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# Note

## Synthesis of pseudo-laminarabiose, -cellobiose, and -maltose (D-glucopyranosyl 5a-carba-D- and L-glucopyranoses)*

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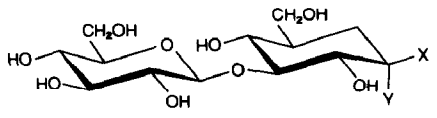
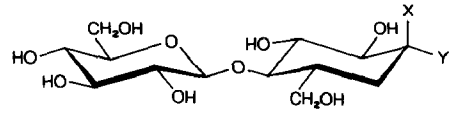
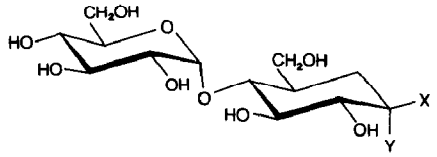
In connection with the synthesis of pseudo-trehalose[2], disaccharide analogues of naturally occurring disaccharides, having the reducing unit replaced by a carbocyclic ring, have been synthesized as the totally acetylated derivatives. Synthesis of pseudo-α- (**1A** and **1B**) and -β-laminarabiose (**2A** and **2B**), pseudo-α- (**3A** and **3B**) and -β-cellobiose (**4A** and **4B**), and pseudo-α- (**5A** and **5B**) and -β-maltose (**6A** and **6B**), was achieved by coupling of the protected 5a-carba-α- and -β-DL-glucopyranose with the appropriate glucosyl donors. Elucidation of the structures and absolute configurations of the products was based on $^1$H-n.m.r. spectra and optical rotations. These analogues are the α- and β-glucosides containing 5a-carba-D- (**A** series) or -L-glucopyranose (**B** series) as



**1A,B** X = H, Y = OH
**2A,B** X = OH, Y = H



**3A,B** X = OH, Y = H
**4A,B** X = H, Y = OH



**5A,B** X = H, Y = OH
**6A,B** X = OH, Y = H

Scheme 1. For convenience, the structures depict only the diastereomeric pseudo-disaccharides (**A** series) which contain 5a-carba-D-glucopyranoses as aglycons.

* Pseudo-sugars, Part XXVII. For Part XXVI, see ref. 1.
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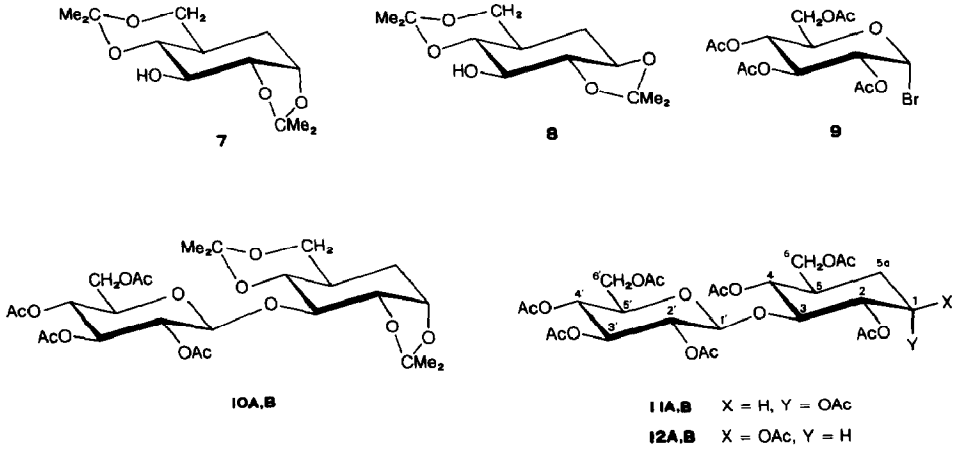
the aglycon. These are possible substrate analogue[2] or inhibitors of glucoside hydrolases, and are also useful as model compounds for conformational analyses of natural oligosaccharides by HSEA calculations[3] based on $^1$H- and $^{13}$C-n.m.r. spectral data.

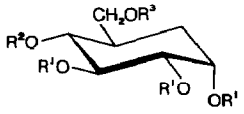
*Pseudo-α-* and *β-laminarabiose.* — Condensation of equimolar amounts of 5a-carba-1,2:4,6-di-*O*-isopropylidene-α-DL-glucopyranose[4] (**7**) with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**9**) in benzene in the presence of mercury(II) cyanide for 15 h at reflux temperature afforded, after chromatography on silica gel, the pseudo-disaccharide derivatives **10A** (34%), $[\alpha]_D$ +22° ($CHCl_3$), and **10B** (38%), $[\alpha]_D$ −49° ($CHCl_3$). Removal of the isopropylidene groups of **10A** and **10B** with aqueous 50% acetic acid, followed by acetylation with acetic anhydride in pyridine at room temperature gave the respective crystalline octaacetates **11A** (98%), $[\alpha]_D$ ~0° ($CHCl_3$), and **11B** (86%), $[\alpha]_D$ −29° ($CHCl_3$), the $^1$H-n.m.r. spectra of which contained doublets (*J* 8.7 Hz) attributable to the anomeric protons at δ 4.82 and 4.78, respectively, indicative of their being β-glucosides. In this case, the difference in the specific rotations was sufficient to assign the absolute configurations of **11A** and **11B**, assuming a contribution of $[\alpha]_D$ +57° ($CHCl_3$) by the carba-sugar moiety (5a-carba-α-D-glucopyranose pentaacetate[5]) to the molecular rotation.



