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Note

Synthesis of glycosidic and 2-deoxyglycosidic ortholactones from 1-bromoglycosyl cyanides

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The orthosomycin group of oligosaccharide antibiotics[1] are characterised by unique spiro-ortholactone linkages between the glycoside units. These bioactive ortholactones may be derived from either normal glyconolactones or 2-deoxy systems, as exemplified by the substructures **1** and **2**[2] in everninomycin C, and have stimulated efforts towards the synthesis of carbohydrate ortholactones. Yoshimura et al.[3] have developed a method that involves the interaction of a glyconolactone with a silylated diol in the presence of trimethylsilyl triflate, but which apparently has not been applied to 2-deoxylactones. Sinaÿ and co-workers[4] have reported the glycosyloxyselenation of a glycal derivative, which has been applied[5] to the synthesis of a tetrasaccharide fragment of the orthosomycins, but which seems to be applicable only to 2-deoxy systems of type **2**. Other approaches to carbohydrate ortholactones involve the oxidative photocyclisation of hydroxyalkyl glycosides[6], one example of which has been reported[7] in the 2-deoxy series, and the formation of 2-deoxyglycosidic ortholactones by Pd(II)-catalysed reactions of pyranoid glycals with alcohols[8]. A further route has been reported via the interaction of glycopyranosyl 1,1-dihalides with alcohols in the presence of silver or mercury salts[9]. This method has not been applied to 2-deoxy systems, but the formation of the 1,1-dihalides[10] could present a problem in these and other more complex structures.

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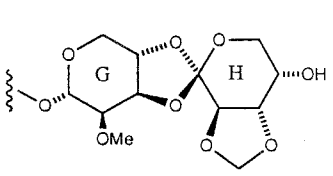

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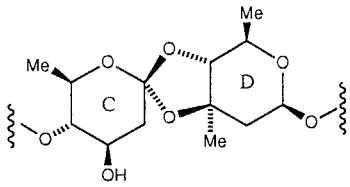

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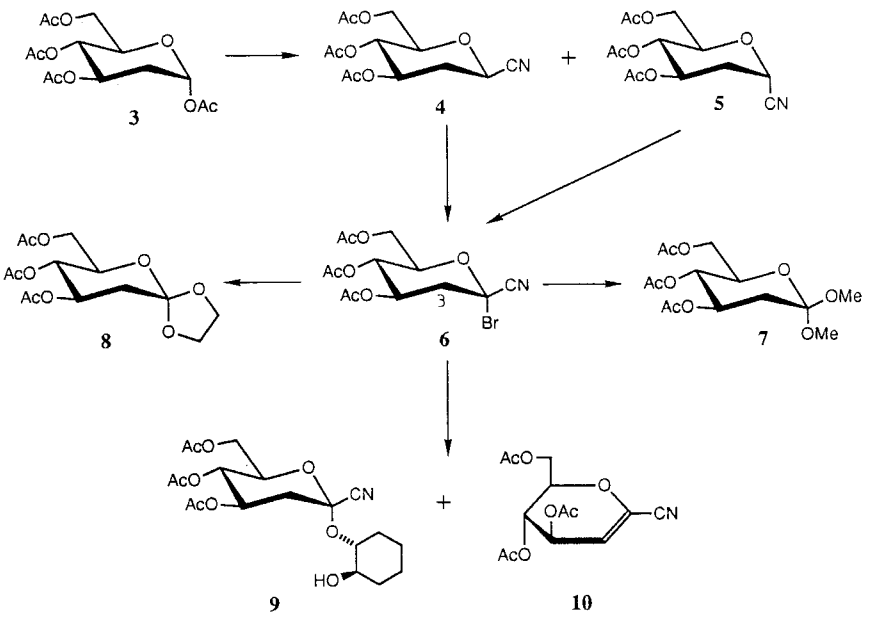
We now report that readily available[11] 1-bromoglycosyl cyanides can give ortholactones on treatment with alcohols in the presence of a soluble silver salt and 2,6-lutidine, and that this chemistry is also applicable readily to 2-deoxyglycosyl systems.

