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Carbohydrate Research 337 (2002) 161–166

CARBOHYDRATE RESEARCH

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Crystal and molecular structure of methyl 4-*O*-methyl-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside

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Received 30 April 2001; received in revised form 7 November 2001; accepted 7 November 2001

Abstract

The cellulose model compound methyl 4-*O*-methyl-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (**6**) was synthesised in high overall yield from methyl β-D-cellobioside. The compound was crystallised from methanol to give colourless prisms, and the crystal structure was determined. The monoclinic space group is $P2_1$ with $Z=2$ and unit cell parameters $a=6.6060$ (13), $b=14.074$ (3), $c=9.3180$ (19) Å, $\beta=108.95(3)°$. The structure was solved by direct methods and refined to $R=0.0286$ for 2528 reflections. Both glucopyranoses occur in the $^4C_1$ chair conformation with endocyclic bond angles in the range of standard values. The relative orientation of both units described by the interglycosidic torsional angles [ϕ (O-5′–C-1′–O-4–C-4) −89.1°, φ (C-1′–O-4–C-4–C-5) −152.0°] is responsible for the very flat shape of the molecule and is similar to those found in other cellodextrins. Different rotamers at the exocyclic hydroxymethyl group for both units are present. The hydroxymethyl group of the terminal glucose moiety displays a gauche–trans orientation, whereas the side chain of the reducing unit occurs in a gauche–gauche conformation. The solid state ^{13}C NMR spectrum of compound **6** exhibits all 14 carbon resonances. By using different cross polarisation times, the resonances of the two methyl groups and C-6 carbons can easily be distinguished. Distinct differences of the C-1 and C-4 chemical shifts in the solid and liquid states are found.

Keywords: Crystal structure; Cellulose; Methyl cellobioside; Solid state NMR

1. Introduction

X-ray diffraction methods have been used intensively to study the spatial arrangements and intricate hydrogen bonding patterns of cellulosic chains.[1] To complement the fibre diffraction techniques and clarify the ambiguities pertaining to the conformational orientation of the hydroxymethyl groups and the packing mode of cellulose II, various model glucosides have been investigated. Thus, the crystal and molecular structures of compounds such as cellobiose,[2] a cellobiose complex with NaI,[3] methyl β-cellobioside,[4] methyl β-cellotrioside[5] and β-cellotetraose[6] have been determined and compared with the data obtained from cellulose II.[7,8] In addition, model compounds have been used in conformational studies employing NMR spectroscopy or MD simulations.[9,10] For ongoing structural studies of cellulosic substrates, a 4′-*O*-methyl substituted methyl cellobioside was prepared. Herein we report on the chemical synthesis of methyl 4-*O*-methyl-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (**6**) and the determination of the crystal and molecular structure.

2. Results and discussion

For the synthesis of model compound **6**, known methyl β-cellobioside **1**[11] was selectively protected by reaction with α,α-dimethoxytoluene under acid catalysis

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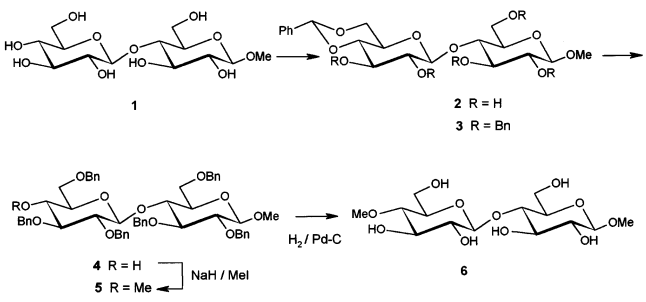
0008-6215/02/$ - see front matter
PII: S0008-6215(01)00299-3

in anhydrous *N*,*N*-dimethylformamide to give the corresponding 4′,6′-*O*-benzylidene compound **2**,[12] which was per-*O*-benzylated and subsequently treated with sodium cyanoborohydride–hydrogen chloride in dry THF to afford compound **4** in 77% yield.[13] Compound **4** reacted smoothly with methyl iodide–sodium hydride to produce the 4′-*O*-methyl ether derivative **5** in 95% yield (Scheme 1). Finally, the benzyl groups where removed by hydrogenolysis with 10% Pd–C as catalyst to give the title compound **6** in 97% yield, which readily crystallised from methanol.



