

Epoxidation and Bis-hydroxylation of C-Phenyl- $\Delta^{2,3}$ -glycopyranosides.

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Abstract: Epoxidation and *cis*-hydroxylation of C-phenyl- $\Delta^{2,3}$ -glycopyranosides have been carried out with a view to developing C-aryl glycoside synthesis. Epoxidation of (2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)benzene and (6-*O-tert*-butyldimethylsilyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)benzene gave predominantly the *allo*-adducts whatever the configuration at the anomeric center. Epoxidation of (4,6-di-*O-tert*-butyldimethylsilyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)benzene gave the *manno*- and *allo*-adducts in a 89:11 and 40:60 ratios for the α - and β -anomers, respectively. Hydroxylation of α -C-phenyl- $\Delta^{2,3}$ -glycopyranosides using OsO₄ afforded the *manno*-adduct only, whatever the substituents at positions 4 and 6, whereas hydroxylation of (2,3-dideoxy- β -D-*erythro*-hex-2-enopyranosyl)benzene and (4,6-di-*O-tert*-butyldimethylsilyl-2,3-dideoxy- β -D-*erythro*-hex-2-enopyranosyl)benzene gave the *manno*- and *allo*-adducts in 25:75 and 80:20 ratios, respectively.

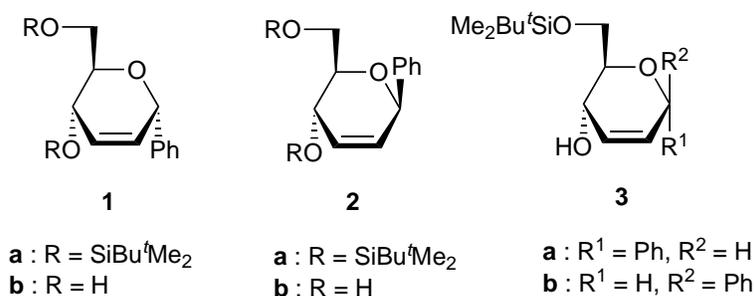
Keywords: (2,3-Unsaturated-glycopyranosyl)benzene, epoxidation, *cis*-hydroxylation.

Introduction

There is a great interest in C-aryl glycosides. This is due to their occurrence in many natural products possessing important medicinal and therapeutic properties [1-3], as well as to their use as valuable chiral building blocks [4-6]. However, it is important to obtain the two anomers of these C-

aryl glycopyranosides with the highest stereoselectivity. Several synthetic methods are now available for the stereoselective and even stereospecific preparation of *C*-aryl glycopyranosides possessing a double bond in the 2,3-position [7-14]. It is to be noted that these unsaturated glycosides are useful precursors of the corresponding saturated *C*-aryl glycosides by simple functionalization of this unsaturation. Whereas epoxidation or hydroxylation of 2,3-dideoxy-hex-2-pyranosides has been well studied [15], there have not been any such systematic studies in the case of *C*-glycopyranosides, although some examples of *cis*-hydroxylation of *C*-aryl glycopyranosides appeared in the literature [14, 16]. We report in this paper some stereochemical aspects concerning the epoxidation and *cis*-hydroxylation of both anomers of some *C*-phenyl- $\Delta^{2,3}$ -glycopyranosides (Scheme 1).

Scheme 1



Results and Discussion

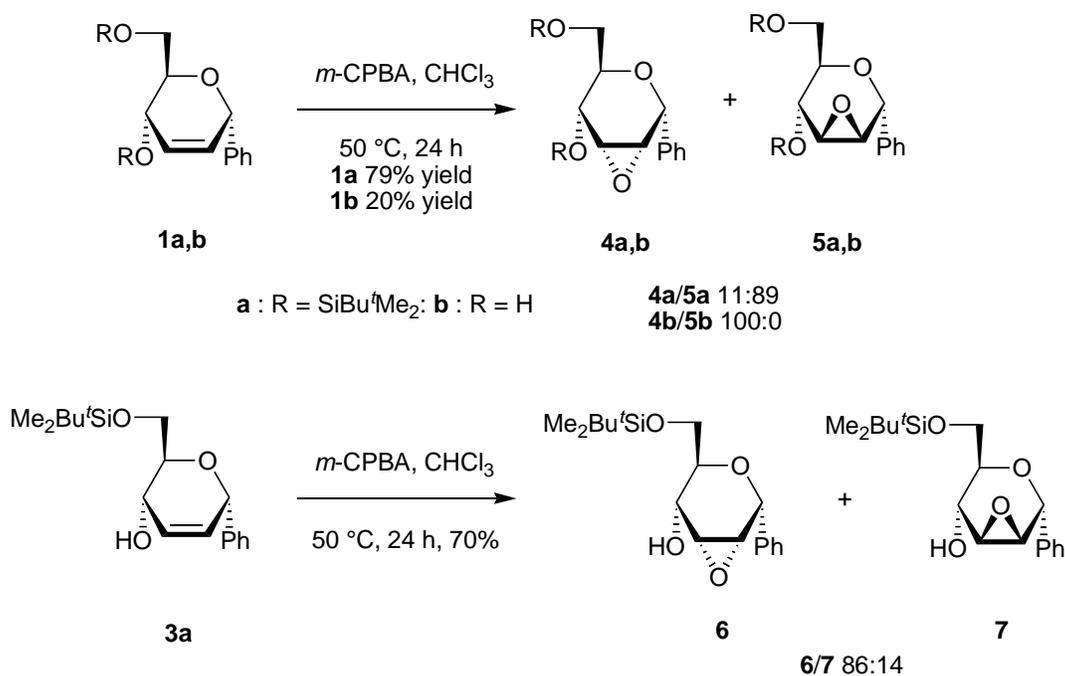
The different *C*-phenyl- $\Delta^{2,3}$ -glycopyranosides having the α - and the β -configuration used in this study are shown in Scheme 1. The synthesis of bis-silylated 2,3-unsaturated-*C*-phenyl glycopyranosides **1a** and **2a** has already been described [12]. The deprotected unsaturated *C*-phenyl glycopyranosides **1b** and **2b** were obtained by a simple desilylation of compounds **1a** and **2a**, whereas monosilylation of **1b** and **2b** with *tert*-butyldimethylsilyl chloride afforded compounds **3a** and **3b**, respectively.

