154. Glycosylidene Carbenes

Part 9[1])

Regioselective Glycosidation of Diols and Triols: Intra- and Intermolecular Hydrogen Bonds

by **Peter Uhlmann** and **Andrea Vasella***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

(30.VII.92)

Glycosidation of the *myo*-inositol derivatives **2** and **3** by the diazirine **1** yields 90% of a diastereoisomer pair of β-D-glycosides in a 1:1 ratio, *i.e.* **5**/**6** and **7**/**8**, respectively (*Scheme 1*). The crystal structure of **3** shows a strong intramolecular H-bond, which persists in solution, as indicated by FT-IR and ^{1}H-NMR spectra. Yields and diastereoselectivity are lower for the glycosidation of **24** by **1** (*Scheme 3*). The resulting 1,2- and 1,4-linked disaccharides **25**–**28** were isolated as their acetates **29**–**32**. The previously determined crystal structure of **24** shows no intramolecular H-bonds. The yield of the glycosidation of **24**, but not of **3**, depends upon the concentration, indicating that activation of **24** by intermolecular H-bonds is required. Glycosidation of **2** and **3** with the trichloroacetimidate **14** gave mixtures of four (**5**, **6**, **15**, and **16**), and six (**7**, **8**, and **17**–**20**) disaccharides, respectively (*Scheme 2*).

Introduction. – Glycosidation by 1-azisugars [2–4] involves formation of a glycosylidene carbene, which is protonated by an OH group to form an ion pair. Combination of the ions leads to glycosides.

Glycosidation of monofunctional alcohols [2] and of phenols [3] by 1-azisugars shows a strong influence of the kinetic acidity on yields and stereoselectivity. Yields reflect the competition between protonation of the intermediate carbene, which is faster for more strongly acidic hydroxy compounds [5], and side reactions, such as the formation of lactone azines [6]. Stereoselectivity reflects the competition between stabilizing interactions of the intermediate glycosyl cation with the 2-benzyloxy group, the glycosyl acceptor, or the solvent. Strongly acidic hydroxy compounds are relatively poor nucleophiles. In noncoordinating solvents, the glycosyl cation resulting from the protonation of the glycosylidene carbene by such a hydroxy compound is stabilized by coordination with the 2-benzyloxy group [7], while solvation of the glycosyl cation by poorly acidic and, thus, more nucleophilic alcohols is more efficient than the one by the 2-benzyloxy group and occurs from the α- and the β-side, leading to loss of anomeric selectivity [2].

In the presence of stoichiometric amounts of the diazirine **1**, methyl orsellinate is monoglycosylated at HO–C(4). This shows that regioselective glycosidation of phenols is possible when the reactivity of an OH group is lowered by an intramolecular H-bond. For mono- and oligosaccharides, which are less acidic than phenols, one expects regioselective

[1]) Part 8: [1].

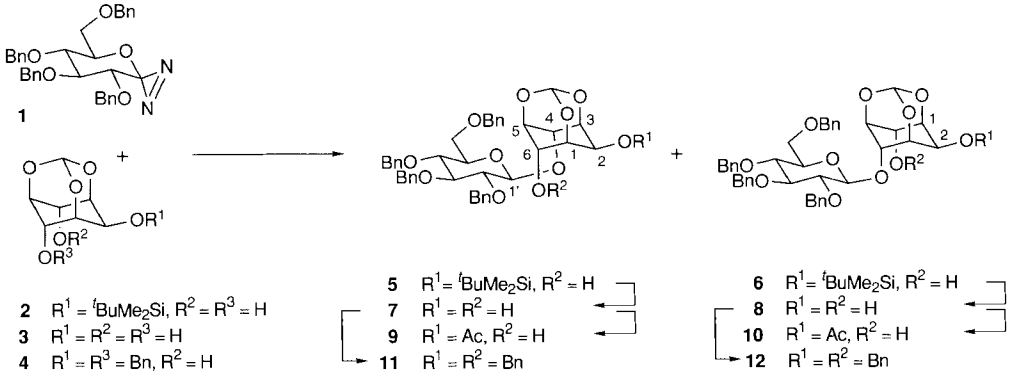
glycosidation in high yields and with good stereoselectivity, when one of the OH groups functions as an H-bond acceptor, as such an OH group possesses an increased kinetic acidity. This should be more important than the concomitant lowered degree of acidity for an H-bond donating OH group[2]) [9].

Intramolecular H-bonds are evidenced by ^{1}H-NMR spectroscopy and by the shift to lower frequencies and the broadening of OH absorption bands in the IR spectra of diluted solutions of alcohols [10]. The observation that intramolecular H-bonds in crystals of saccharides are much less frequent than intermolecular H-bonds may also serve as a guideline [11]. Intramolecular H-bonds in crystals of saccharides may only exist, if they are particularly favourable, in which case they may persist in solution. Perusal of these data [11] [12] leads to the conclusion that the strongest H-bonds in pyranosides should occur in diaxial 1,3-diols, followed by *cis*-1,2-diols and 2- or 4-hydroxytetrahydro-2*H*-pyrans (where the OH group functions only as H-donor). *trans*-Diequatorial 1,2-diols should only form weak H-bonds [13]. We [2] and others [14] have postulated that alkoxyalkyl carbenes should be protonated more rapidly by dimeric or oligomeric than by monomeric alcohols. Hence, one may expect competition between intra- and intermolecularly H-bonded species, particularly when intramolecular H-bonds are unfavourable and the concentration of the alcohol is high.

We have studied the effect of these factors on regioselectivity, yield, and stereoselectivity in the glycosidation of a series of 1,3- and 1,2-diols and some triols. We report the results of the glycosidation of the *myo*-inositol-derived diol **2** [15] and triol **3** [15] on the one hand, and of 1,6-anhydroglucose **24**, on the other hand. While the triol **3** may form an intramolecular H-bond between the two axial OH groups, this may not be so for **24**, on account of the *anti-reflex* effect [16], which leads to a relatively large distance between O–C(2) and O–C(4). To compare the carbene-mediated glycosidation by **1** with a glycosidation of the *Koenigs-Knorr* type, we also examined the trichloroacetimidate **13** as a glycosyl donor.

Results and Discussion. – 1. *Glycosidation of the* myo-*Inositol Derivatives* **2** *and* **3**. Reaction of the diol **2** with 0.9 equiv. of **1** (see *Scheme 1*) in 1,4-dioxane at room

Scheme 1. *Glycosidation of* myo-*Inositol Derivatives with* **1**

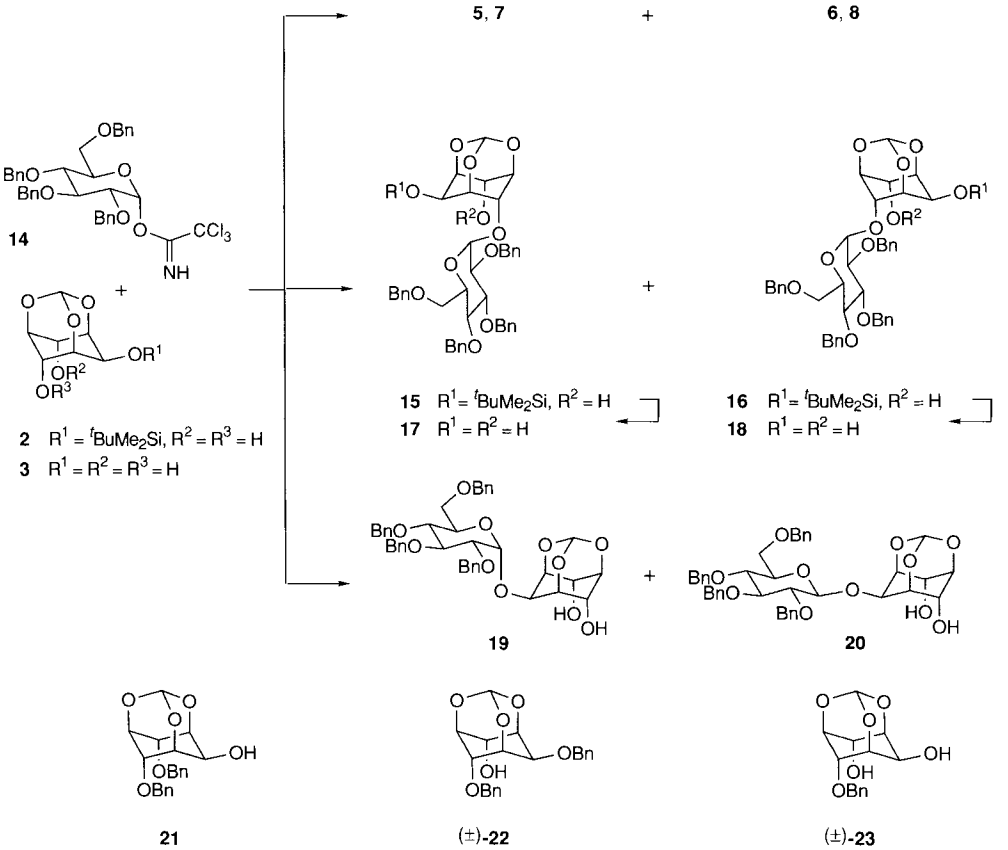


[2]) There is precedence for regioselectivity in the reaction of diols and triols with CH_2N_2. For a pertinent case, relating regioselectivity to the existence of intramolecular H-bonds, see [8].

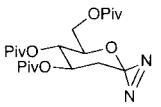
temperature gave 90% of the β-D-glycosides **5** and **6** in a ratio of 1:1, in agreement with the ratio determined by ^{1}H-NMR spectroscopy of the crude product. The β-D-configuration of the monoaddition products was established by ^{1}H-NMR spectroscopy. The *d*'s of H–C(1') appear at 4.61 ppm (J = 7.6 Hz) for **5** and at 4.55 ppm (J = 7.7 Hz) for **6**. The absolute configuration of **5** and **6** was determined by chemical correlation with compound **11**, the glycosidation product of enantiomerically pure **4** [17] with **1**. Desilylation of the glycosides **5** and **6** with $Bu_4NF \cdot 3\ H_2O$ in THF gave the products **7** and **8**, each in 90% yield, which were treated with BnBr/NaH in DMF to afford 96 and 93% of the benzylated glycosides **11** and **12**, respectively.

Glycosidation of the triol **3** with 0.8 equiv. of **1** (see *Scheme 1*) in 1,4-dioxane at room temperature gave, in 90% yield, a 1:1 mixture of the β-D-glycosides **7** and **8**, resulting exclusively from the monoglycosidation of the axial OH groups[3]). Monoacetylation and

Scheme 2. *Glycosidation of* myo-*Inositol Derivatives with* **14**



[3]) Extensive loss of diastereoselectivity was observed in the glycosidation of **3** with the 2-deoxydiazirine **13** [7].



13

partial separation by FC afforded pure samples of the diastereoisomeric monoacetates **9** and **10**, which were deacetylated to **7** and **8**.

Glycosidation of the diol **2** with the trichloroacetimidate **14** (see *Scheme 2*) in CH_2Cl_2 and in the presence of $BF_3 \cdot Et_2O$ at 0° yielded 79% of a mixture of all four monoglycosylated products **5**, **6**, **15**, and **16** in a ratio of 28:53:8:11, as determined by ^{1}H-NMR spectroscopy and HPLC of the crude product. The absolute configuration of the *myo*-inositol-derived moiety of the α-D-glycosides was not determined. In their ^{1}H-NMR spectra, the *d*'s of H–C(1') appear at 4.97 ppm (J = 3.8 Hz) for **15** and 4.78 ppm (J = 3.7 Hz) for **16**. Desilylation of **15** and **16** gave the diols **17** and **18**, respectively, each in 85% yield.