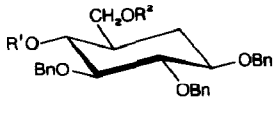

Scheme 2. The structures **7**, **8**, and **13**–**21** depict only the enantiomers corresponding to the D-series of normal hexopyranoses.

Similar condensation of 5a-carba-1,2:4,6-di-*O*-isopropylidene-β-DL-glucopyranose[4] (**8**) with **9** afforded 53% of an inseparable mixture of the condensates, which was *O*-deisopropylidenated and then acetylated to give, after chromatography, crystalline pseudo-disaccharide octaacetates **12A** (24%), $[\alpha]_D$ −13° ($CHCl_3$), and **12B** (26%), $[\alpha]_D$ −31° ($CHCl_3$). The $^1$H-n.m.r. spectra of **12A** and **12B** revealed doublets (*J* 8.2 Hz) for H-1 at δ 4.62 and 4.59, respectively, indicative of their being β-glucosides. Using the small difference of the values of each optical rotation, the former compound was tentatively assigned as the D,D-diastereoisomer and the latter as the D,L-diastereoisomer [5a-carba-β-D-glucopyranose pentaacetate[6]: $[\alpha]_D$ +13.8° ($CHCl_3$)].

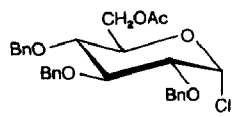
*Pseudo-α- and β-cellobiose.* — First, the appropriately protected carba-sugar to be used as the aglycon for the coupling was prepared as follows: Treatment of 5a-carba-α-DL-glucopyranose[4] (**13**) with an equal amount of α,α-dimethoxytoluene in the presence of *p*-toluenesulfonic acid for 3 h at 50° gave the 4,6-*O*-benzylidene derivative[10] **14** (63%), which was characterized by converting it conventionally into the crystalline triacetate **15** (98%) and tribenzyl ether **16** (72%). Compound **16** was *O*-debenzylidenated with aqueous 80% AcOH (**16**→**17**) and then selectively acetylated with acetyl chloride and imidazole[7] to give the 6-acetate **18** (69%).




| | R¹ | R² | R³ |
|---|---|---|---|
| **13** | H | H | H |
| **14** | H | CHPh | |
| **15** | Ac | CHPh | |
| **16** | Bn | CHPh | |
| **17** | Bn | H | H |
| **18** | Bn | H | Ac |




| | R¹ | R² |
|---|---|---|
| **19** | CHPh | |
| **20** | H | H |
| **21** | H | Ac |

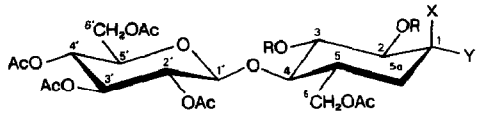



**22**

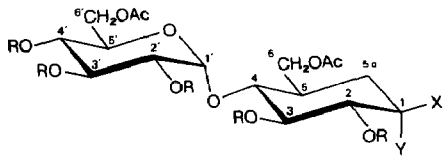
Coupling of **9** with **18** was carried out in $CH_2Cl_2$ in the presence of silver triflate and tetramethylurea for 3 h at 50° to give the protected pseudo-disaccharides **23A** (32%), $[\alpha]_D$ +29° ($CHCl_3$), and **23B** (39%), $[\alpha]_D$ −45° ($CHCl_3$). Compound **23A** was hydrogenolyzed in EtOAc with 10% Pd–C and then acetylated conventionally to give the crystalline octaacetate **24A** (73%), $[\alpha]_D$ +15° ($CHCl_3$), the $^1$H-n.m.r. spectrum (400 MHz, in $CDCl_3$) of which contained a doublet (*J* 8.3 Hz) for the anomeric proton at δ 4.52, indicative of their being β-glucoside. In a similar manner, **23B** was converted into the octaacetate **24B** (84%), $[\alpha]_D$ −53° ($CHCl_3$); $^1$H-n.m.r., $\delta_H$ 4.67 (*J* 7.8 Hz, H-1′). The absolute structures of **23A** and **23B** were convincingly established as depicted in the Scheme on the basis of the optical rotations.

6-*O*-Acetyl-1,2,3-tri-*O*-benzyl-5a-carba-β-DL-glucopyranose (**21**) was prepared from 1,2,3-tri-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-DL-glucopyranose[8] (**19**) in 83% yield by *O*-debenzylidenation (**19**→**20**) and selective acetylation. Condensation of **21** with **9** under the aforementioned conditions afforded the condensates **25A** (32%) and **25B** (39%). Hydrogenolysis of **25A** and **25B** followed by acetylation gave the crystalline pseudo-disaccharide octaacetates **26A** (52%), $[\alpha]_D$ −4° ($CHCl_3$), $\delta_H$ 4.51 (*J* 8.1 Hz, H-1′), and **26B** (64%), $[\alpha]_D$ −23° ($CHCl_3$), $\delta_H$ 4.66 (*J* 8.1 Hz, H-1′), respectively, the absolute configurations of which were tentaviely assigned on the basis of their optical rotations.