We studied first the epoxidation of these substrates using as the epoxidation reagent *m*-chloroperbenzoic acid in CHCl₃ at 50 °C for 24 h. Epoxidation of bis-silylated pseudo-glucal **1a** possessing the α -configuration gave in 79% yield a 11:89 mixture of the α -*allo*- and α -*manno*-epoxides **4a** and **5a**, which were separated by column chromatography, whereas the non-protected pseudo-glucal **1b** gave only the α -*allo* isomer **4b**, albeit in a quite low yield (20%) (Scheme 2); even prolonged reaction times did not improve this yield, degradation products being observed in these cases. Epoxidation of the monosilylated pseudo-glucal **3a** (Scheme 2) gave the reverse selectivity to that observed for the bis-silylated compound **1a**; a 86:14 mixture of the α -*allo*- and α -*manno*-epoxides **6** and **7** was now obtained in 70% yield, the α -*allo*-epoxide being now predominant. These results are quite different from those observed in the epoxidation of alkyl 2,3-dideoxy-hex-2-pyranosides [15].

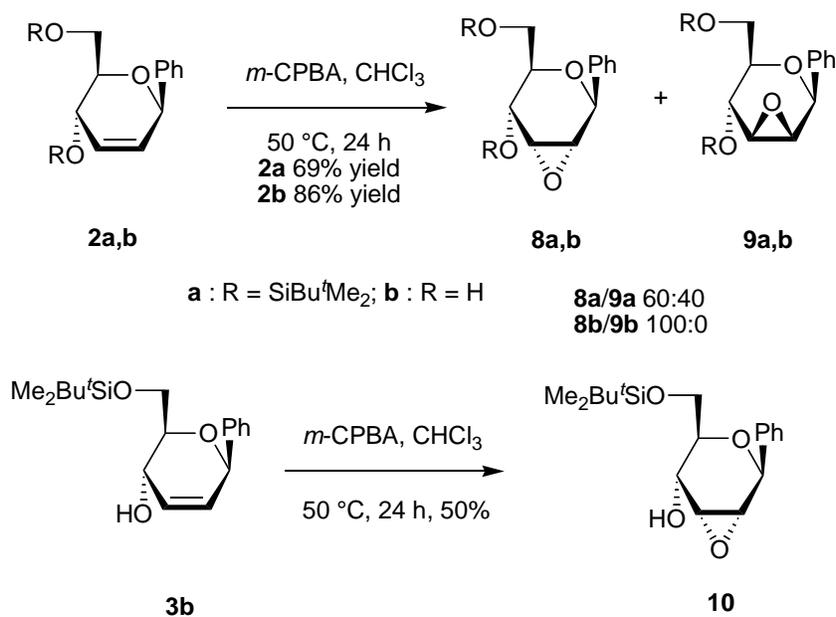
The *allo* or *manno* configuration of those epoxides was established through comparison of the coupling constants $J_{1,2}$ and $J_{3,4}$ [15, 17, 18], these two values being always higher for the α -*allo* than for the α -*manno* derivative. Effectively no H-1/H-2 or H-3/H-4 couplings were observed for compounds **5a** and **7**, whilst compounds **4a** and **6** showed $J_{1,2} = 3.6$ and 3.4 Hz, and $J_{3,4} = 1.7$ and 2.3

Hz, respectively. The observed stereoselectivities could be rationalized by assuming that the epoxidation of compound **1a** is under steric control, the peracid attacking on the β face because of the increased steric requirements on α face imparted by the two substituents at C-1 and C-4, whereas the epoxidation of compounds **1b** and **3a** was reversed, due to the *cis*-directing influence of the allylic hydroxyl group at position 4.

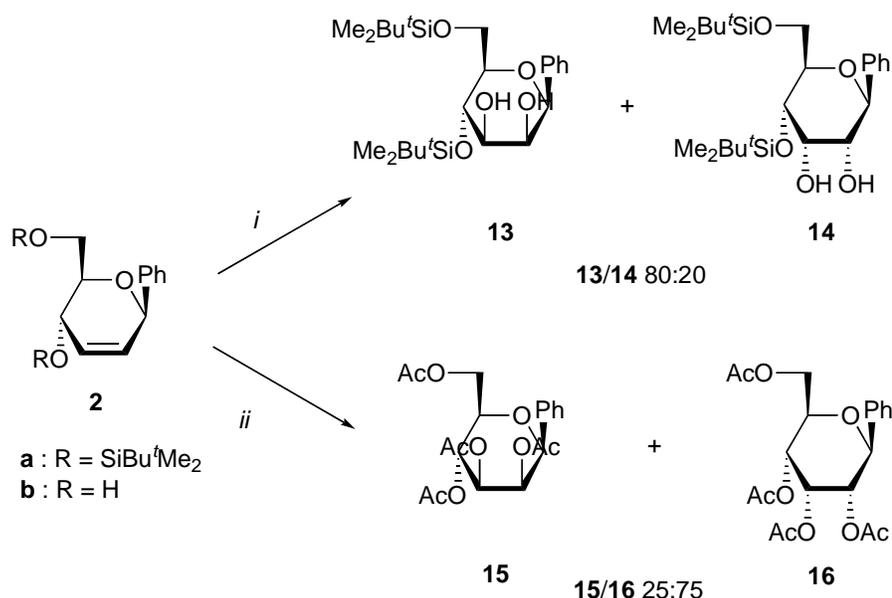
Scheme 2



Scheme 3



Scheme 5



Reactants: i) OsO₄, NMO, H₂O/acetone, 70% yield; ii) OsO₄, NMO, H₂O/acetone, then Ac₂O, pyridine, 75% yield