Scheme 1.

Table 1
Crystallographic data for disaccharide **6**

Empirical formula	$C_{14}H_{26}O_{11}$
Formula weight	370.36
Crystal dimensions (mm)	$0.55 \times 0.35 \times 0.2$
Crystal system	monoclinic
Space group	$P2_1$
Temperature (K)	220(2)
Wavelength (Å)	1.54178
Unit cell dimensions	
a (Å)	6.6060 (13)
b (Å)	14.074 (3)
c (Å)	9.3180(19)
β (°)	108.95(3)
Cell volume (Å^3)	819.4(3)
Z	2
F(000)	396
Calculated density (g/cm^3)	1.501
Absorption coefficient (cm^{-1})	11.28
θ Range for data collection	5.02–70.08
Index ranges	$-8 \le h \le 7$, $-12 \le k \le 17$, $-4 \le l \le 11$
Reflections for cell	32 ($20.5 < \theta < 21.5°$)
Reflections collected	2712
Independent reflections	2566 ($R_{int} = 0.0132$)
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2566/1/331
Goodness-of-fit on F^2	0.877
Conventional R [$F > 4\sigma(F)$]	$R_1 = 0.0286$ for 2528 data
Weighted R (F^2 and all data)	$wR_2 = 0.0915$
Absolute structure parameter	−0.11(16)
Extinction coefficient	0.036(2)

Unambiguous ^{13}C NMR assignments of the spectrum of **6**, recorded in D_2O, were achieved via HMBC-measurements, which allowed the differentiation of the two methyl groups. The spectral data were in good agreement with those of other cellodextrins.[14] Compared to substitution by a β-glucopyranosyl residue, methyl ether substitution at C-4′ resulted in pronounced downfield-shifts of the ^{13}C NMR signals for C-4′ (79.94 ppm) and C-3′ (75.96 ppm), respectively.

Crystals were obtained from a saturated solution of **6** (5 mg) in MeOH (1 mL) at 40 °C and gradual cooling to room temperature. A colorless prism ($0.55 \times 0.35 \times 0.2$ mm) was selected for the measurements. The crystal data and details of the intensity-data collection are given in Table 1. X-ray diffraction data were collected at 220 K using a $\omega/2\theta$ scan mode. Unit-cell dimensions were obtained by a least-squares fit. The structure was solved by direct methods with SHELXL-97 and refined to a final $R = 0.0286$ for 2528 reflections (Table 2). The conformation of the molecule and the numbering of atoms is shown in Fig. 1.

Molecular geometry.—Both glucopyranosyl units occur in the $^4C_1$ chair conformation with endocyclic bond angles and bond lengths in the range of standard values (Tables 3 and 4). The observed values match those of cellobiose[2] and of methyl β-cellobioside, which was crystallised as a 1:1 complex with methanol.[4]

The effect of methyl substitution at O-4′ leads to a slight increase in the exocyclic C-4′–C-3′–O-3′ bond angle (112.54°) compared to the values found for cellobiose (108.1°) and methyl β-cellobioside (110.2°). The interglycosidic torsional angles [ϕ (O-5′–C-1′–O-4–C-4) − 89.1°, φ (C-1′–O-4–C-4–C-5) − 152.0°] are in close agreement with those found in other cellodextrins such as methyl β-cellotrioside.[5] Different rotamers at the exocyclic hydroxymethyl group for both units are present. Whereas the hydroxymethyl group of the terminal glucose moiety displays a clear *gt* conformation (as is thought to occur in cellulose II), that of the reducing unit occurs in a *gg* orientation.

