform). The $^1$H-n.m.r. spectral data are shown in Table I.

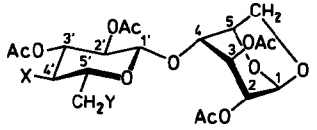
TABLE I

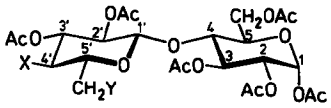
PARTIAL $^1$H-N.M.R. SPECTRAL DATA FOR COMPOUNDS **18a, 18b, 19a,** AND **19b**[a]

| *Proton* | *Chemical shifts (δ)* | | | | *Coupling constants (Hz)* | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **18a** | **18b** | **19a** | **19b** | | **18a** | **18b** | **19a** | **19b** |
| H-1 | 5.43(s) | 5.43(s) | 5.44(s) | 5.44(s) | $J_{1,2}$ | 0 | 0 | 0 | 0 |
| H-2 | 4.57(s) | 4.56(s) | 4.52(s) | 4.53(s) | $J_{2,3}$ | 0 | 0 | 0 | 0 |
| H-3 | 5.10(s) | 5.10(s) | 5.16(s) | 5.17(s) | $J_{3,4}$ | 0 | 0 | 0 | 0 |
| H-4 | 3.52(s) | 3.53(s) | 3.54(s) | 3.54(s) | $J_{4,5}$ | 0 | 0 | 0 | 0 |
| H-5 | 4.58(d) | 4.57(d) | 4.57(d) | 4.58(d) | $J_{5,6a}$ | 0 | 0 | 0 | 0 |
| H-6a | 3.95(d) | 3.96(d) | 3.97(d) | 3.97(d) | $J_{5,6b}$ | 6 | 5.6 | 6 | 6 |
| H-6b | 3.79(dd) | 3.79(dd) | 3.79(dd) | 3.80(dd) | $J_{6a,6b}$ | 7.5 | 7.5 | 7.5 | 7.5 |
| H-1′ | 4.76(d) | 4.78(d) | 4.73(d) | 4.74(d) | $J_{1',2'}$ | 7.5 | 7.8 | 7.5 | 7.5 |
| H-2′ | 4.97(dd) | 4.91(dd) | 4.95(dd) | — | $J_{2',3'}$ | 10 | 10 | 10 | — |
| H-3′ | 4.90(t) | 4.97(t) | 4.85(t) | — | $J_{3',4'}$ | 10 | 10 | 10 | 10 |
| H-4′ | 2.78(t) | 3.02(t) | 2.48(t) | 2.69(t) | $J_{4',5'}$ | 10 | 10 | 10 | 10 |
| H-5′ | 3.45(ddd) | 3.44(ddd) | 3.31(dq) | 3.34(dq) | $J_{5',6'a}$ | 2 | 2 | 6 | 6 |
| H-6′a | 4.56(dd) | 4.49(dd) | | | $J_{5',6'b}$ | 6 | 5.4 | 6 | 6 |
| H-6′b | 4.02(dd) | 4.17(dd) | | | $J_{6'a,6'b}$ | 11.7 | 11.7 | — | — |
| H-1″ | 3.28(d) | 3.64(d) | 3.39(d) | 3.66(d) | $J_{1'',2''}$ | 0 | 0 | 0 | 0 |
| H-2″ | 5.85(s) | 5.74(s) | 5.83(s) | 5.75(s) | $J_{4'',5''}$ | 7.5 | 7.5 | 7.5 | 7.7 |
| H-4″ | 5.65(d) | 5.69(d) | 5.67(d) | 5.72(d) | $J_{5'',6''}$ | 10.5 | 10.3 | 10.5 | 10.5 |
| H-5″ | 5.20(dd) | 5.19(dd) | 5.23(dd) | 5.22(dd) | $J_{1'',6''}$ | 8 | 9 | 8 | 8 |
| H-6″ | 4.95(dd) | 4.92(dd) | 4.96(dd) | — | $J_{7''a,7''b}$ | 13 | 13 | 13 | 13 |
| H-7″a | 4.67(d) | 4.67(d) | 4.66(d) | 4.67(d) | | | | | |
| H-7″b | 4.35(d) | 4.28(d) | 4.35(d) | 4.35(d) | | | | | |
| $CH_3$ | | | 1.30(d) | 1.34(d) | | | | | |

[a]Measured at 400 MHz in $CDCl_3$.

