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CHIRAL MACROCYCLIC COMPOUNDS FROM LACTOSE DERIVATIVES*

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ABSTRACT

The reaction of benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-isopropylidene-β-lactoside with 1,11-ditosyloxy-3,6,9-trioxaundecane gave benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-isopropylidene-3,2′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (**2**, 47%). Acid hydrolysis of **2** and condensation of the product with 1,14-ditosyloxy-3,6,9,12-tetraoxatetradecane afforded benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-(3,6,9,12-tetraoxatetradecane-1,14-diyl)-3,2′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (29%). Similarly, the reaction of benzyl 2,6,2′,4′,6′-penta-*O*-benzyl-β-lactoside with $Ts[OCH_2CH_2]_4OTs$ gave benzyl 2,6,2′,4′,6′-penta-*O*-benzyl-3,3′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (78%). ^{1}H-N.m.r. spectroscopy has been used to study the formation of host–guest complexes with some of these macrocyclic compounds and benzyl ammonium thiocyanate.

INTRODUCTION

The synthesis of chiral macrocyclic compounds is a topic of current interest[1–3]. Chirality and rigidity of the host molecules seem to be necessary in order to achieve chiral recognition of guest molecules[4,5]. Monosaccharides and alditols have been used in the synthesis of chiral crown ethers[6–8] and we have prepared new chiral macrocyclic polyhydroxyethers from cyclomalto-hexaose and -heptaose (α- and β-cyclodextrins)[9]. We now report the synthesis of new chiral macrocyclic ethers from partially benzylated benzyl lactoside derivatives[10,11] bearing an unsubstituted hydroxyl group in each monosaccharide unit. A polyethylene glycol linkage between the units has been introduced in order to obtain more rigid, chiral crown ethers than those synthesised using monosaccharide and alditol derivatives.

*Dedicated to Professor N. K. Kochetkov.

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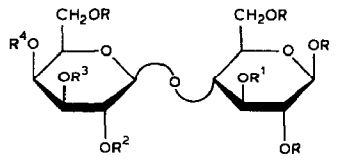
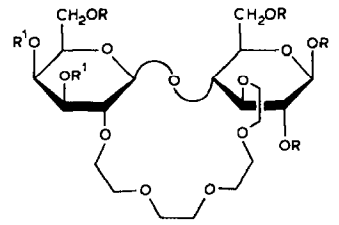
RESULTS AND DISCUSSION

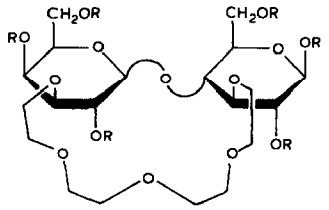
The reaction of benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-isopropylidene-β-lactoside[11] (**1**) with 1,11-ditosyloxy-3,6,9-trioxaundecane ($Ts[OCH_2CH_2]_4OTs$) in the presence of potassium hydroxide gave, after column chromatography, the chiral crown ether benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-isopropylidene-3,2′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (**2**, 47%). The mass spectrum of **2** contained a peak for M^+ at *m/z* 900, and the ^1H- and ^{13}C-n.m.r. spectra contained signals for the tetraethylene glycol moiety at δ 3.60 (m) and a group of signals between δ 68.3 and 70.9. Acid hydrolysis of **2** afforded benzyl 2,6,6′-tri-*O*-benzyl-3,2′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (**3**). Hydrogenolysis of **3** gave 3,2′-*O*-(3,6,9-trioxaundecane-1,11-diyl)lactose (**4**), acetylation of which yielded the hexaacetate **5**. Reaction of **3** with 1,14-ditosyloxy-3,6,9,12-tetraoxatetradecane ($TsO[CH_2CH_2O]_5Ts$) in the presence of sodium hydride afforded benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-(3,6,9,12-tetraoxatetradecane-1,14-diyl)-3,2′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (**6**, 29%). The ^1H-n.m.r. spectrum of **6** showed three well-defined, non-overlapping regions assigned to the aromatic, benzylic, and anomeric, methine, and methylene protons, in the ratios 20:10:48 in agreement with the proposed structure.