The packing of the molecules in the unit cell is shown in Fig. 2. The disaccharides align in a near perpendicular relative orientation. Intermolecular hydrogen bonds extend from HO-2 to O-2′ and from HO-6 to O-2, leading to the *gg* orientation of the primary hydroxyl group at C-6 of the reducing glucopyranosyl unit. Intramolecular hydrogen-bonds extend from O-3(H)–O-5′ with a distance of 2.82 Å and from O-3(H)–O-6′ with a distance of 3.16 Å.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for disaccharide **6**

Atom	*x*	*y*	*z*	U_{eq}
C-1	7102(3)	3238(2)	3645(2)	25(1)
O-1	6714(3)	3494(1)	2140(2)	32(1)
C-1M	8574(5)	3457(2)	1693(3)	42(1)
C-2	5044(3)	3395(2)	4015(2)	25(1)
O-2	4453(3)	4369(1)	3899(2)	35(1)
C-3	5314(3)	3050(2)	5606(2)	27(1)
O-3	3254(3)	3103(2)	5771(2)	41(1)
C-4	6237(3)	2052(2)	5872(2)	24(1)
O-4	7020(2)	1818(1)	7462(2)	24(1)
C-5	8186(3)	1946(2)	5328(2)	23(1)
O-5	7609(2)	2259(1)	3787(2)	25(1)
C-6	8977(3)	938(2)	5352(2)	28(1)
O-6	7475(3)	349(1)	4306(2)	36(1)
C-1′	5554(3)	1445(2)	8089(2)	22(1)
C-2′	6731(3)	827(2)	9446(2)	22(1)
O-2′	7808(2)	68(1)	9001(2)	26(1)
C-3′	5093(3)	414(2)	10114(2)	23(1)
O-3′	6081(3)	−171(1)	11389(2)	28(1)
C-4′	3694(3)	1185(2)	10455(2)	22(1)
O-4′	1853(2)	767(1)	10700(2)	29(1)
C-4′M	1987(4)	628(3)	12235(3)	43(1)
C-5′	2857(3)	1874(2)	9125(2)	22(1)
O-5′	4569(2)	2200(1)	8619(2)	24(1)
C-6′	1809(4)	2743(2)	9522(2)	29(1)
O-6′	1015(3)	3358(1)	8267(2)	32(1)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

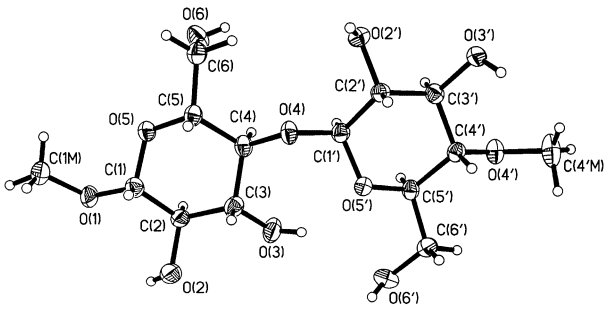


Fig. 1. Perspective view and atom labelling of methyl 4′-*O*-methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside **6**.

The solid state ^{13}C NMR spectrum using cross polarisation and rotation at the magic angle spinning (CP-MAS, Fig. 3) displays all 14 expected carbon resonances. Furthermore, the linewidth of 18 Hz is extraordinarily narrow and TPPM decoupling is required. Only one of the C-6 carbons has a rather broad resonance (56 Hz) which is subject to further investigations. As indicated in Fig. 3 and Table 4, the following lines can be assigned unambiguously: C-1,1′ at 105.3 and 104.9 ppm, C-4,4′ at 83.6 and 80.7 ppm, C-6,6′ signals

Table 3
Selected bond-lengths and their standard deviation for non-hydrogen atoms

Bond lengths (Å)	
C-1–O-1	1.388(2)
C-1–O-5	1.414(3)
C-1–C-2	1.524(3)
O-1–C-1M	1.421(3)
C-2–O-2	1.420(3)
C-2–C-3	1.514(3)
C-3–O-3	1.420(3)
C-3–C-4	1.519(3)
C-4–O-4	1.440(2)
C-4–C-5	1.536(3)
O-4–C-1′	1.386(2)
C-5–O-5	1.430(2)
C-5–C-6	1.509(3)
C-6–O-6	1.412(3)
C-1′–O-5′	1.415(3)
C-1′–C-2′	1.524(3)
C-2′–O-2′	1.417(3)
C-2′–C-3′	1.528(3)
C-3′–O-3′	1.418(2)
C-3′–C-4′	1.525(3)
C-4′–O-4′	1.434(2)
C-4′–C-5′	1.528(3)
O-4′–C-4′M	1.417(3)
C-5′–O-5′	1.435(2)
C-5′–C-6′	1.510(3)
C-6′–O-6′	1.411(3)