The spectra of **18a** and **18b** contained signals (d, *J* 8 Hz; s; dd, *J* 8 and 10.5 Hz) attributed to H-1″, H-2″, and H-6″, respectively, supporting the position (H-1″) of the imino linkage and the (1,5/4,6)-configuration of the cyclohexene moiety. The absolute configurations of **18a** and **18b** were deduced on the basis of the results obtained for the related pseudo-disaccharides[1], in which the branched-chain (1*R*)-conduritol moiety made a levorotatory contribution to the molecular rotation. The signals for H-4′,1″ of **18b** were considerably downfield in comparison with those of **18a**, reflecting the difference in the dihedral angles of the cyclohexene and pyranose rings around the imino bonds. Acetolysis of **18a** and **18b** at room temperature for 2 h afforded the undeca-acetates **20a** (94%), $[\alpha]_D$ −12° (chloroform), and **20b** (97%), $[\alpha]_D$ +68° (chloroform), respectively, the $^1$H-n.m.r. spectra of which indicated that the $\alpha$ anomers had been formed preferentially.

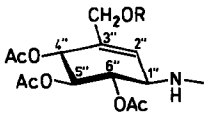




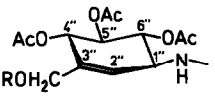
**16a,b, 18a,b** Y = OAc
**17a,b, 19a,b** Y = H

**20a,b** Y = OAc
**21a** Y = H

**a** X =



**b** X =



**16, 17** R = Bz
**18~21** R = Ac

Likewise, condensation of **13** with **15a,b** in *N,N*-dimethylformamide at 45° for 3 days gave a mixture of products (**17a,b**) which was deacylated and then fractionated on Dowex 1-X2 ($HO^-$) resin to give, after acetylation, the octa-acetates **19a** (6.5%), $[\alpha]_D$ −103° (chloroform), and **19b** (7%), $[\alpha]_D$ +20° (chloroform). The $^1$H-n.m.r. spectral data of **19a** and **19b** accorded with those of **18a** and **18b**. Acetolysis of **19a** afforded the deca-acetate **21a** in good yield, the $^1$H-n.m.r. spectrum of which accorded with that of **20a**.

## 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 GX-

400 (400 MHz) spectrometers. T.l.c. was performed on Silica Gel 60 $F_{254}$ (Merck) and column chromatography on Wakogel C-300 (300 Mesh) (Wako Co.). Organic solutions were dried ($Na_2SO_4$) and concentrated at <50° under reduced pressure.

