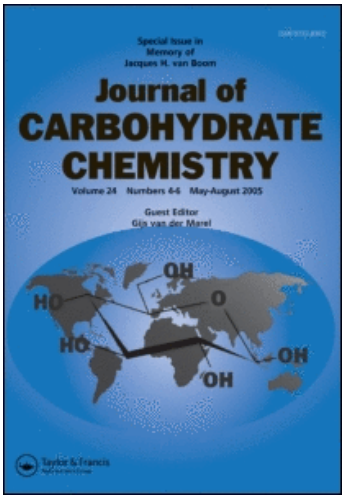

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PREPARATION OF 2,5-ANHYDROHEXITOLS (PART II). INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTION OF CYCLIC SULFATES

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ABSTRACT

The 2-*O*-acetyl-3,4-di-*O*-benzyl-5,6-*O*-cyclic sulfates **5**, **16** and **25**, derived from D-arabinose, D-ribose and D-xylose, respectively, are useful precursors in the synthesis of 2,5-anhydrohexitols. 5-*Exo-tet* cyclization of compounds **5**, **16**, and **25** under the influence of base leads to the predominant or exclusive formation of the corresponding tetrahydrofuran derivatives

INTRODUCTION

In the last decade, cyclic sulfates have proven to be useful intermediates to accomplish regioselective nucleophilic substitutions.[1] Cyclic sulfates, readily accessible from the corresponding 1,2-diol functions, are highly prone to ring-opening by a range of nucleophiles, whereas competing elimination is stereoelectronically unfavorable. The recent development of the asymmetric dihydroxylation reaction,[2] affording direct access to enantiomerically pure diols, has further widened the scope of cyclic sulfate methodology. Apart from 1,2-diols, cyclic sulfates can be prepared from 1,3- and 1,4-diols, which *inter alia* have found useful application in natural product synthesis using

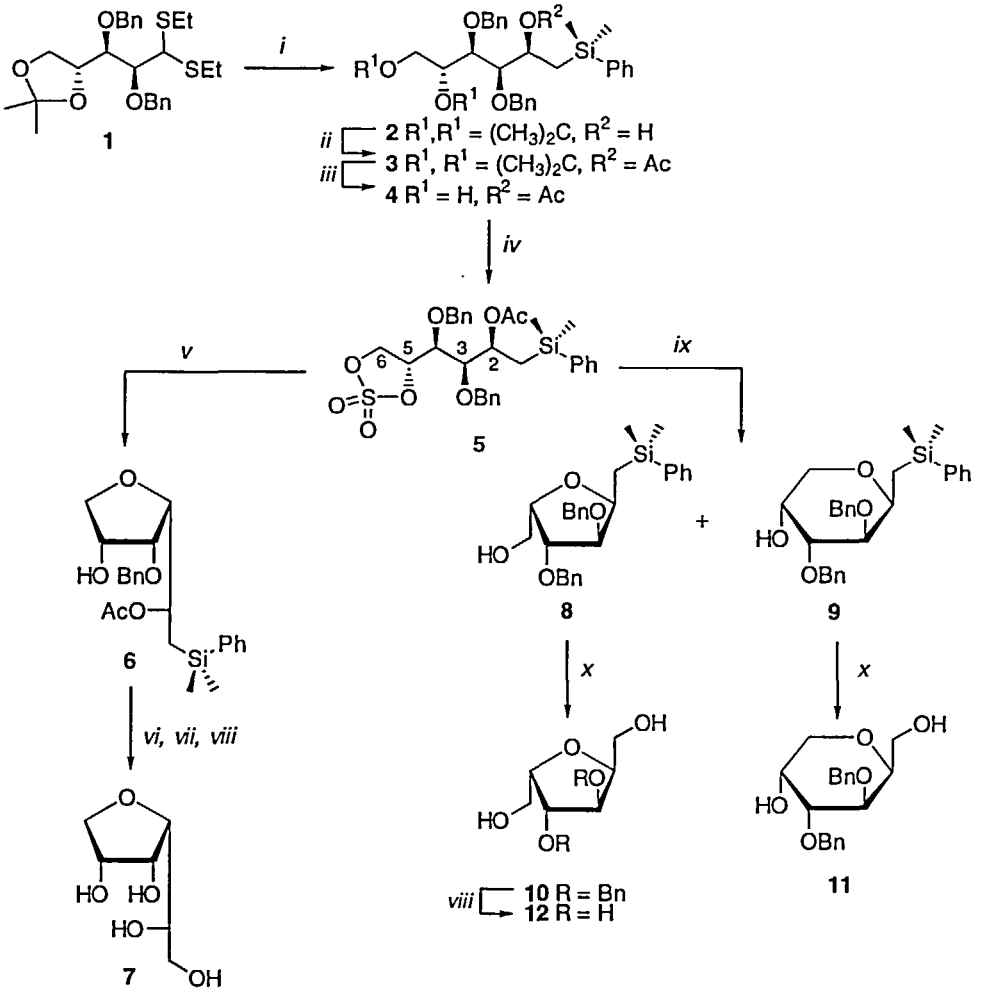
carbohydrates as starting materials.[3,4] For instance, we showed[4a] that azido glycosides could be obtained *via* regioselective diaxial opening of five-membered cyclic sulfates with lithium azide. Furthermore, cyclic sulfates of 1,4-diols in open chain carbohydratesare key intermediates[4b] *en route* towards the eight-carbon monosaccharide KDO (3-deoxy-D-*manno*-2-octulosonic acid). A similar methodology was also applied[4c] in the assembly of polyhydroxylated pyrrolidines, promising glucosidase inhibitors. In contrast to the intermolecular substitution of cyclic sulfates, the intramolecular version of the reaction has to date received scant attention.[5]

In this paper we describe the base-induced cyclization of carbohydrate-derived cyclic sulfates bearing a remote hydroxyl function.

RESULTS AND DISCUSSION

In the preceeding paper we showed that hydrolysis of dithioacetal **1**, followed by Grignard addition of (dimethylphenylsilyl)methylmagnesium chloride to the resulting aldehyde, produced β-hydroxysilane **2** with excellent stereoselectivity (Scheme 1). Deacetonation of compound **2** and acid-mediated cyclization of the resulting triol gave, depending on the nature of the acid, 2,5-anhydrohexitols with high stereocontrol.[6]

It occurred to us that transformation of β-hydroxysilane **2** into cyclic sulfate **5**, followed by a favored[7] 5-*exo-tet* cyclization, may present an alternative route to 2,5-anhydrohexitols. It was expected that base treatment of **5** would result in intramolecular nucleophilic attack of O-2 at the cyclic sulfate. Thus, cyclic sulfate **5** was prepared from β-hydroxysilane **2** involving acetylation to **3** and removal of the 5,6-isopropylidene function with aqueous acetic acid. Reaction of the resulting diol **4** with thionyl chloride and pyridine in ethyl acetate, followed by oxidation according to the Sharpless protocol ($RuCl_3$, $NaIO_4$)[8] led to the cyclic sulfate **5**. In the first instance, cyclization of **5** under the influence of $NaHCO_3$, in aqueous THF for 2 h at 65 °C, was investigated. TLC analysis of the reaction mixture showed complete conversion of cyclic sulfate **5** into a highly polar sulfate derivative. Mild acid hydrolysis, followed by work-up and purification led to the isolation of 1,4-anhydro-L-gulitol derivative **6**. The identity of **6** was ascertained by NMR analysis (^1H, ^{13}C), showing the absence of one benzyl group, as well as by the three-step transformation of **6** into known[9] 1,4-anhydro-L-gulitol (**7**).