Thus 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose[12] (**3**) was treated with trimethylsilyl cyanide and boron trifluoride etherate in nitromethane[13] to give a 1:1 mixture of the nitriles **4** and **5** (Scheme 1), fractional crystallisation of which after chromatography gave 35% of each crystalline isomer[14]. The configuration of these compounds was clear from ^{1}H NMR data ($J_{2,3}$ 12.15 Hz for the β-nitrile **4** and 5.99 Hz for the α anomer **5**). Treatment of either **4** or **5**, or of a mixture, with *N*-bromosuccinimide and dibenzoyl peroxide in refluxing carbon tetrachloride[11] gave the same glycosyl bromide **6** in good yield, although **4** reacted much more rapidly than **5**. The stereochemistry of **6** (axial bromine) was anticipated[11], and confirmed[11,15] by the small $^3J_{C\text{-}1,H\text{-}3ax}$ value (2.5 Hz).

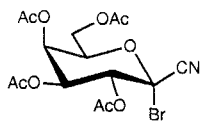
Treatment of **6** with methanol in the presence of silver triflate and 2,6-lutidine gave the oily ortholactone **7** (56%). A similar reaction in the absence of silver



Scheme 1.

triflate gave a mixture of the two possible epimeric methoxynitriles[16]. The spiro-ortholactone **8** was obtained readily from **6** by the use of ethylene glycol–silver triflate–2,6-lutidine. An analogous reaction was attempted using the more sterically demanding (*R*,*R*)-*trans*-cyclohexane-1,2-diol, but, after a reaction for 3 h, the cyanoglycoside **9** ($^3J_{CN,H\text{-}2ax}$ 2.06 Hz) (30%) and the alkene **10** (30%) were the main products. Longer reaction times caused the gradual disapearance of **9** and the formation of another less polar material that could not be isolated.

The presence of the extra oxygen substituent in the starting material was also readily accommodated; treatment of the bromonitrile **11**[11,13] with silver triflate and 2,6-lutidine in methanol gave ortholactone **12** (70%), and use of ethylene glycol in a similar reaction gave the spiro compound **13**.



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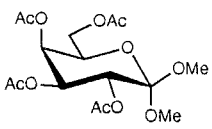

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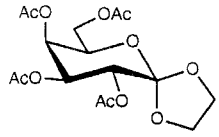

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EXPERIMENTAL

NMR spectra were recorded on solutions in $CDCl_3$ with Bruker WP 200 SY and WH 360 instruments. Mass spectra were obtained using either a VG-updated MS9 or a VG ZABE instrument. Optical rotations were measured at room temperature using a Bendix-NPL 143D automatic polarimeter with a path-length of 1 cm. TLC was performed on Kieselgel HF_{254} type 60 (Merck) and column chromatography on Kieselgel H type 60 (Merck). Melting points were determined on an Electrothermal Mk II apparatus in capillaries and are uncorrected.

*4,5,7-Tri-*O*-acetyl-2,6-anhydro-3-deoxy-*D-gluco- (**4**) *and* -D-manno-*heptononitrile* (**5**).—To a stirred solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-*α*-D-*arabino*-hexopyranose (**3**; 8.0 g, 24 mmol) in nitromethane (150 mL) was added trimethylsilyl cyanide (13 mL, 98 mmol) followed by boron trifluoride etherate (0.5 mL). The mixture was stirred for 3 h at room temperature, the solvent was evaporated in vacuo, and a solution of the residue in water (200 mL) was extracted with ether (3 × 200 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (10:1, toluene–ether) of the residue gave a 1:1 mixture of **4** and **5** that was crystallised from ether to give **4** (2.5 g, 35%), mp 107–108°C; $[\alpha]_D$ +10° (*c* 1.48, $CHCl_3$); R_F 0.5 (ether–toluene, 4:1). NMR data: ^1H (200 MHz), *δ* 2.00 (m, 1 H, H-3*ax*), 2.00, 2.01, 2.06 (3 s, 9 H, 3 OAc), 2.47 (ddd, 1 H, $J_{2,3eq}$ 2.43, $J_{3eq,4}$ 4.57, $J_{3eq,3ax}$ 13.03 Hz, H-3*eq*), 3.60 (ddd, 1 H, $J_{6,7b}$ 2.20, $J_{6,7a}$ 4.90, $J_{5,6}$ 9.69 Hz, H-6), 4.07 (dd, 1 H, $J_{7a,7b}$ 12.55 Hz, H-7b), 4.20 (dd, 1 H, H-7a), 4.35 (dd, 1 H, $J_{2,3ax}$ 12.15 Hz, H-2), 4.9 (m, 2 H, H-4,5); ^{13}C (50 MHz), *δ* 20.5, 20.6, and 20.7 (3 OCO*C*H_3), 34.3 (C-3), 61.8 (C-7), 63.3, 67.7,