*Pseudo-α- and β-maltose.* — Condensation of **18** with 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride[9] (**22**) in 1,2-dichloroethane in the presence of silver triflate and tetramethylurea for 5 h at 100° gave the syrupy diacetates **27A** (28%), $[\alpha]_D$ +59° ($CHCl_3$), and **27B** (29%), $[\alpha]_D$ +13° ($CHCl_3$). Hydrogenolysis of **27A** and **27B** in ethanol with 10% Pd–C gave, after acetylation, the octaacetates **28A** (56%), $[\alpha]_D$ +78°



| | R | X | Y |
|---|---|---|---|
| **23A,B** | Bn | OBn | H |
| **24A,B** | Ac | OAc | H |
| **25A,B** | Bn | H | OBn |
| **26A,B** | Ac | H | OAc |



| | R | X | Y |
|---|---|---|---|
| **27A,B** | Bn | H | OBn |
| **28A,B** | Ac | H | OAc |
| **29A,B** | Bn | OBn | H |
| **30A,B** | Ac | OAc | H |

($CHCl_3$), and **28B** (60%), $[\alpha]_D$ +35° ($CHCl_3$), the $^1$H-n.m.r. spectra of which showed doublets at $\delta$ 5.46 ($J$ 4 Hz) and 5.13 ($J$ 3.7 Hz) due to the α-anomeric protons, respectively. The structures were deduced from the optical rotations.

Coupling of **21** with **22** under similar conditions (3 h at 100°) gave in 58% yield an inseparable mixture of the diacetates **29A** and **29B**, which was similarly hydrogenolyzed in EtOAc, with subsequent acetylation, giving, after chromatography, the octaacetates **30A** (28%), $[\alpha]_D$ +56° ($CHCl_3$), $\delta_H$ 5.45 ($J$ 4 Hz, H-1′), and **30B** (31%), $[\alpha]_D$ +50° ($CHCl_3$), $\delta_H$ 5.12 ($J$ 3.7 Hz, H-1′). Although there was only a small difference between the optical rotations of **30A** and **30B**, the chemical shifts of the signals of their anomeric protons are likely to be correlated with those of the corresponding diastereoisomeric pseudo-α-disaccharides, allowing the prediction of their absolute configurations.

Biological assays and conformational analysis of pseudo-disaccharides prepared in this study are under way.

## 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 $MeSi_4$) with Jeol JNM-FX90A (90 MHz), GSX-270 (270 MHz), or JNM GX-400 FT (400 MHz) spectrometers. T.l.c. was performed on Silica Gel 60 GF (Merck) with detection by charring with $H_2SO_4$. Column chromatography was conducted on Wakogel C-200 (200 mesh) or C-300 (300 mesh). Organic solutions were evaporated at < 50° under diminished pressure.

*3-O-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-5a-carba-1,2:4,6-di-O-isopropylidene-α-D-glucopyranose* (**10A**) *and its diastereoisomer* (**10B**). — A mixture of 5a-carba-1,2:4,6-di-*O*-isopropylidene-α-DL-glucopyranose[4] (**7**, 0.30 g, 1.2 mmol), $Hg(CN)_2$ (1.5 g, 4.1 mmol), powdered Drierite (1 g), and benzene (45 mL) was heated at reflux to remove 15 mL of benzene by distillation. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**9**, 1.4 g, 4.5 mmol) was then added and the mixture was stirred for 25 h at 95°. The mixture was treated with $Et_3N$, insoluble material was removed by filtration, and the filtrate was evaporated. The residue was roughly fractionated on a column of silica

gel with 1:5 acetone–hexane as eluent to give a mixture of **10A** and **10B**, which was again eluted from a column of silica gel with 1:8 EtOAc–$CHCl_3$ to afford **10A** (230 mg, 34%), m.p. 172–174° (from EtOH), $[\alpha]_D^{17}$ +22° (*c* 1, $CHCl_3$), and **10B** (262 mg, 38%), m.p. 174–176° (from EtOH), $[\alpha]_D^{17}$ −49° (*c* 0.8, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): for **10A**, $\delta$ 2.15 and 2.08 (2 s, each 6 H, 4 Ac), 1.56, 1.50, 1.43, and 1.37 (4 s, each 3 H, 2 $CMe_2$); for **10B**, $\delta$ 2.15 and 2.09 (2 s, 3 and 9 H, 4 Ac), 1.56, 1.46, and 1.39 (3 s, 3, 6, and 3 H, 2 $CMe_2$).