Table 4
Selected geometric and spectroscopic parameters for cellobiose, methyl cellobioside and disaccharide **6**

Parameter	Cellobiose[2]	Me cellobioside[4] [a]	**6**
Selected bond angles (°)			
C-1′–O-4–C-4	116.1	115.8	117.0
C-1–O-1–OMe		113.1	113.1
C-4′–C-3′–O-3′	108.1	110.2	112.5
Linkage torsion angles (°)			
ϕ (O-5′–C-1′–O-4–C-4)	−76.3	−88.9	−89.1
ψ (C-1′–O-4–C-4–C-5)	−132.3	−160.7	−152.0
Hydroxymethyl group torsion angles (°)			
χ (O-5–C-5–C-6–O-6)	+65.5	−55.1	−54.3
(O-5′–C-5′–C-6′–O-6′)	+48.7	+52.4	+59.0
Chemical shift (ppm) for carbon atom			
C-1 or C-1′	104.9	106.5	105.3/104.9
C-4 or C-4′	84.9	85.5	83.6/80.7
C-6 or C-6′			63.3/59.9

[a] The compound crystallised as solvate complex with methanol.

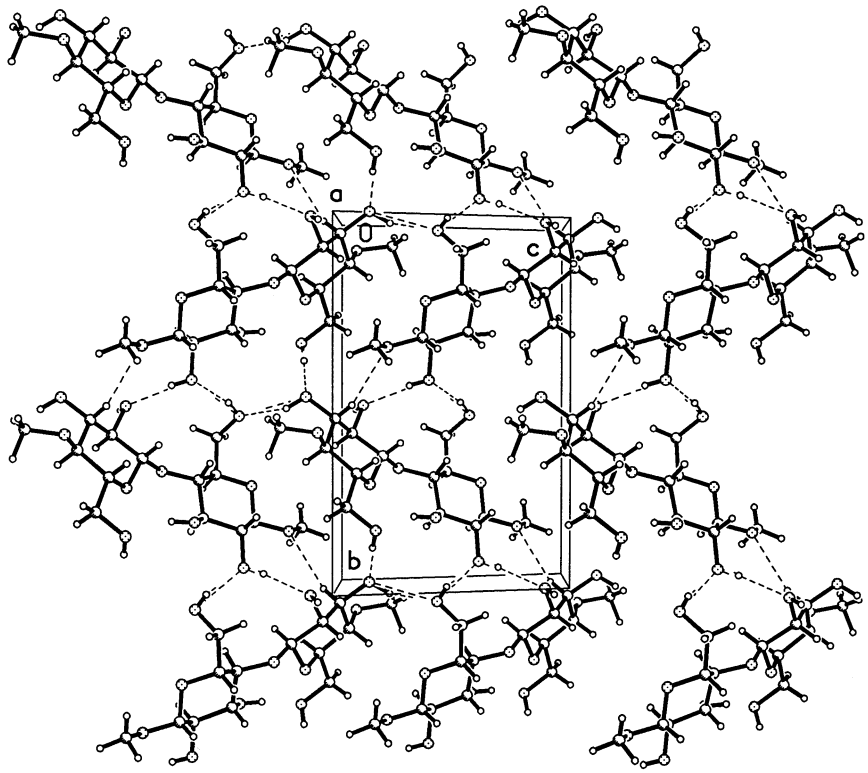


Fig. 2. View of packing mode and unit cell of compound **6**. Hydrogen bonds are drawn in dashed lines.