*2,3,2',3'-Tetra-O-acetyl-1,6-anhydro-6'-O-benzoyl-4'-O-methanesulfonyl-β-lactose* (**6**). — To a solution of 2,3,2',3'-tetra-*O*-acetyl-1,6-anhydro-β-lactose[7] (**5**; 434 mg, 0.88 mmol) in pyridine (10 mL) was added benzoyl chloride (0.28 mL, 2.4 mmol) with cooling (ice). The mixture was stirred at room temperature for 4 days and then concentrated with the addition of water. The residue was treated with methanesulfonyl chloride (0.56 mL, 7.2 mmol) in pyridine (10 mL) at room temperature for 2 days, the mixture was concentrated, and a solution of the residue in ethyl acetate (70 mL) was washed with aqueous sodium hydrogencarbonate and water, dried, and concentrated. Elution of the residue from a column of silica gel (30 g) with 2-butanone–toluene (1:3) gave **6** (420 mg, 71%), isolated as a syrup, $[\alpha]_D^{25}$ −23° (*c* 1.6, chloroform). $^1$H-N.m.r. data (90 MHz): δ 7.70 (m, 5 H, Bz), 5.40 (s, 1 H, H-1), 5.27 (t, 1 H, *J* 3 Hz, H-4'), 5.23–4.93 (m, 3 H, H-3,2',3'), 4.84 (d, 1 H, *J* 7.5 Hz, H-1'), 4.62–4.26 (m, 3 H, H-2,5,6'a), 4.14 (dd, 1 H, *J* 6 and 7.5 Hz, H-6'b), 3.86 (d, 1 H, *J* 7.5 Hz, H-6*endo*), 3.65 (dd, 1 H, *J* 6 and 7.5 Hz, H-6*exo*), 3.51 (s, 1 H, H-4), 3.13 (s, 3 H, Ms), 2.13–1.88 (4 s, 12 H, 4 OAc).

*Anal.* Calc. for $C_{28}H_{34}O_{17}S$: C, 49.85; H, 5.08. Found: C, 50.06; H, 5.11.

*2,3,2',3'-Tetra-O-acetyl-1,6-anhydro-4'-azido-6'-O-benzoyl-4'-deoxy-β-cellobiose* (**7**). — A mixture of **6** (520 mg, 0.77 mmol), sodium azide (224 mg, 3.45 mmol), and *N,N*-dimethylformamide (6 mL) was stirred at 100° for 24 h. T.l.c. (2-butanone–toluene, 3:8; 2 developments) then revealed a major ($R_F$ 0.57) and a minor spot ($R_F$ 0.60). The mixture was diluted with ethyl acetate, washed with water, dried, and concentrated. The residue was crystallised from ethanol to give **7** (324 mg, 68%), m.p. 146–147°, $[\alpha]_D^{26}$ −13° (*c* 1.7, chloroform). $^1$H-N.m.r. data (90 MHz): δ 8.13–7.27 (m, 5 H, Bz), 5.36 (s, 1 H, H-1), 5.30–5.00 (m, 2 H, H-3,3'), 4.98–4.65 (m, 2 H, H-1',2'), 4.60–4.30 (m, 4 H, H-2,5, C$H_2$OBz), 3.84 (d, 1 H, *J* 7.5 Hz, H-6*endo*), 3.78–3.54 (m, 3 H, H-4',5',6*exo*), 3.49 (s, 1 H, H-4), 2.09–1.93 (4 s, 12 H, 4 OAc).

*Anal.* Calc. for $C_{27}H_{31}N_3O_{14}$: C, 52.18; H, 5.03; N, 6.76. Found: C, 51.95; H, 5.18; N, 6.53.

*4'-Amino-1,6-anhydro-4'-deoxy-β-cellobiose* (**9**). — To a solution of **7** (250 mg, 0.40 mmol) in methanol (4 mL) was added methanolic M sodium methoxide (1.0 mL). The mixture was stirred at room temperature for 2 h, then neutralised with Amberlite IR-120B ($H^+$) resin, and concentrated to give the syrupy hydroxy compound **8** (137 mg, 98%), $[\alpha]_D^{25}$ −34° (*c* 0.7, methanol). This compound was hydrogenated in methanol (5 mL) in the presence of Raney nickel T-4[8] (0.3 mL) at an initial pressure of hydrogen of 50 p.s.i. (Parr apparatus) for 19 h. The catalyst was removed and the filtrate was concentrated to give syrupy **9** (125 mg, ~100%), $[\alpha]_D^{20}$ −66° (*c* 1.7, methanol).