Glycosidation of the triol **3** with the trichloroacetimidate **14** (see *Scheme 2*) lead to a mixture of the six possible monoglycosylated products in 73% yield after flash chromatography. Four products corresponded (HPLC) to the α- and β-D-glycosides **7**, **8**, **17**, and **18** (see above). Acetylation, partial separation by prep. HPLC, and deacetylation afforded pure samples of two additional products **19** and **20**, derived from glycosidation of the equatorial OH group. The ratio **7**/**8**/**17**/**18**/**19**/**20** of 20:40:5:10:6:19 was determined by ^{1}H-NMR spectroscopy of the crude product. The configuration of **7**, **8**, and **17**–**20** was established by ^{1}H- and ^{13}C-NMR (*Table 1*) spectroscopy. The α-D-configura-

Table 1. *Selected ^{13}C-NMR* (50 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of Inositol-glycosides* **5**–**10** *and* **15**–**20**

Compound	**5**	**6**[a])	**7**	**8**	**9**	**10**	**15**	**16**	**17**	**18**[a])	**19**	**20**
C(1)	74.44[b])	74.66	74.24[b])	74.76	71.80	72.25	74.49	75.06	74.79	74.73	72.70[b])	73.29[b])
C(2)	61.15	60.85	60.83	60.39	63.33	62.84	60.45	61.10	60.11	60.60	67.13[c])	67.58[c])
C(3)	72.93	73.62	72.40	73.33	69.82	70.99	71.18[b])	73.24	70.16	72.72	70.49[b])	71.66[b])
C(4)	74.76[b])	74.92	74.85[b])	74.90	74.82	74.33	71.32[b])	71.49	71.16[b])	70.89	68.13[c])	67.81[c])
C(5)	67.88	67.57	67.42	67.41	67.52	67.62	67.86	66.96	67.76	66.57	68.53[c])	68.52[c])
C(6)	69.36	68.28	68.98	67.83	69.32	67.88	68.46	68.34	68.26	67.79	68.13[c])	67.98[c])
CHO_3	102.70	102.61	102.82	102.73	102.64	102.61	102.36	102.65	102.73	102.69	102.39	102.37
C(1')	103.89	102.53	103.75	102.60	103.95	102.31	95.16	96.50	94.59	96.61	97.42	102.91
C(2')	82.01	81.42	81.62	81.15	81.55	80.93	78.07	78.35	78.45	78.15	80.46	81.73
C(3')	84.23	84.82	84.36	84.76	84.17	84.79	81.66	81.91	81.74	81.72	81.78	84.39
C(4')	77.23	77.64	77.28	77.55	77.23	77.63	77.00	77.08	77.06	77.00	77.85	77.61
C(5')	76.80	75.15	75.96	75.14	75.88	75.21	71.41[a])	71.69	71.36[b])	71.39	71.90	74.51
C(6')	68.43	68.44	68.47	68.49	68.49	68.54	67.86	67.96	68.03	67.71	69.03	69.19

[a]) Assignment based upon a 2D-C,H-correlated spectrum.
[b])[c]) Assignment may be interchanged.

tion of **17**, **18**, and **19** is evidenced by the *d*'s of H–C(1') at 4.77–4.96 ppm (J = 3.7–3.9 Hz), while the *d*'s of H–C(1') of the β-D-glycosides **7**, **8**, and **20** appear at 4.53–4.62 ppm (J = 7.3–7.8 Hz). In the ^{13}C-NMR spectra of **19** and **20**, the C(2) signal is shifted by *ca.* 7 ppm to lower field (67.13 and 67.58 ppm), as compared to the C(2) signals of **7**, **8**, **17**, and **18** (60.11–60.83 ppm), indicating the 1,2-linkage.

The results of the glycosidation of **3** and **2** with **1** strongly indicate an intramolecular H-bond between the axial OH groups, leading to good yields, diastereoselectivity and, for the triol **3**, regioselectivity. The donor **1** did not discriminate between the enantiotopic,

axial OH groups in **3** and **2**, while the trichloroacetimidate **14** lead to a 1:2 ratio of the corresponding isomers. The 1:2 ratio appears to result from kinetic control of glycosidation[4]). In the carbene-mediated glycosidation, protonation and not, as a rule, interaction with the O-center determines the site of reaction. The less 'compact' transition state lowers the probability of diastereodifferentiating interactions between donor and acceptor.

The structure of **3** in the solid state was established by X-ray analysis, which showed the expected intramolecular H-bond between HO–C(4) and HO–C(6), characterised by a short O···O distance of 2.768 Å and a O–H–O angle of 144° (see *Fig. 1*). There are two intermolecular H-bonds, one between HO–C(2) (donor) and HO–C(4′) (O···O, 2.767 Å; O–H–O, 156°) and the other between HO–C(6) (donor) and HO–C(2″) (O···O, 2.828 Å; O–H–O, 172°).

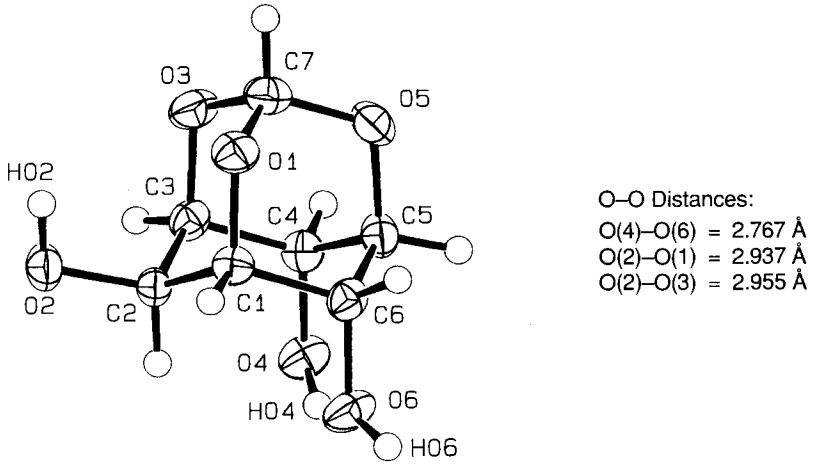


Fig. 1. *Intramolecular O–O distances of the triol* **3**. For experimental conditions, selected bond angles, and torsion angles, see *Exper. Part*[5]).

FT-IR Spectroscopy confirmed the existence of a strong intramolecular H-bond between HO–C(4) and HO–C(6) in solution. The FT-IR spectrum of a 0.1M solution of **3** in 1,4-dioxane was difficult to interprete, as it showed a broad peak (half-width 300 cm^{-1}) at 3430 cm^{-1} with a shoulder at 3370 cm^{-1}, indicating intermolecular H-bonds to the solvent and intramolecular H-bonds. To detect and quantify the intramolecular H-bonds, FT-IR spectra of **3** and **21–23** [17] were measured in CCl_4 at a concentration of 0.05M. For all derivatives, the band of HO–C(4,6) is shifted to lower frequencies ($\Delta\tilde{\nu}$ = 122–135 cm^{-1}). This indicates a strong intramolecular H-bond between the two *cis*-related axial OH groups. The equatorial OH group is involved in a weaker in-

---

[4]) Under the conditions of the *Schmidt* glycosidation (CH_2Cl_2, 0.2 equiv. of $BF_3 \cdot Et_2O$, 0°, 6 h), pure samples of **5** and **6** did not interconvert. Acid-catalysed equilibration has been observed in a related case [18]. Diastereodifferentiating interactions of glycosyl donor and acceptor are known [19].

[5]) Atomic coordinates, bond lengths, and angles were deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EZ, England.

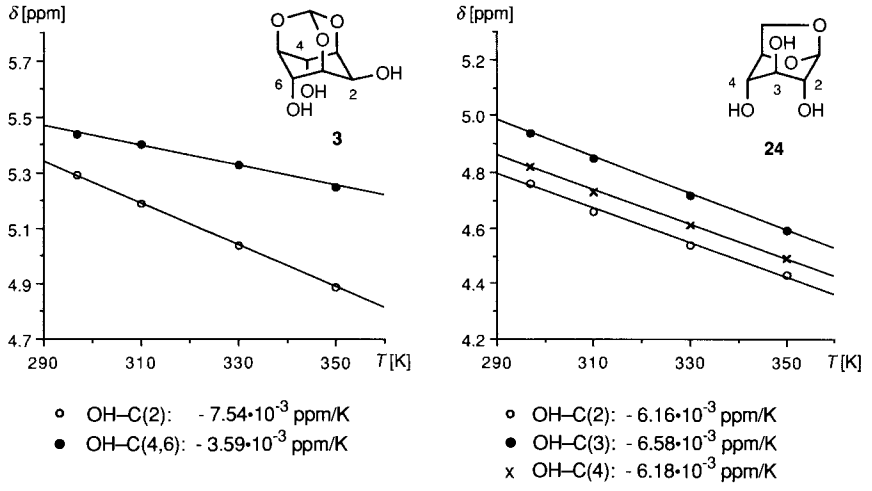


Fig. 2. *Temperature dependence of the chemical shift of the hydroxyl groups of* **3** *and* **24** *in* ^{1}*H-NMR* (300 MHz, (D_6)DMSO)

tramolecular (bifurcated?) H-bond ($\Delta\tilde{\nu} = 58$–60 cm^{-1}) to the orthoester O-atoms (O–C(1,3)). The strong intramolecular H-bond between the *cis*-related axial OH groups is further evidenced in ^{1}H-NMR spectroscopy by a typical temperature dependence [20] ($\Delta\delta/\Delta T = -3.6 \cdot 10^{-3}$ ppm/K; see *Fig. 2*) and a large positive isotope shift of $+2.53 \cdot 10^{-2}$ ppm after partial deuteration [21] of **3** with CD_3OD in (D_6)DMSO. The smaller $\Delta\delta/\Delta T$ value ($-7.54 \cdot 10^{-3}$ ppm/K) for the equatorial OH group does not indicate an intramolecular H-bond for HO–C(2) in DMSO.

2. *Glycosidation of 1,6-Anhydroglucose* (**24**). Reaction of the triol **24** with 0.8 equiv. of **1** in 1,4-dioxane (see *Scheme 3*) afforded 60% of a mixture of two anomeric pairs of the 1,2- and 1,4-linked regioisomers in a ratio **25**/**26**/**27**/**28** of 28:31:17:24, as determined by HPLC of the crude product. Acetylation and partial separation gave pure samples of **29**–**32**. In the ^{1}H-NMR spectra of 1,2-linked disaccarides **29** and **30**, the signals of H–C(3) and H–C(4) (assigned by irradiation) are shifted to lower field (4.61–5.01 ppm), as compared to those of H–C(2) (3.40 and 3.51 ppm, respectively). In the 1,4-linked products, H–C(2) and H–C(3) resonated at lower field (4.59–5.31 ppm) than H–C(4) (3.47 and 3.64 ppm, respectively). (For ^{13}C-NMR, see *Table 2.*)

The result of the glycosidation of **24** is markedly different from the one of **3** and **2**. Yields and diastereoselectivity are sensibly lowered, indicating the lack of a strong H-bond between the *cis*-related axial HO–C(2) and HO–C(4). The crystal structure of **24** [22] shows no intramolecular H-bonds. The O···O distance between O–C(2) and O–C(4) of 3.299 Å is relatively large due to the *anti-reflex* effect [16] and not in a favourable range for an intramolecular H-bond. All OH groups are intermolecularly bonded, although some O···O distances would allow intramolecular H-bonds. FT-IR spectra (CCl_4, 0.05M) of the monobenzylated derivatives **33** and **34**, prepared from **24** [23], show a shift for the HO–C(3,4) bands in **33** and for the HO–C(2,3) bands in **34** of *ca.* 75 cm^{-1} to a lower frequency, probably due to the intramolecular H-bonds C(5)–O···HO–C(2), C(5)–O···HO–C(4), and C(1)–O···HO–C(3). All OH groups

Scheme 3. *Glycosidation of 1,6-Anhydroglucose with* **1**

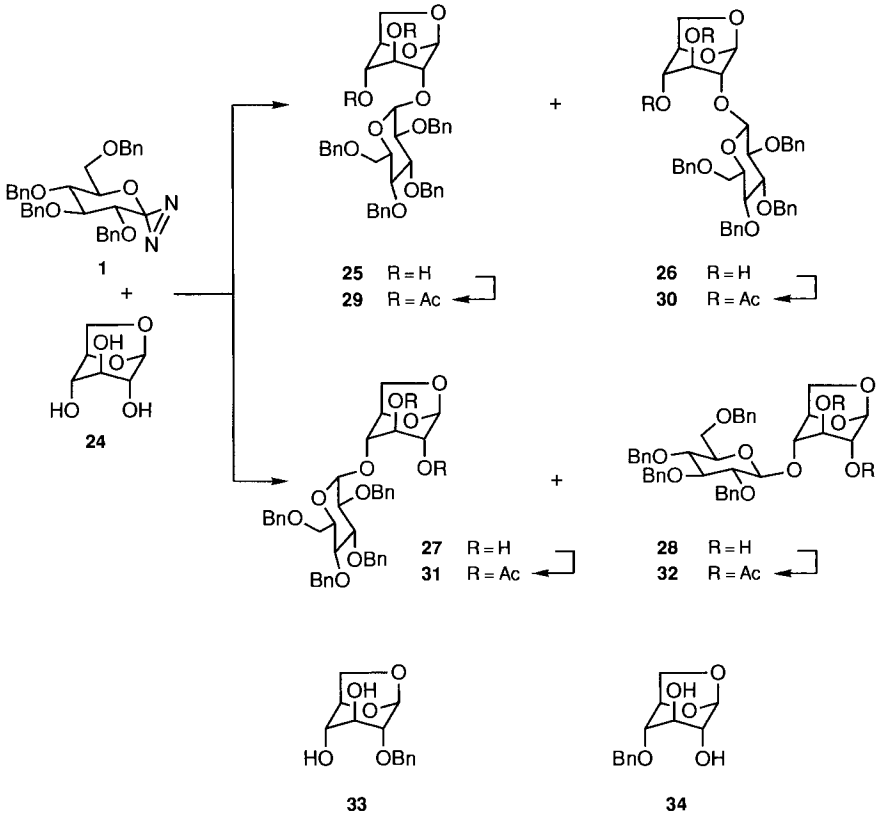


Table 2. *Selected* ^{13}*C-NMR* (50 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of Glycosides* **29–32**

Compound	**29**	**30**	**31**	**32**[a])
C(1)	100.23	101.98	98.95	99.02
C(2)	73.69[b])	75.39[b])	68.93	68.70
C(3)	70.45[c])	71.27[b])	70.20	69.33
C(4)	70.96[c])	71.32[b])	74.99[b])	75.94
C(5)	75.44[b])	74.08[b])	74.78[b])	73.41
C(6)	65.45	65.83	65.17	64.80
C(1′)	98.2	103.93	97.59	102.90
C(2′)	80.01	82.11	79.70	82.11
C(3′)	81.62	85.11	81.59	84.60
C(4′)	77.48	78.19	77.64	77.41
C(5′)	71.02[c])	75.01[b])	71.08	74.81
C(6′)	68.29	69.32	68.85	68.79

[a]) Assignment based upon a 2D-C,H-correlated spectrum.
[b])[c]) Assignment may be interchanged.

in the ^{1}H-NMR spectra ((D$_6$)DMSO) of the triol **24** show similar chemical-shift values. There is no evidence for intramolecular H-bonds. The $\delta\Delta/\delta T$ values are in the range of $-6.16 \cdot 10^{-3}$ to $-6.58 \cdot 10^{-3}$ ppm/K (see *Fig. 2*). No isotope shift was observed.