Reagents and conditions

(*i*) (a) HgO, BF_3·Et_2O, 80% THF (b) $PhMe_2SiCH_2MgCl$, Et_2O, 0 °C (90%); (*ii*) Ac_2O, pyridine, 3 h (100%); (*iii*) 80% HOAc, 15 h (91%); (*iv*) (a) $SOCl_2$, pyridine, EtOAc, 0 °C, 5 min (b) $RuCl_3$, $NaIO_4$, CH_3CN, CH_2Cl_2, H_2O, 0.5 h (88%); (*v*) (a) $NaHCO_3$, 90% THF, reflux, 2 h (b) H_2SO_4, 50 °C, 1 h (87%); (*vi*) KBr, AcO_2H, NaOAc, AcOH, 2 h (64%); (*vii*) KO*t*-Bu, MeOH, 8 h (91%); (*viii*) H_2, Pd-C, 12 h (**7**: 100%, **12**: 96%); (*ix*) (a) LiOMe, MeOH, 3 h (b) H_2SO_4, 50 °C, 3 h (**8**+**9**: 86%, ratio 5:2); (*x*) KBr, NaOAc, AcO_2H, AcOH, 3 h (**10**: 50%, **11**: 21%).

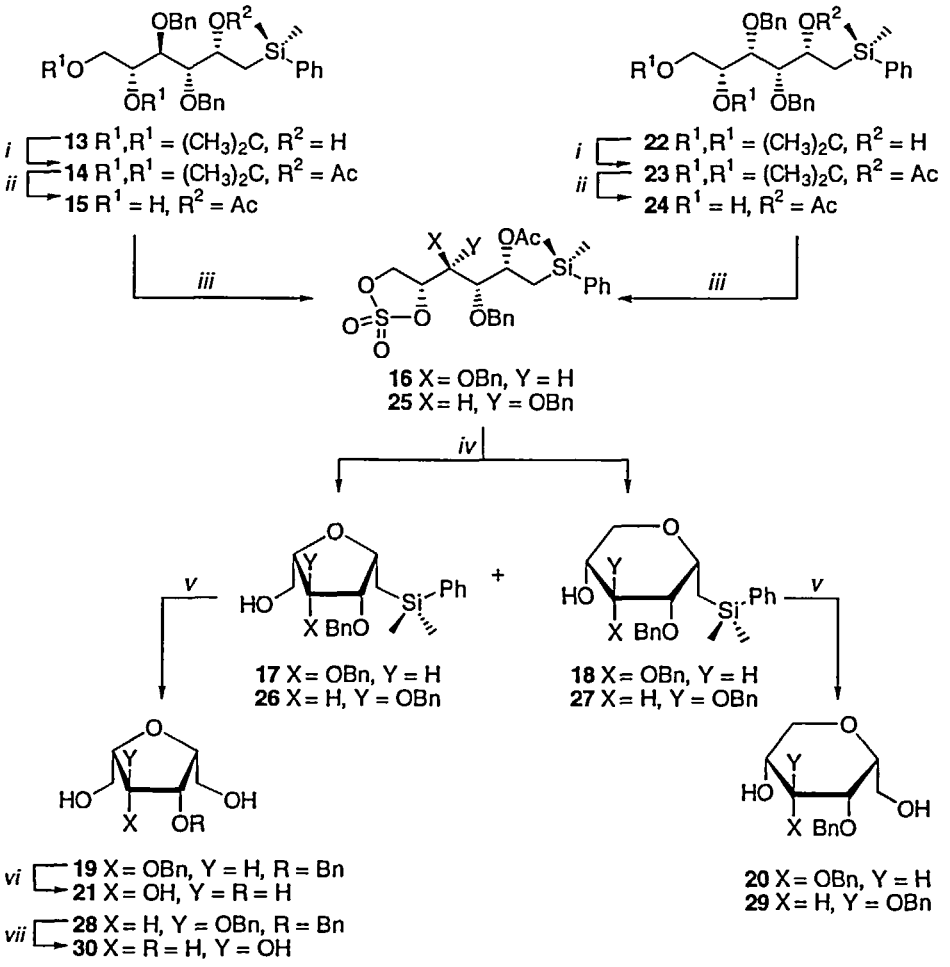
Scheme 1

The unexpected formation of **6** can be explained by debenzylating cycloetherification[4d,10] of **5** *via* nucleophilic attack of the C-3 oxygen at the primary C-6 position.[11]

Next, we attempted to induce the projected cyclization by subjecting **5** to K_2CO_3 in a mixture of MeOH and THF[12] (1 h). In this case an intractable mixture of products was isolated after acid hydrolysis of the intermediate sulfate ester. On the contrary, spectroscopic analysis of the crude products obtained by reaction of **5** with LiOH in THF/MeOH revealed the presence of two isomeric products **8** and **9** (ratio 5:2), the identity of which was readily corroborated by comparison of the carbon NMR spectra with those of previously prepared[6,13] **8** and **9**. The preferential formation of **8** over **9** shows that 5-*exo-tet* cyclization is favored over the corresponding 6-*exo-tet* process. Moreover, side-products resulting from competing attack of methoxide anion at C-6 or at sulfur of the cyclic sulfate function in **5** could not be detected. It is of interest to note that attempts to influence the regioselectivity of the cyclization by variation of the methoxide counterions and solvents were unsuccessful.

Oxidative unmasking of the silyl function in the mixture of cyclic products **8** and **9**, followed by separation of the resulting products, gave homogeneous alcohols **10** and **11**. Hydrogenolysis of the major product **10** afforded known[14] 2,5-anhydro-L-iditol **12**, the spectroscopic data of which are in all aspects identical with an authentic sample. Likewise, removal of benzyl protective groups from compound **11** gave 1,5-anhydro-L-gulitol.[15]

The scope of the intramolecular substitution of cyclic sulfates was further evaluated using the diastereomeric cyclic sulfates **16** and **25** (Scheme 2). Thus, β-hydroxysilane adducts **13** and **22**, obtained[6] from suitably protected diethyl dithioacetals of D-ribose and D-xylose, respectively, were converted into the corresponding cyclic sulfates by acetylation (Ac_2O, pyridine), deacetonation (80% HOAc), treatment with thionyl chloride and finally oxidation with $RuCl_3/NaIO_4$. The cyclic sulfates **16** and **25** were subjected to LiOMe in MeOH or MeOH/THF,[12] respectively. In a similar way as described for arabinose-derived **5**, nucleophilic ring opening of **16** and **25** and subsequent acidic hydrolysis resulted in the formation of intractable mixtures of the isomeric products **17/18** (ratio 6:1) and **26/27** (ratio 4:1), respectively. Treatment of the mixture of **17** and **18** with KBr and peracetic acid resulted in oxidative cleavage of the carbon-silicon bond to give, after separation on silica gel,



Reagents and conditions

(*i*) Ac_2O, pyridine, 2 h (**14**: 83%, **23**: 96%); (*ii*) 80% HOAc, 16 h (**15**: 83%, **24**: 92%); (*iii*) (a) $SOCl_2$, pyridine, EtOAc, 0 °C (b) $RuCl_3$, $NaIO_4$, CH_3CN, CH_2Cl_2, H_2O (**16**: 79%, **25**: 74%); (*iv*) LiOMe, MeOH, 2 h. 2. H_2SO_4, 50 °C, 6 h (**17+18**: 70%, ratio 6:1, **26+27**: 66%, ratio 4:1); (*v*) KBr, AcO_2H, NaOAc, AcOH (**19**: 64%, **20**: 11%, **28**: 57%, **29**: 14%); (*vi*) H_2, Pd-C, MeOH (**21**: 87%, **30**: 97%).