70.1, 76.6, 115.8 (CN), 169.4, 169.9, and 170.5 (3 CH_3COO). Mass spectrum: *m/z* 300 $(M+H)^+$, 256 $(M-Ac)^+$, 240 $(M-OAc)^+$, 226 $(M+CH_2OAc)^+$. *Anal.* Calcd for $C_{13}H_{17}NO_7$: C, 52.2; H, 5.7; N, 4.7. Found: C, 52.2; H, 5.7; N, 4.7.

Further crystallisation of the material in the mother liquors gave **5** (2.5 g, 35%); mp 90–91°C; $[\alpha]_D$ +81.5° (*c* 1.06, $CHCl_3$); R_F 0.55. NMR data: ^1H (200 MHz), δ 2.00 (m, 1 H, H-3*ax*), 2.00, 2.02, 2.05 (3 s, 9 H, 3 OAc), 2.40 (ddd, 1 H, $J_{2,3eq}$ 1.74, $J_{3eq,4}$ 5.08, $J_{3eq,3ax}$ 13.63 Hz, H-3*eq*), 4.00 (ddd, 1 H, $J_{6,7b}$ 2.10, $J_{6,7a}$ 4.46, $J_{5,6}$ 9.80 Hz, H-6), 4.05 (dd, 1 H, $J_{7a,7b}$ 12.4 Hz, H-7b), 4.30 (dd, 1 H, H-7a), 4.90 (dd, 1 H, $J_{2,3eq}$ 1.65, $J_{2,3ax}$ 5.99 Hz, H-2), 4.95 (t, 1 H, $J_{4,5}$ 9.55 Hz, H-5), 5.20 (ddd, 1 H, $J_{3ax,4}$ 11.50 Hz, H-4); ^{13}C (50 MHz), δ 20.5 (2 C) and 20.7 (3 CH_3COO), 32.9 (C-3), 61.5 (C-7), 62.8, 68.0, 68.8, 73.8, 115.7 (CN), 169.5, 169.6, 170.3 (3 CH_3COO). Mass spectrum: *m/z* 300 $(M+H)^+$, 256 $(M-Ac)^+$, 240 $(M-OAc)^+$, 226 $(M-CH_2OAc)^+$. *Anal.* Found: C, 51.9; H, 5.6; N, 4.6.

*4,5,7-Tri-*O*-acetyl-2,6-anhydro-2-bromo-3-deoxy-*D*-gluco-heptononitrile* (**6**).—(*a*) To a solution of **4** (2.5 g, 8.4 mmol) in CCl_4 (50 mL) were added *N*-bromosuccinimide (1.9 g, 10.6 mmol) and benzoyl peroxide (0.32 g, 1.3 mmol). The mixture was boiled under reflux for 2 h, cooled, and filtered. The solid was washed with cold CCl_4, and the filtrate and washings were combined and concentrated. Column chromatography (10:1 toluene–ether) of the residue and recrystallisation from ether–hexane gave **6** (1.9 g, 60%); mp 124–125°C; $[\alpha]_D$ +161° (*c* 1.0, $CHCl_3$); R_F 0.65 (4:1 ether–toluene). NMR data: ^1H (200 MHz), δ 2.02, 2.03, 2.07 (3 s, 9 H, 3 OAc), 2.45 (dd, 1 H, $J_{3ax,4}$ 10.78, $J_{3ax,3eq}$ 13.81 Hz, H-3*ax*), 2.95 (dd, 1 H, $J_{3eq,4}$ 4.97, H-3*eq*), 4.0 (m, 3 H, H-6,7a,7b), 5.10 (t, 1 H, $J_{4,5}=J_{5,6}=9.7$ Hz, H-5), 5.40 (ddd, 1 H, H-4); ^{13}C (50 MHz), δ 20.5 and 20.6 (2 C) (3 CH_3COO), 44.3 (C-3), 60.6 (C-7), 66.9, 68.0, and 74.5 (C-4,5,6), 76.7 (C-2), 115.0 (CN), 169.3, 169.6, and 170.3 (3 CH_3COO). *Anal.* Calcd for $C_{13}H_{16}BrNO_7$: C, 41.3; H, 4.2; Br, 20.7; N, 3.7. Found: C, 41.1; H, 4.2; Br, 21.2; N, 3.7.