It is unclear to which extent the glycosidation of **24** reflects the intrinsic reactivity of the OH groups of the monomeric species. That no 1,3-linked regioisomers are observed may be explained by the assumption that HO–C(3) is involved in a weak, deactivating intramolecular H-bond to O–C(1), while HO–C(2) and HO–C(4) compete for O–C(5) as H-bond acceptor. However, HO–C(2) or HO–C(4) may act as acceptors in intermolecular H-bonds, which would enhance their reactivity. The dependence of intermolecular H-bonds upon concentration should distinguish them from intramolecular H-bonds, such as they exist in the *myo*-inositols **3** and **2**. To examine the role of intermolecular H-bonds in the glycosidation of **3** and **24**, we have studied the dependence of the yield of disaccarides upon the concentration of **3** and **24** individually and in a competition experiment (see *Fig. 3*). The reaction of the triols **3** and **24** with 1 equiv. of **1** was examined

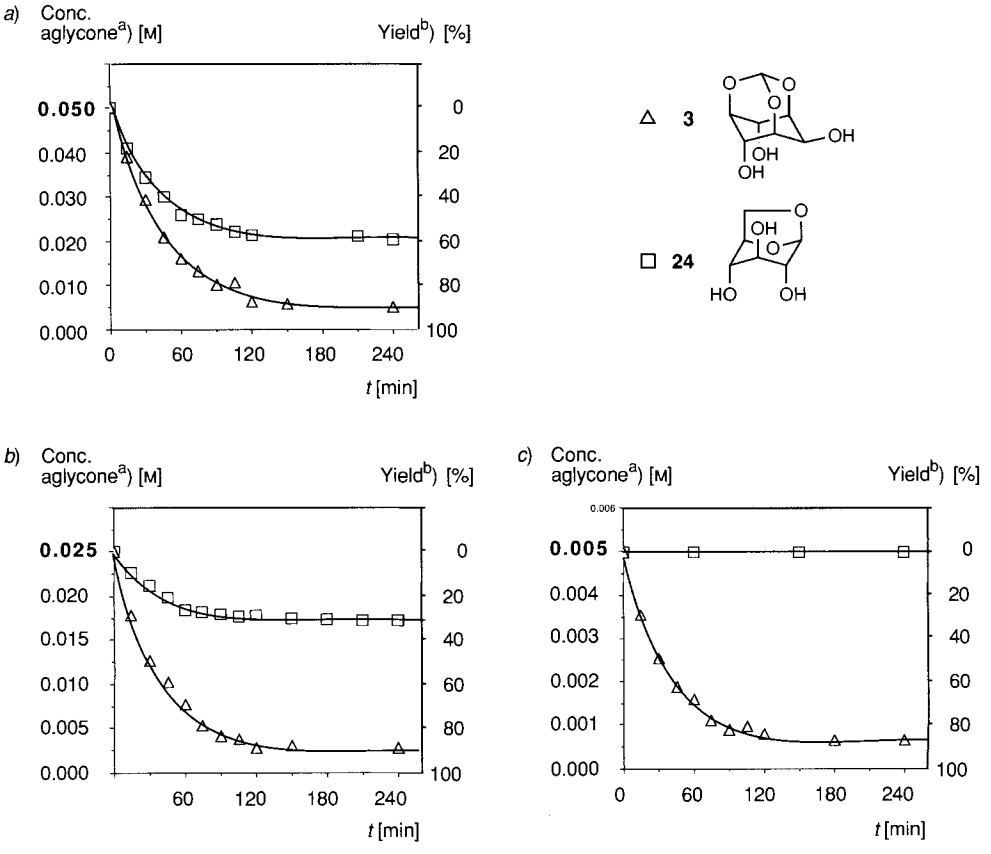


Fig. 3. *Dependence of the glycosidation of* **3** *and* **24** *with* **1** *on the concentration.*
a) The concentration of the aglycone was calculated from the amount of glycosides formed.
b) The concentration of products was monitored by HPLC.

for 0.05M, 0.025M, and 0.005M solutions in 1,4-dioxane at room temperature, and the formation of products was monitored by HPLC. The reaction mixture was concentrated after 4 h, and the disaccharides were separated from by-products by FC. Glycosides were obtained in the same ratio as described above. The overall yield in the glycosidation of **3** did not depend upon its concentration and was in the range of 90%, while the overall yield in the glycosidation of **24** decreased with decreasing concentration, reaching 60% at 0.05M and 31% at 0.025M. Less than 5% of glycosides were observed (HPLC) for a concentration of 0.005M. In a competition experiment between **3** and **24**, a mixture of **1**, **3**, and **24** in equimolar amounts was stirred at room temperature at different concentrations (0.2M, 0.05M, and 0.005M) in 1,4-dioxane for 4 h. FC of the crude product gave mixtures of the glycosides derived from **3** and from **24**. According to the weight of the fractions, the ratio between **7**, **8** (derived from **3**) and **25**–**28** (derived from **24**) was determined as 3:2 at a concentration of 0.2M, 3:1 at 0.05M, and *ca.* 20:1 at 0.005M. These results reflect the enhanced reactivity of associated glycosyl acceptors which do not possess intramolecular H-bonds to OH groups. Determination of the molecular weight of the triols **3** and **24** by osmometry in 1,4-dioxane at a concentration of *ca.* 0.025M showed an average molecular weight of 344 (M_r 190.16) for **3** and 331 (M_r 162.15) for **24**, corresponding to dimers.

These results show the important role of intra- and intermolecular H-bonds to OH groups in carbene-mediated glycosidations. The dependence of intramolecular H-bonds and of the glycosidation by 1-azisugars upon the structure of the glycosyl acceptor, the extent to which intermolecular H-bonds are required for a successful glycosidation, and means of enhancing the kinetic acidity of individual OH groups remain to be explored.

We thank Dr. *A. Linden* for determining the X-ray structure, Mr. *D. Nanz*, Mr. *Th. Plüss*, and Mr. *M. Vöhler* for their help with the NMR experiments, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. Solvents were freshly distilled. Reagents were from *Fluka* or *Aldrich*, and used as received. Powdered 4-Å molecular sieves (*Union Carbide*) were dried *i.v.* for 6 h at 280° and stored under Ar. Anal. TLC: *Merck* precoated silica gel *60 F254* plates; detection by treatment with a soln. of 5% $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ and 0.1% $Ce(SO_4)\cdot 4\,H_2O$. Flash chromatography (FC): silica gel *Merck 60* (40–63 μm). Medium-pressure liquid chromatography (MPLC): silica gel *Merck 60* (15–40 μm). High-performance liquid chromatography (HPLC): anal. *Spherisorb* silica (5 μm) 250 × 4.6 mm column; prep. *Spherisorb* silica gel (5 μm) 250 × 20 mm column. M.p.'s: uncorrected. Optical rotations: in a 1-dm cell; at 25° at 365, 436, 546, 578, and 589 nm; values at 589 nm from a regression curve. IR Spectra: 0.025M solns. in CCl_4. FT-IR Spectra: calibrated between 3800 and 3500 cm^{-1} against the known values of *trans*-1,2-cyclohexanediol [24]; the values of 3629 and 3636 cm^{-1} were used as standards [25] [26] for free equatorial and axial OH groups. ^1H- and ^{13}C-NMR Spectra: at 300 and 400 (^1H) and at 50 MHz (^{13}C); chemical shifts in ppm rel. to TMS, coupling constants J in Hz. MS: EI and CI (isobutane, NH_3) at 70 eV.

General Procedure for the Glycosidation with **1**. A mixture of the aglycon and dried, powdered 4-Å molecular sieves (25 mg/ml) in the indicated solvent (0.05M) was stirred for 30 min at r.t. under Ar. After the addition of **1** (0.8–1.1 equiv.), the mixture was stirred at the indicated temp., until all **1** had disappeared. Filtration through *Celite* and evaporation gave the crude product.

Glycosidation of **2** *with* **1**. The reaction of **1** (820 mg, 1.49 mmol) with **2** (502 mg, 1.65 mmol) in 1,4-dioxane (30 ml) for 4 h at r.t. followed by FC (pentane/Et_2O 3:2) of the crude product gave 559 mg (45%) of **5** and 549 mg (45%) of **6** as colourless oils. Crystallisation from Et_2O/hexane at −25° gave white needles of **5** and **6**, resp.

Glycosidation of **2** *with* **14**. A mixture of **2** (50 mg, 0.16 mmol) and powdered 4-Å molecular sieves (25 mg/ml) in CH_2Cl_2 (10 ml) was stirred for 1 h at r.t. under Ar, cooled to 0°, and then treated with **14** (135 mg, 0.20 mmol) and

$BF_3 \cdot Et_2O$ (4 µl, 0.03 mmol). The soln. was stirred for 30 min at 0°, treated with Et_3N (20 µl), filtered through *Celite*, and evaporated. MPLC (hexane/AcOEt 3:1) afforded 107 mg (79%) of a mixture of **5** (28%), **6** (53%), **15** (8%), and **16** (11%). Prep. HPLC (hexane/AcOEt 3:1; 16 ml/min) afforded pure samples of **15** and **16**.

*1*D*-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-(2,3,4,6-tetra-O-benzyl-β-*D*-glucopyranosyl)*-myo-*inositol* (**5**): R_f (pentane/Et_2O 3:2) 0.18. M.p. 103°. $[\alpha]_D^{25} = +13.0$ ($c = 1.10$, EtOH). IR: 3520*w* (OH_{ax}), 3067*w*, 3032*w*, 2921*m*, 2859*m*, 1497*w*, 1454*m*, 1361*m*, 1307*w*, 1253*w*, 1209*w*, 1168*s*, 1141*m*, 1075*s*, 1029*m*, 1005*s*, 972*m*, 948*m*, 900*w*, 879*m*, 852*m*, 726*w*, 698*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.16 (*m*, 20 arom. H); 5.52 (*d*, $J = 1.1$, CHO_3); 4.89 (*d*, $J = 11.1$, 1 H, PhCH_2); 4.80 (*d*, $J = 12.6$, 1 H, PhCH_2); 4.79 (*d*, $J = 11.1$, 1 H, PhCH_2); 4.78 (*d*, $J = 11.0$, 1 H, PhCH_2); 4.71 (*d*, $J = 11.0$, 1 H, PhCH_2); 4.61 (*d*, $J = 7.6$, irrad. at 3.45→*s*, H–C(1′)); 4.58–4.51 (*m*, H–C(4), H–C(3), H–C(6), 3 H of PhCH_2); 4.34 ('*q*', $J \approx 1.2$, H–C(2)); 4.13 ('*quint.*', $J \approx 2.0$, H–C(1), H–C(5)); 3.69–3.53 (*m*, H–C(3′), H–C(4′), H–C(5′), 2 H–C(6′), OH); 3.45 (*dd*, $J = 7.6, 8.9$, H–C(2′)); 0.93 (*s*, *t*-BuSi); 0.12 (*s*, MeSi); 0.11 (*s*, MeSi). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.24 (*s*); 137.67 (2*s*); 137.61 (*s*); 128.47–127.47 (*m*); 103.89 (*d*, C(1′)); 102.72 (*d*, CHO_3); 84.23 (*d*, C(3′)); 82.01 (*d*, C(2′)); 77.23 (*d*, C(4′)); 76.80 (*d*, C(5′)); 75.58 (*t*); 75.14 (*t*); 75.04 (*t*); 74.76 (*d*, C(4) or C(1)); 74.44 (*d*, C(1) or C(4)); 73.51 (*t*); 72.93 (*d*, C(3)); 69.36 (*d*, C(6)); 68.43 (*t*, C(6′)); 67.88 (*d*, C(5)); 61.15 (*d*, C(2)); 25.91 (*q*); 18.37 (*s*); –4.60 (*q*); –4.69 (*q*). CI-MS: 827 (65, $[M + 1]^+$), 737 (11), 523 (11), 415 (75), 367 (14), 341 (13), 325 (17), 305 (58), 299 (11), 289 (11), 271 (18), 247 (14), 235 (14), 181 (60), 179 (15), 107 (100). Anal. calc. for $C_{47}H_{58}O_{11}Si$ (827.07): C 68.26, H 7.07; found: C 67.97, H 6.96.