Conclusions

We have shown that epoxidation and *cis*-hydroxylation of both anomers of *C*-phenyl- $\Delta^{2,3}$ -glycopyranosides are highly selective, the selectivity depending mostly on the substituent at position 4. Epoxidation of *C*-phenyl- $\Delta^{2,3}$ -glycopyranosides having a free hydroxyl group at position 4 afforded predominantly, if not only, the *allo*-epoxide, whatever the anomer used. When the hydroxyl function at position 4 was protected as a *tert*-butyldimethylsilyl ether, the α -anomer gave predominantly the *manno*-epoxide, when the β -anomer afforded a 60:40 mixture of the two-adducts. *Cis*-dihydroxylation of *C*-phenyl- $\Delta^{2,3}$ - α -glycopyranosides afforded the *manno*-adduct as the unique compound. For the *cis*-dihydroxylation of *C*-phenyl- $\Delta^{2,3}$ - β -glycopyranosides, the presence of the free hydroxyl group at C-4 caused formation of the *allo*-adduct as the major isomer, when the *allo*-adduct was obtained predominantly when the hydroxyl function was protected with a *tert*-butyldimethylsilyl group

Experimental

General

Solvents were purified by standard methods and dried if necessary. Melting points (uncorrected) were determined with a capillary melting point apparatus Büchi SMP-20. Optical rotations were recorded using a Perkin-Elmer 241 polarimeter. Thin-layer chromatography was performed using Merck silica gel 60 F₂₅₄ precoated aluminium plates, 0.2 mm thickness. Column chromatography was performed on silica gel (Merck 60, 70–230 mesh). NMR spectra were recorded on a Bruker 300 MHz spectrometer (operating at 300.13 MHz for ¹H, and 75.01 MHz for ¹³C).

Preparation of compounds **1a,b**.

A solution of the unsaturated bis-silylated *C*-phenyl glycopyranoside **1a** (or **2a**) (3 g, 7.7 mmol) [12], and $\text{NBu}_4\text{F}\cdot 3\text{H}_2\text{O}$ (2.43 g, 7.7 mmol) in THF (50 mL) was stirred at rt for 2 h. After evaporation of the solvent, CH_2Cl_2 was added (50 mL), and the solution was washed with brine. Evaporation of the solvent under reduced pressure gave a residue that was purified by column chromatography on silica using petroleum ether/ethyl acetate as the eluent to give compound **1b** (or **2b**).

(2,3-Dideoxy- α -D-erythro-hex-2-enopyranosyl)benzene (**1b**). Yield 80%, oil, R_f 0.40 (petroleum ether-ethyl acetate 1:4), $[\alpha]_{\text{D}}^{20}$ -72 (*c* 1, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 2.10 (bs, 2H, OH), 3.45 (ddd, 1H, $J = 8.5, 4.4, 4.0$ Hz, H-5), 3.78 (m, 2H, H-6), 4.28 (d, 1H, $J = 8.5$ Hz, H-4), 5.29 (s, 1H, H-1), 6.08 (m, 2H, H-2, H-3), 7.34 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ 63.0 (C-6), 64.6 (C-4), 73.1 (C-5), 74.5 (C-1), 128.8, 128.9, 129.3, 129.8, 130.8 and 140.1 (C-2, C-3, C_{arom}); Anal. calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.89; H, 6.84. Found: C, 70.05; H, 6.61.

(2,3-Dideoxy- β -D-erythro-hex-2-enopyranosyl)benzene (**2b**). Yield 75%, oil, R_f 0.40 (petroleum ether-ethyl acetate 1:4), $[\alpha]_{\text{D}}^{20}$ +192 (*c* 0.8, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 1.94 (bs, 2H, OH), 3.59 (ddd, 1H, $J = 8.7, 5.2, 4.1$ Hz, H-5), 3.86 (dd, 1H, $J = 11.6, 5.2$ Hz, H-6), 3.96 (dd, 1H, $J = 11.6, 4.1$ Hz, H-6), 4.35 (ddd, 1H, $J = 8.7, 1.6, 1.2$ Hz, H-4), 5.18 (bs, 1H, H-1), 5.84 (d, 1H, $J = 10.4$ Hz, H-2 or H-3), 5.92 (d, 1H, $J = 10.4$ Hz, H-3 or H-2), 7.34 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ 63.3 (C-6), 64.3 (C-4), 77.5 (C-5), 79.5 (C-1), 127.4, 128.4, 128.7, 129.0 and 131.1 (C-2, C-3, C_{arom}); Anal. calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.89; H, 6.84. Found: C, 69.81; H, 6.77.

Preparation of compounds **3**.

To a solution of the unsaturated *C*-phenyl glycopyranoside **1b** (or **2b**) (1 g, 4.8 mmol), imidazole (32 mg, 05 mmol) and triethylamine (1 mL, 6.7 mmol) in CH_2Cl_2 (8 mL) maintained at rt was added a solution of *tert*-BuMe₂SiCl (990 mg, 6.6 mmol) in CH_2Cl_2 (10 mL). After being stirred at rt for 24 h, the solution was poured into cold water (10 mL), and the mixture was extracted with CH_2Cl_2 . (3x10 mL). After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica using petroleum ether/diethyl ether as the eluent to give compound **3a** (or **3b**).