at 63.3 and 59.9 ppm and $-OCH_3$ at 63.8 and 58.4 ppm. The discrimination between C-6 and $-OCH_3$ resonances can easily be achieved by comparing the CPMAS spectra with 100 μs and 1 ms cross polarisation times. For the shorter cross polarisation time, the $-OCH_3$ signals have only about 50% intensity compared to C-6 because of the methyl group rotation. The observed chemical shift difference between the C-6 and C-6′ signals would be consistent with the results by Horii, indicating a range of 60–62 ppm for CH_2OH carbons in the gauche–gauche orientation versus 62.5–64.5 ppm for those occurring in the gauche–trans conformation.[15] It is worth noting that substantial differences of the chemical shifts for the carbons C-1 and C-4 are observed in the liquid and solid state NMR spectra. The chemical shifts of carbons involved in the glycosidic linkage are sensitive to conformational changes, which in contrast to the solid state become motionally averaged in solution. Further NMR experiments with labelled model compounds will be performed in order to obtain unambiguous assignments for all carbons and thus provide a reliable model system for the interpretation of solid state NMR-spectroscopic studies of native and regenerated celluloses.[16]

3. Experimental

General methods.—Synthetic methods were as described recently.[17] X-ray diffraction data were collected with a Stoe Stadi-4 diffractometer.

The NMR measurements were recorded on a Bruker DMX400 spectrometer, using a double channel CP-MAS probehead. The spinning frequency of the 4 mm ZrO_2-CRAMPS-rotor was 12,500 Hz and was stabilised to ± 2 Hz. The ^{13}C CPMAS spectra were acquired at a radio frequency of 100.3 MHz. The 90° proton pulse was set to 2.5 μs, a ^{13}C B_1-field of 50 kHz during the ramped (50% ramp on proton channel) CP sequence with a mixing time of 1 ms or 100 μs were used. The TPPM-sequence[18] with a flip angle of 168.5° (pulse length 4.5 μs) and a phase shift of 10° was applied to decouple the protons during the acquisition time.

Methyl 4,6-O-benzylidene-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (**2**).—Methyl cellobioside **1**

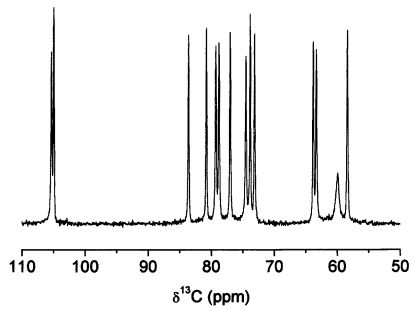


Fig. 3. CPMAS NMR spectrum of disaccharide **6**.

(1.00 g, 2.81 mmol), α,α-dimethoxytoluene (0.63 mL, 4.21 mmol), *p*-toluene–sulfonic acid (0.05 g) and anhyd DMF (50 mL) were stirred at rt for 3 days. A second portion of α,α-dimethoxytoluene (0.42 mL, 2.81 mmol) was added and the mixture was heated to 50 °C under reduced pressure (50 mbar) for 2 h. After addition of triethylamine (3 mL), the reaction mixture was evaporated. Column chromatography of the residue (10:1 EtOAc–MeOH) gave **2** as colourless crystals (0.782 g, 63%), mp 150–152 °C, lit. 151–152 °C (EtOH);[12] $[\alpha]_D^{20}$ −32° (*c* 1.2, MeOH), lit. $[\alpha]_D^{20}$ −37° (*c* 1.9, DMF).[12] ^{1}H NMR (CD_3OD): δ 7.35–7.58 (m, 5 H, Ph), 5.63 (s, 1 H, C*H*Ph), 4.61 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.35 (dd, 1 H, $J_{5',6b'}$ 3.7, $J_{6a',6b'}$ 10.2 Hz, H-6b′), 4.25 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.90–3.96 (m, 1 H, H-6b), 3.88 (dd, 1 H, $J_{5',6a'}$ 3.9 Hz, H-6a′), 3.83 (dd, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.7 Hz, H-4), 3.60–3.75 (m, 2 H, H-5, H-3′), 3.50–3.57 (m, 5 H, H-5′, 1-OMe, H-3, H-4′), 3.30–3.50 (m, 2 H, H-6a, H-2′) and 3.28 (dd, 1 H, $J_{2,3}$ 8.3 Hz, H-2).