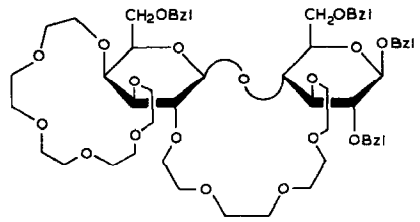
1 R = Bzl, $R^1 = R^2 = H, R^3 = R^4 = CMe_2$
7 R = $R^2 = R^4$ = Bzl, $R^1 = R^3 = H$
9 R = $R^1 = R^2 = R^4 = H, R^3$ = Allyl
10 R = $R^2 = R^4$ = Bzl, $R^1 = H, R^3$ = Allyl



2 R = Bzl, $R^1 = CMe_2$
3 R = Bzl, $R^1 = H$
4 R = $R^1 = H$ (α, β)
5 R = R^1 = Ac (α, β)



11 R = Bzl
12 R = H (α,β)
13 R = Ac (α,β)



6

Benzyl 2,6,2′,4′,6′-penta-*O*-benzyl-β-lactoside (**7**) has been isolated[10] as a product of partial benzylation of benzyl β-lactoside (**8**) and characterised as the corresponding 3,3′-diacetate. We prepared **7** by allylation of benzyl β-lactoside (**8**), *via* stannylation with dibutyltin oxide followed by treatment with allyl bromide, to give benzyl 3′-*O*-allyl-β-lactoside (**9**, 66%). Partial benzylation of **9** under phase-transfer conditions afforded benzyl 3′-*O*-allyl-2,6,2′,4′,6′-penta-*O*-benzyl-β-lactoside (**10**, 32%), and deallylation then gave 41% of **7**. Reaction of **7** with $TsO[CH_2CH_2O]_4Ts$ in the presence of potassium hydroxide gave benzyl 2,6,2′,4′,6′-penta-*O*-benzyl-3,3′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (**11**, 10%). The f.a.b.-mass spectrum of **11** contained a peak at *m/z* 1063 for [M + Na^+], and the ^1H- and ^{13}C-n.m.r. spectra contained signals (m) for the tetraethylene glycol moiety between δ 3.35 and 3.78 and a group of signals between δ 68.5 and 73.1, respectively. F.a.b.-m.s. of **11** in the presence of an equimolecular mixture of Li, Na, K, Rb, and Cs salts indicated[12,13] that **11** showed the best binding ability for Na^+. Hence, when sodium hydroxide was used instead of potassium hydroxide in the reaction of **7** with $TsO[CH_2CH_2O]_4Ts$, 78% of **11** was obtained, indicating the better template effect of Na^+ than of K^+. Hydrogenolysis of **11** gave **12**, acetylation of which afforded **13**.

Evidence for host–guest complex formation of **2, 6,** and **11** with benzyl ammonium thiocyanate was obtained by ^1H-n.m.r. spectroscopy. The chemical shifts of the signals in the spectra of solutions of **2, 6,** and **11** in $CDCl_3$ showed drastic changes when recorded after the addition of benzyl ammonium thiocyanate. Integration of the signals for the benzylic protons of the guest molecule and the methylene and methine protons of the hosts indicated the formation of a 1:3 host–guest complex for **2**, a 1:2 complex for **6**, and a 1:2 complex for **11**. Similar experiments with the α,β-acetate **5** revealed a 1:1 complex. The spectrum of benzyl 2,3,6,2′,6′-penta-*O*-benzyl-3′,4′-*O*-isopropylidene-β-lactoside did not show any change under these conditions.

The synthesis of cyclic polyethers from other partially substituted disaccharides, using polyethylene glycol chains of different lengths, and the study of the relationship between the formation of the macrocyclic compounds and the conformation of the disaccharide glycosidic bond is under investigation.

EXPERIMENTAL

General methods. — All cyclisation reactions were carried out under argon. T.l.c. was performed on Silica Gel GF_{254} (Merck) with detection by charring with sulfuric acid. Flash column chromatography was performed on Merck silica gel (230–400 mesh). ^1H- (300 MHz) and ^{13}C-n.m.r. spectra (75 MHz) were recorded with a Varian XL-300 spectrometer. Optical rotations were determined with a Perkin–Elmer 141 polarimeter. The f.a.b.-mass spectra were obtained by using a polyethylene glycol matrix and an MS-50 Krator instrument fitted with a 1.2T magnet, having a mass range up to 1.300 u.m.a., and an f.a.b. 11NF Ion Tech atom

gun. The e.i.-mass spectra were recorded with a Hitachi–Perkin–Elmer RMU-6MG instrument.

