31. Glycosylidene Carbenes

Part 15

Synthesis of Disaccharides from Allopyranose-Derived Vicinal 1,2-Diols. Evidence for the Protonation by a H-Bonded Hydroxy Group in the σ-Plane of the Intermediate Carbene, Followed by Attack on the Oxycarbenium Ion in the π-Plane

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The α-D-*allo*-diol **9** possesses an intramolecular H-bond (HO–C(3) to O–C(1)) in solution and in the solid state (*Fig. 2*). In solution, it exists as a mixture of the tautomers **9a** and **9b** (*Fig. 3*), which possess a bifurcated H-bond, connecting HO–C(2) with both O–C(1) and O–C(3). In addition, **9a** possesses the same intramolecular H-bond as in the solid state, while **9b** is characterized by an intramolecular H-bond between HO–C(3) and O–C(4). In solution, the β-D-anomer **12** is also a mixture of tautomers, **12a** and presumably a dimer. The H-bonding in **9** and **12** is evidenced by their IR and ^{1}H-NMR spectra and by a comparison with those of **3–8**, **10**, and **11**. The expected regioselectivity of glycosidation of **9** and **12** by the diazirine **1** or the trichloroacetimidate **2** is discussed on the basis of the relative degree of acidity/nucleophilicity of individual OH groups, as governed by H-bonding. Additional factors determining the regioselectivity of glycosidation by **1** are the direction of carbene approach/proton transfer by H-bonded OH groups, and the stereoelectronic control of both the proton transfer to the alkoxy-alkyl carbene (in the σ-plane) and the combination of the thereby formed ions (π-plane of the oxycarbenium ion). Glycosidation of **9** by the diazirine **1** or the trichloroacetimidate **2** proceeded in good yields (75–94%) and with high regioselectivity. Glycosidation of **9** and **12** by **1** or **2** gave mixtures of the disaccharides **14–17** and **18–21**, respectively (*Scheme 2*). As expected, glycosidation of **12** by **1** or by **2** gave a nearly 1:1 mixture of regioisomers and a slight preference for the β-D-anomers (*Table 4*). Glycosidation of the α-D-anomer **9** gave mostly the 1,3-linked disaccharides **16** and **17** (α-D > β-D) along with the 1,2-linked disaccharides **14** and **15** (α-D < β-D, 1,2-/1,3-linked glycosides *ca.* 1:4), except in THF and at low temperature, where the β-D-configurated 1,2-linked disaccharide **15** is predominantly formed. Similarly, glycosidation of **9** with **2** yielded mainly the 1,3-linked disaccharides (1,2-/1,3-linked products *ca.* 1:3 and α-D/β-D *ca.* 1:4). Yields and selectivity depend upon the solvent and the temperature. The regioselectivity and the unexpected stereoselectivity of the glycosidation of **9** by **1** evidences the combined effect of the above mentioned factors, which also explain the lack of regio-complementarity in the glycosidation of **9** by **1** and by **2** (*Scheme 3*). THF solvates the intermediate oxycarbenium ion, as evidenced by the strong influence of this solvent on the regio- and stereoselectivity, particularly at low temperatures, where kinetic control leads to a stereoelectronically preferred axial attack of THF on the oxycarbenium ion.

Introduction. – The regioselectivity of the glycosidation of diols and triols by a diazirine-derived glycosylidene carbene depends on the relative acidity of OH groups [1] (*cf.* [2] [3]), which is governed by intramolecular H-bonds. We have shown that the reactivity of H-bond-donating phenolic [4] and alcoholic OH groups [5] towards a diazirine-derived glycosylidene is depressed, that a triol is selectively glycosylated at a (free or intermolecularly H-bonded) H-bond-accepting OH group [6], and that the

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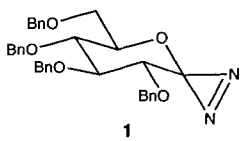
regioselectivity of the glycosidation of 1,2-diols correlates with the relative strength of intramolecular H-bonds [7]. This is illustrated by the glycosidation of the α-D-*altro*-diol **3** with the diazirine **1** [5]. The major products are 1,2-linked disaccharides, as expected from the relative strength of the H-bonds linking, on the one hand, HO–C(3) either to the MeO group or to O–C(4) [7], and, on the other hand, HO–C(2) to O–C(5). In keeping with the stronger H-bond involving HO–C(3) as a H-donor and enhancing its nucleophilicity, *Koenigs-Knorr*-type glycosidation of **3** by the trichloroacetimidate **2** [8] resulted predominantly in 1,3-linked disaccharides. In this example, the kinetically more acidic HO–C(2) and the more nucleophilic HO–C(3) are *trans*-diaxially arranged and do not sterically interact. The ion pairs which are formed by protonation of the carbene derived from **1** by either HO–C(2) or HO–C(3) remain in intimate contact – the reactions of the monotosylates **4** or **6** with **1** do not lead to epoxides [5] – and, therefore, HO–C(2) and HO–C(3) do not (in a product-determining way) interact during glycosidation.

This leads to the question if the rate of protonation of a glycosylidene carbene by individual OH groups is the only or the only important factor determining the regioselectivity of glycosidation. The 1,2-*cis*-axial,equatorial and 1,2-*trans*-diequatorial diols which we have studied either possessed OH groups which did not interact with each other [5] or which formed cooperative [9], more or less unidirectional (linear) H-bonds with an alkoxy group as chain terminator [7]. The situation is different for the α-D-*allo*-diol **9**, where the 1,2-*cis* OH groups can interact with each other and with the same alkoxy group, *viz.* O–C(1) and/or O–C(4). One expects the axial HO–C(3) to form a six-membered H-bond with the axial MeO group (*cf.* [6]). This H-bond reduces the kinetic acidity of HO–C(3) and enhances its nucleophilic properties. HO–C(2) can only form a five-membered, and thus weaker H-bond to O–C(3) and/or to the anomeric MeO group. As a consequence, the intermediate carbene should preferentially deprotonate HO–C(2) and,



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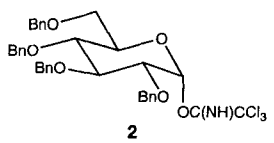

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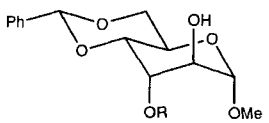

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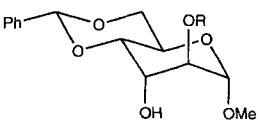
5 R = Me



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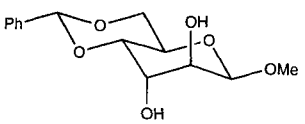

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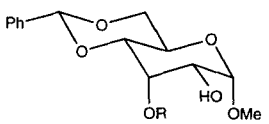

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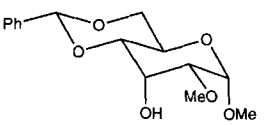

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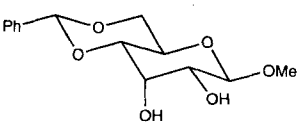

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if no other factor intervenes, glycosylate this OH group. Conversely, the electrophilic glycosyl donor **2** should preferentially glycosylate HO–C(3). A different regioselectivity is expected for the anomeric *β*-D-*allo*-diol **12**, where HO–C(3) can form a H-bond with O–C(4) or O–C(2), while HO–C(2) can form a H-bond only to the *cis*-oriented O–C(3) or to the *trans*-diequatorial O–C(1).