*1*L*-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-(2,3,4,6-tetra-O-benzyl-β-*D*-glucopyranosyl)*-myo-*inositol* (**6**): R_f (pentane/Et_2O 3:2) 0.11. M.p. 88°. $[\alpha]_D^{25} = +7.60$ ($c = 1.04$, EtOH). IR: 3549*w* (OH_{ax}), 3067*w*, 3032*w*, 2929*m*, 2859*m*, 1497*w*, 1454*m*, 1361*m*, 1307*w*, 1275*w*, 1253*w*, 1209*w*, 1168*s*, 1144*m*, 1111*s*, 1073*s*, 1029*m*, 1005*s*, 970*m*, 948*m*, 882*w*, 853*m*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.12 (*m*, 20 arom. H); 5.52 (*d*, $J = 1.2$, CHO_3); 4.86 (*s*, 2 H, PhCH_2); 4.80 (*d*, $J = 11.0$, 2 H, PhCH_2); 4.72 (*d*, $J = 10.7$, 1 H, PhCH_2); 4.69 ('*dt*', $J \approx 1.9, 3.9$, H–C(4)); 4.57 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.55 (*d*, $J = 7.7$, irrad. at 3.42→*s*, H–C(1′)); 4.54 (*d*, $J = 9.7$, 1 H, PhCH_2); 4.51 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.47 (*m*, H–C(6)); 4.34 ('*sext.*', $J \approx 2.0$, H–C(3)); 4.29 ('*sept.*', $J \approx 1.7$, H–C(5)); 4.27 ('*q*', $J \approx 1.4$, H–C(2)); 4.15 ('*sext.*', $J \approx 1.9$, H–C(1)); 3.74–3.64 (*m*, H–C(3′), H–C(4′), 2 H–C(6′)); 3.49 (*m*, H–C(5′)); 3.42 (*m*, H–C(2′)); 3.25 (*d*, $J = 9.7$, OH); 0.94 (*s*, *t*-BuSi); 0.15 (*s*, MeSi); 0.15 (*s*, MeSi). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.09 (*s*); 137.70 (*s*); 137.64 (*s*); 137.23 (*s*); 128.69–127.61 (*m*); 102.61 (*d*, CHO_3); 102.53 (*d*, C(1′)); 84.82 (*d*, C(3′)); 81.42 (*d*, C(2′)); 77.64 (*d*, C(4′)); 75.61 (*t*); 75.37 (*t*); 75.15 (*d*, C(5′)); 75.04 (*t*); 74.92 (*d*, C(4)); 74.66 (*d*, C(1)); 73.62 (*d*, C(3)); 73.46 (*t*); 68.44 (*t*, C(6′)); 68.28 (*d*, C(6)); 67.57 (*d*, C(5)); 60.85 (*d*, C(2)); 25.92 (*q*); 18.35 (*s*); –4.52 (*q*); –4.70 (*q*). CI-MS: 827 (16, $[M + 1]^+$), 415 (44), 361 (12), 325 (14), 305 (100), 289 (11), 287 (14), 271 (14), 247 (19), 235 (15), 217 (22), 197 (10), 187 (14), 181 (48), 179 (20), 139 (12), 107 (84), 105 (10), 91 (75). Anal. calc. for $C_{47}H_{58}O_{11}Si$ (827.07): C 68.26, H 7.07; found: C 68.47, H 7.13.

*1*D*-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-(2,3,4,6-tetra-O-benzyl-α-*D*-glucopyranosyl)*-myo-*inositol* (**15**): R_f (pentane/Et_2O 3:2) 0.27. $[\alpha]_D^{25} = +36.7$ ($c = 0.98$, EtOH). IR: 3517*w* (OH_{ax}), 3090*w*, 3067*w*, 3032*w*, 2929*m*, 2859*m*, 1738*w*, 1606*w*, 1497*w*, 1454*m*, 1362*m*, 1306*w*, 1259*m*, 1208*w*, 1168*s*, 1071*s*, 1028*s*, 1003*s*, 976*m*, 956*m*, 896*w*, 881*m*, 850*m*, 726*w*, 697*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34–7.14 (*m*, 20 arom. H); 5.52 (*d*, $J = 1.2$, CHO_3); 4.97 (*d*, $J = 3.8$, H–C(1′)); 4.88–4.79 (*m*, 4 H, PhCH_2); 4.69 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.61 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.61 ('*dt*', $J \approx 1.9, 3.9$, H–C(4)); 4.51 (*d*, $J = 10.8$, 1 H, PhCH_2); 4.50 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.43 (*m*, H–C(6)); 4.30 ('*sext.*', $J \approx 1.9$, H–C(3)); 4.27–4.25 (*m*, H–C(2), H–C(5)); 4.14 ('*sext.*', $J \approx 2.0$, H–C(1)); 3.86 ('*t*', $J \approx 9.3$, H–C(3′)); 3.81 ('*dt*', $J \approx 10.1, 2.9$, H–C(5′)); 3.74–3.63 (*m*, H–C(4′), H–C(6′), OH); 3.61 (*dd*, $J = 3.8, 9.6$, irrad. at 4.97→*d*, $J = 9.6$, H–C(2′)); 0.91 (*s*, *t*-BuSi); 0.07 (*s*, MeSi); 0.07 (*s*, MeSi). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.85 (*s*); 137.51 (*s*); 137.24 (*s*); 137.17 (*s*); 128.15–126.97 (*m*); 102.36 (*d*, CHO_3); 95.16 (*d*, C(1′)); 81.66 (*d*, C(3′)); 78.07 (*d*, C(2′)); 77.00 (*d*, C(4′)); 75.25 (*t*); 74.69 (*t*); 74.49 (*d*, C(1)); 73.30 (*t*); 73.21 (*t*); 71.41 (*d*); 71.32 (*d*); 71.18 (*d*); 68.46 (*d*, C(6)); 67.86 (*d*, *t*, C(5), C(6′)); 60.45 (*d*, C(2)); 25.44 (*q*); 17.82 (*s*); –4.97 (*q*); –5.04 (*q*). CI-MS: 844 (23, $[M + 18]^+$), 827 (83), 737 (18), 730 (10), 324 (16), 305 (100), 227 (30), 216 (16), 198 (12), 191 (10), 108 (36). Anal. calc. for $C_{47}H_{58}O_{11}Si$ (827.07): C 68.26, H 7.07; found: C 68.40, H 7.29.

*1*L*-2-O-[(*tert*-Butyl)dimethylsilyl]-1,3,5-O-methylidyne-4-O-(2,3,4,6-tetra-O-benzyl-α-*D*-glucopyranosyl)*-myo-*inositol* (**16**): R_f (pentane/Et_2O 3:2) 0.22. $[\alpha]_D^{25} = +52.8$ ($c = 0.97$, EtOH). IR: 3506*w* (OH_{ax}), 3067*w*, 3032*w*, 2930*m*, 2858*m*, 1738*w*, 1497*w*, 1454*m*, 1391*w*, 1362*m*, 1308*w*, 1258*m*, 1208*w*, 1168*s*, 1142*s*, 1072*s*, 1028*m*, 1004*s*, 976*m*, 951*m*, 896*w*, 880*m*, 851*m*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.16 (*m*, 20 arom. H); 5.53 (*d*, $J = 1.1$, CHO_3); 4.85–4.79 (*m*, 4 H, PhCH_2); 4.78 (*d*, $J = 3.7$, irrad. at 3.56→*s*, H–C(1′)); 4.64 (*d*, $J = 12$, 1 H, PhCH_2); 4.57 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.56–4.48 (*m*, H–C(4), H–C(6)); 4.50 (*d*, $J = 11.2$, 1 H, PhCH_2); 4.45 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.31–4.29 (*m*, H–C(2), OH); 4.18 (*m*, H–C(3), H–C(5)); 4.08 ('*sext.*', $J \approx 2.1$, H–C(1)); 3.77 (*m*, H–C(5′)); 3.70–3.59 (*m*, H–C(3′), H–C(4′), 2 H–C(6′)); 3.56 (*dd*, $J = 3.7, 9.6$, H–C(2′)); 0.96 (*s*, *t*-BuSi); 0.17 (*s*, MeSi). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.24 (*s*); 138.13 (*s*); 137.62 (*s*); 137.15 (*s*); 128.92–127.31 (*m*);

102.65 (*d*, CHO_3); 96.50 (*d*, C(1')); 81.91 (*d*, C(3')); 78.35 (*d*, C(2')); 77.08 (*d*, C(4')); 75.70 (*t*); 75.06 (*d*, C(1)); 74.70 (*t*); 74.32 (*t*); 73.52 (*t*); 73.24 (*d*, C(3)); 71.69 (*d*, C(5')); 71.49 (*d*, C(4)); 68.34 (*d*, C(6)); 67.96 (*t*, C(6')); 66.96 (*d*, C(5)); 61.10 (*d*, C(2)); 26.10 (*q*); 18.53 (*s*); −4.39 (*q*); −4.60 (*q*). CI-MS: 844 (8, $[M + 18]^+$), 827 (75), 738 (17), 541 (12), 333 (17), 324 (21), 305 (100), 216 (19), 198 (13), 108 (33), 106 (17), 91 (13). Anal. calc. for $C_{47}H_{58}O_{11}Si$ (827.07): C 68.26, H 7.07; found: C 68.07, H 7.24.

*1*D-*1,3,5*-O-*Methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)*-myo-*inositol* (**7**). $Bu_4NF \cdot 3\ H_2O$ (115 mg, 0.36 mmol) was added to a soln. of **5** (300 mg, 0.36 mmol) in THF (5 ml) at 0°. The mixture was stirred for 24 h at 24°, diluted with AcOEt (15 ml), and washed with brine (3 × 10 ml). The org. layer was dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 1:1) afforded 232 mg (90%) of 7 as a colourless oil. R_f (pentane/Et_2O 1:4) 0.17. $[\alpha]_D^{25} = +6.4$ (*c* = 1.06, EtOH). IR: 3583*w* (OH_{eq}), 3544*w* (OH_{ax}), 3090*w*, 3067*w*, 3032*w*, 2868*w*, 1742*w*, 1497*w*, 1454*m*, 1402*w*, 1360*m*, 1298*w*, 1262*w*, 1236*w*, 1209*w*, 1164*s*, 1082*s*, 1028*m*, 1011*s*, 993*s*, 958*m*, 911*w*, 891*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.16 (*m*, 20 arom. H); 5.46 (*d*, *J* = 1.3, CHO_3); 4.89 (*d*, *J* = 11.1, 1 H, PhCH_2); 4.82 (*d*, *J* = 11.1, 1 H, PhCH_2); 4.80 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.74 (*s*, 2 H, PhCH_2); 4.57 (*d*, *J* = 7.8, irrad. at 3.42→*s*, H–C(1')); 4.57–4.50 (*m*, H–C(3), H–C(4), H–C(6), 3 H of PhCH_2); 4.20 ('*sext.*', *J* ≈ 1.8, H–C(1)); 4.15 (*m*, H–C(5)); 4.08 (*m*, H–C(2)); 3.70–3.52 (*m*, H–C(3'), H–C(4'), H–C(5'), 2 H–C(6'), OH); 3.42 (*dd*, *J* = 7.8, 8.7, H–C(2')); 3.05 (br. *s*, OH). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.20 (*s*); 137.80 (*s*); 137.67 (2*s*); 128.74–127.72 (*m*); 103.75 (*d*, C(1')); 102.82 (*d*, CHO_3); 84.36 (*d*, C(3')); 81.62 (*d*, C(2')); 77.28 (*d*, C(4')); 75.96 (*d*, C(5')); 75.62 (*t*); 75.20 (*t*); 75.07 (*t*); 74.85 (*d*, C(4) or C(1)); 74.24 (*d*, C(1) or C(4)); 73.45 (*t*); 72.40 (*d*, C(3)); 68.98 (*d*, C(6)); 68.47 (*t*, C(6')); 67.42 (*d*, C(5)); 60.83 (*d*, C(2)). CI-MS: 730 (100, $[M + 18]^+$), 324 (12), 108 (10). Anal. calc. for $C_{41}H_{44}O_{11}$ (712.80): C 69.09, H 6.49; found: C 69.09, H 6.49.