The ^{1}H-n.m.r. experiments on the formation of host–guest complexes were carried out using 0.01M solutions of the host molecules in $CDCl_3$.

Benzyl 2,6,6′-tri-O-benzyl-3′,4′-O-isopropylidene-3,2′-O-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (**2**). — A stirred mixture of benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-isopropylidene-β-lactoside[11] (**1**; 0.7 g, 0.9 mmol) and potassium hydroxide (1.09 g, 19.4 mmol) in dry tetrahydrofuran (10 mL) was heated at 45° for 15 min. The temperature was then raised to 65° and a solution of $TsO[CH_2CH_2O]_4Ts$ (1.17 g, 2.34 mmol) in dry tetrahydrofuran (8 mL) was added dropwise during 4 h. Stirring was continued for 18 h, and the mixture was then cooled, filtered, and concentrated. Flash column chromatography (4:1 chloroform–ethyl acetate) of the residue gave **2** (0.4 g, 47%) as a syrup, $[\alpha]_D^{25}$ −17° (*c* 0.3, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 7.20–7.40 (m, 20 H, 4 Ph), 4.52 (d, 1 H, H-1), 4.45 (d, 1 H, H-1′); ^{13}C, 138.4, 138.3, 138.2, 137.4 (C-ipso), 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, (aromatic), 109.6 (*C*Me$_2$), 102.3, 102.4 (C-1,1′), 82.0, 81.8, 78.8, 75.6, 74.9, 74.6, 73.4, 73.2, 73.0, 71.9, 71.6, 71.0, 70.8, 70.6, 70.5, 69.3, 69.1, 68.4, 27.2, and 26.0 p.p.m.

Anal. Calc. for $C_{51}H_{64}O_{14}$: C, 68.00; H, 7.11. Found: C, 67.79; H, 7.35.

Benzyl 2,6,6′-tri-O-benzyl-3,2′-O-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside (**3**). — To a stirred solution of **2** (1.35 g, 15 mmol) in ethanol (100 mL) was added aqueous 70% acetic acid (25 mL). The solution was heated to 75° for 48 h, then cooled, and concentrated. Flash column chromatography (20:1 chloroform–methanol) of the residue yielded **3** (1.1 g, 85%) as a syrup, $[\alpha]_D^{25}$ −17° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 7.26–7.35 (m, 20 H, Ph), 4.45 (d, 1 H, anomeric), 4.35 (d, 1 H, anomeric); ^{13}C, 138.3, 137.6 (C-ipso), 128.3, 127.9, 127.5 (aromatic), 102.6, 101.2 (C-1,1′), 83.2, 81.9, 79.3, 74.6, 73.5, 72.5, 72.3, 71.6, 70.9, 70.4, 69.6, 69.2, and 68.8 p.p.m.

Anal. Calc. for $C_{48}H_{60}O_{14} \cdot 2\ H_2O$: C, 64.28; H, 7.14. Found: C, 64.43; H, 7.07.

3,2′-O-(3,6,9-Trioxaundecane-1,11-diyl)lactose (**4**). — A solution of **3** (0.290 g, 0.34 mmol) in ethanol (20 mL) was hydrogenated over 10% Pd/C (330 mg) overnight, then filtered, and concentrated to give **4** (140 mg, 83%) as a syrup, $[\alpha]_D^{25}$ +25° (*c* 0.9, methanol). N.m.r. data (CD_3OD): ^{13}C, 101.9, 101.7 (C-1′α,β), 98.0, 93.7 (C-1α,β), 82.6, 80.5, 80.4, 80.3, 77.3, 77.0, 76.8, 75.6, 74.9, 74.8, 74.2, 72.9, 72.8, 72.6, 72.4, 72.2, 71.8, 71.7, 71.5, 71.2, 70.6, and 62.8, 62.1, 61.8 p.p.m. (C-6,6′α,β).