A portion (80 mg, 0.25 mmol) of **9** was treated with acetic anhydride (2 mL) in pyridine (2 mL) at room temperature overnight. The mixture was concentrated

and the product was eluted from a column of silica gel (4 g) with ethanol–toluene (1:10) to give the syrupy hexa-*N,O*-acetyl derivative **10** (135 mg, 95%), $[\alpha]_D^{24}$ −35° (*c* 2, chloroform). $^1$H-N.m.r. data (90 MHz): δ 6.26 (d, 1 H, *J* 9 Hz, NH), 5.45 (s, 1 H, H-1), 5.19 (s, 1 H, H-3), 5.05 (t, 1 H, *J* 10.5 Hz, H-3′), 4.82 (d, 1 H, *J* 7.5 Hz, H-1′), 4.62 (d, 1 H, *J* 6 Hz, H-5), 4.58 (s, 1 H, H-2), 4.31–4.06 (m, 2 H, C*H*$_2$OAc), 4.00 (d, 1 H, *J* 7.5 Hz, H-6*endo*), 3.80 (dd, 1 H, *J* 6 and 7.5 Hz, H-6*exo*), 3.59 (s, 1 H, H-4), 2.15–1.93 (clusters, 18 H, NAc and 5 OAc).

*Anal.* Calc. for $C_{24}H_{33}NO_{15}$: C, 50.09; H, 5.78; N, 2.43. Found: C, 50.08; H, 5.68; N, 2.11.

*1,6-Anhydro-4′-azido-4′,6′-dideoxy-6′-iodo-β-cellobiose* (**11**). — Compound **8** (260 mg, 0.74 mmol) was treated with *N*-iodosuccinimide (510 mg, 0.74 mmol) in *N,N*-dimethylformamide (14 mL), and triphenylphosphine (130 mg, 1.85 mmol) was added. The mixture was stirred at 50° for 23 h and then cooled to 0–5°, methanol was added, and the mixture was stirred at room temperature for 1 h and then concentrated. The residue was eluted from a column of silica gel (30 g) with chloroform–methanol (10:1) to give **11** (260 mg, 76%), isolated as a syrup, $[\alpha]_D^{25}$ −37° (*c* 0.9, methanol). $^1$H-N.m.r. data (90 MHz, $CD_3OD$): δ 5.31 (s, 1 H, H-1), 4.51 (d, 1 H, *J* 7.5 Hz, H-1′), 4.08 (d, 1 H, *J* 6 Hz, H-5), 3.75 (d, 1 H, *J* 7.5 Hz, H-6a), 3.69 (dd, 1 H, *J* 6 and 10.8 Hz, H-6b), 3.43 (dd, 1 H, *J* 5 and 10.8 Hz, H-6′a), 3.27 (dd, 1 H, *J* 3 and 10.8 Hz, H-6′b), 3.40 (s, 1 H, H-4), 2.98 (ddd, 1 H, *J* 3, 5, and 10 Hz, H-5′).

A portion (21 mg) of **11** was acetylated in the usual way, to give the syrupy tetra-acetate **12** (28 mg, 100%), $[\alpha]_D^{26}$ −20° (*c* 1.3, chloroform). $^1$H-N.m.r. data (90 MHz): δ 5.41 (bs, 1 H, H-1), 5.22 (t, 1 H, *J* 9.5 Hz, H-3′), 5.12 (t, 1 H, *J* 1.2 Hz, H-3), 4.60 (dt, 1 H, *J* 1.2, 1.2, and 6 Hz, H-5), 4.54 (t, 1 H, *J* 1.2 Hz, H-2), 3.95 (dd, 1 H, *J* 1.2 and 7.5 Hz, H-6a), 3.77 (dd, 1 H, *J* 6 and 7.5 Hz, H-6b), 3.61 (t, 1 H, *J* 9.5 Hz, H-4′), 3.53 (dd, 1 H, *J* 3 and 11.5 Hz, H-6′a), 3.34 (dd, 1 H, *J* 5 and 11.5 Hz, H-6′b), 3.51 (bs, 1 H, H-4), 3.04 (ddd, 1 H, *J* 3, 5, and 9.5 Hz, H-5′), 2.18, 2.10, and 2.03 (3 s, 3, 6, and 3 H, 4 OAc).