*Anal.* Calc. for $C_{27}H_{40}O_{14}$: C, 55.10; H, 6.85. Found: for **10A**, C, 55.08; H, 6.67; for **10B**, C, 55.11; H, 6.72.

*5a-Carba-3-*O*-(β-*D*-glucopyranosyl)-α-*D*-glucopyranose octaacetate* (**11A**) *and its diastereoisomer* (**11B**). — Compound **10A** (46 mg, 0.08 mmol) was treated with aq. 50% AcOH for 3 h at room temperature, and the mixture was evaporated. The residue was acetylated with $Ac_2O$ (1 mL) in pyridine (1 mL) overnight at room temperature. The crude product was eluted from a short column of active alumina with $CHCl_3$ to give **11A** (52 mg, 98%), m.p. 197–199° (from EtOH); $[\alpha]_D^{19}$ ~0° (*c* 1.4, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 4.82 (d, 1 H, $J_{1,2}$ 8.7 Hz, H-1), 2.23, 2.17, 2.14, 2.08, 2.05, and 2.01 (6 s, 3, 6, 6, 3, 3, and 3 H, 8 Ac).

*Anal.* Calc. for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: C, 51.63; H, 5.98.

Compound **10B** (76 mg, 0.13 mmol) was similarly converted into the octaacetate **11B** (75 mg, 86%); m.p. 169–170° (from EtOH), $[\alpha]_D^{19}$ −29° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 4.78 (d, 1 H, $J_{1,2}$ 8.7 Hz, H-1), 2.20, 2.18, 2.14, 2.11, 2.09, and 2.04 (6 s, 3, 3, 3, 3, 9, and 3 H, 8 Ac).

*Anal.* Found: C, 51.37; 6.07.

*5a-Carba-3-*O*-(β-*D*-glucopyranosyl)-β-*D*-glucopyranose octaacetate* (**12A**) *and its diastereoisomer* (**12B**). — A mixture of 5a-carba-1,2:4,6-di-*O*-isopropylidene-β-DL-glucopyranose[4] (**8**, 0.24 g, 0.93 mmol) and **9** (1.1 g, 2.8 mmol) in benzene (20 mL) was treated with $Hg(CN)_2$ (1.0 g, 4.1 mmol) and powdered Drierite (0.75 g) for 15 h at reflux temperature. The mixture was processed as in the preparation of **10A** and **10B** to give an inseparable mixture of the condensates, which was similarly *O*-deisopropylidenated and acetylated to give a mixture of **12A** and **12B**. The mixture was eluted from a column of silica gel with 1:5 EtOAc–$CHCl_3$ as eluent to afford **12A** (72 mg, 46%), m.p. 157.5–158.5° (from EtOH), $[\alpha]_D^{14}$ −13° (*c* 1, $CHCl_3$), and **12B** (76 mg, 49%), m.p. 173.5–175.5° (from EtOH), $[\alpha]_D^{14}$ −31° (*c* 1.2, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): for **12A**, $\delta$ 4.62 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 3.78 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10 Hz, H-3), 2.12, 2.08, 2.07, 2.03, 2.02, and 1.99 (6 s, 3, 3, 6, 3, 6, and 3 H, 8 Ac); for **12B**, $\delta$ 4.59 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 3.74 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10 Hz, H-3), 2.15, 2.08, 2.06, 2.04, 2.03, 2.02, 2.01, and 1.98 (8 s, each 3 H, 8 OAc).

*Anal.* Calc. for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: for **12A**, C, 51.10; H, 5.80; for **12B**, C, 51.64; H, 5.89.

4,6-O-*Benzylidene-5a-carba-*α*-*DL*-glucopyranose* (**14**). — To a solution of carba-α-DL-glucopyranose[4] (**13**, 2.7 g, 15 mmol) in *N*,*N*-dimethylformamide (DMF, 15 mL) was added α,α-dimethoxytoluene (2.7 mL, 18 mmol) and *p*-toluenesulfonic acid monohydrate (2 mg) and the mixture was stirred at 55° under diminished pressure (aspirator) for 3 h. The mixture was made neutral with $NaHCO_3$ and evaporated. The residue was

eluted from a column of silica gel with 1:10 MeOH–$CHCl_3$ as eluent to give **14** (2.5 g, 63%); m.p. 189.5–191.5° (from EtOH).

*Anal.* Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.82. Found: C, 62.76; H, 6.56.

Conventional acetylation of **14** (55 mg, 0.21 mmol) gave the triacetate **15** (79 mg, 98%); m.p. 158.5–159.5° (from EtOH); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.40–7.13 (m, 5 H, Ph), 5.42 (s, 1 H, PhC*H*), 4.81 (dd, 1 H, $J_{1,2}$ 3.3, $J_{2,3}$, 10.5 Hz, H-2), 4.07 (dd, 1 H, $J_{5,6eq}$ 3.9, $J_{6eq,6ax}$ 11.4 Hz, H-6*eq*), 3.50 (dd, 1 H, $J_{5,6ax}$ 11 Hz, H-6*ax*), 3.48 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.3 Hz, H-4), 2.09, 2.00, and 1.96 (3 s, each 3 H, 3 Ac).