(6-*O-tert*-Butyldimethylsilyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)benzene (**3a**). Yield 66%, oil, R_f 0.47 (petroleum ether-diethyl ether 2:1), $[\alpha]_{\text{D}}^{20}$ -75 (*c* 1, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 0.05 (s, 3H, SiMe), 0.07 (s, 3H, SiMe), 0.88 (s, 9H, CMe_3), 3.01 (bs, 1H, OH), 3.46 (ddd, 1H, $J = 7.7, 7.5, 5.5$ Hz, H-5), 3.71 (dd, 1H, $J = 9.6, 7.7$ Hz, H-6), 3.83 (dd, 1H, $J = 9.6, 5.5$ Hz, H-6), 4.26 (d, 1H, $J = 7.5$ Hz, H-4), 5.23 (s, 1H, H-1), 6.05 (m, 2H, H-2, H-3), 7.35 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -5.5 (SiMe), -5.4 (SiMe), 18.2 (CMe_3), 25.9 (CMe_3), 65.7 (C-6), 67.0 (C-4), 71.4 (C-5), 73.9 (C-1), 128.0, 128.4, 128.5, 129.6 and 139.5 (C-2, C-3, C_{arom}); Anal. calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{Si}$: C, 67.46; H, 8.81. Found: C, 66.81; H, 8.81.

(6-*O*-*tert*-Butyldimethylsilyl-2,3-dideoxy- β -*D*-erythro-hex-2-enopyranosyl)benzene (**3b**). Yield 82%, oil, R_f 0.36 (petroleum ether-diethyl ether 2:1), $[\alpha]_D^{20} +120$ (c 0.9, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 0.10 (s, 6H, SiMe), 0.90 (s, 9H, CMe_3), 3.40 (bs, 1H, OH), 3.65 (ddd, 1H, $J = 8.1, 5.1, 4.4$ Hz, H-5), 3.77 (dd, 1H, $J = 9.5, 8.1$ Hz, H-6), 4.03 (dd, 1H, $J = 9.5, 5.1$ Hz, H-6), 4.40 (dd, 1H, $J = 4.4, 1.5$ Hz, H-4), 5.15 (s, 1H, H-1), 5.83 (dd, 1H, $J = 10.3, 1.5$ Hz, H-3),), 5.90 (d, 1H, $J = 10.3$ Hz, H-3), 7.21 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -5.5 (SiMe), -5.6 (SiMe), 18.2 (CMe_3), 25.9 (CMe_3), 66.5 (C-6), 67.9 (C-4), 77.2, and 77.3 (C-1, C-5), 127.3, 128.2, 128.3, 130.4 and 140.5 (C-2, C-3, C_{arom}); Anal. calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{Si}$: C, 67.46; H, 8.81. Found: C, 67.40; H, 8.75.

General procedure for the epoxidation.

A solution of the unsaturated carbohydrate (0.23 mmol) and *m*-CPBA (1.17 g, 0.69 mmol) in CHCl_3 (10 mL) was stirred at 50 °C for 24 h. The solution was neutralized with a saturated aqueous solution of NaHCO_3 , the organic phase was separated, and the aqueous phase was extracted with CHCl_3 (2x10 mL). The organic phases were dried over Na_2SO_4 . After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica using the appropriate eluent.

(4,6-*Di-O-tert*-butyldimethylsilyl-2,3-anhydro- α -*D*-allopyranosyl)benzene (**4a**). Yield 9%, oil, R_f 0.18 (petroleum ether-ethyl acetate-triethylamine 40:1:1), $[\alpha]_D^{20} +18$ (c 0.9, CH_2Cl_2); $^1\text{H-NMR}$ (CDCl_3) δ 0.13 (s, 6H, SiMe), 0.17 (s, 3H, SiMe), 0.20 (s, 3H, SiMe), 0.94 (s, 9H, CMe_3), 0.98 (s, 9H, CMe_3), 3.54 (dd, 1H, $J = 4.2, 1.7$ Hz, H-3), 3.48-3.57 (m, 1H, H-5), 3.75 (dd, 1H, $J = 11.2, 6.1$ Hz, H-6), 3.95 (dd, 1H, $J = 11.2, 1.9$ Hz, H-6), 3.98 (dd, 1H, $J = 4.2, 3.6$ Hz, H-2), 4.02 (dd, 1H, $J = 9.1, 1.7$ Hz, H-4), 5.26 (bd, 1H, $J = 3.6$ Hz, H-1), 7.31-7.61 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -5.2 (SiMe), -5.0 (SiMe), -4.7 (SiMe), -4.0 (SiMe), 18.1 (CMe_3), 18.6 (CMe_3), 25.8 (CMe_3), 26.1 (CMe_3), 55.8 and 57.5 (C-2, C-3), 63.4 (C-6), 66.9 (C-4), 71.1 (C-5), 72.4 (C-1), 126.5, 127.4, 128.5 and 139.1 (C_{arom}); Anal. calcd for $\text{C}_{24}\text{H}_{42}\text{O}_4\text{Si}_2$: C, 63.95; H, 9.39. Found: C, 63.61; H, 9.38.