(*b*) Reaction of **5** (2.5 g) as in (*a*), but employing a reflux period of 24 h, also gave **6** (1.9 g, 60%).

*3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-deoxy-1,1-dimethoxy-*D*-glucitol* (**7**).—To a solution of **6** (0.4 g, 1.1 mmol) in CH_2Cl_2 (3 mL) and MeOH (10 mL) were added 2,6-lutidine (0.37 mL) and silver triflate (0.6 g, 2.3 mmol). The mixture was stirred in the dark for 2 days at room temperature, more silver triflate (0.6 g) was added, and the mixture was stirred for a further 3 days, filtered through Celite, and concentrated in vacuo. Column chromatography (10:1 toluene–ether) of the residue gave **7** (0.20 g, 56%), isolated as a colourless syrup; $[\alpha]_D$ +52° (*c* 0.9, $CHCl_3$) [lit.[8] mp 53–56°C; $[\alpha]_D$ +55° (*c* 3.8, $CHCl_3$)]; R_F 0.54 (3:1 ether–toluene). NMR data: ^1H (200 MHz), δ 1.71 (dd, 1 H, $J_{2ax,3}$ 11.39, $J_{2ax,2eq}$ 12.54 Hz, H-2*ax*), 2.00, 2.01, 2.04 (3 s, 9 H, 3 OAc), 2.46 (dd, 1 H, $J_{2eq,3}$ 5.10 Hz, H-2*eq*), 3.20 and 3.28 (2 s, each 3 H, 2 OMe), 3.81 (ddd, 1 H, $J_{5,6b}$ 2.34, $J_{5,6a}$ 4.93, $J_{4,5}$ 9.78 Hz, H-5), 4.05 (dd, 1 H, $J_{6a,6b}$ 12.21 Hz, H-6b), 4.20 (dd, 1 H, H-6a), 4.98 (t, 1 H, $J_{4,5}=J_{3,4}=9.53$ Hz, H-4), 5.10 (ddd, 1 H, H-3); ^{13}C (50 MHz), δ 20.6 (2C) and 20.8 (3 CH_3COO), 34.8 (C-2), 48.0 and 50.1 (2 OCH_3), 62.3 (C-6), 69.0, 70.1, 70.3

(C-3,4,5), 112.2 (C-1), 169.7, 170.0, and 170.6 (3 CH_3COO). Mass spectrum: m/z 303 $(M - OMe)^+$, 261 $(M - CH_2OAc)^+$.