*Anal.* Calc. for $C_{20}H_{24}O_8$: C, 61.22; H, 6.16. Found: C, 61.44; H, 6.20.

Compound **14** (129 mg, 0.48 mmol) was treated with NaH (0.17 g, 3.5 mmol) and $PhCH_2Cl$ (0.33 mL, 2.9 mmol) in DMF (15 mL) for 16 h at room temperature. The mixture was treated with MeOH and then evaporated. The residue was extracted with EtOAc, and the extract was dried and evaporated. The product was purified on a column of silica gel with 1:6 EtOAc–hexane to give the tribenzyl ether **16** (187 mg, 72%); m.p. 115–116°; $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.91–7.25 (m, 20 H, 4 Ph), 5.80 (s, 1 H, PhC*H*), 5.07 (d, 2 H, *J* 3 Hz, PhC$H_2$), 4.88 (s, 4 H, 2 PhC$H_2$), 4.03 (m, 1 H, H-1), 2.41 (m, 1 H, H-5).

*Anal.* Calc. for $C_{35}H_{36}O_5$: C, 78.33; H, 6.76. Found: C, 78.29; H, 6.76.

*6-O-Acetyl-1,2,3-tri-O-benzyl-5a-carba-α-*DL*-glucopyranose* (**18**). — A mixture of **16** (322 mg, 0.60 mmol) and aq. 80% AcOH (20 mL) was heated for 5 min at 90°, and evaporated to give the crude diol **17**. To a solution of imidazole (123 mg, 1.8 mmol) in $CHCl_3$ (10 mL) was added dropwise AcCl (64 $\mu$L, 0.90 mmol). A solution of crude **17** in $CHCl_3$ (10 mL) was added to the filtered solution, and the mixture was heated at reflux for 28 h and then evaporated to dryness. Chromatography of the residue on silica gel with 1:15 butanone–PhMe gave **18** (202 mg, 69%) as a syrup; $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.76–7.42 (m, 15 H, 3 Ph), 5.05 (ABq, 2 H, *J* 12.3 and 30.9 Hz, C$H_2$OAc), 4.83 and 4.77 (2 s, each 2 H, 2 PhC$H_2$), 3.97 (t, 1 H, $J_{5,6} = J_{6,6'}$ = 9.6 Hz, H-6), 3.46 (dd, 1 H, $J_{5,6'}$ 3 Hz, H-6'), 2.60 (bs, 1, OH), 2.08 (s, 3 H, OAc).

*Anal.* Calc. for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.84; H, 7.05.

*6-O-Acetyl-1,2,3-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-5a-carba-α-*D*-glucopyranose* (**23A**) *and its diastereoisomer* **23B**. — To a mixture of **18** (250 mg, 0.51 mmol) in $CH_2Cl_2$ (10 mL) were added in turn silver triflate (328 mg, 1.3 mmol), tetramethylurea (324 $\mu$L, 2.0 mmol), and a solution of **9** (839 mg, 2.9 mmol) in $CH_2Cl_2$ (10 mL), and the mixture was stirred for 3 h at 50° in the dark. The mixture was treated with $Et_3N$ and insoluble material was removed by filtration. The filtrate was evaporated and the residue was eluted from a column of silica gel with 1:15 butanone–$PhMe_3$ as an eluent to give crystalline **23A** (135 mg, 32%), m.p. 163–164° (from EtOH), $[\alpha]_D^{15}$ +29° (*c* 1.3, $CHCl_3$), and syrupy **23B** (163 mg, 39%), $[\alpha]_D^{15}$ −45° (*c* 1.3, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): for **23A**, $\delta$ 7.81–7.34 (m, 15 H, 3 Ph), 4.97, 4.66, and 4.57 (3 s, each 2 H, 3 PhC$H_2$), 2.11, 2.08, 2.03, and 2.01 (4 s, 3, 3, 6, and 3 H, 5 OAc); for **23B**, $\delta$ 7.81–7.41 (m, 15 H, 3 Ph), 5.30, 4.88, and 4.81 (3 s, each 2 H, 3 PhC$H_2$), 2.18, 2.14, 2.11, and 2.05 (4 s, 3, 3, 6, and 3 H, 5 Ac).

*Anal.* Calc. for $C_{44}H_{52}O_{15}$: C, 64.38; H, 6.38. Found: for **23A**, C, 64.03; H, 6.27; for **23B**, C, 64.25; H, 6.84.