Conventional treatment of **4** (140 mg) with acetic anhydride (1 mL) in pyridine (1 mL) gave, after column chromatography (ethyl acetate), the hexaacetate **5** (200 mg) as a syrup, $[\alpha]_D^{25}$ +25° (*c* 0.3, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 6.23 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1α), 5.63 (d, 1 H, *J* 7.9 Hz, H-1β), 5.36 (d, 1 H, $J_{3',4'}$ 3.5 Hz, H-4′α), 5.34 (d, 1 H, *J* 3.4 Hz, H-4′β), 4.96 (dd, 1 H, $J_{3',2'}$ 9.71 Hz, H-3′α), 4.66 (d, 1 H, $J_{1',2'}$ 7.64 Hz, H-1′α), 4.59 (d, 1 H, $J_{1',2'}$ 7.64 Hz, H-1′β),

4.56–4.49 (H-6′α,β), 4.34–4.29 (dd, H-6α,β), 4.20–3.55 (H-3,4,5,2′α,β and -CH_2-O), 2.15–2.03 (12 s, 6 Ac); ^{13}C, 170.0, 169.6, 169.3 (CO), 102.6, 102.4 (C-1′, *α,β-galacto*), 92.4, 90.0 (C-1, *α,β-gluco*), 79.2, 77.1, 76.8, 76.6, 76.4, 76.3, 75.0, 73.5, 73.4, 72.6, 72.3, 72.1, 71.7, 71.3, 70.9, 67.9, 63.1, 63.0, 61.4, and 20.28 (Ac) p.p.m..

Anal. Calc. for $C_{32}H_{48}O_{20}$: C, 51.06; H, 6.42. Found: C, 50.74; H, 6.62.

*Benzyl 2,6,6′-tri-*O*-benzyl-3′,4′-*O*-(3,6,9,12-tetraoxatetradecane-1,14-diyl)-3,2′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside* (**6**). — A suspension of NaH (110 mg, 458 mmol) in dry tetrahydrofuran (11 mL) was boiled under reflux and stirred under argon as a solution of **3** (470 mg, 0.55 mmol) and $TsO[CH_2CH_2O]_5Ts$ (328 mg, 0.60 mmol) in dry tetrahydrofuran (33 mL) was added dropwise during 10 h. After stirring for 21 h, the suspension was cooled to room temperature, quenched by the addition of several drops of water, and then concentrated *in vacuo*. A solution of the residue in dichloromethane (10 mL) was washed with 0.2M hydrochloric acid and saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated. Column chromatography (16:1 chloroform–methanol) of the residue afforded **6** (166 mg, 29%) as a syrup, $[\alpha]_D^{25}$ −20° (*c* 0.5, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 7.20–7.4 (m, 20 H, 5 Ph), 5.0–4.34 (10 H, 4 $PhCH_2$ and H-1,1′), 4.0–3.1 (48 H); ^{13}C, 138.5, 138.2, 137.5 (C-ipso), 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4 (aromatic), 102.4, 101.0 (C-1,1′), 83.4, 82.2, 81.4, 78.2, 75.3, 75.2, 74.7, 74.3, 73.4, 73.1, 72.2, 71.5, 71.4 (d), 71.2, 71.0, 70.9 (d), 70.7, 70.6 (d), 70.4, 70.3, 70.2, 70.0, 69.8, and 68.7 (d). Mass spectrum (f.a.b.): *m/z* 1086 $[M + Na]^+$ (74%).

Anal. Calc. for $C_{58}H_{78}O_{18}$: C, 65.54; H, 7.34. Found: C, 65.36; H, 7.70.