We report on the regio- and stereoselectivity of the glycosidation of **9** [10] and **12** [10] by **1** and **2** and discuss its significance for a qualitative mechanistic understanding of the formal insertion of an alkoxy alkyl carbene into H–O bonds.

Results and Discussion. – 1. *Hydrogen Bonds of the Diols* **9** *and* **12**; *Factors Determining the Regioselectivity*. As shown by the X-ray analysis, **9** adopts a slightly flattened $^4C_1$ conformation. The synclinal arrangement of O(5) and C(14) (dihedral angle 63°; *Fig. 1*, *Table 1*) is in agreement with the *exo*-anomeric effect. A strong intramolecular H-bond between HO–C(3) and O–C(1) is indicated by the O(3)···O(1), O(3)–H, and O(1)···H distances of 2.769, 0.86, and 1.98 Å, respectively. This bent H-bond (O(3)–H···O(1)

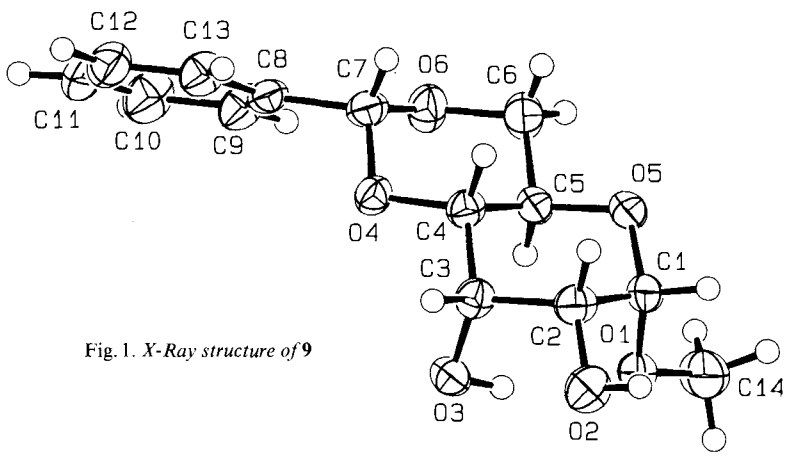

Fig. 1. *X-Ray structure of* **9**

Table 1. *Selected Atom Distances and Bond and Dihedral Angles of the X-Ray Structure of* **9**. For numbering, see *Fig. 1*.

Atom distances [Å]		Bond or dihedral angles [°]			
C(1)–O(1)	1.409 (2)	C(1)–O(1)–C(14)	113.6 (2)	O(5)–C(1)–O(1)–C(14)	62.6 (3)
O(1)–C(14)	1.434 (3)	O(1)–C(1)–O(5)	111.6 (2)	O(5)–C(1)–C(2)–O(2)	176.7 (2)
C(1)–O(5)	1.423 (2)	C(1)–O(5)–C(5)	112.3 (1)	O(1)–C(1)–C(2)–O(2)	54.0 (2)
C(2)–O(2)	1.417 (3)	O(1)–C(1)–C(2)	107.7 (2)	O(2)–C(2)–C(3)–O(3)	– 55.5 (2)
C(3)–O(3)	1.439 (2)	C(1)–C(2)–C(3)	111.3 (2)	O(1)–C(1)–O(5)–C(5)	63.3 (2)
C(5)–O(5)	1.436 (2)	C(2)–C(3)–C(4)	106.9 (2)	O(1)–C(1)–C(2)–C(3)	– 68.4 (2)
O(2)–H	0.83 (3)	C(2)–O(2)–H	107 (2)	C(2)–C(3)–O(3)–H	– 36 (2)
O(3)–H	0.86 (3)	C(3)–O(3)–H	102 (2)	H–C(1)–C(2)–H	54 (2)
C(1)···C(3)	2.530	O(3)–H···O(1)	151.5	H–C(2)–C(3)–H	– 62 (2)
O(1)···O(3)	2.768	C(1)–C(2)–C(3)–C(4)	–54.1 (2)	H–C(3)–C(4)–H	62 (2)
O(1)···O(2)	2.773	C(2)–C(3)–C(4)–C(5)	58.3 (2)	H–C(2)–O(2)–H	– 49 (2)
O(2)···O(3)	2.811	C(3)–C(4)–C(5)–O(5)	–62.0 (2)	H–C(3)–O(3)–H	–154 (3)

angle 152°) is part of a chair-like ring (H–C(3)–O(3)–H and H–C(1)–O(1)···H angles –154 and 156°, resp.). HO–C(2) is turned away from O–C(3) and O–C(1) (H–C(2)–O(2)–H –49°) and involved in an intermolecular H-bond to O–C(3) of an adjacent molecule (distances O(2)···O(3′) 2.874 Å, O(2)–H 0.86 Å, O(3′)···H 1.96 Å, and bond angle O(2)–H···O(3′) 167°), linking the molecules into infinite one-dimensional chains running parallel to the *a*-axis (*Fig. 2*). In this way, O–C(3) of **9** functions both as an H-donor and an H-acceptor.

In agreement with the X-ray structure, the IR spectrum of **9** in KBr shows two broad OH bands of equal intensity (3440 and 3380 cm^{-1}). As expected, H-bonding in the anomer **12** is different and characterized by a narrow band at 3480 and two broad bands at 3340 and 3250 cm^{-1}.