Scheme 2

diastereomerically pure alcohols **19** and **20**. Analogously, oxidative unmasking and separation of **26** and **27** afforded homogeneous products **28** and **29**. Removal of the benzyl groups in tetrahydrofurans **19** and **28** led to a near quantitative isolation[16] of 2,5-anhydroallitol[17] (**21**) and 2,5-anhydro-L-glucitol[18] (**30**).

In conclusion, the cyclic sulfates **5**, **16** and **25**, derived from D-arabinose, D-ribose and D-xylose, respectively, are useful precursors for the synthesis of 2,5-anhydrohexitols (*C*-glycosides).[19] In this respect, it is of interest to note that the above described methodology is complementary to the previously reported[6] acid-mediated synthesis of functionalized tetrahydrofurans.

EXPERIMENTAL

General methods and materials. Toluene was distilled from P_2O_5 and stored over 4Å molecular sieves, THF and Et_2O were freshly distilled from $LiAlH_4$. All reactions were performed under strictly anhydrous conditions unless noted otherwise. Reactions were followed by TLC analysis on Schleicher and Schüll DC Fertigfolien F 1500 LS 254. Compounds were visualized by UV light (254 nm) and spraying with 20% H_2SO_4 in MeOH followed by charring at 140 °C. Column chromatography was performed on silica gel 60, 230-400 mesh (Merck). Optical rotations were measured in $CHCl_3$ on a Propol automatic polarimeter. ^1H NMR spectra and ^{13}C NMR spectra (50.1 MHz) were recorded in deuterated chloroform using a Jeol JNM-FX 200 spectrometer. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard.

2-*O*-Acetyl-3,4-di-*O*-benzyl-5,6-*O*-isopropylidene-1-deoxy-1-dimethylphenylsilyl-D-glucitol (3). To a stirred solution of compound **2** (3.80 g, 7.31 mmol) in pyridine (30 mL) and Ac_2O (15 mL) was added DMAP (0.1 g). After 3 h, solvents were removed *in vacuo* and the residual oil was coevaporated with 1,4-dioxane (4x 4 mL). The residue was purified on silica gel (elution: Et_2O/light petroleum, 1/4 1/3, v/v) to afford **3** as a solid, yield 4.10 g (100%). R_f 0.8 (Et_2O/light petroleum, 1/1, v/v). $[\alpha]_D^{20}$ +19.3° (*c* 1). Mp 56-57 °C. ^1H NMR: δ 7.48-7.21 (m, 15H, CH, arom), 5.32 (dt, 1H, H-2, $J_{1a,2}$ $J_{2,3}$ 5.8 Hz, $J_{1b,2}$ 8.3 Hz), 4.68 (AB, 2H, CH_2, Bn, *J* -11.3 Hz), 4.54 (AB, 2H, CH_2, Bn, *J* -11.6), 4.15 (dt, 1H, H-5, $J_{4,5}$ 4.7 Hz, $J_{5,6a}$ $J_{5,6b}$ 6.8 Hz), 3.92 (dd, 1H, H-6a, $J_{6a,6b}$ -8.1 Hz), 3.88 (dd, 1H, H-6b), 3.78 (t, 1H, H-4, $J_{3,4}$ 4.7 Hz), 3.43 (dd, 1H, H-3), 1.73 (s, 3H, CH_3, Ac), 1.41,

1.31 (2x s, 6H, CH_3, isoprop), 1.22-1.10 (m, 1H, H-1a), 0.90-0.78 (m, 1H, H-1b), 0.29, 0.24 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 169.6 (C=O), 138.2, 138.0 (Cq, arom), 133.3, 128.7-127.3 (CH, arom), 108.2 (Cq, isoprop), 81.8, 78.2, 76.3 (C-3, C-4, C-5), 74.3, 73.6 (CH_2, Bn), 71.2 (C-2), 65.6 (C-6), 26.3, 24.8 (CH_3, isoprop), 20.6 (CH_3, Ac), 17.9 (C-1), -2.6, -3.0 ($SiCH_3$).

Anal. Calcd for $C_{33}H_{42}O_6Si$ (562.78): C, 70.43; H, 7.52. Found: C, 70.06; H, 7.36.

2-*O*-Acetyl-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-glucitol (4). After stirring compound **3** (4.10 g, 7.31 mmol) in 80% aqueous AcOH (80 mL) for 15 h, solvents were removed *in vacuo*, the residue coevaporated with toluene (3x 4 mL) and applied onto a column of silica gel. Elution with Et_2O/light petroleum (1/1 2/1, v/v) afforded compound **4** as an oil, yield 3.47 g (91%). R_f 0.3 (Et_2O/light petroleum, 3/1, v/v). ^1H NMR: δ 7.52-7.24 (m, 15H, CH, arom), 5.39 (ddd, 1H, H-2, $J_{1a,2}$ 5.8 Hz, $J_{1b,2}$ 8.6 Hz, $J_{2,3}$ 4.7 Hz), 4.56 (AB, 2H, CH_2, Bn, J -11.3 Hz), 4.54 (AB, 2H, CH_2, Bn, J -12.0), 3.70-3.64 (m, 4H, H-4, H-5, H-6), 3.54 (t, 1H, H-3, $J_{3,4}$ 4.7 Hz), 2.94 (bs, 1H, OH), 2.13 (bs, 1H, OH), 1.79 (s, 3H, CH_3, Ac), 1.33 (dd, 1H, H-1a, $J_{1a,1b}$ -14.8 Hz), 0.88-0.82 (m, 1H, H-1b), 0.30, 0.26 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 170.1 (C=O), 138.1, 137.6 (Cq, arom), 133.3, 128.7-127.5 (CH, arom), 81.0, 77.5 (C-3, C-4), 73.9, 73.3 (CH_2, Bn), 71.3, 70.8 (C-2, C-5), 63.0 (C-6), 20.7 (CH_3, Ac), 18.3 (C-1), -2.7, -2.9 ($SiCH_3$).

Anal. Calcd for $C_{30}H_{38}O_6Si$ (522.71): C, 68.93; H, 7.33. Found: C, 68.74; H, 7.01.

2-*O*-Acetyl-3,4-di-*O*-benzyl-5,6-*O*-(cyclic sulfate)-1-deoxy-1-dimethylphenylsilyl-D-glucitol (5). To a cooled (0 °C) solution of diol **4** (0.78 g, 1.5 mmol) in EtOAc (10 mL) was added $SOCl_2$ (0.20 g, 1.65 mmol) and a mixture of pyridine (0.26 g, 3.30 mmol) and EtOAc (2 mL). After 30 min, TLC-analysis (Et_2O/light petroleum, 1/1, v/v) revealed the conversion of **5** into two more apolar products (R_f 0.7 and 0.8). EtOAc (20 mL) and H_2O (5 mL) were added, the layers separated and the organic layer washed with brine (5 mL). The aqueous phases were combined and extracted with EtOAc (20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was coevaporated with MeCN to remove traces of pyridine before dissolving in a mixture of MeCN (4 mL), CH_2Cl_2 (4 mL) and H_2O (6 mL). To the rapidly stirred mixture was added $NaIO_4$ (0.64 g, 3.0 mmol) and catalytic $RuCl_3$. After 15 min, the mixture was