*1,2-O-(3,4,6-tri-O-acetyl-2-deoxy-*D*-arabino-hexopyranosylidene)ethanediol* (**8**).—To a solution of **6** (1.0 g, 2.6 mmol) in CH_2Cl_2 (10 mL) and ethylene glycol (10 mL) were added 2,6-lutidine (1 mL) and silver triflate (1.5 g, 5.8 mmol). The mixture was stirred at room temperature in the dark for 2 days, more silver triflate (0.6 g) was added, stirring was continued for 3 days, the mixture was filtered through Celite, and the solvent was evaporated in vacuo. Column chromatography (10:1 toluene–ether) of the residue and recrystallisation from EtOAc–hexane gave **8** (0.44 g, 50%), mp 154–156°C; $[\alpha]_D$ +44° (*c* 1.05, $CHCl_3$); lit.[7] mp 144–145°C, $[\alpha]_D$ +48.7° (acetone); R_F 0.51 (3:1, ether–toluene). NMR data: ^1H (360 MHz), δ 2.01, 2.03, 2.07 (3 s, 9 H, 3 OAc), 2.12 (dd, 1 H, $J_{2ax,3}$ 11.90, $J_{2ax,2eq}$ 12.50 Hz, H-2*ax*), 2.30 (dd, 1 H, $J_{2eq,3}$ 5.43 Hz, H-2*eq*), 3.95 (ddd, 1 H, $J_{5,6a}$ 2.35, $J_{5,6b}$ 4.42, $J_{4,5}$ 10.06 Hz, H-5), 4.05 (m, 4 H, 0.75 OCH_2CH_2O and H-6), 4.18 (m, 1 H, 0.25 OCH_2CH_2O), 4.25 (dd, 1 H, $J_{6a,6b}$ 12.28 Hz, H-6b), 5.05 (t, 1 H, $J_{4,5} = J_{3,4} = 9.75$ Hz, H-4), 5.26 (ddd, 1 H, H-3); ^{13}C (50 MHz), δ 20.6 (2 C), 20.8 (3 CH_3COO), 38.2 (C-2), 62.3 (C-6), 64.0 (CH_2O), 64.9 (CH_2O), 68.8, 70.2, 70.4 (C-3,4,5), 118.4 (C-1), 169.7, 170.0, 170.7 (3 CH_3COO). Mass spectrum: m/z 333 $(M + H)^+$, 259 $(M - CH_2OAc)^+$, 200 $(M - CH_2OAc - OAc)^+$.

*(1R,2R)-2-Hydroxycyclohexyl 3,4,6-tri-O-acetyl-1-cyano-2-deoxy-α-*D*-arabino-hexopyranoside* (**9**) *and 4,5,7-tri-O-acetyl-2,6-anhydro-3-deoxy-*D*-arabino-hept-2-enononitrile* (**10**).—To a stirred solution of **6** (0.4 g, 1.05 mmol) in CH_2Cl_2 (10 mL) were added (*R,R*)-*trans*-cyclohexane-1,2-diol (0.3 g, 2.6 mmol), 2,6-lutidine (0.37 mL), and silver triflate (0.6 g, 2.3 mmol). The mixture was stirred in the dark for 3 h, filtered through Celite, and concentrated to dryness. The residue was partitioned between water and CH_2Cl_2, and the organic phase was dried ($MgSO_4$) and concentrated. Column chromatography (20:1 toluene–ether) of the residue gave, first, **10** (94 mg, 30%), mp 79–81°C; $[\alpha]_D$ −47° (*c* 1.10, $CHCl_3$); R_F 0.62 (3:1 ether–toluene). NMR data: ^1H (200 MHz), δ 2.04, 2.05, 2.06 (3 s, 9 H, 3 OAc), 4.1–4.5 (m, 3 H, H-6,7a,7b), 5.20 (t, 1 H, $J_{5,6} = J_{4,5} = 5.5$ Hz, H-5), 5.35 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-4), 5.70 (d, 1 H, H-3); ^{13}C (50 MHz), δ 20.5 (3 CH_3COO), 60.2 (C-7), 65.5, 65.8, and 75.7 (C-4,5,6), 112.2 (C-3), 112.7 (CN), 130.7 (C-2), 169.1, 169.6, 170.2 (3 CH_3COO). Mass spectrum: m/z 298 $(MH)^+$, 238 $(M - OAc)^+$. *Anal.* Calcd for $C_{13}H_{15}NO_7$: C, 52.5; H, 5.1; N, 4.7. Found: C, 52.3; H, 5.0; N, 4.7.

Eluted second was **9** (0.13 g, 30%), isolated as a colourless syrup; $[\alpha]_D$ +38° (*c* 1.26, $CHCl_3$); R_F 0.3. NMR data: ^1H (200 MHz), δ 1.5 (m, 8 H, 4 CH_2), 2.05, 2.06, 2.09 (3 s, 9 H, 3 OAc), 2.30 (t, 1 H, $J_{2ax,2eq} = J_{2ax,3} = 13.1$ Hz, H-2*ax*), 2.70 (dd, 1 H, $J_{2eq,3}$ 5.10 Hz, H-2*eq*), 3.5 (m, 1 H, C*H*OR), 3.9 (m, 1 H, C*H*OH), 4.05 (ddd, 1 H, $J_{5,6a}$ 2.25, $J_{5,6b}$ 5.35, $J_{4,5}$ 9.8 Hz, H-5), 4.13 (d, 1 H, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.22 (dd, 1 H, H-6b), 5.03 (t, 1 H, *J* 9.6 Hz, H-4), 5.25 (ddd, 1 H, $J_{3,4}$ 9.23, H-3); ^{13}C (50 MHz), δ 20.5 (2 C) and 20.7 (3 CH_3CO), 23.4, 24.0, 31.1, 32.3, 39.9, 61.8 (C-6), 67.7, 68.3, 70.1, 72.4, 84.4, 95.7 (C-1), 115.1 (CN), 169.5, 169.9, and 170.3 (3