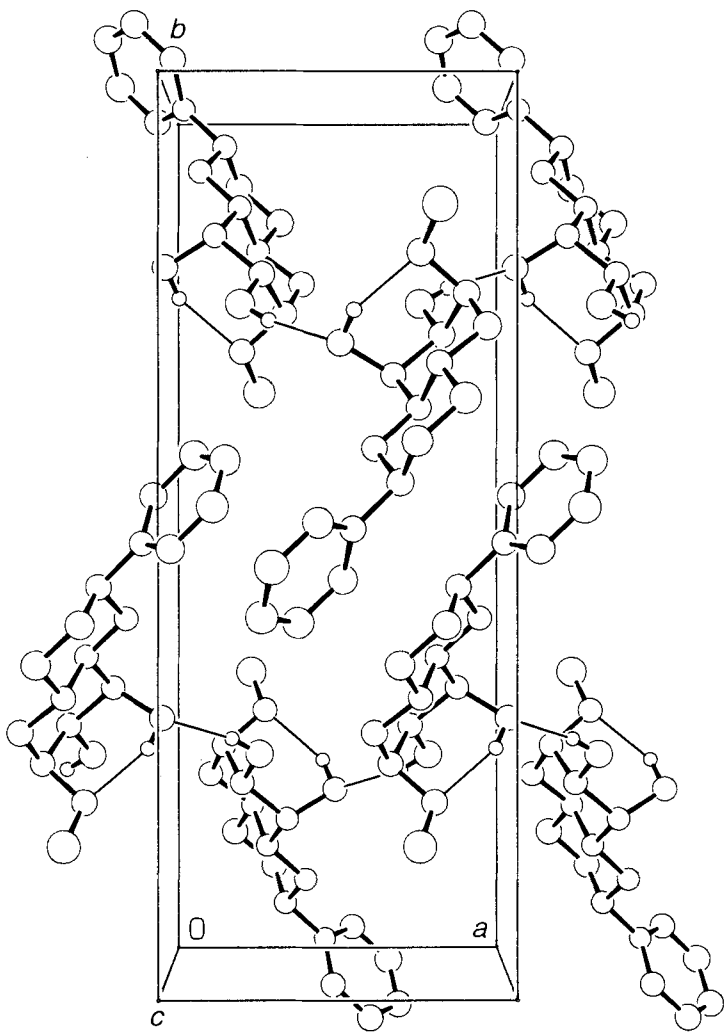

Fig. 2. *Hydrogen bonds in the solid state of* **9**

The IR spectra of **3** (CH_2Cl_2, *Table 2*) [5] show only bands for intramolecularly bonded OH groups, one at 3520 cm^{-1} for O(3)–H···OMe in a six-membered ring (3554 cm^{-1} in CCl_4) and one at 3598 cm^{-1} for the O(2)–H···O(5) group (3630 cm^{-1} in CCl_4; **3a** in *Fig. 3*). The band for O(3)–H···O(4) in a *cis*-annulated five-membered ring (see **3b**) is

Table 2. *FT-IR OH Bands* [cm^{-1}] *of the Diols* **3**–**12**

Diol	Solvent	Intramolecularly bonded OH[a])	Intermolecularly bonded OH[b])
3 [5]	CH_2Cl_2	3598, 3520	
3 [12] [13]	CCl_4	3630, 3602, 3554	
4 [5]	CH_2Cl_2	3596	
5 [12] [13]	CCl_4	3629, 3602	
6 [5]	CH_2Cl_2	3575[c]), 3524	
7 [12] [13]	CCl_4	3596, 3548	
8 [12]	CCl_4	3600	
9	CH_2Cl_2	3566 (br.), *ca.* 3540 (sh, br.)	*ca.* 3500
9 [13]	CCl_4	3610, 3581, 3547	
10 [13]	CCl_4	3567	
11 [13]	CCl_4	3609, 3552	
12	CH_2Cl_2	3586 (br.)	3473
12	CCl_4	3605 (br.)	

[a]) No dependence upon concentration (0.1M–0.005M) of solutions in CH_2Cl_2. [b]) Broad band, with tailing to *ca.* 3300 cm^{-1}; present at 0.1M (**9**, **12**) and 0.05M (**12**). [c]) Not at 3595 cm^{-1}, as published.

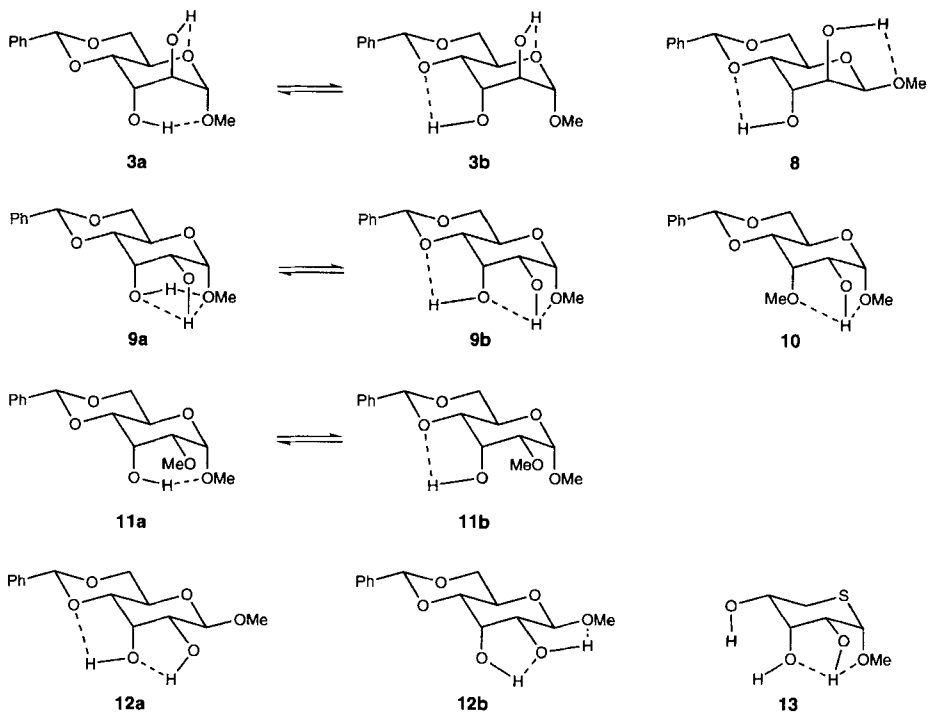

Fig. 3. *Intramolecular hydrogen bonds in the diols* **3** *and* **8**–**12**, *as deduced from IR* (OH bands of CH_2Cl_2 or CCl_4 solutions) *and* ^{1}*H-NMR spectroscopy* (vicinal J(OH,H) of $CDCl_3$ solutions), *and of* **13**, *as deduced from X-ray analysis*

only present in the spectrum of **3** in CCl_4[2]). Similar bands are found in the spectra of the β-D-anomer **8** [12] [13] and of the 2-*O*-protected altrosides **6** [5] and **7** [12] [13] (*Table 2*). The assignment is corroborated by the spectra of the 3-*O*-protected altrosides **4** [5] and **5** [12] [13].

Further assignments were based on a comparison of the IR spectra of the α-D-allosides **9**–**11** in CCl_4 [13]. Like the corresponding altroside **7**, the 2-*O*-methyl-alloside **11** exhibits an OH band at 3552 cm^{-1} for an H-bond in a six-membered ring, denoting the presence of the tautomer **11a** (*Fig. 3*) and a band at 3609 cm^{-1} for an H-bond in a five-membered ring with O–C(4) (**11b**) and/or O–C(2) as H-bond acceptors. The second possibility raises the question about a bifurcated H-bond (to both O–C(2) and O–C(1)) for which, however, there is no evidence, as the band at 3552 cm^{-1} for **11** is very similar to the corresponding one of **7**. This corroborates the rule that intramolecular H-bonds in six-membered rings are stronger than those in five-membered rings, but also that anomeric OR groups are poorer acceptors [9]. The equatorial HO–C(2) of the 3-*O*-methyl-alloside **10** can form an intramolecular H-bond to O–C(3) or to O–(1) (both leading to *cis*-annulated five-membered rings). This should give rise to an IR band in CCl_4 at *ca.* 3600 cm^{-1}. The band is, however, observed at 3567 cm^{-1} [13] and evidences a bifurcated H-bond[3]), as depicted for **10** in *Fig. 3*.