(4,6-*Di-O-tert*-butyldimethylsilyl-2,3-anhydro- α -*D*-mannopyranosyl)benzene (**5a**). Yield 70%, oil, R_f 0.20 (petroleum ether-ethyl acetate-triethylamine 40:1:1), $[\alpha]_D^{20} +21$ (c 0.9, CH_2Cl_2); $^1\text{H-NMR}$ (CDCl_3) δ 0.06 (s, 3H, SiMe), 0.08 (s, 3H, SiMe), 0.15 (s, 3H, SiMe), 0.22 (s, 3H, SiMe), 0.92 (s, 9H, CMe_3), 0.95 (s, 9H, CMe_3), 3.27 (ddd, 1H, $J = 9.0, 6.7, 2.2$ Hz, H-5), 3.36 (d, 1H, $J = 3.7$ Hz, H-2 or H-3), 3.60 (d, 1H, $J = 3.7$ Hz, H-2 or H-3), 3.65 (dd, 1H, $J = 11.1, 6.7$ Hz, H-6), 3.77 (d, 1H, $J = 9.0$ Hz, H-4), 3.83 (dd, 1H, $J = 11.1, 2.2$ Hz, H-6), 5.27 (s, 1H, H-1), 7.31-7.61 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -5.2 (SiMe), -5.1 (SiMe), -4.8 (SiMe), -4.3 (SiMe), 18.0 (CMe_3), 18.5 (CMe_3), 25.8 (CMe_3), 26.0 (CMe_3), 52.4 and 56.9 (C-2, C-3), 63.6 (C-4), 63.6 (C-6), 72.3 (C-5), 73.1 (C-1), 127.6, 128.0, 128.7 and 137.5 (C_{arom}); Anal. calcd for $\text{C}_{24}\text{H}_{42}\text{O}_4\text{Si}_2$: C, 63.95; H, 9.39. Found: C, 63.72; H, 9.42.

(2,3-Anhydro- α -*D*-allopyranosyl)benzene (**4b**). Yield 20%, oil, R_f 0.24 (diethylether), $[\alpha]_D^{20} -6.0$ (c 0.7, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 2.84 (bs, 2H, OH), 3.31 (ddd, 1H, $J = 8.8, 4.5, 3.4$ Hz, H-5), 3.50 (dd, 1H, $J = 4.3, 1.7$ Hz, H-3), 3.63 (dd, 1H, $J = 11.8, 4.5$ Hz, H-6), 3.69 (dd, 1H, $J = 11.8, 3.4$ Hz, H-6), 3.79 (dd, 1H, $J = 4.3, 3.6$ Hz, H-2), 3.93 (dd, 1H, $J = 8.8, 1.7$ Hz, H-4), 5.06 (d, 1H, $J = 3.6$ Hz, H-1),

7.16-7.34 (m, 5H, H_{arom}); ¹³C-NMR (CDCl₃) δ 55.6 and 58.2 (C-2, C-3), 62.8 (C-6), 66.2 (C-4), 71.4 (C-5), 72.4 (C-1), 126.9, 128.2, 129.9 and 138.8 (C_{arom}); Anal. calcd for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.65; H, 6.46.

(6-*O*-*tert*-Butyldimethylsilyl-2,3-anhydro- α -D-allopyranosyl)benzene (**6**). Yield 60%, oil, *R*_f 0.40 (petroleum ether-ethyl acetate 2:1), [α]_D²⁰ -22 (*c* 1.2, CHCl₃); ¹H-NMR (CDCl₃) δ 0.00 (s, 6H, SiMe), 0.81 (s, 9H, CMe₃), 2.48 (bs, 1H, OH), 3.51 (dt, 1H, *J* = 7.1, 5.3 Hz, H-5), 3.66 (dd, 1H, *J* = 4.1, 2.3 Hz, H-3), 3.86 (d, 1H, *J* = 5.3 Hz, H-6), 3.93 (dd, 1H, *J* = 4.1, 3.4 Hz, H-2), 4.10 (dd, 1H, *J* = 7.1, 2.3 Hz, H-4), 5.21 (d, 1H, *J* = 3.4 Hz, H-1), 7.30-7.54 (m, 5H, H_{arom}); ¹³C-NMR (CDCl₃) δ -5.1 (SiMe), 18.1 (CMe₃), 18.7 (CMe₃), 26.3 (CMe₃), 55.2 and 57.7 (C-2, C-3), 65.0 (C-6), 67.6, 71.4, and 72.1 (C-1, C-4, C-5), 127.0, 128.1, 128.8 and 138.8 (C_{arom}); Anal. calcd for C₁₈H₂₈O₄Si (mixture **6** + **7**): C, 64.25; H, 8.39. Found: C, 64.26; H, 8.59.

(6-*O*-*tert*-Butyldimethylsilyl-2,3-anhydro- α -D-mannopyranosyl)benzene (**7**). Yield 10%, oil, *R*_f 0.54 (petroleum ether-ethyl acetate 2:1), [α]_D²⁰ -21 (*c* 1.2, CHCl₃); ¹H-NMR (CDCl₃) δ 0.00 (s, 3H, SiMe), 0.03 (s, 3H, SiMe), 0.83 (s, 9H, CMe₃), 2.50 (bs, 1H, OH), 3.17 (ddd, 1H, *J* = 8.7, 5.3, 4.3 Hz, H-5), 3.44 (d, 1H, *J* = 3.6, Hz, H-2 or H-3), 3.55 (d, 1H, *J* = 3.6 Hz, H-2 or H-3), 3.58 (dd, 1H, *J* = 9.4, 4.3 Hz, H-6), 3.70 (dd, 1H, *J* = 9.4, 5.3 Hz, H-6), 3.87 (d, 1H, *J* = 8.7 Hz, H-4), 5.11 (s, 1H, H-1), 7.32-7.46 (m, 5H, H_{arom}); ¹³C-NMR (CDCl₃) δ -5.3 (SiMe), -5.2 (SiMe), 18.5 (CMe₃), 26.2 (CMe₃), 51.9 and 55.3 (C-2, C-3), 66.3 (C-6), 66.9, 69.4, and 72.9 (C-1, C-4, C-5), 128.6, 128.9, 129.1 and 136.8 (C_{arom}).