filtered, rinsed with CH_2Cl_2 (20 mL), washed with cold H_2O (5 mL) and dried ($MgSO_4$). The oil obtained after concentration was purified by flash chromatography (elution: CH_2Cl_2/light petroleum, 3/2, v/v) to give **5** as white crystals, yield 0.76 g (88%). R_f 0.5 (Et_2O/light petroleum, 1/1, v/v). $[\alpha]_D^{20}$ +9.0° (*c* 1). Mp 97-98 °C (decomp). ^1H NMR: δ 7.49-7.16 (m, 15H, CH, arom), 5.32 (ddd, 1H, H-2, $J_{1a,2}$ 5.6 Hz, $J_{1b,2}$ 8.3 Hz, $J_{2,3}$ 6.4 Hz), 4.81 (ddd, 1H, H-5, $J_{4,5}$ 3.1 Hz, $J_{5,6a}$ $J_{5,6b}$ 6.1 Hz), 4.77 (dd, 1H, H-6a, $J_{6a,6b}$ -9.1 Hz), 4.64 (AB, 2H, CH_2, Bn, *J* -12.4 Hz), 4.45 (AB, 2H, CH_2, Bn, *J* -11.6 Hz), 4.30 (dd, 1H, H-6b), 4.00 (t, 1H, H-4, $J_{3,4}$ 4.2 Hz), 3.40 (dd, 1H, H-3), 1.76 (s, 3H, CH_3, Ac), 1.14 (dd, 1H, H-1a, $J_{1a,1b}$ -14.6 Hz), 1.11 (dd, 1H, H-1b), 0.31, 0.25 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 169.7 (C=O), 137.9, 136.8, 136.5 (Cq, arom), 133.4, 129.1-127.7 (CH, arom), 83.0, 80.4, 76.0 (C-3, C-4, C-5), 74.7, 74.2 (CH_2, Bn), 70.5 (C-2), 69.2 (C-6), 20.8 (CH_3, Ac), 17.7 (C-1), -2.8, -3.0 ($SiCH_3$).

Anal. Calcd for $C_{30}H_{36}O_8SSi$ (584.76): C, 61.62; H, 6.21. Found: C, 61.46; H, 6.16.

2-*O*-Acetyl-3,6-anhydro-4-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-glucitol (6). Cyclic sulfate **5** (0.31 g, 0.52 mmol) was dissolved in 90% aqueous THF (5 mL) and $NaHCO_3$ (88 mg, 1.04 mmol) was added. The mixture was heated to reflux for 2 h, cooled to 50 °C, and H_2SO_4 (2 drops) was added. After stirring at 50 °C for 1 h, the mixture was cooled to rt, a saturated solution of $NaHCO_3$ was added and the mixture extracted with Et_2O (2x 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated before purification on silica gel to afford **6** as a colorless oil, yield 0.19 g (87%). R_f 0.2 (Et_2O/light petroleum, 1/1, v/v). $[\alpha]_D^{20}$ +1.1° (*c* 1). ^1H NMR: δ 7.45-7.25 (m, 10H, H-arom), 5.34 (dt, 1H, H-2, $J_{1a,2}$ $J_{2,3}$ 5.8 Hz, $J_{1b,2}$ 8.3 Hz), 4.56 (AB, 2H, CH_2, Bn, *J* -11.6 Hz), 4.23 (m, 1H, H-5), 4.02 (dd, 1H, H-4, $J_{3,4}$ 7.0 Hz, $J_{4,5}$ 5.4 Hz), 3.84 (dd, 1H, H-6a, $J_{5,6a}$ 2.6 Hz, $J_{6a,6b}$ -9.8 Hz), 3.72 (dd, 1H, H-3), 3.65 (dd, 1H, H-6b, $J_{5,6b}$ 4.3 Hz), 3.01 (d, 1H, OH, *J* 9.4 Hz), 1.80 (s, 3H, CH_3, Ac), 1.25 (dd, 1H, H-1a, $J_{1a,1b}$ -14.6 Hz), 1.17 (dd, 1H, H-1b), 0.30, 0.26 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 170.1 (C=O), 138.4, 137.1 (Cq, arom), 133.4, 128.8-127.6 (CH, arom), 81.4, 78.9 (C-3, C-4), 73.2, 72.6 (CH_2, Bn, C-6), 70.7, 70.0 (C-2, C-5), 20.8 (CH_3, Ac), 18.9 (C-1), -2.3, -2.9 ($SiCH_3$).

Anal. Calcd for $C_{23}H_{30}O_5Si$ (414.57): C, 66.64; H, 7.29. Found: C, 66.59; H, 7.25.

1,4-Anhydro-L-gulitol (7). A solution of NaOAc (0.5 g) in AcOH (5 mL) was added to **6** (0.19 g, 0.45 mmol), followed by KBr (72 mg, 0.54 mmol). The mixture was cooled (10 °C) and AcOOH (2.5 mL, 30% in AcOH) was added dropwise in the dark. After 2 h, the mixture was diluted with EtOAc (30 mL) and poured into a cooled (0 °C) solution of $Na_2S_2O_3$ (5 mL, 15%). The layers were separated and to the organic phase was added aqueous $NaHCO_3$ (10 mL, 15%), followed by solid $NaHCO_3$ until no more gas evolved. The organic phase was washed with H_2O (10 mL), dried ($MgSO_4$) and solvents were evaporated *in vacuo*. The residue was coevaporated with toluene (2x 5 mL) and purified on silica gel to give 2-*O*-acetyl-3,6-anhydro-4-*O*-benzyl-D-glucitol, yield 85 mg (64%). R_f 0.5 (EtOAc/MeOH, 19/1, v/v). $[\alpha]_D^{20}$ +11.1° (*c* 1). ^{1}H NMR: δ 7.41-7.25 (m, 5H, H-arom), 5.16 (q, 1H, H-2, $J_{1a,2}$ $J_{2,3}$ 5.5 Hz, $J_{1b,2}$ 8.1 Hz), 4.62 (AB, 2H, CH_2, Bn, *J* -11.4 Hz), 4.29 (m, 1H, H-5), 4.22-4.18 (m, 2H, H-3, H-4), 3.96 (dd, 1H, H-6a, $J_{5,6a}$ 1.7 Hz, $J_{6a,6b}$ -10.1 Hz), 3.85 (m, 1H, H-1), 3.73 (dd, 1H, H-6b, $J_{5,6b}$ 3.6 Hz), 3.04 (d, 1H, OH, *J* 8.4 Hz), 2.20 (bs, 1H, OH), 2.06 (s, 3H, CH_3, Ac). ^{13}C{^{1}H} NMR: δ 170.6 (C=O), 136.9 (Cq, arom), 128.5, 128.1, 127.7 (CH, arom), 79.9, 77.1 (C-3, C-4), 73.2 (CH_2, Bn, C-6), 72.6, 70.0 (C-2, C-5), 62.4 (C-1), 21.0 (CH_3, Ac). The resulting alcohol (85 mg, 0.29 mmol) was dissolved in MeOH (3 mL) and KO*t*-Bu was added (6 mg, 0.05 mmol). The mixture was stirred for 8 h, neutralized with Dowex-H^+, filtered and concentrated. The residue was applied onto a column of silica gel and elution effected with EtOAc/MeOH (99/1, v/v) to give 3,6-anhydro-4-*O*-benzyl-D-glucitol as an oil, yield 67 mg (91%). R_f 0.4 (EtOAc/MeOH, 19/1, v/v). $[\alpha]_D^{20}$ -21.3° (*c* 0.5). ^{1}H NMR: δ 7.40-7.26 (m, 5H, H-arom), 4.68 (AB, 2H, CH_2, Bn, *J* -11.6 Hz), 4.29-3.73 (m, 8H, H-1, H-2, H-3, H-4, H-5, H-6). ^{13}C{^{1}H} NMR: δ 137.2 (Cq, arom), 128.5, 128.0, 127.7 (CH, arom), 79.0, 78.2 (C-3, C-4), 73.9, 72.4 (CH_2, Bn, C-6), 69.0 (C-2, C-5), 64.4 (C-1). The deacetylated product (67 mg, 0.26 mmol) was dissolved in MeOH (2 mL) and degassed before the addition of 10% Pd-C (20 mg). An H_2 atmosphere was introduced and the mixture stirred until TLC-analysis showed the absence of UV positive products. The catalyst was removed by filtration over Hyflo followed by rinsing with MeOH. Concentration afforded **7**, pure enough for spectral analysis, yield 43 mg (100%). $[\alpha]_D^{20}$ +8.7° (*c* 1, H_2O). Mp 107 °C. ^{1}H NMR (COSY): δ 4.41 (dt, 1H, H-2, $J_{2,3}$ 4.8 Hz, $J_{1a,2}$ $J_{1b,2}$ 6.6 Hz), 4.27 (t, 1H, H-3, $J_{3,4}$ 4.2 Hz), 3.96 (dd, 1H, H-1a, $J_{1a,1b}$ -9.0 Hz), 3.92 (dt,