As expected, the IR spectrum of **9** in CCl_4 [13] exhibits bands for the three types of H-bonds present in **10** and **11**: one at 3547 cm^{-1} (OH bonded in a six-membered ring), one at 3610 cm^{-1} (OH bonded in a *cis*-annulated five-membered ring), and one at 3581 cm^{-1} for HO–C(2) in a bifurcated H-bond. By comparison, *cis*-5-hydroxy-2-phenyl-1,3-dioxane, possessing a bifurcated H-bond, absorbs at 3587 cm^{-1} in CCl_4 solution [17]. The spectra of **9** in CH_2Cl_2 at concentrations of 0.1, 0.05, 0.025, 0.01, and 0.004M are poorly resolved, showing broadened bands for intramolecularly bonded OH groups at 3566 (H-bond in a five-membered ring, see **9b**) and at *ca.* 3540 cm^{-1} (shoulder, bifurcated H-bond, see **9a**/**9b**). A weak shoulder extending to *ca.* 3350 cm^{-1} for intermolecularly bonded OH groups is present at concentrations $\geq$ 0.05M. The absorption of the H-bond in the 6-membered ring (**9a**) is probably hidden by the band of the bifurcated H-bond. The β-D-anomer **12** shows a broad band at 3605 cm^{-1} (CCl_4, < 0.005M) and at 3586 cm^{-1} (CH_2Cl_2) for intramolecularly bonded OH, and a broad band at 3473 cm^{-1} (CH_2Cl_2, at $c \geq 0.025$M with a tailing to 3200 cm^{-1}) for intermolecularly bonded OH. This indicates that **12a** is favoured, but the broad bands do not allow to exclude the isomer **12b**.

The ^{1}H-NMR spectrum in $CDCl_3$ shows that **9** adopts the $^4C_1$ conformation also in solution (*Table 3*). HO–C(2) resonates as a *d* (J = 11.7 Hz) at 2.88 and HO–C(3) as a *d* (J = 6.5 Hz) at 2.58 ppm. The large J(OH,H) of HO–C(2) is only compatible with a dihedral angle of *ca.* 180° for H–C(2)–O–H [17]. This shows that HO–C(2) is involved in an intramolecular H-bond in solution, in contradistinction to the solid state, where HO–C(2) forms an intermolecular H-bond (see above). To calculate the distances between H–OC(2) and the neighbouring H-acceptors, we changed the dihedral angle for H–C(2)–O–H in the X-ray structure of **9** from – 49 to 180°. This leads to a distance of 2.44 Å between H–OC(2) and O(3) and to one of 2.46 Å between H–OC(2) and O(1), and

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[2]) A solvent shift of *ca.* 20–30 cm^{-1} is observed by changing the solvent from CCl_4 to CH_2Cl_2 [11] [7].

[3]) Bifurcated H-bonds play an important role in the solid state (compare [9] [14] [15]) and in oligo- and polymers (*cf.* [16]).

Table 3. *Selected ^{1}H-NMR* (400 MHz) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Diols* **9** *and* **12** *at Room Temperature*

H or *J*	**9** ($CDCl_3$)	**9** ((D_6)DMSO)	**12** ($CDCl_3$)	**12** ((D_6)DMSO)
H–C(1)	4.77	4.59	4.63	4.45
H–C(2)	3.72	3.56	3.52	3.24
H–C(3)	4.30	3.98	4.40	4.00
H–C(4)	3.56	3.53	3.61	3.53
H–C(5)	4.10	3.92	4.01	3.80
H–C(6)	4.39	4.23	4.41	4.23
H′–C(6)	3.76	3.65	3.77	3.64
MeO	3.50	3.30	3.59	3.37
PhC*H*	5.59	5.59	5.58	5.58
OH–C(2)	2.88	4.59	2.60	5.01
OH–C(3)	2.58	4.39	2.47	5.07
J(1,2)	4.3	4.1	7.9	8.0
J(2,3)	3.3	3.5	3.2	2.9
J(3,4)	2.7	2.6	2.5	2.2
J(4,5)	9.7	9.4	9.6	9.3
J(5,6)	5.1	5.2	5.2	4.9
J(5′,6)	10.3	10.6	10.0	10.4
J(6,6′)	10.4	10.3	10.4	10.0
J(2,OH)	11.7	9.5	6.0	6.7
J(3,OH)	6.5	5.1	< 1.5	3.9

to bond angles of 108° for O(3)···H–O(2) and 103° for O(1)···H–O(2). These values meet the geometric requirements of a bifurcated H-bond[4]). The three O-atoms and the H-atom involved in this H-bond are not in the same plane (sum of bond angles O(3)···H–O(2), O(1)···H–O(2), and O(3)···H···O(1) = 280°). For intermolecular H-bonds, the sum of these three angles is usually larger than 350° [14]. If one assumes a similar dihedral angle H–C(3)–O–H of **9a** in solution as it is found for the solid state (−150°), one has to interprete *J*(3,OH) of 6.5 Hz as evidencing a nearly 1:1 mixture **9a**/**9b**, meaning that the heterodromic H-bonding system in **9a** [9] competes with the H-bonding system of **9b**, in spite of the unusually small ring present in **9a** and the poor acceptor quality of the anomeric MeO group.

The ^{1}H-NMR spectrum ($CHCl_3$) of the β-D-anomer **12** is not compatible with **12a** as the only tautomer. *J*(2,OH) for **12a** should be 9–10 Hz and for **12b** *ca.* 1.5 Hz, whereas *J*(3,OH) is small for both tautomers. The experimental value (*J*(2,OH) = 6.0 Hz) suggests a mixture between **12a** and either a dimer (or oligomer) or **12b**, in both cases with a similar H–C(2)–O(2)–H dihedral angle. The absence of a distinct IR band for an

[4]) At least one case of a monosaccharide derivative, the 5-thio-α-D-ribopyranoside **13** (see *Fig. 3*), is known, where an intramolecular bifurcated H-bond is present in the solid state [18]. Similar distances (O(3)···H 2.53 Å, O(1)···H 2.65 Å), bond angles (O(2)–H···O(3) 116°, O(2)–H···O(1) 100°, sum of O(2)–H···O(3), O(2)–H···O(1), and O(3)···H···O(1) = 287°) and dihedral angles (H–C(2)–O(2)–H 169°, S–C(1)–O(1)–C 71°) are observed, as they are calculated for the corresponding conformer of **9**. The absence of a H-bond between HO–C(3) and MeO–C(1) in **13** correlates with longer C(3)···C(1) (2.61 Å; **9**: 2.53 Å) and O(3)···O(1) distances (2.99 Å; **9**: 2.77 Å) for the thiopyran derivative. HO–C(3) and HO–C(4) of **13** are engaged in intermolecular H-bonds. HO–C(4) is bonded to HO–C(2) of an adjacent molecule, forming a four-center H-bond in the solid state.

intramolecular H-bond in a *trans* five-membered ring (see above), the intrinsic weakness of H-bonds in such a ring, and the poorer acceptor properties of the anomeric OR group, however, speak against the presence of substantial amounts of **12b**.