*Benzyl 3′-*O*-allyl-β-lactoside* (**9**). — A stirred mixture of benzyl β-lactoside (**8**; 5 g, 11.6 mmol), dibutyltin oxide (3.75 g, 15.06 mmol), and molecular sieves (3 Å, 15 g) in acetonitrile (250 mL) was boiled under reflux overnight. Tetrabutylammonium bromide (1.85 g, 5.74 mmol) and allyl bromide (50.0 g, 0.41 mol) were then added and heating was continued for 6 h. The solution was cooled, filtered, and concentrated. Column chromatography (6:1 ethyl acetate–methanol) of the residue gave **9** (3.6 g, 66%), m.p. 159–160°, $[\alpha]_D^{25}$ −18° (*c* 0.6, methanol). N.m.r. data (CD_3OD): ^{1}H, δ 7.20–7.40 (m, 5 H, Ph), 6.00 (m, 1 H, allyl), 5.34 (m, 1 H, allyl), 5.17 (m, 1 H, allyl), 4.40 (d, 2 H, H-1,1′); ^{13}C, 138.9 (C-ipso), 136.4 (*C*H=), 129.2, 129.1, 128.6 (aromatic), 117.5 (CH_2=), 104.9, 103.1 (C-1,1′), 81.9, 80.6, 76.8, 76.4, 76.3, 74.7, 71.8, 71.7, 71.5, 66.9 and 62.4, 61.9 (C-6,6′).

Anal. Calc. for $C_{22}H_{32}O_{11}$: C, 55.92; H, 6.82. Found: C, 56.19; H, 6.90.

*Benzyl 3′-*O*-allyl-2,6,2′,4′,6′-penta-*O*-benzyl-β-lactoside* (**10**). — A mixture of **9** (1.51 g, 3.20 mmol), benzene (60 mL), aqueous 20% sodium hydroxide (30 mL), tetrabutylammonium hydrogensulfate (0.8 g), and benzyl bromide (4.0 g, 23.6 mmol) was vigorously stirred for 32 h. The organic layer was then separated, washed with water, M sulfuric acid, and water, dried (Na_2SO_4), and concentrated. Column chromatography (7:3 hexane–ethyl acetate) of the residue gave **10** (0.93 g, 32%) as a syrup, $[\alpha]_D^{25}$ −14° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 7.20–

7.40 (m, 30 H, 6 Ph), 5.92 (m, 1 H, allyl), 5.32 (m, 1 H, allyl), 5.18 (m, 1 H, allyl); ^{13}C, 138.8, 138.4, 138.3, 138.2, 137.5 (C-ipso), 134.6 (*C*H=), 128.4–127.3 (aromatic), 116.9 (*C*H_2=) 103.7, 101.9 (C-1,1'), 82.2, 81.7, 81.4, 78.8, 75.4, 75.2, 74.7, 74.5, 74.2, 73.7, 73.6, 73.0, 72.9, 71.7, 71.0, 68.7, and 68.6 p.p.m.

Anal. Calc. for $C_{57}H_{62}O_{11}$: C, 74.16; H, 6.77. Found: C, 74.18; H, 7.10.

Benzyl 2,6,2',4',6'-penta-O-*benzyl-β-lactoside* (**7**). — A stirred mixture of **10** (1.47 g, 1.60 mmol), 10% Pd/C (70 mg), and toluene-*p*-sulphonic acid (50 mg) in ethanol–water (5:1, 24 mL) was boiled under reflux for 44 h, and then filtered through Celite which was washed with hot chloroform (100 mL). The combined filtrate and washings were washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (4:1 hexane–ethyl acetate) of the residue yielded **7** (0.58 g, 41%) as a syrup, $[\alpha]_D^{25}$ −10° (*c* 0.9, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 7.15–7.40 (m, 30 H, 6 Ph), 5.00–4.20 (m), 3.9–3.10 (m); ^{13}C, 138.7, 138.6, 138.2, 138.0, 137.9, 137.4 (C-ipso), 128.7–127.0 (aromatic), 103.5, 101.8 (C-1,1'), 81.3, 79.3, 75.4, 75.1, 75.0, 74.9, 74.6, 74.1, 73.9, 73.7, 73.5, 73.1, 70.9, 68.6, and 68.3 p.p.m.

Anal. Calc. for $C_{54}H_{58}O_{11}$: C, 73.44; H, 6.62. Found: C, 72.99; H, 6.93.