*5a-Carba-4-O-(β-D-glucopyranosyl)-α-D-glucopyranose octaacetate* (**24A**) *and its diastereoisomer* **24B**. — A solution of **23A** (60 mg, 0.073 mmol) in EtOAc (10 mL) was hydrogenated in the presence of 10% Pd–C (10 mg) in a Parr apparatus (at an initial hydrogen pressure of 3.4 kg/cm$^2$) for 3 days at room temperature. The catalyst was removed by filtration and the filtrate was evaporated and the residue was acetylated conventionally. The product was eluted from a column of silica gel with 1:8 butanone–PhMe to give **24A** (36 mg, 73%), m.p. 196.5–198.5° (from EtOH), $[\alpha]_D^{12}$ +15° (*c* 0.4, $CHCl_3$); $^1$H-n.m.r. (400 MHz, $CDCl_3$): $\delta$ 5.38 (m, 1 H, H-1), 5.35 (dd, 1 H, $J_{2,3}$ 10.7, $J_{3,4}$ 9.3 Hz, H-3), 5.16 (t, 1 H, $J_{2',3'} = J_{3',4'}$ = 9.3 Hz, H-3'), 5.09 (t, 1 H, $J_{4',5'}$ 9.3 Hz, H-4'), 4.96 (dd, 1 H, $J_{1',2'}$ 8.3 Hz, H-2'), 4.86 (dd, 1 H, $J_{1,2}$ 2.9 Hz, H-2), 4.52 (d, 1 H, H-1'), 4.41 (dd, 1 H, $J_{5',6'a}$ 4.4, $J_{6',6'}$ 12.2 Hz, H-6'a), 4.31 (dd, 1 H, $J_{5,6a}$ 2.4, $J_{6,6}$ 11.2 Hz, H-6a), 4.13 (dd, 1 H, $J_{5,6b}$ 4.9 Hz, H-6b), 4.03 (dd, 1 H, $J_{5',6'b}$ 2.4 Hz, H-6'b), 3.66 (m, 1 H, H-5'), 3.63 (t, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 2.13, 2.12, 2.08, 2.05, 2.02, 2.01, and 1.99 (7 s, 3, 3, 3, 3, 3, 3, and 6 H, 8 Ac).

*Anal.* Calc. for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: C, 51.39; H, 5.72.

Compound **23B** (62 mg, 0.075 mmol) was hydrogenated similarly in EtOH (10 mL) for 20 h, and then acetylated. The product was eluted from a column of silica gel to give **24B** (43 mg, 84%) as a syrup; $[\alpha]_D^{12}$ −53° (*c* 1.3, $CHCl_3$); $^1$H-n.m.r. (400 MHz, $CDCl_3$): $\delta$ 5.40 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 9.3 Hz, H-3), 5.37 (m, 1 H, H-1), 5.11 (t, 1 H, $J_{3',4'} = J_{4',5'}$ = 9.3 Hz, H-4'), 4.99 (t, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 9.3 Hz, H-2'), 4.84 (dd, 1 H, $J_{1,2}$ 2.9 Hz, H-2), 4.67 (d, 1 H, H-1'), 4.17–4.08 (m, 4 H, 2 C$H_2$OAc), 3.72 (dd, 1 H, $J_{4,5}$ 10.8 Hz, H-4'), 3.64 (ddd, 1 H, $J_{5',6'a}$ 2.9, $J_{5',6'b}$ 3.4 Hz, H-5'), 2.15, 2.11, 2.10, 2.05, 2.02, 2.00, and 1.99 (7 s, 3, 3, 3, 3, 6, 3, and 3 H, 8 Ac).

*Anal.* Found: C, 51.75; H, 6.27.

*6-O-Acetyl-1,2,3-tri-O-benzyl-5a-carba-β-DL-glucopyranose* (**21**). — A mixture of 1,2,3-tri-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-DL-glucopyranose[8] (**19**, 330 mg, 0.62 mmol) and aq. 80% AcOH (20 mL) was heated for 5 min at 90° and evaporated to give crude diol **20**. Without purification, **20** was selectively acetylated as described in the preparation of **18** to give **21** (250 mg, 83%) as needles; m.p. 94–95° (from EtOH); $^1$H-n.m.r. (90 MHz, $CDCl_3$): $\delta$ 7.49–7.22 (m, 15 H, 3 Ph), 5.20–4.57 (m, 6 H, 3 PhC$H_2$), 4.21 (d, 2 H, *J* 5.4 Hz, C$H_2$OAc), 2.53 (bs, 1 H, OH), 2.04 (s, 3 H, Ac).

*Anal.* Calc. for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.22; H, 6.90.

*6-O-Acetyl-1,2,3-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-5a-carba-β-D-glucopyranose* (**25A**) *and its diastereoisomer* **25B**. — To a mixture of **21** (178 mg, 0.36 mmol) in 1,2-dichloroethane (10 mL) were added in turn silver triflate (280 mg, 1.1 mmol), tetramethylurea (0.20 mL, 1.6 mmol), and a solution of **9** (430 mg, 1.1 mmol) in 1,2-dichloroethane (10 mL). The mixture was stirred for 20 h at 90°, processed as in the preparation of **23A** and **23B**, and the products were chromatographed on silica gel with 1:8 butanone–PhMe to give **25A** (94 mg, 32%), m.p. 140–143° (from EtOH), $[\alpha]_D^{30}$ −12° (*c* 0.3, $CHCl_3$), and **25B** (116 mg, 39%), $[\alpha]_D^{30}$ −19° (*c* 1.2, $CHCl_3$); $^1$H-n.m.r. (90 MHz, $CDCl_3$): for **25A**, $\delta$ 2.09, 2.06, 1.99, 1.96, and 1.93 (3 s, each 3 H, 5 OAc); for **25B**, $\delta$ 2.09 and 2.03 (2 s, 3 and 12 H, 5 Ac).