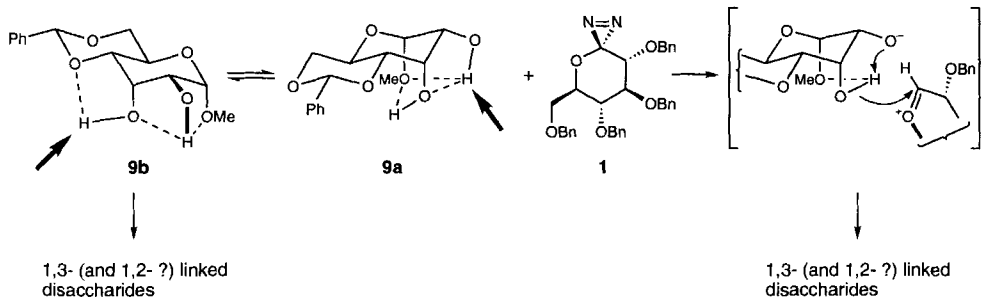
Only minor differences of J(OH,H) are observed for solutions of **9** and **12** in $CDCl_3$ or (D_6)DMSO. This is in contrast to the behaviour of the corresponding *manno*-2,3-diols [7] and suggests a higher stability of the H-bonds in **9** and **12**.

For solutions in (D_6)DMSO, the chemical shift for both OH groups of **9** and of **12** depends quite strongly upon the temperature [7] [6] [19]. The $\Delta\delta/\Delta T$ values for HO–C(2) (**9**: – 5.8 ppb/K; **12**: – 7.6 ppb/K) and for HO–C(3) (**9**: – 6.5 ppb/K; **12**: – 8.4 ppb/K) indicate at the best weak intramolecular H-bonds which appear to be stronger in **9** than in **12**. A linear dependence of these chemical-shift values upon the temperature is also observed for solutions in $CDCl_3$ (*cf.* [20]). The $\Delta\delta/\Delta T$ values (HO–C(2) of **9**: – 2.9 ppb/K; HO–C(2) of **12**: – 4.4 ppb/K; HO–C(3) of **9**: – 4.6 ppb/K; HO–C(3) of **12**: – 5.2 ppb/K) evidence that the intramolecular H-bonds are stronger in $CDCl_3$ solution. Their relative stability remains unchanged. The vicinal J(H,OH) for both OH groups of **9** and **12** in $CDCl_3$ solution depend only weakly upon the temperature (5% enhancement at 243 K relative to the values at 318 K), indicating that the corresponding rotamer equilibria do not change within this temperature range. No signals for isotopomers nor even line broadening of the OH signals are observed upon partial deuteration [6] [21–23] of **9** and **12** with CD_3OD in (D_6)DMSO.

On the basis of the relative strength of the H-bonds in the β-D-alloside **12** and the equilibrium between **12a** and **12b**, one expects that the glycosylidene carbene derived from **1** will be protonated to a similar extent by either OH group. A prediction of the regioselectivity for the protonation of the α-D-anomer **9** is more difficult. In **9a**, the bifurcated H-bond in a five-membered ring is weaker than the H-bond forming a six-membered ring, as evidenced by the $\Delta\upsilon$ values (CCl_4) of 48 and 89 cm^{-1} [13]. One predicts a preferred protonation by HO–C(2). $\Delta\nu$ Values (CCl_4) evidence that the bifurcated H-bond of **9b** is stronger than the H-bond linking HO–C(3) to O–C(4) (48 *vs.* 19 cm^{-1} [13]). For this tautomer, one has to predict a slightly preferred protonation by HO–C(3).

Two additional factors must be considered to predict the regioselectivity of glycosidation, *viz.* the direction of approach of the glycosylidene carbene and the consequence of the stereoelectronic control of the protonation of the carbene and of the combination of the thereby formed ion pair. If it is indeed so that the glycosylidene carbene is protonated by a H-bonded and not by a free OH group (there is no evidence for free OH groups), then the H-bonds will also determine the direction from which the carbene approaches. The angle dependence of the strength of H-bonds implies that a linear approach of a basic carbene is preferred for free OH groups, resulting in a C(1′)···H–O angle of roughly 180°. The attack angle for H-bonded OH groups should reflect the preferred geometry of bifurcated H-bonds, where the sum of bond angles around the H atom is 360°. One expects an approach angle of 120° for a symmetric, bifurcated H-bond. Similarly, one expects a tetrahedral angle for the attack of a basic reagent on a bifurcated H-bond. Protonation by HO–C(2) of **9a** implies that the carbene attacks from below the plane of the pyranose ring (bold arrow in *Scheme 1*), while protonation by a free OH group would imply an approach of the carbene from above and sideon of this plane. Protonation by HO–C(3) of **9b** will lead to an approach of the carbene more or less from the direction of the O–C(4) bond, forming an obtuse angle with H–O(3).

Scheme 1



Protonation of the carbene in the σ-plane leads to a geometrical arrangement of the ions which does not allow their combination. Reorientation of the ions to permit the required interaction of the oxy anion with the π-orbitals of the oxycarbenium ion will tend to avoid (partial) dissociation which is energetically costly, particularly in a poorly coordinating solvent. Attack on the oxycarbenium ion by HO–C(3), which is already located in the π-plane of the oxycarbenium ion, or by the corresponding oxy anion derived by a rapid proton transfer to $^-$O–C(2), should be more favourable (*Scheme 1*). If so, protonation by HO–C(2) will lead to glycosidation of HO–C(3). The consequence of this stereoelectronic factor on the fate of the ion pairs derived from protonation by HO–C(3) are less clear. The results which we have so far obtained with similar systems, however, lead to the prediction that protonation by HO–C(3) will mostly lead to its glycosidation.

2. *Glycosidation of the Allopyranosides* **9** *and* **12**. Glycosidation of the anomers **9** and **12** by **1** or **2** gave mixtures of the four disaccharides **14**–**17** and **18**–**21**, respectively (*Scheme 2* and *Table 4*). The ratio of the products was determined by anal. HPLC. No trisaccharides were detected. The individual disaccharides derived from the α-D-anomer **9** were isolated on a preparative scale by prep. HPLC. The disaccharides derived from the β-D-anomer **12** were more difficult to separate, requiring a combination of flash chromatography and HPLC. The mixture **18**/**19** was separated only after acetylation to **22** and **23**, which were each deacetylated to yield the crystalline monoalcohols **18** and **19**.