(4,6-*Di-O-tert*-butyldimethylsilyl-2,3-anhydro- β -D-allopyranosyl)benzene (**8a**). Yield 32%, oil, *R*_f 0.22 (petroleum ether-ethyl acetate-triethylamine 50:1:1), [α]_D²⁰ +116 (*c* 1.2, CH₂Cl₂); ¹H-NMR (CDCl₃) δ 0.02 (s, 3H, SiMe), 0.03 (s, 3H, Me), 0.17 (s, 3H, SiMe), 0.19 (s, 3H, SiMe), 0.90 (s, 9H, CMe₃), 0.95 (s, 9H, CMe₃), 3.33-3.40 (m, 2H, H-2, H-3), 3.49 (ddd, 1H, *J* = 9.0, 2.9, 2.7 Hz, H-5), 3.77-3.88 (m, 2H, H-6), 4.27 (dd, 1H, *J* = 9.0, 1.5 Hz, H-4), 4.90 (s, 1H, H-1), 7.29-7.44 (m, 5H, H_{arom}); ¹³C-NMR (CDCl₃) δ -5.2 (SiMe), -5.1 (SiMe), -4.7 (SiMe), -4.2 (SiMe), 18.1 (CMe₃), 18.4 (CMe₃), 25.8 (CMe₃), 26.0 (CMe₃), 55.4 and 60.5 (C-2, C-3), 62.3 (C-6), 65.9 (C-4), 74.7 (C-5), 76.0 (C-1), 126.6, 127.9, 128.4 and 139.7 (C_{arom}); Anal. calcd for C₂₄H₄₂O₄Si₂: C, 63.95; H, 9.39. Found: C, 63.93; H, 9.34.

(4,6-*Di-O-tert*-butyldimethylsilyl-2,3-anhydro- β -D-mannopyranosyl)benzene (**9a**). Yield 20%, oil, *R*_f 0.18 (petroleum ether-ethyl acetate-triethylamine 50:1:1), [α]_D²⁰ +89 (*c* 1.1, CH₂Cl₂); ¹H-NMR (CDCl₃) δ 0.01 (s, 3H, SiMe), 0.04 (s, 3H, SiMe), 0.15 (s, 3H, SiMe), 0.19 (s, 3H, SiMe), 0.88 (s, 9H, CMe₃), 0.94 (s, 9H, CMe₃), 3.22 (ddd, 1H, *J* = 9.1, 5.1, 2.0 Hz, H-5), 3.33-3.40 (s, 2H, H-2, H-3), 3.72 (dd, 1H, *J* = 11.5, 5.1 Hz, H-6), 3.83 (dd, 1H, *J* = 11.5, 2.0 Hz, H-6), 3.90 (d, 1H, *J* = 9.1 Hz, H-4), 4.83 (s, 1H, H-1), 7.30-7.48 (m, 5H, H_{arom}); ¹³C-NMR (CDCl₃) δ -5.1 (2xSiMe), -4.9 (SiMe), -4.4 (SiMe), 18.0 (CMe₃), 18.5 (CMe₃), 25.8 (CMe₃), 26.0 (CMe₃), 53.4 and 57.4 (C-2, C-3), 62.6 (C-4), 63.1 (C-6), 75.7 (C-5), 80.5 (C-1), 128.0, 128.3, 128.4 and 138.7 (C_{arom}); Anal. calcd for C₂₄H₄₂O₄Si₂: C, 63.95; H, 9.39. Found: C, 63.95; H, 9.38.

(2,3-Anhydro- β -D-allopyranosyl)benzene (**8b**). Yield 80%, oil, R_f 0.26 (diethyl ether); $^1\text{H-NMR}$ (CDCl_3) δ 2.80 (bs, 2H, OH), 3.46 (d, 1H, $J = 4.4$ Hz, H-2), 3.50-3.58 (m, 2H, H-3, H-5), 3.78 (dd, 1H, $J = 11.7, 5.5$ Hz, H-6), 3.90 (dd, 1H, $J = 11.7, 3.7$ Hz, H-6), 4.10 (dd, 1H, $J = 9.2, 1.8$ Hz, H-4), 4.89 (s, 1H, H-1), 7.25-7.50 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ 54.9 and 60.3 (C-2, C-3), 62.4 (C-6), 65.9 (C-4), 74.0 (C-5), 76.3 (C-1), 126.7, 128.4, 128.7 and 138.7 (C_{arom}); Anal. calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4$: C, 64.85; H, 6.35. Found: C, 64.94; H, 6.28.

(6-*O*-*tert*-Butyldimethylsilyl-2,3-anhydro- β -D-allopyranosyl)benzene (**10**). Yield 50%, oil, R_f 0.32 (petroleum ether-diethyl ether 2:1), $[\alpha]_{\text{D}}^{20} +100$ (c 0.9, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 0.10 (s, 6H, SiMe), 0.93 (s, 9H, CMe_3), 3.32 (d, 1H, $J = 3.9$ Hz, OH), 3.44 (d, 1H, $J = 4.3$ Hz, H-2), 3.57 (dd, 1H, $J = 4.3, 2.2$ Hz, H-3), 3.60 (ddd, 1H, $J = 9.0, 6.9, 4.9$ Hz, H-5), 3.79 (dd, 1H, $J = 10.1, 6.9$ Hz, H-6), 3.96 (dd, 1H, $J = 10.1, 4.9$ Hz, H-6), 4.19 (ddd, 1H, $J = 9.0, 3.9, 2.2$ Hz, H-4), 4.91 (s, 1H, H-1), 7.38 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -1.3 (2xSiMe), 18.7 (CMe_3), 26.3 (CMe_3), 55.2 and 57.7 (C-2, C-3), 65.0 (C-6), 67.6 (C-4), 71.4 (C-5), 72.1 (C-1), 127.0, 128.1, 128.8 and 138.8 (C_{arom}); Anal. calcd for $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Si}$: C, 64.25; H, 8.39. Found: C, 64.28; H, 8.79.