*1*L-*1,3,5*-O-*Methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)*-myo-*inositol* (**8**). Similarly to **5**, **6** (300 mg) was desilylated to give 229 mg (89%) of **8**. R_f (pentane/Et_2O 1:4) 0.17. $[\alpha]_D^{25} = +4.0$ (*c* = 1.10, EtOH). IR: 3583*w* (OH_{eq}), 3548*w* (OH_{ax}), 3067*w*, 3032*w*, 2868*w*, 1742*m*, 1497*w*, 1454*m*, 1410*w*, 1360*m*, 1297*w*, 1239*m*, 1209*w*, 1164*s*, 1079*s*, 1028*m*, 1012*s*, 994*s*, 958*m*, 888*w*, 726*w*, 698*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.14 (*m*, 20 arom. H); 5.47 (*d*, *J* = 1.3, CHO_3); 4.85 (*s*, 2 H, PhCH_2); 4.79 (*d*, *J* = 10.8, 1 H, PhCH_2); 4.78 (*d*, *J* = 11.0, 1 H, PhCH_2); 4.71 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.68 ('*dt*', *J* ≈ 1.9, 4.0, H–C(4)); 4.59 (*d*, *J* = 12.2, 1 H, PhCH_2); 4.55 (*d*, *J* = 12.2, 1 H, PhCH_2); 4.54 (*d*, *J* = 11.6, 1 H, PhCH_2); 4.53 (*d*, *J* = 7.7, irrad. at 3.44→*s*, H–C(1')); 4.48 (*m*, H–C(6)); 4.41 ('*sext.*', *J* ≈ 2.0, H–C(3)); 4.28 ('*sept.*', *J* ≈ 1.8, H–C(5)); 4.21 ('*sext.*', *J* ≈ 2.0, H–C(1)); 4.11 (br. *d*, *J* ≈ 8.8, H–C(2)); 3.70–3.59 (*m*, H–C(3'), H–C(4'), 2 H–C(6')); 3.47 (*m*, H–C(5')); 3.44 ('*t*', *J* ≈ 8.2, H–C(2')); 3.36 (*d*, *J* = 10.3, OH); 3.03 (br. *d*, *J* ≈ 11, OH). ^{13}C-NMR ($CDCl_3$): 138.13 (*s*); 137.79 (*s*); 137.74 (*s*); 137.36 (*s*); 128.68–127.45 (*m*); 102.73 (*d*, CHO_3); 102.60 (*d*, C(1')); 84.76 (*d*, C(3')); 81.15 (*d*, C(2')); 77.55 (*d*, C(4')); 75.54 (*t*); 75.20 (*t*); 75.14 (*d*, C(5')); 75.01 (*t*); 74.90 (*d*, C(4)); 74.76 (*d*, C(1)); 73.59 (*t*); 73.33 (*d*, C(3)); 68.49 (*t*, C(6')); 67.83 (*d*, C(6)); 67.41 (*d*, C(5)); 60.39 (*d*, C(2)). CI-MS: 733 (11), 732 (46), 731 (100, $[M + 18]^+$), 324 (12), 108 (11). Anal. calc. for $C_{41}H_{44}O_{11}$ (712.80): C 69.09, H 6.22; found: C 69.37, H 6.36.

*1*D*-*1,3,5*-O-*Methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*glucopyranosyl)*-myo-*inositol* (**17**). Similarly to **5**, **15** (243 mg) was desilylated to give 178 mg (85%) of **17**. R_f (pentane/Et_2O 1:4) 0.17. $[\alpha]_D^{25} = +39.2$ (*c* = 1.0, EtOH). IR: 3583*w* (OH_{eq}), 3525*w* (OH_{ax}), 3067*w*, 3032*w*, 2929*w*, 6867*w*, 1497*w*, 1457*m*, 1410*w*, 1361*m*, 1296*w*, 1261*w*, 1209*w*, 1164*s*, 1082*s*, 1028*m*, 1015*s*, 992*s*, 958*m*, 916*w*, 889*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.13 (*m*, 20 arom. H); 5.48 (*d*, *J* = 1.2, CHO_3); 4.88 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.82 (*d*, *J* = 11.8, 2 H, PhCH_2); 4.80 (*d*, *J* = 12.4, 1 H, PhCH_2); 4.79 (*d*, *J* = 3.9, H–C(1')); 4.63 ('*dt*', *J* ≈ 1.8, 3.9, H–C(4)); 4.61 (*d*, *J* = 11.4, 2 H, PhCH_2); 4.49 (*d*, *J* ≈ 10, 1 H, PhCH_2); 4.48 (*d*, *J* ≈ 12, 1 H, PhCH_2); 4.45 (br. *s*, H–C(6)); 4.26 (*m*, H–C(3), H–C(5)); 4.20 ('*sext.*', *J* ≈ 1.9, H–C(1)); 4.12 (br. *s*, H–C(2)); 3.80 ('*t*', *J* ≈ 9.3, H–C(3')); 3.77–3.61 (*m*, H–C(4'), H–C(5'), 2 H–C(6'), OH); 3.57 (*dd*, *J* = 3.8, 9.6, H–C(2')); 3.03 (br. *s*, OH). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.22 (*s*); 137.78 (*s*); 137.49 (*s*); 137.37 (*s*); 128.64–127.59 (*m*); 102.73 (*d*, CHO_3); 94.59 (*d*, C(1')); 81.74 (*d*, C(3')); 78.45 (*d*, C(2')); 77.06 (*d*, C(4')); 75.66 (*t*); 75.08 (*t*); 74.79 (*d*, C(1)); 74.00 (*t*); 73.49 (*t*); 71.36 (*d*, C(5') or C(4)); 71.16 (*d*, C(4) or C(5')); 70.16 (*d*, C(3)); 68.26 (*d*, C(6)); 68.03 (*t*, C(6')); 67.76 (*d*, C(5)); 60.11 (*d*, C(2)). CI-MS: 730 (100, $[M + 18]^+$), 324 (11). Anal. calc. for $C_{41}H_{44}O_{11}$ (712.80): C 69.09, H 6.22; found: C 68.86, H 6.46.

*1*L*-*1,3,5*-O-*Methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*glucopyranosyl)*-myo-*inositol* (**18**). Similarly to **5**, **16** (100 mg) was desilylated to give 75 mg (87%) of **18**. R_f (pentane/Et_2O 1:4) 0.24. $[\alpha]_D^{25} = +55.0$ (*c* = 1.0, EtOH). IR: 3584*w* (OH_{eq}), 3501*w* (OH_{ax}), 3067*w*, 3032*w*, 2929*w*, 1734*w*, 1497*w*, 1454*m*, 1407*w*, 1362*w*, 1300*w*, 1261*m*, 1209*m*, 1011*s*, 993*s*, 957*m*, 909*w*, 887*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.13 (*m*, 20 arom. H); 5.47 (*d*, *J* = 1.1, CHO_3); 4.87 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.83 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.81 (*d*, *J* = 10.8, 1 H, PhCH_2); 4.79 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.77 (*d*, *J* = 3.9, irrad. at 3.56→*s*, H–C(1')); 4.64 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.58 (*d*, *J* = 12.1, 1 H, PhCH_2); 4.59–4.53 (*m*, H–C(4), H–C(6)); 4.49 (*d*, *J* = 10.8, 1 H, PhCH_2); 4.47 (*d*, *J* = 12.1, 1 H, PhCH_2); 4.34 (br. *d*, *J* ≈ 8.7, OH); 4.23 ('*sext.*', *J* ≈ 2.0, H–C(1)); 4.20 ('*sept.*', *J* ≈ 1.8, H–C(5)); 4.15–4.10 (*m*, H–C(2), H–C(3)); 3.81 ('*t*', *J* = 9.0, H–C(3')); 3.73–3.60 (*m*, H–C(4'), H–C(5'), 2 H–C(6')); 3.56 (*dd*, *J* = 3.8,

9.6, H–C(2')); 3.06 (br. *d*, *J* = 11.5, OH). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.14 (*s*); 137.72 (*s*); 137.47 (*s*); 137.05 (*s*); 128.64–127.76 (*m*); 102.69 (*d*, CHO_3); 96.61 (*d*, C(1')); 81.72 (*d*, C(3')); 78.15 (*d*, C(2')); 77.00 (*d*, C(4')); 75.74 (*t*); 75.13 (*t*); 74.73 (*d*, C(1)); 74.31 (*t*); 73.47 (*t*); 72.72 (*d*, C(3)); 71.39 (*d*, C(5')); 70.89 (*d*, C(4)); 67.79 (*d*, C(6)); 67.71 (*t*, C(6')); 66.57 (*d*, C(5)); 60.60 (*d*, C(2)). CI-MS: 730 (100, $[M + 18]^+$), 547 (23), 541 (15), 392 (13), 324 (23), 216 (19), 108 (19). Anal. calc. for $C_{41}H_{44}O_{11}$ (712.80): C 69.09, H 6.22; found: C 68.85, H 6.41.

*1*D-*2*-O-*Acetyl-1,3,5*-O-*methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)*-myo-*inositol* (**9**). At 0°, a mixture of **7** (35 mg, 0.049 mmol), Et_3N (13 µl, 0.093 mmol), 4-(dimethylamino)pyridine (6.0 mg, 0.049 mmol), and Ac_2O (6 µl, 0.063 mmol) in CH_2Cl_2 (0.65 ml) was stirred under Ar for 15 min. Evaporation and FC (pentane/Et_2O 1:1) of the residue afforded 24 mg (65%) of **9**. Colourless oil. R_f (pentane/Et_2O 1:2) 0.31. $[\alpha]_D^{25} = +1.0$ (*c* = 1.21, EtOH). IR: 3546*w* (OH_{ax}), 3090*w*, 3067*w*, 3032*w*, 2827*w*, 1742*s*, 1497*w*, 1454*m*, 1371*m*, 1239*s*, 1210*w*, 1168*s*, 1073*s*, 1029*m*, 1002*s*, 976*s*, 949*m*, 910*w*, 856*w*, 822*w*, 726*w*, 698*s*, 604*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.15 (*m*, 20 arom. H); 5.52 (*d*, *J* = 1.2, CHO_3); 5.35 ('*q*', *J* ≈ 1.7, H–C(2)); 4.91 (*d*, *J* = 11.1, 1 H, PhCH_2); 4.85 (*d*, *J* = 11.2, 1 H, PhCH_2); 4.80 (*d*, *J* = 11.6, 2 H, PhCH_2); 4.74 (*d*, *J* = 11.2, 1 H, PhCH_2); 4.61 (*d*, *J* = 7.6, irrad. at 3.46→*s*, H–C(1')); 4.58–4.47 (*m*, H–C(3), H–C(4), H–C(6), 3 H of PhCH_2); 4.29 (*m*, H–C(1), H–C(5)); 3.69–3.54 (*m*, H–C(3'), H–C(4'), H–C(5'), 2 H–C(6'), OH); 3.46 (*dd*, *J* = 7.6, 8.8, H–C(2')); 2.20 (*s*, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.27 (*s*); 138.24 (*s*); 137.88 (*s*); 137.70 (*s*); 137.65 (*s*); 128.68–127.45 (*m*); 103.95 (*d*, C(1')); 102.64 (*d*, CHO_3); 84.17 (*d*, C(3')); 81.55 (*d*, C(2')); 77.23 (*d*, C(4')); 75.88 (*d*, C(5')); 75.57 (*t*); 75.04 (2*t*); 74.82 (*d*, C(4)); 73.47 (*t*); 71.80 (*d*, C(1)); 69.82 (*d*, C(3)); 69.32 (*d*, C(6)); 68.49 (*t*, C(6')); 67.52 (*d*, C(5)); 63.33 (*d*, C(2)); 21.11 (*q*). CI-MS: 755 (12, $[M + 1]^+$), 523 (18), 431 (16), 415 (67), 397 (12), 341 (12), 325 (25), 323 (30), 307 (40), 283 (13), 271 (25), 269 (16), 253 (11), 247 (13), 233 (77), 217 (37), 193 (10), 187 (36), 181 (100), 179 (42), 107 (24), 91 (71). Anal. calc. for $C_{43}H_{46}O_{12}$ (754.84): C 68.42, H 6.14; found: C 68.68, H 6.22.