The constitution of the disaccharides **14**–**21** is evidenced mainly by the signals for two monosaccharide moieties in the ^{1}H- and ^{13}C-NMR spectra and by OH signals in the IR and ^{1}H-NMR spectra. The configuration of the new anomeric center is deduced from the chemical shifts of H–C(1′) and C(1′) and from the J(1′,2′) values (*Tables 5* and *6* in the *Exper. Part*). According to the values of the vicinal J(H,OH), the disaccharides possess similar intramolecular H-bonds as the corresponding diols. The larger J(H,OH) value for the 1,2-linked disaccharides **14** and **15** indicate a stronger preference for the O(3)–H···O(1) than for the O(3)–H···O(4) H-bond. Not surprisingly, the 1,3-linked disaccharides **16** and **17** possess bifurcated H-bonds. The value of 8.5 Hz for J(2,OH) of the 1,3-linked disaccharide **21** is as expected for a H-bond between HO–C(2) and O–C(3). The corresponding value for **20** (10.8 Hz), however, corresponds to a larger dihedral angle, evidencing a bifurcated H-bond of HO–C(2) with O–C(3) and probably O–C(2′) as acceptors (*Fig. 4*). Further evidence for this H-bond is found in the ^{1}H-NMR spectrum. There is an upfield shift ($\Delta\delta$ = 0.4 and 0.9 ppm, resp.) for the signals for

Scheme 2

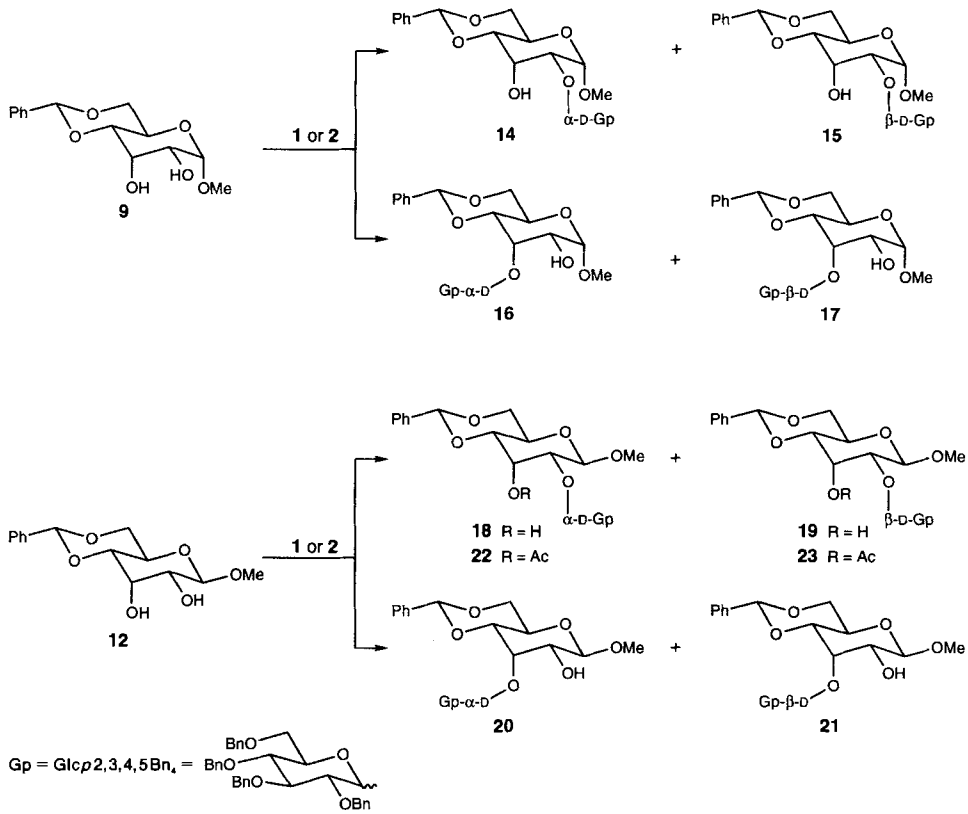
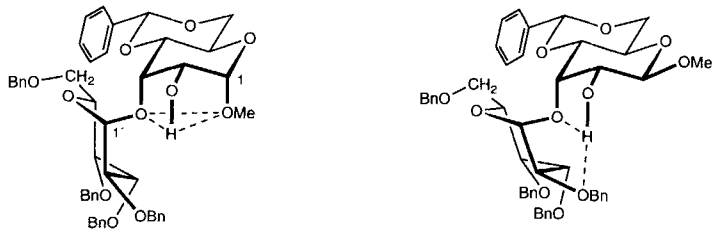


Table 4. *Glycosidation of the* allo-*Diols* **9** *and* **12** *with the Diazirine* **1** *and the Trichloroacetimidate* **2**

Glycosyl donor	Diol (equiv.)	Conditions	Total yield [%]	Regioselectivity RO–C(2)/RO–C(3)	Stereoselectivity (α-D/β-D) of	
					RO–C(2)	RO–C(3)
1	**12** (0.75)	$ClCH_2CH_2Cl$, 23°, 5 h	69	54:46	40:60	45:55
1	**12** (0.75)	dioxane, 23°, 5 h	80	51:49	32:68	38:62
2	**12** (0.9)	CH_2Cl_2, $BF_3 \cdot Et_2O$, −30°, 0.5 h	90	46:54	11:89	31:69
1	**9** (1.3)	CH_2Cl_2, 24°, 5 h	90	23:77	41:59	81:19
1	**9** (1.3)	CH_2Cl_2, *hv*, −85°, 3 h	82	21:79	44:56	89:11
1	**9** (1.3)	$ClCH_2CH_2Cl$, 23°, 5 h	83	32:68	49:51	74:26
1	**9** (1.3)	CCl_4, 23°, 5 h	30	8:92	49:51	94: 6
1	**9** (1.3)	toluene, 70°, 2 h	79	20:80	32:68	72:28
1	**9** (1.3)	dioxane, 24°, 5 h	81	28:72	39:61	89:11
1	**9** (1.3)	dioxane, 0.5 equiv. of BuLi, 23°, 5 h	38	32:68	59:41	83:17
1	**9** (1.3)	THF, 24°, 5 h	75	40:60	25:75	66:34
1	**9** (1.3)	THF, *hv*, −85°, 4 h	79	72:28	10:90	67:33
2	**9** (0.9)	CH_2Cl_2, $BF_3 \cdot Et_2O$, −30°, 0.5 h	94	28:72	24:76	23:77

H–C(6′) and H′–C(6′) of the 3-*O*-α-D-glucosylated products **16** and **20**, which can be rationalized by a shielding effect of the Ph group of the benzylidene moiety in a conformation which is in keeping with the above mentioned bifurcated H-bond, as illustrated in *Fig. 4*.



16 **20**

Fig. 4. *Preferred rotamers around the newly formed glycosidic bond of* **16** *and* **20**, *as deduced from the upfield shift of the 2 H–C(6′)* (**16** and **20**) *and the presence of a bifurcated H-bond* (**20**)

Glycosidation of the β-D-anomer **12** by **1** in $ClCH_2CH_2Cl$ or in dioxane solution gave a nearly 1:1 mixture of regioisomers (*Table 4*). There is a slight preference for the β-D-anomers, as it has been observed for other diols [7] and for monoalcohols [24].