*Anal.* Calc. for $C_{44}H_{52}O_{15}$: C, 64.38; H, 6.38. Found: for **25B**, C, 64.08; H, 6.32; for **25B**, C, 64.52; H, 6.48.

*5a-Carba-4-O-(β-D-glucopyranosyl)-β-D-glucopyranose octaacetate* (**26A**) *and its diastereoisomer* **26B**. — Compound **25A** (69 mg, 0.084 mmol) was hydrogenolyzed and acetylated as in the preparation of **24A**. The product was chromatographed on silica gel with 1:4 butanone–PhMe to give **26A** (29 mg, 52%) as needles; m.p. 201–203° (from EtOH), $[\alpha]_D^{25}$ −4° (*c* 0.5, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): δ 5.15 (t, 1 H, $J_{2',3'} = J_{3',4'}$ = 8.8 Hz, H-3'), 5.09 (t, 1 H, $J_{1,2} = J_{2,3}$ = 9.5 Hz, H-2), 4.93 (dd, 1 H, $J_{1',2'}$ 8.1 Hz, H-2'), 4.87 (m, 1 H, H-1), 4.51 (d, 1 H, H-1'), 4.40 (dd, 1 H, $J_{5',6'a}$ 4.4, $J_{6',6'}$ 12.5 Hz, H-6'a), 4.36 (dd, 1 H, $J_{5,6a}$ 2.9, $J_{6,6}$ 11.4 Hz, H-6a), 4.07 (dd, 1 H, $J_{5,6b}$ 2.6 Hz, H-6b), 4.04 (dd, 1 H, $J_{5',6'b}$ 2.6 Hz, H-6'b), 2.11, 2.08, 2.03, 2.01, and 1.98 (5 s, 3, 3, 3, 12, and 3 H, 8 Ac).

*Anal.* Calc. for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: C, 51.32; H, 5.89.

Compound **25B** (92 mg, 0.11 mmol) was similarly converted into the octaacetate **26B** (49 mg, 64%) as needles; m.p. 147–148° (from EtOH); $[\alpha]_D^{25}$ −23° (*c* 1.1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): δ 5.09 (dd, 1 H, $J_{2,3}$ 7.7, $J_{3,4}$ 8.8 Hz, H-3), 5.06 (t, 1 H, $J_{2',3'} = J_{3',4'}$ = 9.5 Hz, H-3'), 4.96 (dd, 1 H, $J_{1,2}$ 9.9 Hz, H-2), 4.92 (m, 1 H, H-1), 4.66 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1'), 4.19 (dd, 1 H, $J_{5,6a}$ 3.3, $J_{6,6}$ 11 Hz, H-6a), 4.14 (d, *J* 2.7 Hz, H-6',6'), 4.08 (dd, 1 H, $J_{5,6b}$ 5.5, H-6b), 3.73 (dd, 1 H, $J_{4,5}$ 10.6 Hz, H-4), 3.64 (m, 1 H, H-5'), 2.11, 2.10. 2.03, 2.02, 2.01. and 1.99 (6 s, 3, 3, 6, 6, 3, and 3 H, 8 Ac).

*Anal.* Found: C, 50.63; H, 5.78.

*6-O-Acetyl-1,2,3-tri-O-benzyl-4-O-(6-O-acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl)-5a-carba-α-D-glucopyranose* (**27A**) *and its diastereoisomer* **27B**. — Coupling of **18** (278 mg, 0.57 mmol) and 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride[9] (**22**, 560 mg, 1.1 mmol) was carried out as in the preparation of **25A** and **25B** for 5 h at 100° to give **27A** (153 mg, 28%), $[\alpha]_D^{16}$ +59° (*c* 0.8, $CHCl_3$), and **27B** (160 mg, 29%), $[\alpha]_D^{16}$ +13° (*c* 0.7, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): for **27A**, δ 7.34–7.14 (m, 30 H, 6 Ph), 5.77 (d, 1 H, $J_{1',2'}$ 4.7 Hz, H-1'), 5.07–4.47 (m, 12 H, 6 PhC$H_2$), 2.04 and 2.01 (2 s, each 3 H, 2 Ac); for **27B**, δ 7.38–7.16 (m, 30 H, 6 Ph), 5.16 (d, 1 H, $J_{1',2'}$ 4.7 Hz, H-1'), 5.07–4.47 (m, 12 H, 6 PhC$H_2$), 2.02 and 2.00 (2 s, each 3 H, 2 Ac).

*Anal.* Calc. for $C_{59}H_{64}O_{12}$: C, 73.42; H, 6.68. Found: for **27A**, C, 73.01; H, 6.48; for **27B**, C, 72.96; H, 6.57.