1H, H-5, $J_{5,6a}$ 3.4 Hz, $J_{5,6b}$ $J_{4,5}$ 6.3 Hz), 3.89 (dd, 1H, H-4), 3.72 (dd, 1H, H-6a, $J_{6a,6b}$ -11.7 Hz), 3.70 (dd, 1H, H-1b), 3.60 (dd, 1H, H-6b). $^{13}C\{^1H\}$ NMR: δ 80.8 (C-4), 71.9, 71.6, 71.1 (C-2, C-3, C-5), 70.8 (C-1), 63.2 (C-6).

2,5-Anhydro-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-L-iditol (8) and 2,6-Anhydro-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-glucitol (9). To a solution of cyclic sulfate **5** (0.17 g, 0.29 mmol) in a mixture of dry THF (1 mL) and MeOH (2 mL) was added a freshly prepared solution of LiOMe in MeOH (0.35 mL, 1 M). After 3 h, TLC analysis indicated the complete conversion of **5** into baseline material. Concentrated H_2SO_4 (2 drops) was added and stirring continued at 50 °C for 3 h. Work-up was executed as described in the preparation of **6** to give **8** and **9** as a mixture of isomers (ratio 5:2) after silica gel column chromatography (elution: Et_2O/light petroleum, 1/1, v/v), yield 0.11 g (86%). R_f 0.7 (Et_2O/light petroleum, 3/1, v/v). Compound **8**: ^1H NMR: δ 7.54-7.20 (m, 15H, H-arom), 4.43 (AB, 2H, CH_2, Bn, J -11.8 Hz), 4.31 (AB, 2H, CH_2, Bn, J -11.6 Hz), 4.22 (ddd, 1H, H-2, $J_{1a,2}$ 7.6 Hz, $J_{1b,2}$ 7.3 Hz, $J_{2,3}$ 3.5 Hz), 4.13 (q, 1H, H-5), 4.04 (dd, 1H, H-4, $J_{3,4}$ 1.5 Hz, $J_{4,5}$ 5.3 Hz), 3.77 (dd, 1H, H-6a, $J_{5,6a}$ 5.5 Hz, $J_{6a,6b}$ -11.6 Hz), 3.67 (dd, 1H, H-6b, $J_{5,6b}$ 4.9 Hz), 3.60 (dd, 1H, H-3), 1.32 (dd, 1H, H-1a, $J_{1a,1b}$ -14.3 Hz), 1.19 (dd, 1H, H-1b), 0.33, 0.31 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 138.9, 137.8, 137.4 (Cq, arom), 133.5, 128.7-127.3 (CH, arom), 82.9, 82.7 (C-3, C-4), 78.5, 77.5 (C-2, C-5), 72.2, 71.5 (CH_2, Bn), 61.6 (C-6), 15.7 (C-1), -2.2, -2.7 ($SiCH_3$). Compound **9**: ^1H NMR: δ 7.53-7.18 (m, 15H, H-arom), 4.43 (s, 2H, CH_2, Bn), 4.40 (AB, 2H, CH_2, Bn, J -11.8 Hz), 4.00-3.94 (m, 1H, H-5), 3.76-3.68 (m, 3H, H-2, H-3, H-4), 3.35-3.21 (m, 2H, H-6), 2.04 (d, 1H, OH, J 8.6 Hz), 1.29 (dd, 1H, H-1a, $J_{1a,1b}$ -14.8 Hz, $J_{1a,2}$ 9.2), 0.87 (dd, 1H, H-1b, $J_{1b,2}$ 5.4 Hz), 0.31, 0.29 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 137.9, 137.7 (Cq, arom), 133.6, 128.9-127.7 (CH, arom), 76.4, 75.6 (C-3, C-4), 73.2, 72.7 (CH_2, Bn), 72.2 (C-2), 66.9 (C-6), 64.5 (C-5), 17.4 (C-1), -1.8, -2.8 ($SiCH_3$).

2,5-Anhydro-3,4-di-*O*-benzyl-L-iditol (10) and 1,5-Anhydro-2,3-di-*O*-benzyl-L-gulitol (11). Treatment of the mixture of **8** and **9** (0.48 g, 1.05 mmol) with KBr and AcO_2H was executed as described for oxidative unmasking of **6**. The crude product was applied onto a silica gel column and elution effected with Et_2O to give **11**, yield 75 mg (21%). R_f 0.3 (Et_2O). $[\alpha]_D^{20}$ +19.9° (*c* 1). ^1H NMR: δ 7.37-7.25 (m, 10H, H-arom), 4.56 (s,

2H, CH_2, Bn), 4.50 (AB, 2H, CH_2, Bn, *J* -12.2 Hz), 4.05-3.95 (m, 1H, H-2), 3.91-3.36 (m, 7H, H-1, H-3, H-4, H-5, H-6), 2.10 (bs, 1H, OH), 1.73 (bs, 1H, OH). $^{13}C\{^1H\}$ NMR: δ 137.4, 137.2 (Cq, arom), 128.6-127.8 (CH, arom), 74.7, 73.4 (C-3, C-4, C-5), 72.9, 72.6 (CH_2, Bn), 66.7 (C-1), 64.6 (C-2), 62.3 (C-6). Further elution (Et_2O/MeOH, 49/1, v/v) afforded **10**, yield 0.18 g (50%). R_f 0.2 (Et_2O). $[\alpha]_D^{20}$ +38.8° (*c* 1). ^1H NMR: δ 7.38-7.26 (m, 10H, H-arom), 4.54 (AB, 4H, CH_2, Bn, *J* -12.0 Hz), 4.26 (q, 2H, H-2, H-5, *J* 4.5 Hz), 4.14 (bd, 2H, H-3, H-4), 3.86-3.83 (m, 4H, H-1, H-6), 2.33 (s, 1H, OH). $^{13}C\{^1H\}$ NMR: δ 137.3 (Cq, arom), 128.4, 127.9, 127.5 (CH, arom), 82.3, 79.9 (C-2, C-3, C-4, C-5), 72.1 (CH_2, Bn), 61.4 (C-1, C-6).