Glycosidation of the α-D-anomer **9** with **1** in CH_2Cl_2, $ClCH_2CH_2Cl$, toluene, or dioxane leads in yields between 79 and 90% and with a regioselectivity of *ca.* 3:7 to 2:8 mostly to 1,3-linked disaccharides. The highest regioselectivity (8:92) was realized in CCl_4, but the yield dropped to 30%. The diastereoselectivity of the 1,2-linked (minor) products is low, except for the reaction in toluene (**14**/**15** 32:68). Surprisingly, there is a clear preference for the formation of the α-D-anomers of the 1,3-linked products, with a ratio **16**/**17** ranging from 72:28 to 94:6. BuLi lowered the yield, but did not otherwise influence the outcome of the glycosidation.

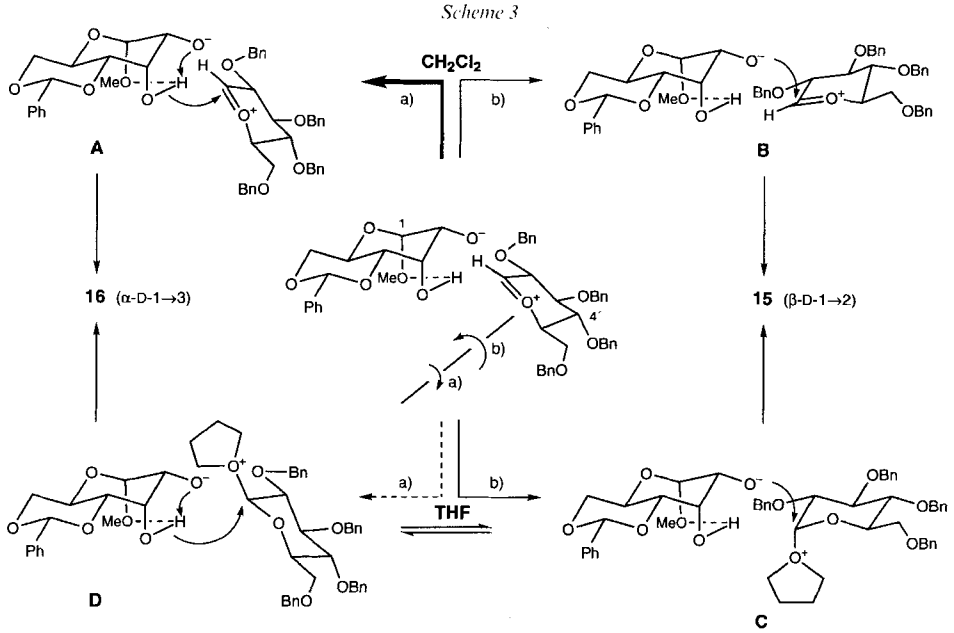
The glycosidation of **9** by **1** in THF differs clearly from the one in the other solvents. Glycosidation at room temperature led to a lower regioselectivity with a ratio of 4:6 for the 1,2-/1,3-linked disaccharides (*Table 4*). A higher proportion of the β-D-anomers of both regioisomers was formed (**14**/**15** 25:75, **16**/**17** 66:34), as it had been observed for monoalcohols [24]. Glycosidation in THF at −85° (photolytic conditions) led to a still higher regioselectivity, reaching a ratio of 72:28 in favour of the 1,2-linked disaccharides, in contrast to the low-temperature glycosidation in CH_2Cl_2, where the 1,3-linked products dominate. Lowering the temperature of the glycosidation in THF did not influence the diastereoselectivity for the 1,3-linked disaccharides, whereas the β-D/α-D ratio for the 1,2-linked disaccharides was increased to 9:1.

The glycosidation of **9** and **12** with the trichloroacetimidate **2** in CH_2Cl_2 [8] shows the expected regioselectivity, which differs only slightly from the glycosidations with the diazirine **1**, and the expected preference for the β-D-anomers (*Table 4*, see analogous reactions in [7]).

The low degree of regioselectivity and the slight preference for the β-D anomers in the glycosidation of the β-D-alloside **12** is in keeping with expectation. The preferred glycosidation of HO–C(3) of the α-D-anomer **9** in most solvents – except in THF at low temperature – is also as predicted. The preferential formation of the α-D-anomer of the major regioisomer may be the result either of the orientation of the attacking carbene,

which is carried over to the intermediate oxycarbenium ion, or the result of a stereoelectronically controlled axial attack of the neighbouring $^{-}O-C(3)$ or HO–C(3) on the intermediate oxycarbenium ion, which is sufficiently long-lived to rotate around the axis through C(1′) and C(4′). The correlation of preferred glycosidation of HO–C(3) and unusual stereoselectivity lends credential to the proposed combination of the effects of regioselective protonation by a H-bonded OH group, the preferred direction of attack of the carbene, and the geometrical requirements for proton transfer to the carbene and the combination of the ion pair. This is visualized in *Scheme 3*. The α-D-anomer **16** is formed

Scheme 3



if the transfer of a proton from HO–C(3) to $^{-}O-C(2)$ parallels a relative movement of the carbocation according to a) leading to **A**. A relative movement according to b) leads to attack by $^{-}O-C(2)$ (**B**), and to the β-D-anomer **15**. It implies a (partial) dissociation of the ion pair. Hence, the preferred pathway under all conditions, except in THF at low temperature, is formation of **16**.

For reactions in THF, one expects that solvation competes with the nucleophilic attack of the oxyanion on the oxycarbenium ion. Solvation from the axial side is kinetically preferred. Partial dissociation and attack by the nearest oxyanion $^{-}O-C(2)$ is now facilitated and proceeds with inversion of the configuration at the anomeric center of the tetrahydrofuranylium cation *via* **C** leading to **15**, the main product under these conditions. Higher temperatures lower the regioselectivity (more of the 1,3-linked disaccharides is formed) and increase the proportion of the α-D-configurated 1,2-linked disaccharide **14**. This indicates an increased participation of the β-D-configurated tetrahydrofuranylium cation (**D**).

We thank Dr. *A. Linden* for the X-ray analysis, Messrs. *Th. Plüss, D. Nanz,* and *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. See [5] [7]. Powdered 4-Å molecular sieves (*Union Carbide*) were dried *i.v.* for 6 h at 150° and stored under Ar. High-performance liquid chromatography (HPLC): anal. 250 × 4.6 mm column with *Zorbax sil* for **14–17** and **20/21**, anal. 250 × 4.6 mm column with *Spherisorb* silica (5 μm) for **18/19**, prep. 250 × 20 mm column with *Spherisorb* silica (5 μm); retention times (t_R) for anal. HPLC in min. The diols **9** [10] and **12** [10], the diazirine **1** [25] [4], and the trichloroacetimidate **2** [26] were prepared according to the literature. For the determination of the dependency of the chemical shifts of the OH groups, ^{1}H-NMR spectra of **9** and **12** (10 mg, 0.035 mmol) in $CDCl_3$ soln. were recorded at 243, 263, 283, 298, and 318 K and in (D_6)DMSO soln. at 298, 308, 328, and 348 K. For ^{1}H-NMR data of **9** and **12** at r.t., see *Table 3.*

X-Ray Analysis of **9**: $C_{14}H_{18}O_6$ (282.3). Orthorhombic $P2_12_12_1$; $a = 8.3038$ (8), $b = 21.5975$ (6), $c = 7.574$ (1) Å; $V = 1358.3$ (2) Å^3; $D_{calc} = 1.380$ Mg/m^3; $Z = 4$. The measurements were made in the ω-2θ scan mode on a *Rigaku-AFC5R* diffractometer (graphite monochromator, MoK_α, $\lambda = 0.71069$ Å) with a 12 kW rotating anode generator at 21°, 2θ(max) = 60°, scan speed 16.0°/min in ω, scan width $(1.21 + 0.35 \tan\theta)$°. Of the 2727 total collected reflections, 2641 were unique, $R = 0.0365$, $R_w = 0.0339$. The structure was solved with the direct-methods routine of SHELXS-86 [27] which revealed the position of all non-H-atoms which were refined anisotropically. The H-atoms were located in a difference *Fourier* map, and their positions were allowed to refine together with individual isotropic temperature factors.