Methyl 2,3-di-O-*benzyl-4,6*-O-*benzylidene-β*-D-*glucopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**3**).—Sodium hydride (3.83 g, 160 mmol) was added to a solution of **2** (7.10 g, 16.0 mmol) in anhyd DMF (150 mL). The mixture was stirred under argon for 1 h. Benzyl bromide (19.0 mL, 160 mmol) was added and the mixture was stirred overnight at rt. The solution was poured onto satd aq NH_4Cl and extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and evaporated. Chromatography (toluene→7:1 toluene–EtOAc) of the crude product gave **3** as colourless crystals (9.95 g, 71%), mp 144–146 °C (EtOH), lit. 143–145 °C (4:1 hexane–EtOAc);[13] $[\alpha]_D^{20}$ +1° (*c* 0.9, $CHCl_3$), lit. $[\alpha]_D^{20}$ +4° (*c* 2.1, $CHCl_3$).[13] ^{1}H NMR data ($CDCl_3$): δ 7.22–7.50 (m, 30 H, 6 × Ph), 5.48 (s, 1 H, CHPh), 4.68–4.91 (m, 8 H, CH_2Ph), 4.58 (d, 1 H, *J* 12.1 Hz, CH_2Ph), 4.53 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.38 (d, 1 H, *J* 12.1 Hz, CH_2Ph), 4.28 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.82 (dd, 1 H, $J_{5',6b'}$ 5.1, $J_{6a',6b'}$ 10.6 Hz, H-6b′), 3.98 (dd, 1 H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.2 Hz, H-4), 3.83 (dd, 1 H, $J_{5,6b}$ 3.7, $J_{6a,6b}$ 10.8 Hz, H-6b), 3.67 (dd, 1 H, $J_{5,6a}$ 1.2 Hz, H-6a), 3.30–3.61 (m, 10 H, H-3′, H-4′, 1-OMe, H-3, H-6a′, H-2, H-2′, H-5) and 3.09–3.18 (m, 1 H, H-5′).

Methyl 2,3,6-tri-O-*benzyl-β*-D-*glucopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**4**).—A solution of HCl in anhyd Et_2O (2.5 M) was added dropwise to a solution of **3** (4.72 g, 5.35 mmol) and $NaCNBH_3$ (3.36 g, 53.5 mmol) in dry THF (100 mL) containing powdered 3 Å molecular sieves, until the evolution of gas ceased. The molecular sieves were filtered off after 30 min, and EtOAc was added. The mixture was extracted twice with satd $NaHCO_3$ and once with brine. The organic layer was dried over $MgSO_4$ and evaporated. Column chromatography (9:1 toluene–EtOAc) yielded a **4** as colourless syrup (3.63 g, 77%); $[\alpha]_D^{20}$ +8° (*c* 0.4, $CHCl_3$), lit. $[\alpha]_D^{20}$ +7° (*c* 1.5, $CHCl_3$).[13] ^{1}H NMR data ($CDCl_3$): δ 7.19–7.36 (m, 30 H, 6 × Ph), 4.93 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.67–4.87 (m, 7 H, CH_2Ph), 4.59 (d, 1 H, *J* 12.1 Hz, CH_2Ph), 4.47 (d, 1 H, $J_{1',2'}$ 7.2 Hz, H-1′), 4.40–4.46 (m, 3 H, CH_2Ph), 4.27 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.96 (dd, 1 H, $J_{3,4}$ 9.1, $J_{4,5}$ 9.1 Hz, H-4), 3.82 (dd, 1 H, $J_{5,6b}$ 4.2, $J_{6a,6b}$ 11.0 Hz, H-6b), 3.70 (dd, 1 H, $J_{5,6a}$ 2.2, Hz, H-6a), 3.46–3.64 (m, 7 H, H-6a′, H-6b′, 1-OMe, H-4′, H-3), 3.29–3.41 (m, 4 H, H-2, H-5, H-3′, H-2′), 3.20–3.28 (m, 1 H, H-5′) and 2.86 (d, 1 H, $J_{4',OH}$ 1.5 Hz, OH).