*Anal.* Calc. for $C_{20}H_{26}IN_3O_{12}$: C, 38.29; H, 4.18; N, 6.70. Found: C, 38.68; H, 4.17; N, 6.47.

*4′-Amino-1,6-anhydro-4′,6′dideoxy-β-cellobiose* (**13**). — A solution of **11** (159 mg, 0.35 mmol) in ethanol (8 mL) and pyridine (1.3 mL) was hydrogenated in the presence of Raney nickel (0.6 mL) at an initial hydrogen pressure of 50 p.s.i. at room temperature for 15 h. The catalyst was removed and the filtrate was concentrated to give syrupy **13** (105 mg, 100%).

A portion (15 mg) of **13** was acetylated in the usual way to give, after column chromatography (ethanol–toluene, 1:10), the penta-*N,O*-acetyl derivative **14** (24 mg, 94%), m.p. 141–144°, $[\alpha]_D^{25}$ −40° (*c* 1, chloroform). $^1$H-N.m.r. data (90 MHz): δ 5.76 (d, 1 H, *J* 10 Hz, NH), 5.41 (s, 1 H, H-1), 5.18 (s, 1 H, H-3), 5.04 (dd, 1 H, *J* 7.5 and 9 Hz, H-2′), 4.99 (t, 1 H, *J* 9 Hz, H-3′), 4.76 (d, 1 H, *J* 7.5 Hz, H-1′), 4.58 (d, 1 H, *J* 6 Hz, H-5), 4.50 (s, 1 H, H-2), 3.96 (d, 1 H, *J* 7.5 Hz, H-6a), 3.75 (dd, 1 H, *J* 6 and 7.5 Hz, H-6b), 3.54 (s, 1 H, H-4), 2.11, 2.02, and 1.92 (3 s, 6, 6, and 3 H, NAc and 4 OAc).

*Anal.* Calc. for $C_{22}H_{31}NO_{13}$: C, 51.06; H, 6.04; N, 2.71. Found: C, 50.59; H, 5.87; N, 2.49.

*2,3,2',3',6'-Penta-O-acetyl-1,6-anhydro-4'-deoxy-4'-[(1R)-(1,5/4,6)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenylamino]-β-cellobiose* (**18a**) *and its (1S)-diastereoisomer* (**18b**). — A mixture of **9** (129 mg, 0.40 mmol), DL-(1,2,4/3)-3,4-di-*O*-acetyl-1,2-anhydro-5-benzoyloxymethyl-5-cyclohexene-1,2,3,4-tetrol[6] (**15a,b**; 135 mg, 0.39 mmol), *N,N*-dimethylformamide (2 mL), and 2-propanol (4 mL) was heated in a sealed tube at 55° for 6 days, and then treated with acetic anhydride (2 mL) and pyridine (5 mL) at room temperature overnight. The mixture was concentrated, and a solution of the residue in ethyl acetate was washed with aqueous sodium hydrogencarbonate, dried, and concentrated. The syrupy residue was eluted from a column of silica gel (12 g) with 2-butanone–toluene (1:10) to give a syrupy mixture (69 mg, 19%) of **16a** and **16b** which was treated with methanolic M sodium methoxide (0.1 mL) in methanol (2 mL) at room temperature for 2 h. T.l.c. then revealed two spots [$R_F$ 0.22 and 0.18; chloroform–methanol (1:1)]. The mixture was washed through a short column of Amberlite IR-120B ($H^+$) resin (0.5 mL) with aqueous 0.5% ammonia, the eluate was concentrated, and a solution of the residue in water was washed with ethyl acetate. The aqueous layer was washed through a short column of Dowex 1-X2 ($HO^-$) resin (5 mL) with water to give two hydroxy compounds, $R_F$ 0.22, $[\alpha]_D^{23}$ −112° (*c* 0.8, water) (15.3 mg, 8%), and $R_F$ 0.18, $[\alpha]_D^{23}$ +7° (*c* 0.8, water) (15.6 mg, 8.3%).