2,5-Anhydro-L-iditol (12). Compound **10** (0.18 g, 0.52 mmol) was hydrogenated as described for the synthesis of **7** to give crude **12** as an oil, yield 82 mg (96%). Crystallization from EtOH afforded white crystals (50 mg). See previous paper.

2-*O*-Acetyl-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-5,6-di-*O*-isopropylidene-D-altritol (14). Compound **13**[14] (2.40 g, 4.60 mmol) was acetylated as described in the synthesis of **3** to give **14** as an oil after purification by silica gel, yield 2.14 g (83%). R_f 0.8 (Et_2O/light petroleum, 1/1, v/v). $[\alpha]_D^{20}$ +16.3° (*c* 0.5). ^1H NMR: δ 7.49-7.25 (m, 15H, H-arom), 5.34 (m, 1H, H-2), 4.66 (s, CH_2, Bn), 4.53 (AB, 2H, CH_2, Bn, *J* -11.8 Hz), 4.27 (dt, 1H, H-5, $J_{4,5}$ 5.4 Hz, $J_{5,6a}$ $J_{5,6b}$ 6.4 Hz), 3.91 (m, 2H, H-6), 3.79 (dd, 1H, H-4, $J_{3,4}$ 3.2 Hz), 3.39 (dd, 1H, H-3, $J_{2,3}$ 5.4 Hz), 1.65 (s, 3H, CH_3, Ac), 1.39, 1.32 (2x s, 6H, CH_3, isoprop), 1.19 (m, 2H, H-1), 0.30, 0.27 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 169.6 (C=O), 138.1, 138.0, 137.7 (Cq, arom), 133.2, 128.4-127.3 (CH, arom), 108.1 (Cq, isoprop), 81.4, 78.9, 75.2 (C-3, C-4, C-5), 73.4, 73.2 (CH_2, Bn), 70.0 (C-2), 65.8 (C-6), 26.2, 24.8 (CH_3, isoprop), 20.6 (CH_3, Ac), 18.5 (C-1), -2.8, -3.1 ($SiCH_3$).

Anal. Calcd for $C_{33}H_{42}O_6Si$ (562.78): C, 70.43; H, 7.52. Found: C, 70.23; H, 7.42.

2-*O*-Acetyl-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-altritol (15). Compound **14** (2.14 g, 3.81 mmol) was deacetonated as described in the synthesis of **3** to give **15** as an oil after silica gel column chromatography, yield 1.64 g (83%). R_f 0.5 (Et_2O). ^1H NMR: δ 7.50-7.24 (m, 15H, CH, arom), 5.37 (m, 1H, H-2), 4.60 (AB, 2H, CH_2, Bn, *J* -11.6 Hz), 4.56 (s, 2H, CH_2, Bn), 3.92-3.58 (m, 5H, H-3, H-4, H-5, H-6), 3.17 (bs, 1H, OH), 2.18 (bs, 1H, OH), 1.70 (s, 3H, CH_3, Ac), 1.17 (dd, 1H, H-1a, $J_{1a,1b}$ -11.2

Hz, $J_{1a,2}$ 5.2 Hz), 0.85 (dd, 1H, H-1b, $J_{1b,2}$ 4.7 Hz), 0.31, 0.28 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 170.3 (C=O), 138.1, 137.8, 137.7 (Cq, arom), 133.2, 128.5-127.3 (CH, arom), 82.2, 79.0 (C-3, C-4), 73.5, 72.8 (CH_2, Bn), 71.2, 70.5 (C-2, C-5), 63.4 (C-6), 20.6 (CH_3, Ac), 18.5 (C-1), -2.7, -3.2 ($SiCH_3$).

Anal. Calcd for $C_{30}H_{38}O_6Si$ (522.71): C, 68.93; H, 7.33. Found: C, 68.73; H, 7.30.

2-*O*-Acetyl-3,4-di-*O*-benzyl-5,6-*O*-(cyclic sulfate)-1-deoxy-1-dimethylphenylsilyl-D-altritol (16). Diol **15** (0.58 g, 1.03 mmol) was treated with thionylchloride and subsequently oxidized with $RuCl_3$ as described in the preparation of **5** to give **16** as an oil after silica gel column chromatography, yield 0.48 g (79%). R_f 0.6 (Et_2O/light petroleum, 1/1, v/v). $[\alpha]_D^{20}$ +28.8° (*c* 2). ^1H NMR: δ 7.48-7.18 (m, 15H, CH, arom), 5.17-5.07 (m, 2H, H-2, H-5), 4.63 (m, 1H, H-6a), 4.48 (AB, 2H, CH_2, Bn, *J* -11.1 Hz), 4.33 (d, 2H, CH_2, Bn, *J* -2.0), 4.33 (dd, 1H, H-6b, $J_{5,6b}$ 6.7 Hz, $J_{6a,6b}$ -8.8 Hz), 3.97 (m, 1H, H-4), 3.52 (dd, 1H, H-3, $J_{2,3}$ 5.6 Hz, $J_{3,4}$ 3.4 Hz), 1.70 (s, 3H, CH_3, Ac), 1.08-0.96 (m, 2H, H-1), 0.32, 0.29 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 169.9 (C=O), 137.6, 136.7 (Cq, arom), 133.4, 128.8-127.7 (CH, arom), 82.1, 80.8, 76.4 (C-3, C-4, C-5), 74.3, 73.6 (CH_2, Bn), 69.5 (C-2), 69.3 (C-6), 20.6 (CH_3, Ac), 17.9 (C-1), -2.8, -3.0 ($SiCH_3$).

Anal. Calcd for $C_{30}H_{36}O_8SSi$ (584.76): C, 61.62; H, 6.21. Found: C, 61.45; H, 6.17.

2,5-Anhydro-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-L-galactitol (17) and 2,6-Anhydro-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-altritol (18). Cyclic sulfate **16** (0.30 g, 0.51 mmol) was treated with LiOMe, followed by H_2SO_4 as described for the cyclization of **5**. After purification, compounds **17** and **18** were obtained as a mixture of isomers (ratio 6:1), yield 0.16 g (70%). R_f 0.4 (Et_2O/light petroleum, 3/1, v/v). Compound **17**: $[\alpha]_D^{20}$ +15.4° (*c* 2). ^1H NMR: δ 7.54-7.25 (m, 15H, H-arom), 4.63 (AB, 2H, CH_2, Bn, *J* -11.6 Hz), 4.57 (AB, 2H, CH_2, Bn, *J* -12.1 Hz), 4.22 (dd, 1H, H-6a, $J_{5,6a}$ 4.0 Hz, $J_{6a,6b}$ -7.9 Hz), 4.06 (dd, 1H, H-6b, $J_{5,6b}$ 4.7 Hz), 3.96 (ddd, 1H, H-2, $J_{1a,2}$ 8.6 Hz, $J_{1b,2}$ 4.0 Hz, $J_{2,3}$ 6.2 Hz), 3.74-3.68 (m, 3H, H-3, H-4, H-5), 2.56 (t, 1H, OH, *J* 4.2 Hz), 1.43 (dd, 1H, H-1a, $J_{1a,1b}$ -14.5 Hz), 1.14 (dd, 1H, H-1b), 0.31 (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 138.0, 137.6 (Cq, arom), 133.6, 128.5-127.3 (CH, arom), 80.9, 78.4, 77.4, 77.2 (C-2, C-3, C-4, C-5), 73.5, 72.9 (CH_2, Bn), 62.3 (C-6), 16.9 (C-1), -2.1, -2.3

($SiCH_3$). Compound **18**: $^{13}C\{^1H\}$ NMR: δ 138.2, 137.6 (Cq, arom), 133.4, 128.4-127.3 (CH, arom), 77.5, 76.1 (C-3, C-4), 73.1, 72.8 (CH_2, Bn), 70.1 (C-2), 67.2 (C-6), 63.5 (C-5), 17.8 (C-1), -2.3, -2.9 ($SiCH_3$).