General procedure for the bis-hydroxylation.

A solution of the unsaturated carbohydrate (1 mmol), *N*-methylmorpholine oxide (470 mg, 4 mmol), and OsO_4 (5 mg, 0.02 mmol, 2%) in acetone/water (4 mL/1 mL) was stirred at rt until all the starting carbohydrate has disappeared as shown by TLC. Na_2SO_3 (500 mg) was then added, and the solution was stirred at rt for 0.5 h. After addition of brine (10 mL), the mixture was extracted with ethyl acetate (3x10 mL). Evaporation of the solvent under reduced pressure gave a residue that was purified by column chromatography on silica using the corresponding eluent for the silylated products. When starting from dihydroxy compounds **2a** and **2b**, the crude mixture was directly acetylated using a standard procedure, and the tetraacetates were purified by chromatography.

(4,6-Di-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranosyl)benzene (**11**). Yield 70%, oil, R_f 0.40 (petroleum ether-ethyl acetate 4:1), $[\alpha]_{\text{D}}^{20} +17$ (c 1.0, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 0.04 (s, 3H, SiMe), 0.06 (s, 3H, SiMe), 0.08 (s, 3H, SiMe), 0.10 (s, 3H, SiMe), 0.85 (s, 9H, CMe_3), 0.95 (s, 9H, CMe_3), 2.25 (bs, 1H, OH), 2.25 (d, 1H, $J = 7.4$ Hz, OH), 3.60 (ddd, 1H, $J = 5.9, 5.0, 3.7$ Hz, H-5), 3.74 (ddd, 1H, $J = 7.4, 6.6, 2.9$ Hz, H-3), 3.80 (dd, 1H, $J = 11.0, 5.0$ Hz, H-6), 3.96 (dd, 1H, $J = 6.6, 5.9$ Hz, H-4), 4.03 (dd, 1H, $J = 11.0, 3.7$ Hz, H-6), 4.27 (bdd, 1H, $J = 5.9, 2.9$ Hz, H-2), 4.90 (d, 1H, $J = 5.9$ Hz, H-1), 7.40 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -5.0 (SiMe), -4.9 (SiMe), -4.5 (SiMe), -4.0 (SiMe), 18.5 (CMe_3), 18.7 (CMe_3), 26.2 (2x CMe_3), 64.4 (C-6), 70.8, 71.2 and 72.2 (C-1, C-4, C-5), 77.6, and 77.7 (C-2, C-3), 127.3, 128.3, 129.0 and 138.7 (C_{arom}); Anal. calcd for $\text{C}_{24}\text{H}_{44}\text{O}_5\text{Si}_2$: C, 61.50; H, 9.47. Found: C, 61.50; H, 9.77.

(2,3,4,6-Tetra-*O*-acetyl- α -D-mannopyranosyl)benzene (**12**). Yield 43%, white solid, m.p. 136 °C, R_f 0.60 (petroleum ether-ethyl acetate 1:1), $[\alpha]_{\text{D}}^{20} +46$ (c 1.0, CHCl_3); $^1\text{H-NMR}$ (CDCl_3) δ 2.01 (s, 3H, Me), 2.06 (s, 3H, Me), 2.13 (s, 3H, Me), 2.17 (s, 3H, Me), 3.77 (ddd, 1H, $J = 8.8, 6.1, 2.6$ Hz, H-5), 4.14 (dd, 1H, $J = 12.0, 6.1$ Hz, H-6), 4.38 (dd, 1H, $J = 12.0, 2.6$ Hz, H-6), 5.12 (d, 1H, $J = 2.9$ Hz, H-

1), 5.17 (dd, 1H, $J = 9.1, 3.1$ Hz, H-3), 5.35 (dd, 1H, $J = 9.1, 8.8$ Hz, H-4), 6.20 (dd, 1H, $J = 3.1, 2.9$ Hz, H-2), 7.35-7.55 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ 21.1 (2xMe), 21.2 (Me), 21.4 (Me), 62.8 (C-6), 67.2 (C-4), 69.6 (C-2), 70.1 (C-3), 71.5 (C-5), 76.2 (C-1), 126.8, 128.9, 129.5 and 135.6 (C_{arom}), 170.0 (CO), 170.3 (CO), 170.7 (CO), 171.1 (CO). All the data are in agreement with the literature [21].