The first product was acetylated and the product was eluted from a column of alumina with chloroform to give syrupy **18a** (24.3 mg, 89%), $[\alpha]_D^{20}$ −66° (*c* 1.3, chloroform). For the $^1$H-n.m.r. data (400 MHz), see Table I.

*Anal.* Calc. for $C_{37}H_{49}NO_{22}$: C, 51.69; H, 5.74; N, 1.63. Found: C, 51.34; H, 5.59; N, 1.63.

Acetylation of the second product gave syrupy **18b** (24 mg, 85%), $[\alpha]_D^{20}$ +24° (*c* 1.3, chloroform). For the $^1$H-n.m.r. data (400 MHz), see Table I.

Found: C, 52.02; H, 5.89; N, 1.23.

*1,2,3,6,2',3',6'-Hepta-O-acetyl-4'-deoxy-4'-[(1R)-(1,5/4,6)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenylamino]-α-cellobiose* (**20a**) *and its (1S)-diastereoisomer* (**20b**). — Compound **18a** (21 mg, 0.025 mmol) was treated with acetic anhydride–acetic acid–conc. sulfuric acid (70:30:1, 2 mL) at room temperature for 2 h. The mixture was then poured into ice–water and extracted with ethyl acetate (30 mL), and the extract was washed with saturated aqueous sodium hydrogencarbonate and water, dried, and concentrated to give syrupy **20a** (22 mg, 94%), $[\alpha]_D^{27}$ −12° (*c* 1.1, chloroform). $^1$H-N.m.r. data (90 MHz): δ 6.22 (d, 1 H, *J* 3.5 Hz, H-1), 5.84 (s, 1 H, H-2″), 5.63 (d, 1 H, *J* 7.5 Hz, H-4″), 5.40 (t, 1 H, *J* 10 Hz, H-3), 5.15 (t, 1 H, *J* 10 Hz, H-3′), 5.08–4.70 (m, 4 H, H-2,2′,5″,6″), 4.62–4.04 (m, 6 H, 2 $CH_2$OAc and C=C$CH_2$OAc), 4.04–3.50 (m, 3 H, H-5,5′,1″), 3.30 (t, 1 H, *J* 10 Hz, H-4), 2.86 (t, 1 H, *J* 10 Hz, H-4), 2.86 (t, 1 H, *J* 10 Hz, H-4′, appears on deuteration), 2.17–1.99 (cluster of s, 33 H, 11 OAc).

*Anal.* Calc. for $C_{41}H_{55}NO_{25}$: C, 51.20; H, 5.76; N, 1.46. Found: C, 51.74; H, 5.96; N, 1.59.

Similarly, acetolysis of **18b** (22 mg, 0.026 mmol) gave syrupy **20b** (24 mg, 98%), $[\alpha]_D^{27}$ +68° (*c* 1.2, chloroform). $^1$H-N.m.r. data (90 MHz): δ 6.20 (d, 1 H, *J* 3.3 Hz, H-1), 5.69 (s, 1 H, H-2″), 5.64 (d, 1 H, *J* 7.5 Hz, H-4″), 5.40 (t, 1 H, *J* 10 Hz, H-3), 5.15 (t, 1 H, *J* 10 Hz, H-3′), 5.09–4.70 (m, 4 H, H-2,2′,5″,6″), 4.64–4.10 (m, 6 H, 2 C*H*$_2$OAc and C=C*H*$_2$OAc), 4.08–3.50 (m, 3 H, H-5,5′,1″), 3.30 (t, 1 H, *J* 10 Hz, H-4), 2.98 (t, 1 H, *J* 10 Hz, H-4′, appears on deuteration), 2.17–2.01 (cluster of s, 33 H, 11 OAc).