2,5-Anhydro-3,4-di-*O*-benzyl-L-galactitol (19) and 1,5-Anhydro-2,3-di-*O*-benzyl-L-talitol (20). Treatment of the isomeric mixture of silanes **17** and **18** (0.16 g, 0.35 mmol) with KBr and AcO_2H was executed as described for the oxidative unmasking of **6**. The oil obtained after work-up was applied onto a column of silica gel and elution effected with EtOAc to give **20**, yield 13 mg (11%). R_f 0.2 (EtOAc). $^{13}C\{^1H\}$ NMR: δ 137.4, 137.2 (Cq, arom), 128.6-127.8 (CH, arom), 74.7, 73.4 (C-2, C-3, C-4), 72.9, 72.6 (CH_2, Bn), 66.7 (C-6), 64.6 (C-5), 62.3 (C-1). Further elution gave **19**, yield 77 mg (64%). R_f 0.1 (EtOAc). $[\alpha]_D^{20}$ 0° (*c* 1). ^1H NMR: δ 7.35-7.26 (m, 10H, H-arom), 4.67 (AB, 4H, CH_2, Bn, *J* -11.8 Hz), 4.21-4.10 (m, 4H, H-2, H-3, H-4, H-5), 3.88 (dd, 2H, H-1a, H-6a, $J_{1a,1b}$ $J_{6a,6b}$ -11.7 Hz, $J_{1a,2}$ $J_{5,6a}$ 5.0 Hz), 3.78 (dd, 2H, H-1b, H-6b, $J_{1b,2}$ $J_{5,6b}$ 4.5 Hz), 2.70 (bs, 1H, OH). $^{13}C\{^1H\}$ NMR: δ 138.0 (Cq, arom), 128.6, 128.1, 127.6 (CH, arom), 78.8 (C-2, C-3, C-4, C-5), 73.6 (CH_2, Bn), 61.9 (C-1, C-6).

2,5-Anhydrogalactitol (21). Compound **19** (77 mg, 0.22 mmol) was hydrogenated as described for the synthesis of **7** to give **21** as a syrup, yield 32 mg (87%). R_f 0.4 (MeOH). $[\alpha]_D^{20}$ 0° (*c* 0.3, H_2O). ^1H NMR: see Table 2, previous paper. $^{13}C\{^1H\}$ NMR (MeOD): δ 80.2 (C-2, C-5), 71.8 (C-3, C-4), 60.8 (C-1, C-6).

3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-5,6-di-*O*-isopropylidene-D-iditol (22). A solution of 3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-iditol[6] was dissolved in acetone (3 mL) and 2,2-dimethoxypropane (0.44 mL, 3.55 mmol) and *p*-TsOH (18 mg, 0.07 mmol) were added. After stirring for 1.5 h, a saturated solution of $NaHCO_3$ (4 mL) was added, and 1,4-dioxane was removed *in vacuo*. Et_2O (20 mL) was added, the layers were separated and the organic layer was washed with brine (15 mL), dried ($MgSO_4$) and concentrated. The residue was purified on silica gel (elution: Et_2O/light petroleum, 1/2, v/v) to give **22** as an oil, yield 0.28 g (76%). R_f 0.8 (Et_2O/light petroleum, 3/1, v/v). $[\alpha]_D^{20}$ 15.2° (*c* 2.0). ^1H NMR: δ 7.53-7.21 (m, 15H, H-arom), 4.64 (s, 2H, CH_2, Bn), 4.51 (AB, 2H, CH_2, Bn, *J* -11.3 Hz), 4.33 (ddd, 1H, H-5, $J_{4,5}$ 5.5 Hz, $J_{5,6a}$ 6.4 Hz, $J_{5,6b}$ 7.5 Hz), 3.96 (m, 1H, H-2), 3.86 (dd, 1H, H-6a, $J_{6a,6b}$ -8.1 Hz), 3.71 (dd, 1H, H-6b), 3.50 (t, 1H, H-4, $J_{3,4}$ 5.2 Hz), 3.31 (dd, 1H, H-3, $J_{2,3}$ 3.1 Hz), 2.33 (d, 1H, OH, *J*

7.5 Hz), 1.41, 1.33 (2x s, 6H, CH_3, isoprop), 1.10 (dd, 1H, H-1a, $J_{1a,1b}$ -14.7 Hz, $J_{1a,2}$ 9.1 Hz), 1.00 (dd, 1H, H-1b, $J_{1b,2}$ 4.9 Hz), 0.32 (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 139.3, 138.2, 137.9 (Cq, arom), 133.5, 128.7-127.5 (CH, arom), 108.7 (Cq, arom), 83.2, 78.2, 76.2 (C-3, C-4, C-5), 74.1, 73.7 (CH_2, Bn), 68.1 (C-2), 65.8 (C-6), 26.4, 25.5 (CH_3, isoprop), 22.2 (C-1), -2.0, -2.7 ($SiCH_3$).

Anal. Calcd for $C_{31}H_{40}O_5Si$ (520.74): C, 71.50; H, 7.74. Found: C, 71.27; H, 7.68.

2-*O*-Acetyl-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-5,6-di-*O*-isopropylidene-D-iditol (23). Compound **22** (0.28 g, 0.54 mmol) was acetylated and purified as in the synthesis of **3** to give **23** as an oil, yield 0.29 g (96%). R_f 0.4 (Et_2O/light petroleum, 1/1, v/v). ^1H NMR: δ 7.48-7.14 (m, 15H, H-arom), 5.34 (dt, 1H, H-2, $J_{1a,2}$ $J_{2,3}$ 5.8 Hz, $J_{1b,2}$ 8.3 Hz), 4.67 (AB, CH_2, Bn, J -11.3 Hz), 4.48 (AB, 2H, CH_2, Bn, J -11.6 Hz), 4.21 (m, 1H, H-5), 3.81 (dd, 1H, H-6a, $J_{5,6a}$ 6.3 Hz, $J_{6a,6b}$ -8.0 Hz), 3.66 (t, 1H, H-6b, $J_{5,6b}$ 7.9 Hz), 3.53-3.40 (m, 2H, H-3, H-4), 1.77 (s, 3H, CH_3, Ac), 1.40, 1.33 (2x s, 6H, CH_3, isoprop), 1.26 (dd, 1H, H-1a, $J_{1a,1b}$ -14.6 Hz), 1.11 (dd, 1H, H-1b), 0.29, 0.25 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 170.1 (C=O), 138.6, 138.1 (Cq, arom), 133.6, 129.1-127.7 (CH, arom), 109.1 (Cq, isoprop), 81.0, 78.3, 76.4 (C-3, C-4, C-5), 73.9, 73.8 (CH_2, Bn), 71.0 (C-2), 65.8 (C-6), 26.5, 25.8 (CH_3, isoprop), 21.1 (CH_3, Ac), 18.3 (C-1), -2.4, -2.7 ($SiCH_3$).

Anal. Calcd for $C_{33}H_{42}O_6Si$ (562.78): C, 70.43; H, 7.52. Found: C, 70.16; H, 7.46.