*1*L-*2*-O-*Acetyl-1,3,5*-O-*methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)*-myo-*inositol* (**10**). Similarly to **7**, **8** (27 mg) was acetylated to give 20 mg (70%) of **10**. R_f (pentane/Et_2O 1:2) 0.27. $[\alpha]_D^{25} = +4.2$ (*c* = 1.00, EtOH). IR: 3546*w* (OH_{ax}), 3032*m*, 2867*m*, 1744*s*, 1497*w*, 1454*m*, 1372*m*, 1261*m*, 1237*s*, 1167*s*, 1076*s*, 1028*m*, 1002*s*, 976*s*, 948*m*, 909*w*, 725*w*, 698*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.13 (*m*, 20 arom. H); 5.53 (*d*, *J* = 1.3, CHO_3); 5.39 ('*q*', *J* ≈ 1.5, H–C(2)); 4.86 (*m*, 2 H, PhCH_2); 4.79 (*d*, *J* = 11.0, 1 H, PhCH_2); 4.78 (*d*, *J* = 10.8, 1 H, PhCH_2); 4.74 (*d*, *J* = 11.0, 1 H, PhCH_2); 4.70 ('*sext.*', *J* ≈ 1.9, H–C(4)); 4.56 (*d*, *J* = 11.9, 1 H, PhCH_2); 4.56 (*d*, *J* = 7.7, irrad. at 3.46→*s*, H–C(1')); 4.57–4.46 (*m*, H–C(3), H–C(6), 1 H of PhCH_2); 4.51 (*d*, *J* = 12.2, 1 H of PhCH_2); 4.32 (*m*, H–C(1), H–C(5)); 3.71–3.59 (*m*, H–C(3'), H–C(4'), 2 H–C(6')); 3.49 (*ddd*, *J* = 2.3, 4.4, 9.3, H–C(5')); 3.46 ('*t*', *J* ≈ 8.2, H–C(2')); 3.37 (*d*, *J* = 9.8, OH); 2.16 (*s*, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.02 (*s*); 138.14 (*s*); 137.82 (*s*); 137.72 (*s*); 137.29 (*s*); 128.42–127.61 (*m*); 102.61 (*d*, CHO_3); 102.31 (*d*, C(1')); 84.79 (*d*, C(3')); 80.93 (*d*, C(2')); 77.63 (*d*, C(4')); 75.49 (*t*); 75.21 (*d*, *t*, C(5')); 75.03 (*t*); 74.33 (*d*, C(4)); 73.46 (*t*); 72.25 (*d*, C(1)); 70.99 (*d*, C(3)); 68.54 (*t*, C(6')); 67.88 (*d*, C(6)); 67.62 (*d*, C(5)); 62.84 (*d*, C(2)); 21.07 (*q*). CI-MS: 772 (100, $[M + 18]^+$), 539 (27), 233 (24), 198 (14), 151 (73), 108 (27), 106 (12). Anal. calc. for $C_{43}H_{46}O_{12}$ (754.84): C 68.42, H 6.14; found: C 68.24, H 6.27.

*1*D-*2,6-Di*-O-*benzyl-1,3,5*-O-*methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)*-myo-*inositol* (**11**). A soln. of **7** (100 mg, 0.14 mmol) in DMF (1 ml) was added to a mixture of NaH (20 mg, 0.83 mmol) and BnBr (0.1 ml, 0.84 mmol) in DMF (1 ml) under Ar at 0°. The mixture was stirred for 1 h at 0°, treated with MeOH (0.2 ml) and H_2O (5 ml), and then extracted with AcOEt (2 × 15 ml). The org. layer was washed with brine (2 × 5 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 2:1) of the residue afforded 120 mg (96%) of **11**. Colourless oil. R_f (hexane/AcOEt 2:1) 0.28. $[\alpha]_D^{25} = +8.6$ (*c* = 0.48, EtOH). IR: 3090*w*, 3066*w*, 3032*m*, 2867*m*, 1945*w*, 1742*w*, 1606*w*, 1497*m*, 1454*m*, 1362*m*, 1304*w*, 1240*w*, 1208*w*, 1168*s*, 1071*s*, 1028*m*, 1005*w*, 952*m*, 902*w*, 823*w*, 726*m*, 697*s*, 608*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33–7.15 (*m*, 30 arom. H); 5.57 (*d*, *J* = 1.2, CHO_3); 4.83 (*d*, *J* = 11.1, 1 H, PhCH_2); 4.78 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.77 (*d*, *J* = 11.8, 1 H, PhCH_2); 4.73 (*d*, *J* = 11.1, 1 H, PhCH_2); 4.69 ('*sept.*', *J* ≈ 1.7, H–C(4)); 4.61 (*d*, *J* = 11.2, 1 H, PhCH_2); 4.61 (*m*, H–C(3)); 4.59 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.52 (*d*, *J* = 10.9, 1 H, PhCH_2); 4.50 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.48 (*s*, 2 H, PhCH_2); 4.46 (*d*, *J* = 7.8, irrad. at 3.16→*s*, H–C(1')); 4.43 (*d*, *J* = 11.8, 1 H, PhCH_2); 4.38 (*d*, *J* = 11.2, 1 H, PhCH_2); 4.35–4.31 (*m*, H–C(1), H–C(5), H–C(6)); 4.00 ('*q*', *J* = 1.5, H–C(2)); 3.72 (*dd*, *J* = 1.7, 10.4, H_A–C(6')); 3.66 (*dd*, *J* = 4.1, 10.4, H_B–C(6')); 3.57 ('*t*', *J* ≈ 8.9, irrad. at 3.16→*d*, *J* = 9.9, H–C(3')); 3.49 ('*t*', *J* ≈ 8.9, H–C(4')); 3.44 (*m*, H–C(5')); 3.16 (*dd*, *J* = 7.8, 8.9, H–C(2')). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.53 (*s*); 138.23 (*s*); 138.04 (*s*); 137.92 (2*s*); 137.72 (*s*); 128.40–127.22 (*m*); 103.49 (*d*); 103.16 (*d*); 84.23 (*d*); 81.78 (*d*); 77.40 (*d*); 75.40 (*t*); 74.93 (*t*); 74.65 (*d*); 74.54 (*t*); 74.39 (*d*); 73.42 (*t*); 73.29 (*d*); 71.28 (*t*); 70.54 (*d*); 70.47 (*d*); 70.34 (*t*); 69.01 (*d*); 68.75 (*t*); 67.59 (*d*). CI-MS: 910 (99, $[M + 18]^+$), 893 (81), 820 (19), 804 (13), 575 (14), 540 (12), 469 (10), 415 (10), 399 (16), 371 (72), 324 (25), 281 (26), 265 (15), 253 (17), 216 (24), 198 (29), 181 (14), 108 (100), 106 (27), 105 (12), 91 (42), 87 (26).

*1*L-*2,6-Di*-O-*benzyl-1,3,5*-O-*methylidyne-4*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)*-myo-*inositol* (**12**). Similarly to **7**, **8** (100 mg) was benzylated to give 116 mg (93%) of **12**. R_f (hexane/AcOEt 2:1) 0.29. $[\alpha]_D^{25} = +28.6$

(c = 0.58, EtOH). IR: 3090*w*, 3066*w*, 3032*m*, 2866*m*, 1742*w*, 1497*m*, 1454*m*, 1362*m*, 1306*w*, 1240*w*, 1208*w*, 1167*s*, 1095*s*, 1029*m*, 1008*s*, 951*m*, 901*w*, 726*m*, 697*s*, 608*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.04 (*m*, 30 arom. H); 5.54 (*d*, J = 1.2, CHO_3); 4.86 (*d*, J = 10.2, 1 H, PhCH_2); 4.83 (*d*, J = 10.2, 1 H, PhCH_2); 4.75 (*d*, J = 12.2, 1 H, PhCH_2); 4.74 (*m*, H–C(4)); 4.74 (*d*, J = 10.9, 1 H, PhCH_2); 4.70 (*d*, J = 11.2, 1 H, PhCH_2); 4.57 (*d*, J = 12.2, 1 H, PhCH_2); 4.56 (*m*, H–C(3)); 4.55 (*d*, J = 10.9, 1 H, PhCH_2); 4.53 (*d*, J = 7.2, H–C(1′)); 4.52 (*d*, J = 11.9, 1 H, PhCH_2); 4.46 (*d*, J = 11.9, 1 H, PhCH_2); 4.41 (*d*, J = 11.8, 1 H, PhCH_2); 4.34 (*d*, J = 11.2, 1 H, PhCH_2); 4.32 (*d*, J = 11.8, 1 H, PhCH_2); 4.30 (*m*, H–C(5)); 4.26 ('*dt*', $J \approx$ 2.2, 3.7, H–C(6)); 4.22 ('*sext.*', $J \approx$ 1.9, H–C(1)); 2.12 ('*q*', $J \approx$ 1.6, H–C(2)); 3.74–3.58 (*m*, H–C(3′), H–C(4′), 2 H–C(6′)); 3.47 (*m*, H–C(5′)); 3.32 (*m*, H–C(2′)). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.47 (*s*); 138.40 (*s*); 137.96 (*s*); 137.80 (*s*); 137.68 (*s*); 137.24 (*s*); 128.43–127.26 (*m*); 104.88 (*d*); 103.06 (*d*); 84.33 (*d*); 82.09 (*d*); 77.35 (*d*); 75.90 (*d*); 75.57 (*t*); 74.92 (*t*); 74.68 (*d*); 74.37 (*t*); 73.87 (*d*); 73.43 (*t*); 71.54 (*t*); 71.40 (*d*); 70.85 (*d*, *t*); 68.87 (*d*); 68.79 (*t*); 66.25 (*d*). CI-MS: 910 (100, $[M + 18]^+$), 893 (50), 820 (20), 803 (11), 648 (28), 575 (13), 540 (14), 415 (13), 399 (15), 371 (75), 324 (32), 307 (17), 281 (28), 265 (15), 253 (18), 216 (29), 198 (31), 181 (12), 108 (98), 106 (25), 105 (11), 91 (43).

Glycosidation of **3** *with* **1**. The reaction of **1** (200 mg, 0.36 mmol) with **3** (83 mg, 0.44 mmol) in 1,4-dioxane (7 ml) for 4 h at r.t. and FC (pentane/Et_2O 1:4) of the crude product gave 234 mg (90%) of **7**/**8** 1:1 as a colourless oil. Treatment of the product with Ac_2O (1.2 equiv.), Et_3N (2.0 equiv.), and 4-(dimethylamino)pyridine (1.0 equiv.) in CH_2Cl_2 under Ar at 0° and FC (pentane/Et_2O 1:1) gave 67 mg (27%) of **9** and 59 mg (24%) of **10**.

Glycosidation of **3** *with* **14**. A mixture of **3** (277 mg, 1.46 mmol) and powdered 4-Å molecular sieves (25 mg/ml) in 1,4-dioxane (30 ml) was stirred for 1 h at r.t. under Ar, and then treated with **14** (1.1 g, 1.6 mmol) and $BF_3 \cdot Et_2O$ (35 µl, 0.28 mmol). The mixture was stirred for 30 min at r.t., treated with Et_3N (0.2 ml), filtered through *Celite*, and evaporated. FC (pentane/Et_2O 1:2) afforded 755 mg (73%) of a mixture of **7** (20%), **8** (40%), **17** (5%), **18** (10%), **19** (6%), and **20** (19%). Acetylation, partial separation by prep. HPLC (hexane/AcOEt 2:1, 16 ml/min), and deacetylation afforded pure samples of **19** and **20**.

1-D-*1,3,5*-O-*Methylidyne-2*-O-*(2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl)*-myo-*inositol* (**19**): R_f (pentane/Et_2O 1:4) 0.15. $[\alpha]_D^{25} = +50.6$ (c = 1.0, EtOH). IR: 3407*w* (br., 2 OH_{ax}), 3066*w*, 3032*w*, 2927*m*, 1497*w*, 1454*m*, 1362*m*, 1261*m*, 1208*w*, 1167*s*, 1074*s*, 1028*s*, 1002*s*, 949*m*, 726*m*, 698*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.16 (*m*, 20 arom. H); 5.49 (*d*, J = 1.2, CHO_3); 5.02 (*d*, J = 10.9, 1 H, PhCH_2); 4.96 (*d*, J = 3.7, H–C(1′)); 4.86 (*d*, J = 10.8, 1 H, PhCH_2); 4.85 (*d*, J = 10.9, 1 H, PhCH_2); 4.81 (*d*, J = 12.0, 1 H, PhCH_2); 4.65 (*d*, J = 12.0, 1 H, PhCH_2); 4.58 (*d*, J = 11.7, 1 H, PhCH_2); 4.50 (*d*, J = 10.8, 1 H, PhCH_2); 4.48 (*m*, H–C(4) or H–C(6)); 4.43 (*d*, J = 11.8, 1 H, PhCH_2); 4.40 (*m*, H–C(1) or H–C(3), H–C(4) or H–C(6)); 4.30 (*m*, H–C(1) or H–C(3)); 4.16 (*m*, H–C(5)); 4.14 ('*t*', $J \approx$ 9.2, H–C(3′)); 4.11 (*m*, H–C(5′)); 3.99 ('*d*', $J \approx$ 9.2, H–C(2)); 3.72–3.65 (*m*, 2 H–C(6′)); 3.69 (br. *s*, OH); 3.60 (*dd*, J = 3.8, 9.7, irrad. at 4.96→*d*, J = 9.7, H–C(2′)); 3.58 (*dd*, J = 9.0, 10.0, H–C(4′)); 3.38 (br. *s*, OH). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.79 (*s*); 138.20 (*s*); 138.00 (*s*); 137.65 (*s*); 128.52–127.59 (*m*); 102.39 (*d*, CHO_3); 97.42 (*d*, C(1′)); 81.78 (*d*, C(3′)); 80.46 (*d*, C(2′)); 77.85 (*d*, C(4′)); 75.70 (*t*); 75.12 (*t*), 73.47 (*t*); 73.23 (*t*); 72.70 (*d*, C(1) or C(3)); 71.90 (*d*, C(5′)); 70.49 (*d*, C(3) or C(1)); 69.03 (*t*, C(6′)); 68.53 (*d*); 68.13 (2*d*); 67.13 (*d*). CI-MS: 730 (100, $[M + 18]^+$). Anal. calc. for $C_{41}H_{44}O_{11}$ (712.80): C 69.09, H 6.22; found: C 68.93, H 6.41.