Found: C, 51.63; H, 5.91; N, 1.38.

*2,3,2′,3′-Tetra-*O*-acetyl-1,6-anhydro-4′,6′-dideoxy-4′-[(1*R*)-(1,5/4,6)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenylamino]-β-cellobiose* (**19a**) *and its (1*S*)-diastereoisomer* (**19b**). — A mixture of **13** (110 mg, 0.36 mmol), **15a,b** (125 mg, 0.36 mmol), and *N,N*-dimethylformamide (2 mL) was heated in a sealed tube at 45° for 72 h, and then treated with acetic anhydride (3 mL) and pyridine (3 mL) at room temperature overnight. The mixture was processed as described in the preparation of **16a** and **16b**, to give a syrupy mixture (62 mg, 20%) of **17a** and **17b**, which was deacylated; the products were then fractionated on a column of Dowex 1-X2 ($HO^-$) resin (6 mL) by elution with water. The crystalline fractions [11 mg, 6.5%; $R_F$ 0.17 (chloroform–methanol, 2:1); 12 mg, 7%; $R_F$ 0.13] were acetylated. The former gave **19a** (16.4 mg, 87%), $[\alpha]_D^{23}$ −103° (*c* 0.7, chloroform). For the $^1$H-n.m.r. data (400 MHz), see Table I.

*Anal.* Calc. for $C_{35}H_{47}NO_{20}$: C, 52.43; H, 5.91; N, 1.75. Found: C, 52.30; H, 5.80; N, 1.63.

The latter gave syrupy **19b** (18.3 mg, 90%), $[\alpha]_D^{23}$ +20° (*c* 0.8, chloroform). For the $^1$H-n.m.r. data (400 MHz), see Table I.

Found: C, 52.24; H, 5.86; N, 1.50.

*1,2,3,6,2′,3′-Hexa-*O*-acetyl-4′,6′-dideoxy-4′-[(1*R*)-(1,5/4,6)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenylamino]-α-cellobiose* (**21a**). — Compound **19a** (13 mg, 0.016 mmol) was acetolysed and the product was purified by column chromatography to give syrupy **21a** (14.6 mg, 99%), $[\alpha]_D^{20}$ −18° (*c* 0.7, chloroform). $^1$H-N.m.r. data (90 MHz): δ 6.25 (d, 1 H, *J* 3.5 Hz, H-1), 5.82 (s, 1 H, H-2″), 5.65 (d, 1 H, *J* 7.5 Hz, H-4″), 5.41 (t, 1 H, *J* 10 Hz, H-3), 5.21 (dd, 1 H, *J* 7.5 and 10.5 Hz, H-5″), 4.99 (dd, 1 H, *J* 3.5 and 10 Hz, H-2), 4.87 (dd, 1 H, *J* 7.5 and 10 Hz, H-2′), 4.55 (d, 1 H, *J* 7.5 Hz, H-1′), 4.42 (bs, 2 H, C*H*$_2$OAc), 4.21 (d, 1 H, *J* 13 Hz, H-7″a), 4.08 (d, 1 H, *J* 13 Hz, H-7″b), 3.90 (d, 1 H, *J* 10 Hz, H-5), 3.75 (t, 1 H, *J* 10 Hz, H-4), 3.35 (d, 1 H, *J* 8 Hz, H-1″), 3.22 (dq, *J* 6, 6, 6, and 10 Hz, H-5′), 2.45 (t, 1 H, *J* 10 Hz, H-4′, appears on deuteration), 2.17, 2.11, and 2.04 (3 s, 3, 3, and 24 H, 10 OAc), 1.32 (d, 3 H, *J* 6 Hz, methyl).

*Anal.* Calc. for $C_{39}H_{53}NO_{23}$: C, 51.83; H, 5.91; N, 1.55. Found: C, 51.77; H, 5.70; N, 1.35.

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