2-*O*-Acetyl-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-iditol (24). Deacetonation of compound **23** (0.29 g, 0.52 mmol) as described in the synthesis of **3** gave **24** after purification, yield 0.25 g (92%). R_f 0.2 (Et_2O/light petroleum, 3/1, v/v). $[\alpha]_D^{20}$ -4.7° (*c* 2.5). ^1H NMR: δ 7.48-7.22 (m, 15H, CH, arom), 5.27 (m, 1H, H-2), 4.66 (AB, 2H, CH_2, Bn, J -11.6 Hz), 4.57 (AB, 2H, CH_2, Bn, J -11.1), 3.76-3.64 (m, 2H, H-5, H-6a), 3.57-3.46 (m, 3H, H-3, H-4, H-6b), 1.82 (s, 3H, CH_3, Ac), 1.25-1.17 (m, 1H, H-1), 0.31, 0.28 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 170.5 (C=O), 138.2, 138.0, 137.7 (Cq, arom), 133.4, 128.9-127.5 (CH, arom), 80.7, 78.5 (C-3, C-4), 74.5, 74.3 (CH_2, Bn), 70.8, 70.5 (C-2, C-5), 63.9 (C-6), 20.9 (CH_3, Ac), 18.0 (C-1), -2.7, -2.9 ($SiCH_3$).

Anal. Calcd for $C_{30}H_{38}O_6Si$ (522.71): C, 68.93; H, 7.33. Found: C, 68.46; H, 7.27.

2-*O*-Acetyl-3,4-di-*O*-benzyl-5,6-*O*-(cyclic sulfate)-1-deoxy-1-dimethylphenylsilyl-D-iditol (25). Diol **24** (0.25 g, 0.47 mmol) was converted into the corresponding cyclic sulfate as described in the preparation of **5** to give **25** as an oil after silica gel column chromatography, yield 0.20 g (74%). R_f 0.6 (Et_2O/light petroleum, 3/1, v/v). ^1H NMR: δ 7.48-7.20 (m, 15H, CH, arom), 5.32 (dt, 1H, H-2, $J_{1a,2}$ $J_{2,3}$ 5.8 Hz, $J_{1b,2}$ 8.3 Hz), 4.88 (m, 1H, H-5), 4.82 (dd, 1H, H-6a, $J_{5,6a}$ 6.8 Hz, $J_{6a,6b}$ -8.3 Hz), 4.63 (AB, 2H, CH_2, Bn, J -12.3 Hz), 4.50 (AB, 2H, CH_2, Bn, J -11.6), 4.35 (dd, 1H, H-6b, $J_{5,6b}$ 6.0 Hz), 3.82-3.70 (m, 2H, H-3, H-4), 1.76 (s, 3H, CH_3, Ac), 1.26 (dd, 1H, H-1a, $J_{1a,1b}$ -14.6 Hz), 1.11 (dd, 1H, H-1b), 0.30, 0.24 (2x s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 169.8 (C=O), 137.8, 136.9, 136.8 (Cq, arom), 133.4, 129.2-127.8 (CH, arom), 83.0, 79.5, 75.6 (C-3, C-4, C-5), 74.2, 73.8 (CH_2, Bn), 69.9 (C-2), 69.8 (C-6), 20.9 (CH_3, Ac), 18.2 (C-1), -2.8, -3.0 ($SiCH_3$).

Anal. Calcd for $C_{30}H_{36}O_8SSi$ (584.76): C, 61.62; H, 6.21. Found: C, 61.47; H, 6.14.

2,5-Anhydro-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-L-glucitol (26) and 2,6-Anhydro-3,4-di-*O*-benzyl-1-deoxy-1-dimethylphenylsilyl-D-iditol (27). Cyclic sulfate **25** (0.20 g, 0.34 mmol) was treated with LiOMe, followed by H_2SO_4 as described for **5**. Flash chromatography gave compounds **26** and **27** (ratio 4:1), yield 0.10 g (66%). R_f 0.7 (toluene/acetone, 85/15, v/v). Compound **26**: ^1H NMR: δ 7.55-7.25 (m, 15H, CH, arom), 4.47 (s, 2H, CH_2, Bn), 4.30 (AB, 2H, CH_2, Bn, J -12.1 Hz), 4.12), 4.12 (m, 1H, H-2), 3.92 (m, 2H, H-5, H-6a), 3.74 (dd, 1H, H-6b, $J_{5,6b}$ 1.8 Hz; $J_{6a,6b}$ -9.8 Hz), 3.63 (d, 1H, H-4, $J_{4,5}$ 3.7 Hz), 3.56 (d, 1H, H-3, $J_{2,3}$ 3.2 Hz), 1.38 (dd, 1H, H-1a, $J_{1a,1b}$ -14.2 Hz, $J_{1a,2}$ 7.3 Hz), 1.20 (dd, 1H, H-1b, $J_{1b,2}$ 7.5 Hz), 0.31 (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 138.8, 137.6 (Cq, arom), 133.4, 128.6-127.9 (CH, arom), 83.6, 83.2, 79.0 (C-2, C-3, C-4, C-5), 71.7, 70.8 (CH_2, Bn), 63.0 (C-6), 15.2 (C-1), -2.3, -2.7 ($SiCH_3$).

2,5-Anhydro-3,4-di-*O*-benzyl-L-glucitol (28) and 1,5-Anhydro-2,3-di-*O*-benzyl-L-iditol (29). Treatment of the isomeric mixture of silanes **26** and **27** (0.10 g, 0.22 mmol) with KBr and AcO_2H was executed as described for the unmasking of **6**. The oil obtained after work-up was applied onto a column of silica gel (elution: Et_2O/light petroleum, 2/1, v/v) to give **29**, yield 10 mg (14%). R_f 0.4 (Et_2O). $^{13}C\{^1H\}$ NMR: δ 137.6, 137.0 (Cq, arom), 128.8-127.5 (CH, arom), 75.7, 74.1, 73.0 (C-2, C-3, C-4), 71.9, 71.8 (CH_2, Bn), 66.3 (C-6), 64.6 (C-5), 60.9 (C-1).

Anal. Calcd for $C_{20}H_{24}O_5$ (344.41): C, 69.75; H, 7.02. Found: C, 69.43; H, 7.01.

Further elution (3/1, v/v) afforded **28**, yield 0.42 g (57%). R_f 0.3 (Et_2O). $[\alpha]_D^{20}$ +30.9° (*c* 1). ^1H NMR: δ 7.52-7.25 (m, 10H, CH, arom), 4.56 (s, 2H, CH_2, Bn), 4.53 (AB, 2H, CH_2, Bn, *J* -11.8 Hz), 4.18-3.83 (m, 6H, H-1a, H-2, H-4, H-5, H-6), 3.80 (d, 1H, H-3, $J_{2,3}$ 2.8 Hz), 3.66 (dd, 1H, H-1b, $J_{1a,1b}$ -12.0 Hz, $J_{1b,2}$ 4.3 Hz). $^{13}C\{^1H\}$ NMR: δ 137.4, 137.0 (Cq, arom), 128.2-127.3 (CH, arom), 83.5, 83.2, 82.6, 80.4 (C-2, C-3, C-4, C-5), 71.7, 71.5 (CH_2, Bn), 62,4, 61.5 (C-1, C-6).

Anal. Calcd for $C_{20}H_{24}O_5$ (344.41): C, 69.75; H, 7.02. Found: C, 69.69; H, 6.92.

2,5-Anhydro-L-glucitol (30). Compound **28** (42 mg, 0.12 mmol) was hydrogenated as described for the synthesis of **7** to give **30** as a syrup, yield 19 mg (97%). See previous paper.

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