1-D-*1,3,5*-O-*Methylidyne-2*-O-*(2,3,4,6-tetra*-O-*benzyl*-β-D-*glucopyranosyl)*-myo-*inositol* (**20**): R_f (pentane/Et_2O 1:4) 0.15. $[\alpha]_D^{25} = +3.8$ (c = 1.0, EtOH). IR: 3406*w* (br., 2 OH_{ax}), 3066*w*, 3032*w*, 2867*w*, 1606*w*, 1497*w*, 1454*m*, 1359*w*, 1307*w*, 1263*w*, 1209*w*, 1167*s*, 1073*s*, 1028*m*, 1001*s*, 956*s*, 896*w*, 726*w*, 698*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.18 (*m*, 20 arom. H); 5.53 (*d*, J = 0.9, CHO_3); 5.11 (*d*, J = 10.7, 1 H, PhCH_2); 4.97 (*d*, J = 11.0, 1 H, PhCH_2); 4.85 (*d*, J = 10.9, 1 H, PhCH_2); 4.80 (*d*, J = 10.8, 1 H, PhCH_2); 4.78 (*d*, J = 10.5, 1 H, PhCH_2); 4.62 (*d*, J = 7.3, H–C(1′)); 4.56 (*d*, J = 11.8, 1 H, PhCH_2); 4.54 (*d*, J = 11.0, 1 H, PhCH_2); 4.50 (*d*, J = 11.9, 1 H, PhCH_2); 4.47 (br. *s*, H–C(4), H–C(5), H–C(6)); 4.31 (*m*, H–C(1) or H–C(3)); 4.24 (br. *s*, H–C(2)); 4.17 (*m*, H–C(1) or H–C(3)); 3.81 (br. *s*, OH); 3.78–3.49 (*m*, H–C(2′), H–C(3′), H–C(4′), H–C(5′), 2 H–C(6′), OH). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.32 (*s*); 138.14 (*s*); 137.74 (*s*); 137.48 (*s*); 128.43–127.62 (*m*); 102.91 (*d*, C(1′)); 102.73 (*d*, CHO_3); 84.39 (*d*, C(3′)); 81.73 (*d*, C(2′)); 77.61 (*d*, C(4′)); 75.63 (*t*); 74.98 (2*t*); 74.51 (*d*, C(5′)); 73.41 (*t*); 73.29 (*d*, C(1) or C(3)); 71.66 (*d*, C(3) or C(1)); 69.19 (*t*, C(6′)); 68.52 (*d*); 67.98 (*d*); 67.81 (*d*); 67.58 (*d*). CI-MS: 730 (100, $[M + 18]^+$), 350 (17). Anal. calc. for $C_{41}H_{44}O_{11}$ (712.80): C 69.09, H 6.22; found: C 68.90, H 6.44.

Glycosidation of **4** *with* **1**. The reaction of **4** (23 mg, 0.062 mmol) with 6 equiv. of **1** (200 mg, 0.36 mmol) in 1,4-dioxane (1.2 ml) for 36 h at r.t. and FC (hexane/AcOEt 3:1) gave 10 mg (18%) of **11** and 17 mg (74%) of **4**.

Glycosidation of **24** *with* **1**. A soln. of **1** (140 mg, 0.25 mmol) and **24** (50 mg, 0.31 mmol) in 1,4-dioxane (5 ml) was stirred for 4 h at r.t. Evaporation and MPLC (hexane/Et_2O 1:2) of the residue gave 105 mg (60%) of a mixture of **25** (28%), **26** (31%), **27** (17%), and **28** (24%). Prep. HPLC (hexane/AcOEt 1:1; 16 ml/min) gave mixtures **25**/**26** and **27**/**28**. Acetylation (Ac_2O, Et_3N, 4-(dimethylamino)pyridine, CH_2Cl_2) of these fractions and prep. HPLC (hexane/AcOEt 2:1; 16 ml/min) afforded pure samples of **29**, **30**, **31**, and **32**.

*3,4-Di-*O*-acetyl-1,6-anhydro-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**29**): R_f (hexane/AcOEt 1:2) 0.18. t_R (hexane/AcOEt 1:1) 14.90. $[\alpha]_D^{25} = +49.5$ ($c = 1.10$, EtOH). IR: 3066*w*, 3032*w*, 2903*m*, 2867*w*, 1743*s*, 1606*w*, 1497*w*, 1454*m*, 1370*m*, 1240*s*, 1224*s*, 1149*m*, 1074*s*, 1048*s*, 1029*s*, 916*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.16 (*m*, 20 arom. H); 5.48 (br. *s*, H–C(1)); 5.01 (*m*, H–C(3)); 4.96 (*d*, $J = 11.1$, 1 H, PhCH_2); 4.94 (*d*, $J = 3.6$, irrad. at 3.56→*s*, irrad. at 5.48→NOE of 3%, H–C(1′)); 4.84 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.82 (*d*, $J = 11.1$, 1 H, PhCH_2); 4.80 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.63 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.60 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.62–4.60 (*m*, H–C(4), H–C(5)); 4.50 (*d*, $J = 10.9$, 1 H, PhCH_2); 4.45 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.05 (*dd*, $J \approx 0.8$, 7.6, H_A–C(6)); 4.01 ('*t*', $J \approx 9.4$, H–C(3′)); 4.00 (*m*, H–C(5′)); 3.78 (*dd*, $J = 5.7$, 7.6, H_B–C(6)); 3.75 (*dd*, $J = 3.3$, 10.6, H_A–C(6′)); 3.69 (*dd*, $J = 9.1$, 9.9, H–C(4′)); 3.66 (*dd*, $J = 2.1$, 10.6, H_B–C(6′)); 3.56 (*dd*, $J = 3.6$, 9.7, H–C(2′)); 3.40 (br. *s*, irrad. at 5.48→NOE of 5%, H–C(2)); 2.07 (*s*, CH_3); 2.05 (*s*, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.25 (*s*); 169.06 (*s*); 138.78 (*s*); 138.39 (2*s*); 137.97 (*s*); 128.46–127.53 (*m*); 100.23 (*d*, C(1)); 98.20 (*d*, C(1′)); 81.62 (*d*, C(3′)); 80.01 (*d*, C(2′)); 77.48 (*d*, C(4′)); 75.58 (*t*); 75.44 (*d*, C(5) or C(2)); 74.90 (*t*); 73.69 (*d*, C(2) or C(5)); 73.45 (*t*); 73.18 (*t*); 71.02 (*d*, C(5′)); 70.96 (*d*, C(4) or C(3)); 70.45 (*d*, C(3) or C(4)); 68.29 (*t*, C(6′)); 65.45 (*t*, C(6)); 20.93 (2*q*). CI-MS: 786 (100, $[M + 18]^+$), 696 (28), 606 (11), 264 (35), 108 (17). Anal. calc. for $C_{44}H_{48}O_{12}$ (768.86): C 68.74, H 6.29; found: C 68.92, H 6.12.

*3,4-Di-*O*-acetyl-1,6-anhydro-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**30**): R_f (hexane/AcOEt 1:2) 0.16. t_R (hexane/AcOEt 1:1) 17.30. $[\alpha]_D^{25} = -2.0$ ($c = 1.04$, EtOH). IR: 3066*w*, 3032*w*, 2903*m*, 1743*s*, 1497*w*, 1454*m*, 1371*s*, 1305*w*, 1240*s*, 1223*s*, 1152*m*, 1073*s*, 1048*s*, 1030*s*, 930*w*, 875*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.16 (*m*, 20 arom. H); 5.69 (br. *s*, H–C(1)); 5.07 (*d*, $J = 11.3$, 1 H, PhCH_2); 4.95 ('*quint.*', $J \approx 1.5$, H–C(3)); 4.89 (*d*, $J = 10.9$, 1 H, PhCH_2); 4.82 (*d*, $J = 10.9$, 1 H, PhCH_2); 4.75 (*d*, $J = 11.4$, 2 H, PhCH_2); 4.69 (br. *s*, H–C(4)); 4.68 (*d*, $H \approx 7.7$, irrad. at 3.51→*s*, H–C(1′)); 4.62 (*m*, H–C(5)); 4.60 (*d*, $J = 12.2$, 1 H, PhCH_2); 4.55 (*d*, $J = 12.6$, 1 H, PhCH_2); 4.52 (*d*, $J = 13.8$, 1 H, PhCH_2); 4.09 (*dd*, $J = 0.9$, 7.7, H_A–C(6)); 3.81 (*dd*, $J = 5.8$, 7.7, H_B–C(6)); 3.69 (*d*, $J = 3.3$, 2 H–C(6′)); 3.66–3.59 (*m*, H–C(3′), H–C(4′)); 3.63 (br. *s*, irrad. at 5.69→NOE of 7%, H–C(2)); 3.51 ('*t*', $J \approx 8.2$, H–C(2′)); 3.47 ('*dt*', $J \approx 9.4$, 3.0, H–C(5′)); 2.07 (*s*, CH_3); 1.85 (*s*, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.84 (*s*); 169.92 (*s*); 139.17 (*s*); 139.11 (*s*); 138.79 (*s*); 138.73 (*s*); 128.96–126.58 (*m*); 103.93 (*d*, C(1′)); 101.98 (*d*, C(1)); 85.11 (*d*, C(3′)); 82.11 (*d*, C(2′)); 78.19 (*d*, C(4′)); 76.29 (*t*); 75.52 (*t*); 75.39 (*d*, C(2) or C(5′)); 75.01 (*d*, C(5′) or C(2)); 74.92 (*t*); 74.08 (*d*); 73.96 (*t*); 71.32 (*d*); 71.27 (*d*); 69.32 (*t*, C(6′)); 65.83 (*t*, C(6)); 21.60 (*q*); 21.31 (*q*). CI-MS: 786 (100, $[M + 18]^+$), 696 (24), 606 (10), 331 (22), 264 (32), 108 (15). Anal. calc. for $C_{44}H_{48}O_{12}$ (768.86): C 68.74, H 6.29; found: C 68.97, H 6.40.

*2,3-Di-*O*-acetyl-1,6-anhydro-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**31**): R_f (hexane/AcOEt 1:2) 0.27. t_R (hexane/AcOEt 1:1) 10.28. $[\alpha]_D^{25} = +3.0$ ($c = 1.0$, EtOH). IR: 3066*w*, 3032*w*, 2902*w*, 1747*s*, 1497*w*, 1454*m*, 1370*m*, 1241*s*, 1224*s*, 1154*m*, 1075*s*, 1048*s*, 909*m*, 894*m*, 726*m*, 697*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.15 (*m*, 20 arom. H); 5.45 (*m*, H–C(1)); 5.15 (*d*, $J = 3.7$, irrad. at 3.58→*s*, H–C(1′)); 4.98 (*d*, $J = 10.9$, 1 H, PhCH_2); 4.92 (*m*, H–C(3)); 4.86 (*d*, $J = 11.0$, 1 H, PhCH_2); 4.82 (*d*, $J = 10.9$, 1 H, PhCH_2); 4.75 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.70 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.67 (*m*, H–C(5)); 4.59 (*m*, H–C(2)); 4.57 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.48 (*d*, $J = 11.0$, 1 H, PhCH_2); 4.46 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.07 ('*t*', $J \approx 9.2$, H–C(3′)); 4.03 (*m*, H–C(5′)); 3.91 (*dd*, $J = 0.8$, 7.6, H_A–C(6)); 3.69 (*dd*, $J = 5.8$, 7.6, H_B–C(6)); 3.70–3.64 (*m*, 2 H–C(6′)); 3.58 (*dd*, $J = 3.7$, 9.6, H–C(2′)); 3.57 (*dd*, $J = 9.0$, 10.0, H–C(4′)); 3.47 (*m*, H–C(4)); 2.11 (*s*, CH_3); 1.91 (*s*, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.97 (*s*); 169.35 (*s*); 138.77 (*s*); 138.25 (*s*); 138.16 (*s*); 137.93 (*s*); 128.93–127.52 (*m*); 98.95 (*d*, C(1)); 97.59 (*d*, C(1′)); 81.59 (*d*, C(3′)); 79.70 (*d*, C(2′)); 77.64 (*d*, C(4′)); 75.54 (*t*); 74.99 (*d*, C(4) or C(5)); 74.93 (*t*); 74.78 (*d*, C(5) or C(4)); 73.41 (*t*); 72.83 (*t*); 71.08 (*d*, C(5′)); 70.20 (*d*, C(3)); 68.93 (*d*, C(2)); 68.85 (*t*, C(6′)); 65.17 (*t*, C(6)); 20.96 (*q*); 20.57 (*q*). CI-MS: 786 (100, $[M + 18]^+$), 264 (14). Anal. calc. for $C_{44}H_{48}O_{12}$ (768.86): C 68.74, H 6.29; found: C 68.67, H 6.40.