(4,6-Di-*O-tert-butyl*dimethylsilyl- β -D-mannopyranosyl)benzene (**13**) (as a mixture with **14**). Yield 56%, oil, R_f 0.45 (petroleum ether-ethyl acetate 4:1); $^1\text{H-NMR}$ (CDCl_3) δ 0.10 (s, 3H, SiMe), 0.14 (s, 3H, SiMe), 0.15 (s, 3H, SiMe), 0.19 (s, 3H, SiMe), 0.93 (s, 9H, CMe_3), 0.94 (s, 9H, CMe_3), 1.70 (bs, 1H, OH), 2.40 (bs, 1H, OH), 3.31 (ddd, 1H, $J = 9.2, 5.5, 2.9$ Hz, H-5), 3.66 (dd, 1H, $J = 8.8, 3.3$ Hz, H-3), 3.88 (dd, 1H, $J = 9.2, 8.8$ Hz, H-4), 3.93 (m, 2H, H-6), 4.06 (d, 1H, $J = 3.3$ Hz, H-2), 4.60 (s, 1H, H-1), 7.28 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -5.1 (CH_3), -5.0 (CH_3), -4.8 (CH_3), -4.0 (CH_3), 18.4 (CMe_3), 18.5 (CMe_3), 26.0 (CMe_3), 26.1 (CMe_3), 62.3 (C-6), 69.1, 73.1, and 76.3 (C-1, C-4, C-5), 79.4 and 81.5 (C-2, C-3), 126.0, 127.7, 128.4 and 138.0 (C_{arom}); Anal. calcd for $\text{C}_{24}\text{H}_{44}\text{O}_5\text{Si}_2$ (mixture **13** + **14**): C, 61.50; H, 9.47. Found: C, 61.86; H, 9.31.

(4,6-Di-*O-tert-butyl*dimethylsilyl- β -D-allopyranosyl)benzene (**14**) (as a mixture with **13**). Yield 14%, oil, R_f 0.45 (petroleum ether-ethyl acetate 4:1); $^1\text{H-NMR}$ (CDCl_3) δ 0.00 (s, 3H, SiMe), 0.03 (s, 3H, SiMe), 0.07 (s, 3H, SiMe), 0.16 (s, 3H, SiMe), 0.90 (s, 9H, CMe_3), 0.93 (s, 9H, CMe_3), 1.50 (bs, 1H, OH), 2.60 (bs, 1H, OH), 3.50 (dd, 1H, $J = 9.9, 2.9$ Hz, H-2), 3.61 (ddd, 1H, $J = 9.5, 2.9, 1.5$ Hz, H-5), 3.80 (dd, 1H, $J = 11.4, 2.9$ Hz, H-6), 3.87 (dd, 1H, $J = 11.4, 1.5$ Hz, H-6), 4.01 (dd, 1H, $J = 9.5, 2.9$ Hz, H-4), 4.20 (dd, 1H, $J = 2.9, 2.9$ Hz, H-3), 4.50 (d, 1H, $J = 9.9$ Hz, H-1), 7.40 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ -5.2 (CH_3), -5.0 (CH_3), -4.8 (CH_3), -4.5 (CH_3), 18.0 (CMe_3), 18.2 (CMe_3), 25.8 (CMe_3), 26.0 (CMe_3), 62.2 (C-6), 67.8, 71.5 and 73.1 (C-1, C-4, C-5), 76.1 and 77.6 (C-2, C-3), 127.4, 128.0, 128.2 and 137.0 (C_{arom}).

(2,3,4,6-Tetra-*O-acetyl*- β -D-mannopyranosyl)benzene (**15**) (as a mixture with **16**). Yield 19%, oil, R_f 0.30 (petroleum ether-ethyl acetate 1:1); $^1\text{H-NMR}$ (CDCl_3) δ 2.00 (s, 3H, Me), 2.03 (s, 3H, Me), 2.11 (s, 3H, Me), 2.20 (s, 3H, Me), 3.83 (ddd, 1H, $J = 9.5, 5.9, 2.6$ Hz, H-5), 4.21-4.30 (m, 1H, H-6), 4.35 (dd, 1H, $J = 12.5, 5.9$ Hz, H-6), 4.79 (d, 1H, $J = 1.1$ Hz, H-1), 5.25 (dd, 1H, $J = 10.2, 3.3$ Hz, H-3), 5.33 (dd, 1H, $J = 10.2, 9.5$ Hz, H-4), 5.55 (dd, 1H, $J = 3.3, 1.1$ Hz, H-2), 7.30 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ 20.2 (Me), 20.3 (Me), 20.8 (Me), 21.0 (Me), 60.4 (C-6), 66.6 (C-4), 73.1 (C-2), 77.3 (C-3), 77.4 (C-5), 81.8 (C-1), 127.2, 128.7, 129.2, and 136.3 (C_{arom}), 168.7 (CO), 168.9 (CO), 169.2 (CO), 170.6 (CO). All data are in agreement with the literature [21].

(2,3,4,6-Tetra-*O-acetyl*- β -D-allopyranosyl)benzene (**16**) (as a mixture with **15**). Yield 56%, oil, R_f 0.30 (petroleum ether-ethyl acetate 1:1); $^1\text{H-NMR}$ (CDCl_3) δ 1.80 (s, 3H, Me), 2.03 (s, 3H, Me), 2.08 (s, 3H, Me), 2.23 (s, 3H, Me), 4.15-4.27 (m, 3H, H-5, H-6), 4.71 (d, 1H, $J = 10.3$ Hz, H-1), 5.03 (dd, 1H, $J = 10.3, 2.9$ Hz, H-2), 5.12 (dd, 1H, $J = 9.9, 2.6$ Hz, H-4), 5.73 (dd, 1H, $J = 2.9, 2.6$ Hz, H-3), 7.35-7.43 (m, 5H, H_{arom}); $^{13}\text{C-NMR}$ (CDCl_3) δ 20.4 (Me), 20.6 (Me), 20.8 (Me), 21.4 (Me), 62.8 (C-6), 66.6 (C-4), 68.5 (C-2), 70.6 (C-3), 71.4 (C-5), 76.2 (C-1), 126.9, 127.2, 128.4 and 136.9 (C_{arom}), 168.8 (CO), 169.2 (CO), 170.0 (CO), 170.8 (CO).

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