*5a-Carba-4-O-(α-D-glucopyranosyl)-α-D-glucopyranose octaacetate* (**28A**) *and its diastereoisomer* **28B**. — Compound **27A** (65 mg, 0.067 mmol) was hydrogenolyzed and acetylated as in the preparation of **24A** to give **28A** (26 mg, 56%); $[\alpha]_D^{26}$ +78° (*c* 1.3, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): δ 5.57 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10.4 Hz, H-3), 5.46 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1'), 5.42 (t, 1 H, $J_{2',3'} = J_{3',4'}$ = 10.1 Hz, H-3'), 5.36 (m, 1 H, H-1), 5.09 (t, 1 H, $J_{4',5'}$ 10.1 Hz, H-4'), 4.91 (dd, 1 H, H-2'), 4.79 (dd, 1 H, $J_{1,2}$ 4.6 Hz, H-2), 3.89 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 2.17, 2.12, 2.10, 2.08, 2.03, 2.01, 1.99, and 1.97 (8 s, each 3 H, 8 Ac).

*Anal.* Calc. for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: C, 50.80; H, 5.88.

Compound **27B** (48 mg, 0.05 mmol) was similarly converted into the octaacetate **28B** (20 mg, 60%); $[\alpha]_D^{26}$ +35° (*c* 1, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): δ 5.45 (dd, 1 H, $J_{2',3'}$ 10.6, $J_{3',4'}$ 9.5 Hz, H-3'), 5.37 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 8.8 Hz, H-3), 5.13 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1'), 5.12 (t, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 4.90 (dd, 1 H, H-2'), 4.78 (dd, 1 H, $J_{1,2}$ 3.3 Hz, H-2), 4.55 (dd, 1 H, $J_{5,6a}$ 2.9, $J_{6,6}$ 11 Hz, H-6a), 3.56 (dd, 1 H, $J_{4,5}$ 10.6 Hz, H-4), 2.18, 2.09, 2.07, 2.03, 2.01, 2.00, and 1.98 (7 s, 3, 6, 3, 3, 3, 3, and 3 H, 8 Ac).

*Anal.* Found: C, 50.77; H, 5.60.

*5a-Carba-4-O-(α-D-glucopyranosyl)-β-D-glucopyranose octaacetate* (**30A**) *and its diastereoisomer* **30B**. — Coupling of **21** (226 mg, 0.46 mmol) and **22** (1.4 g, 2.8 mmol) was carried out as in the preparation of **25A** and **25B** to give 255 mg (58%) of an inseparable mixture of **29A** and **29B**. A 159-mg portion of the mixture was hydrogenolyzed and acetylated as in the preparation of **24A** to give a mixture of the products, which was chromatographed on silica gel with 8:1 $CHCl_3$–EtOAc to give **30A** (32 mg, 28%) as needles, m.p. 165–167° (from EtOH), $[\alpha]_D^{25}$ + 56° (*c* 0.8, $CHCl_3$), and **30B** (35 mg, 31%) as plates, m.p. 142–144°, $[\alpha]_D^{24}$ + 50° (*c* 0.7, $CHCl_3$); $^1$H-n.m.r. (270 MHz, $CDCl_3$): for **30A**, $\delta$ 5.45 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1'), 5.38 (dd, 1 H, $J_{2',3'}$ 10.6 Hz, H-3'), 5.17 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.2 Hz, H-3), 5.07 (t, 1 H, $J_{1,2}$ 9.2 Hz, H-2), 5.01 (t, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 4.90 (dd, 1 H, $J_{2',3'}$ 10.6 Hz, H-2'), 3.99 (m, 1 H, H-5'), 3.89 (dd, 1 H, $J_{4,5}$ 10.3 Hz, H-4), 2.12, 2.10, 2.05, 2.02, 2.01, 2.00, 1.99, and 1.98 (8 s, each 3 H, 8 Ac); for **30B**, $\delta$ 5.41 (dd, 1 H, $J_{2',3'}$ 10.3, $J_{3',4'}$ 9.5 Hz, H-3'), 5.12 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1'), 5.09 (t, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 4.99 (t, 1 H, $J_{1,2} = J_{2,3}$ = 9.5 Hz, H-2), 4.88 (dd, 1 H, H-2'), 4.57 (dd, 1 H, $J_{5,6a}$ 3.1, $J_{6,6}$ 11 Hz, H-6a), 4.19 (dd, 1 H, $J_{5',6'a}$ 2.6, $J_{6',6'}$ 13 Hz, H-6'a), 4.11 (dd, 1 H, $J_{5,6b}$ 2.2 Hz, H-6b), 4.03 (dd, 1 H, $J_{5',6'b}$ 4.4 Hz, H-6'b), 3.99 (m, 1 H, H-5'), 3.56 (dd, 1 H, $J_{3,4}$ 8.8, $J_{4,5}$ 10.6 Hz, H-4), 2.09, 2.08, 2.07, 2.02, 2.01, and 2.00 (6 s, 3, 3, 3, 6, 3, and 6 H, 8 Ac).

*Anal.* Calc. for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. found: for **30A**, C, 51.04; H, 5.85; for **30B**, C, 50.96; H, 5.86.

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