*2,3-Di-*O*-acetyl-1,6-anhydro-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**32**): R_f (hexane/AcOEt 1:2) 0.25. t_R (hexane/AcOEt 1:1) 11.72. $[\alpha]_D^{25} = -17.6$ ($c = 0.29$, EtOH). IR: 3066*w*, 3032*m*, 2902*m*, 1748*s*, 1497*w*, 1454*m*, 1370*m*, 1306*w*, 1222*s*, 1152*s*, 1070*s*, 1029*s*, 909*m*, 894*m*, 726*m*, 698*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.16 (*m*, 20 arom. H); 5.49 (*m*, H–C(1)); 5.31 (*m*, H–C(3)); 5.07 (*d*, $J = 11.0$, 1 H, PhCH_2); 4.93 (*d*, $J = 11.0$, 1 H, PhCH_2); 4.82 (*d*, $J = 11.7$, 1 H, PhCH_2); 4.80 (*d*, $J = 11.1$, 1 H, PhCH_2); 4.80 (*d*, $J = 11.7$, 1 H, PhCH_2); 4.65 (*d*, $J = 7.8$, irrad. at 3.56→*s*, H–C(1′)); 4.61 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.57 (*d*, $J = 11.0$, 1 H, PhCH_2); 4.59–4.56 (*m*, H–C(2), H–C(5)); 4.50 (*d*, $J = 12.0$, 1 H, PhCH_2); 3.97 (*dd*, $J = 0.5$, 7.6, H_A–C(6)); 3.77 (*dd*, $J = 5.8$, 7.5, H_B–C(6)); 3.73 (*d*, $J = 3.1$, 2 H–C(6′)); 3.69–3.66 (*m*, H–C(3′), H–C(4′)); 3.64 (*m*, H–C(4)); 3.56 (*dd*, $J = 7.8$, 9.1, H–C(2′)); 3.54 (*m*, H–C(5′)); 2.09 (*s*, CH_3); 2.01 (*s*, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.90 (*s*); 169.09 (*s*); 138.48 (*s*); 138.41 (*s*); 138.05 (2*s*); 128.24–127.36 (*m*); 102.90 (*d*, C(1′)); 99.02 (*d*, C(1)); 84.60 (*d*, C(3′)); 82.11 (*d*, C(2′)); 77.41 (*d*, C(4′)); 75.94 (*d*, C(4)); 75.56 (*t*); 74.81 (*d*, *t*, C(5′)); 74.75 (*t*); 73.41 (*d*, C(5)); 73.09 (*t*); 69.33 (*d*, C(3)); 68.79 (*t*, C(6′)); 68.70 (*d*, C(2)); 64.80 (*t*, C(6)); 20.84 (*q*); 20.64 (*q*). CI-MS: 786 (100, $[M + 18]^+$). Anal. calc. for $C_{44}H_{48}O_{12}$ (768.86): C 68.74, H 6.29; found: C 68.67, H 6.40.

X-Ray Analysis of **3**. Crystal data, exper. conditions, selected bond and torsion angles are given in *Tables 3–5*.

Table 3. *Crystal Data and Experiment Conditions for the X-Ray Analysis of* **3**

Molecular formula	$C_7H_{10}O_6$	Temp. of data collection [°C]	24
Formula weight	190.15	Radiation	MoK_α
Crystal structure	monoclinic, centrosymmetric	λ [Å] (graphite monochrom.)	0.70926
Space group	$P2_1/c$	Diffractometer	*Nicolet-R3*
a [Å]	11.7311 (9)	2 Θ Range [°C]	55
b [Å]	6.4007 (7)	No. of reflections measured	2561
c [Å]	11.231 (1)	Observed reflections [$I > 3\sigma(I)$]	1293
V [Å^3]	764.6 (1)	Final R factor	0.0350
Z	4	R_w	0.0365
Calc. density [g/cm^3]	1.652	μ (MoK_α) [cm^{-1}]	1.38

Table 4. *Selected Bond Angles* [°] *for* **3**. E.s.d.'s in Parentheses.

C(2)–C(1)–C(6)	110.4(1)	C(4)–C(3)–O(3)	107.8(1)	C(1)–C(6)–O(6)	110.1(1)
C(2)–C(1)–O(1)	109.0(1)	C(3)–C(4)–C(5)	107.4(1)	C(5)–C(6)–O(6)	109.7(1)
C(6)–C(1)–O(1)	108.2(1)	C(3)–C(4)–O(4)	111.6(1)	O(1)–C(7)–O(3)	111.1(1)
C(1)–C(2)–C(3)	107.4(1)	C(5)–C(4)–O(4)	113.4(1)	O(1)–C(7)–O(5)	111.2(1)
C(1)–C(2)–O(2)	113.1(1)	C(4)–C(5)–C(6)	113.0(1)	O(3)–C(7)–O(5)	111.5(1)
C(3)–C(2)–O(2)	111.8(1)	C(4)–C(5)–O(5)	106.7(1)	C(1)–O(1)–C(7)	110.3(1)
C(2)–C(3)–C(4)	111.2(1)	C(6)–C(5)–O(5)	106.6(1)	C(3)–O(3)–C(7)	110.5(1)
C(2)–C(3)–O(3)	108.8(1)	C(1)–C(6)–C(5)	107.7(1)	C(5)–O(5)–C(7)	111.6(1)

Table 5. *Selected Torsion Angles* [°] *for* **3**. E.s.d.'s in Parentheses.

C(2)–C(1)–C(6)–C(5)	59.9(1)	O(2)–C(2)–C(3)–C(4)	–173.3(1)	C(4)–C(5)–C(6)–C(1)	–58.4(1)
C(2)–C(1)–C(6)–O(6)	–59.6(1)	O(2)–C(2)–C(3)–O(3)	68.1(1)	C(4)–C(5)–C(6)–O(6)	61.4(2)
C(6)–C(1)–C(2)–C(3)	–62.2(1)	C(2)–C(3)–C(4)–C(5)	–59.1(1)	C(4)–C(5)–O(5)–C(7)	60.3(1)
C(6)–C(1)–C(2)–O(2)	174.0(1)	C(2)–C(3)–C(4)–O(4)	65.8(1)	C(6)–C(5)–O(5)–C(7)	–60.6(1)
C(2)–C(1)–O(1)–C(7)	–59.8(1)	C(2)–C(3)–O(3)–C(7)	60.2(1)	O(5)–C(5)–C(6)–C(1)	58.5(1)
O(1)–C(1)–C(2)–C(3)	56.5(1)	C(4)–C(3)–O(3)–C(7)	–60.5(1)	O(5)–C(5)–C(6)–O(6)	178.2(1)
O(1)–C(1)–C(2)–O(2)	–67.4(1)	O(3)–C(3)–C(4)–C(5)	60.0(1)	O(1)–C(7)–O(3)–C(3)	–63.3(1)
C(6)–C(1)–O(1)–C(7)	60.3(1)	O(3)–C(3)–C(4)–O(4)	–175.0(1)	O(3)–C(7)–O(1)–C(1)	63.0(1)
O(1)–C(1)–C(6)–C(5)	–59.3(1)	C(3)–C(4)–C(5)–C(6)	57.6(2)	O(1)–C(7)–O(5)–C(5)	62.8(1)
O(1)–C(1)–C(6)–O(6)	–178.8(1)	C(3)–C(4)–C(5)–O(5)	–59.2(1)	O(5)–C(7)–O(1)–C(1)	–61.8(1)
C(1)–C(2)–C(3)–C(4)	62.1(1)	O(4)–C(4)–C(5)–C(6)	–66.2(2)	O(3)–C(7)–O(5)–C(5)	–61.8(1)
C(1)–C(2)–C(3)–O(3)	–56.5(1)	O(4)–C(4)–C(5)–O(5)	177.0(1)	O(5)–C(7)–O(3)–C(3)	61.3(1)

REFERENCES

[1] A. Vasella, P. Uhlmann, Ch. Waldraff, F. Diederich, C. Thilgen, *Angew. Chem.* **1992,** in press.
[2] K. Briner, A. Vasella, *Helv. Chim. Acta* **1992,** *75,* 621.
[3] K. Briner, A. Vasella, *Helv. Chim. Acta* **1990,** *73,* 1764.
[4] K. Briner, A. Vasella, *Helv. Chim. Acta* **1989,** *72,* 1371.
[5] A. Vasella, K. Briner, N. Soundararajan, M.S. Platz, *J. Org. Chem.* **1991,** *56,* 4741.
[6] K. Briner, Ch. Waldraff, Ch. Witzig, A. Vasella, in preparation.
[7] Y. Takahashi, A. Vasella, *Helv. Chim. Acta* **1992,** *75,* 1563.
[8] A. Gaudemer, J.-L. Fourrey, J. Polonsky, *Bull. Soc. Chim. Fr.* **1967,** 1676.

[9] G. A. Jeffrey, W. Saenger, in 'Hydrogen Bonding in Biological Structures', Springer Verlag, Berlin, 1991.
[10] H. Hönig, H. Weidmann, *Carbohydr. Res.* **1979,** *73,* 260; A. J. Michell, H. G. Higgins, *Tetrahedron* **1965,** *21,* 1109; M. Tichy, *Adv. Org. Chem* **1965,** *5,* 115.
[11] G. A. Jeffrey, *Carbohydr. Res.* **1973,** *28,* 233.
[12] G. A. Jeffrey, J. Mitra, *Acta Crystallogr., Sect. B* **1983,** *39,* 469; C. Ceccarelli, G. A. Jeffrey, R. Taylor, *J. Mol. Struct.* **1981,** *70,* 255.
[13] E. Alvarado, Ph. D. Thesis, University of Alberta, 1987.
[14] D. Griller, M. T. H. Liu, J. C. Scaiano, *J. Am. Chem. Soc.* **1982,** *104,* 5549.
[15] H. W. Lee, Y. Kishi, *J. Org. Chem.* **1985,** *50,* 4402.
[16] C. W. Jefford, B. Waegell, *Tetrahedron Lett.* **1963,** 1981; J.-F. Biellmann, R. Hanna, G. Ourisson, C. Sandris, B. Waegell, *Bull. Soc. Chim. Fr.* **1960,** 1429.
[17] G. Baudin, B. I. Glänzer, K. S. Swaminathan, A. Vasella, *Helv. Chim. Acta* **1988,** *71,* 1367.
[18] K. Bock, T. Skrydstrup, *J. Chem. Soc., Perkin Trans. 1* **1991,** 1181.
[19] N. M. Spijker, C. A. A. van Boeckel, *Angew. Chem. Int. Ed.* **1991,** *30,* 180.
[20] B. R. Leeflang, J. F. G. Vliegenhart, L. M. J. Kroon-Batenburg, B. P. van Eijck, J. Kroon, *Carbohydr. Res.* **1992,** *230,* 41; F. Heatley, J. E. Scott, B. Casu, *ibid.* **1979,** *72,* 13; B. Casu, M. Reggiani, G. G. Gallo, A. Vigevani, *Tetrahedron* **1966,** *22,* 3061.
[21] J. C. Christofides, D. B. Davis, *J. Am. Chem. Soc.* **1986,** *108,* 5738.
[22] Y. J. Park, H. S. Kim, G. A. Jeffrey, *Acta Crystallogr., Sect. B* **1971,** *27,* 220.
[23] M. C. Cruzado, M. Martin-Lomas, *Carbohydr. Res.* **1988,** *175,* 193.
[24] L. Kuhn, *J. Am. Chem. Soc.* **1952,** *74,* 2492.
[25] S. J. Angyal, R. M. Hoskinson, *J. Chem. Soc.* **1962,** 2991.
[26] A. R. H. Cole, G. T. A. Müller, D. W. Thornton, R. L. S. Willix, *J. Chem. Soc.* **1959,** 1218.