CH_3CO). Mass spectrum: m/z 414 $(MH)^+$, 386.1574 $(M - HCN)^+$ (Calcd for $C_{18}H_{26}O_9$: m/z 386.1577).

*2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-1,1-dimethoxy-*D*-galactitol* (**12**).—The bromonitrile **11** (0.2 g, 0.46 mmol) was treated and processed, as in the preparation of **7**, to yield **12** (0.126 g, 70%) as a clear syrup; $[\alpha]_D$ +78° (*c* 1.57, $CHCl_3$); R_F 0.56 (3:1 ether–toluene). NMR data: ^1H (200 MHz), δ 1.97, 2.08, 2.13, 2.18 (4 s, 12 H, 4 OAc), 3.32, 3.42 (2 s, 6 H, 2 OMe), 4.1 (m, 3 H, H-5,6a,6b), 5.25 (dd, 1 H, $J_{3,4}$ 3.38, $J_{2,3}$ 10.61 Hz, H-3), 5.45 (dd, 1 H, $J_{4,5}$ 1.05 Hz, H-4), 5.51 (d, 1 H, H-2); ^{13}C (50 MHz), δ 20.4, 20.5 (2 C) and 20.7 (4 CH_3COO), 48.1 and 51.4 (2 OCH_3), 61.4 (C-6), 65.7, 67.6, 69.1, 70.0 (C-2,3,4,5), 111.2 (C-1), 169.8 (2 C), 170.0 and 170.2 (4 CH_3COO). Mass spectrum: m/z 361.1114 $(M - OMe)^+$ (Calcd for $C_{15}H_{21}O_{10}$: m/z 361.1134), 333 $(M - OAc)^+$, 319 $(M - CH_2OAc)^+$.

*1,2-*O*-(2,3,4,6-Tetra-*O*-acetyl-*D*-galactopyranosylidene)ethanediol* (**13**).—To a solution of **11** (0.1 g, 0.23 mmol) in CH_2Cl_2 (2 mL) and ethylene glycol (1 mL) were added 2,6-lutidine (0.15 mL) and silver triflate (0.2 g, 0.7 mmol). The mixture was stirred in the dark for 2 days at room temperature, more silver triflate (0.2 g) was added, stirring was continued for 5 days, and the mixture was filtered through Celite and concentrated in vacuo. A solution of the residue in water (20 mL) was extracted with CH_2Cl_2 (3 × 20 mL), and the extracts were combined, dried ($MgSO_4$), and concentrated. Column chromatography (20:1 toluene–ether) of the residue gave **13** (36 mg, 40%); mp 158–160°C (from ether–hexane); $[\alpha]_D$ +51° (*c* 0.37, $CHCl_3$), R_F 0.5 (3:1 ether–toluene). NMR data: ^1H (200 MHz), δ 1.97, 2.03, 2.08, 2.15 (4 s, 12 H, 4 OAc), 4.1 (m, 7 H, H-5,6a,6b and OCH_2CH_2O), 5.25 (dd, 1 H, $J_{3,4}$ 3.32, $J_{2,3}$ 10.48 Hz, H-3), 5.45 (dd, 1 H, $J_{4,5}$ 1.15 Hz, H-4), 5.57 (d, 1 H, H-2). Mass spectrum: m/z 391.1220 $(M + H)^+$ (calcd for $C_{16}H_{23}O_{11}$: m/z 391.1240), 347 $(M - Ac)^+$, 331 $(M - OAc)^+$, 317 $(M - CH_2OAc)^+$.

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