Benzyl 2,6,2',4',6'-penta-O-*benzyl-3,3'*-O-*(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside* (**11**). — (*a*) A stirred mixture of **7** (0.52 g, 0.59 mmol) and sodium hydroxide (0.6 g, 15 mmol) in dry tetrahydrofuran (17 mL) was heated at 50° for 20 min. The temperature was then raised to 70° and a solution of $TsO[CH_2CH_2O]_4Ts$ (0.6 g, 1.19 mmol) in dry tetrahydrofuran (20 mL) was added dropwise during 7 h. Stirring was continued for 24 h, and the mixture was then cooled, filtered, and concentrated. Column chromatography (2:1 hexane–ethyl acetate) of the residue gave **11** (480 mg, 78%) as a syrup, $[\alpha]_D^{25}$ −30° (*c* 2.2, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 7.40–7.20 (m, 30 H, 6 Ph), 5.1–4.3 (13 H, 6 PhC*H*$_2$ and H-1'), 4.39 (d, 1 H, *J* 7.88 Hz, H-1); ^{13}C, 139.3, 138.9, 138.4, 138.2, 137.8, 137.4 (C-ipso), 128.2–127.1 (aromatic), 102.4, 100.3 (C-1,1'), 83.3, 81.7, 81.2, 80.7, 75.4, 74.6, 74.5, 74.0, 73.8, 73.2, 73.1, 71.4, 70.8, 70.6, 70.2, 70.1, 70.0, 69.9, 69.6, 69.5, and 68.2 p.p.m. Mass spectrum (f.a.b.): *m/z* 1063 $[M + Na]^+$ (20%), 973 (2).

Anal. Calc. for $C_{62}H_{72}O_{14}$: C, 71.52; H, 6.97. Found: C, 71.09; H, 7.07.

(*b*) A mixture of **7** (70 mg, 0.08 mmol) and potassium hydroxide (80 mg) in dry tetrahydrofuran (2 mL) and $TsO[CH_2CH_2O]_4Ts$ (94 mg, 0.2 mmol) in dry tetrahydrofuran (3 mL) was treated as above to afford **11** (11 mg, 10%) as a syrup.

3,3'-O-*(3,6,9-Trioxaundecane-1,11-diyl)lactose* (**12**). — A solution of **11** (0.34 g) in ethanol (30 mL) was hydrogenated over 10% Pd/C (0.17 g) at room temperature for 5 h, filtered, and concentrated to afford **12** (0.14 g, 85%) as a syrup, $[\alpha]_D^{25}$ +57° (*c* 0.8, methanol). N.m.r. data (CD_3OD): ^{13}C, δ 102.8, 102.7 (C-1'α,β), 98.0, 93.9 (C-1α,β), 84.9, 82.4 (C-3α,β), 81.5, 81.4 (C-3'α,β), 77.2, 76.7, 76.2, 74.9, 74.8, 74.6, 72.7, 72.6, 72.5, 72.4, 72.3, 71.9, 71.7, 71.5, 71.4, 71.0, 67.8, 66.5, and 62.6 p.p.m.

Anal. Calc. for $C_{20}H_{36}O_{14}$: C, 48.00; H, 7.20. Found: C, 48.36; H, 7.35.

Conventional treatment of **12** (140 mg) with acetic anhydride (1 mL) in

pyridine (1 mL) gave, after column chromatography (ethyl acetate), the hexaacetate **13** (0.16 g, 76%), $[\alpha]_D^{25}$ +44.5° (*c* 0.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 6.18 (d, 1 H, *J* 3.5 Hz, H-1α), 5.63 (d, 1 H, *J* 8.9 Hz, H-1β), 5.57 (m, 2 H, H-4′α,β), 5.25, 5.16 (2 d, 2 H, *J* 8.5 Hz, H-1′α,β), 5.04–4.9 (m, 4 H, H-2α,β,2′α,β); ^{13}C, 169.9–167.4 (CO), 100.3, 100.2 (C-1′α,β), 91.4, 89.0 (C-1α,β), 81.3, 78.1, 76.5, 76.3, 76.1, 72.7, 72.5, 72.2, 71.9, 71.8, 71.1, 71.0, 70.4, 70.3, 70.1, 70.0, 69.8, 69.7, 67.6, 67.5, 62.4, 62.1, 62.0, and 20.3 (Ac) p.p.m.

Anal. Calc. for $C_{32}H_{48}O_{20}$: C, 51.06; H, 6.38. Found: C, 50.83; H, 6.51.

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