Methyl 2,3,6-tri-O-*benzyl-4*-O-*methyl-β*-D-*glucopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**5**).—Sodium hydride (0.337 g, 14.1 mmol) was added to a solution of **4** (6.22 g, 7.03 mmol) in dry THF (150 mL). The mixture was stirred under argon for 1 h. Methyl iodide (2.19 mL, 35.1 mmol) was added, and the mixture was stirred overnight at rt. The reaction mixture was poured onto aq satd NH_4Cl and extracted with EtOAc (100 mL). The organic layer was dried over $MgSO_4$ and concentrated. Chromatography of the crude product on silica gel (toluene→7:1 toluene–EtOAc) gave **5** as colourless syrup (5.99 g, 95%); $[\alpha]_D^{20}$ +23° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.16–7.35 (m, 30 H, 6 × Ph), 5.03 (d, 1 H, *J* 11.5 Hz, CH_2), 4.65–4.85 (m, 9 H, CH_2), 4.58 (d, 1 H, *J* 12.1 Hz, CH_2), 4.46 (d, 1 H, $J_{1',2'}$ 7.1 Hz, H-1′), 4.43 (d, 1 H, *J* 11.5 Hz, CH_2), 4.27 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.99 (dd, 1 H, $J_{3,4}$ 9.3, $J_{4,5}$ 9.3 Hz, H-4), 3.81 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.64–3.72 (m, 2 H, H-6b, H-6a′), 3.49–3.60 (m, 5 H, H-3, 1-OMe, H-6b′), 3.47 (s, 3 H, 4′-OMe), 3.28–3.45 (m, 5 H, H-3′, H-2, H-5, H-4′, H-2′) and 3.15–3.20 (m, 1 H, H-5′). Anal. Calcd for $C_{55}H_{62}O_{11}$: C, 73.47; H, 6.95. Found: C, 73.21; H, 6.80.

Methyl 4-O-*methyl-β*-D-*glucopyranosyl-(1→4)-β*-D-*glucopyranoside* (**6**).—A solution of **5** (5.90 g, 6.56 mmol) in dry MeOH (100 mL) was hydrogenated at rt in the presence of 10% Pd–C (0.25 g) for 15 h at atmospheric pressure. The catalyst was removed by filtration, and the filtrate was concentrated to yield **6** as colourless crystals (2.35 g, 97%); mp 196–198 °C (MeOH); $[\alpha]_D^{20}$ −11° (*c* 0.4, water). ^{1}H NMR (D_2O): δ 4.47 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.39 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.98 (dd, 1 H, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 12.3 Hz, H-6a), 3.90 (dd, 1 H, $J_{5',6a'}$ 2.3 Hz, H-6a′), 3.89 (dd, 1 H, $J_{5,6b}$ 4.6 Hz, H-6b), 3.73 (dd, 1 H, $J_{5',6b'}$ 5.3, $J_{6a',6b'}$ 12.4 Hz, H-6b′), 3.56–3.63 (m, 7 H, H-5, H-4, H-3, H-3′, 1-OMe), 3.55 (s, 3 H, 4′-OMe), 3.47 (ddd, 1 H, $J_{4',5'}$ 9.5 Hz, H-5′), 3.25–3.40 (m, 2 H, H-2′, H-2), 3.22 (dd, 1 H, $J_{3',4'}$ 9.5 Hz, H-4′); ^{13}C NMR (D_2O): δ 103.87 (C-1), 103.27 (C-1′), 79.94 (C-4′), 79.42 (C-4), 75.96 (C-3′), 75.79 (C-5), 75.56 (C-5′), 75.11 (C-3), 73.97 (C-2′), 73.68 (C-2), 61.11 (C-6′), 60.83 (C-6, 4′-Me) and 58.02 (1-Me). IR (KBr): 3440 (b), 2916 (s), 2883 (s), 1620 (w), 1452 (m), 1451 (m), 1363 (m), 1165 (s), 1107 (s), 1035 (s), 993 (s). Anal. Calcd for $C_{14}H_{26}O_{11}$: C, 45.40; H, 7.08. Found: C, 45.34; H, 6.80.

4. Supplementary material

The data were deposited at the Cambridge Structural database (Accession number CCDC 172127). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Technical assistance by Maria Hobel is gratefully acknowledged. The authors also thank Dr Andreas Hofinger and Dr Michael Puchberger for recording NMR spectra.

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