General Procedure for the Glycosidation of **9** *and* **12** *with* **1**. a) *Thermal Conditions.* Under Ar, solid **1** was added to a soln. of **9** or **12** in the indicated dry solvent and the mixture stirred at the indicated temp. for the given period of time. For glycosidation in toluene, the diols were dissolved at higher temp. and **1** added at that temp. After disappearance of **1**, the mixture was diluted with CH_2Cl_2, evaporated at or below 40° under vacuum, and purified as described below.

b) *Photolytic Conditions.* Under Ar, the soln. of the diol in the indicated solvent was added to solid **1** at the indicated temp. The mixture was stirred and irradiated (*HPK-125-Philips* high-pressure Hg lamp, *Solidex* glass filter) at the indicated temp. After disappearance of **1**, the solvent was evaporated to give the crude product.

Glycosidation of **9** *with* **1**. The reaction of **1** (100 mg, 0.18 mmol) with **9** (67 mg, 0.24 mmol) in 1,4-dioxane (2 ml) for 4 h at r.t. followed by FC (hexane/AcOEt 7:3) gave **14–17** (118 mg, 81%). Prep. HPLC (hexane/AcOEt 65:35, 16 ml/min) gave **14** (13.2 mg, 9%), **15** (19.8 mg, 14%), and **16/17** (85 mg). A second prep. HPLC (CH_2Cl_2/AcOEt 95:5, 16 ml/min) of **16/17** gave **16** (75.7 mg, 52%) and **17** (9.4 mg, 6%).

Glycosidation of **9** *with* **2**. A mixture of **9** (30 mg, 0.11 mmol) and powdered 4-Å molecular sieves (25 mg/ml) in CH_2Cl_2 (2 ml) was stirred for 30 min at r.t. under Ar, cooled to $-30°$, and then treated with a soln. of **2** (80 mg, 0.12 mmol) in CH_2Cl_2 (2 ml) followed by a soln. of $BF_3 \cdot Et_2O$ (14 μl, 0.12 mmol) in CH_2Cl_2 (1 ml). After stirring for 30 min, addition of Et_3N (0.1 ml), and filtration through *Celite,* the filtrate was evaporated. Purification as described above gave **14** (10.2 mg, 6%), **15** (32.2 mg, 20%), **16** (25 mg, 16%), and **17** (84.1 mg, 52%).

*Methyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-allopyranoside* (**14**). R_f (hexane/AcOEt 3:2) 0.24. Anal. HPLC (hexane/AcOEt 3:2, 1.5 ml/min): t_R 3.74. M.p. 145° (hexane/AcOEt). $[\alpha]_D^{25} = +84.8$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3660*w*, 3540*w* (br.), 3060*w*, 3015*w* (sh), 3000*w*, 2930*w* (br.), 2865*w*, 1610*w* (br.), 1500*w*, 1470*w* (sh), 1455*m*, 1405*w* (sh), 1380*w* (sh), 1365*m*, 1320*w* (br.), 1295*w* (sh), 1240*w* (br.), 1210*w* (sh), 1180*w* (sh), 1160*m* (sh), 1140*m* (sh), 1125*s* (sh), 1100*s* (br.), 1070*s*, 1050*s*, 1030*s* (sh), 1010*s* (sh), 995*m* (sh), 915*w*, 880*w*, 855*w*, 700*s*, 670*w* (sh), 660*w*, 640*w*, 630*w* (sh). ^{1}H-NMR ($CDCl_3$): 7.53–7.49 (*m*, 2 arom. H); 7.39–7.21 (*m*, 21 arom. H); 7.16–7.12 (*m*, 2 arom. H); 5.54 (*s*, PhC*H*); 4.98 (*d*, $J = 11.1$, PhC*H*); 4.91 (*d*, $J = 3.7$, H–C(1′)); 4.845 (*d*, $J \approx 3.0$, H–C(1)); 4.84 (*d*, $J = 10.9$, PhC*H*); 4.83 (*d*, $J = 10.6$, PhC*H*); 4.80 (*d*, $J = 12.0$, PhC*H*); 4.63 (*d*, $J = 12.0$, PhC*H*); 4.61 (*d*, $J = 12.0$, PhC*H*); 4.48 (*d*, $J = 10.8$, PhC*H*); 4.44–4.40 (*m*, H–C(3)); 4.43 (*d*, $J = 12.0$, PhC*H*); 4.38 (*dd*, $J = 5.2$, 10.4, H_{eq}–C(6)); 4.16 (*dt*, $J = 5.2$, 10.0, H–C(5)); 4.13 (*ddd*, $J = 2.4$, 3.5, 10.1, H–C(5′)); 4.08 (*t*, $J \approx 9.3$, H–C(3′)); 3.74 (*dd*, $J = 3.6$, 10.7, H–C(6′)); 3.74 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.67 (*dd*, $J = 9.0$, 10.1, H–C(4′)); 3.67 (*dd*, $J = 2.1$, 10.7, H′–C(6′)); 3.60 (*t*, $J \approx 3.4$, H–C(2)); 3.59 (*dd*, $J = 3.7$, 9.6, H–C(2′)); 3.47 (*s*, MeO); 3.45 (*dd*, $J = 2.5$, 9.7, H–C(4)); 3.27 (*d*, $J = 7.2$, exchangeable with D_2O, OH–C(3)). ^{13}C-NMR ($CDCl_3$): 138.83 (*s*); 138.45 (*s*); 138.20 (*s*); 137.83 (*s*); 137.15 (*s*); 128.98–126.34 (several *d*); 102.01 (*d*); 99.23 (*d*); 98.08 (*d*); 81.62 (*d*); 80.01 (*d*); 78.87 (*d*); 77.57 (*d*); 75.60 (*d*); 75.54 (*t*); 74.91 (*t*); 73.42 (*t*); 72.94 (*t*); 70.86 (*d*); 69.46 (*d*); 69.14 (*t*); 68.51 (*t*); 57.90 (*d*); 55.94 (*q*). CI-MS: 824 (16), 823 (53), 822 (100, $[M + NH_4]^+$), 540 (12), 415 (10), 325 (10), 324 (26), 283 (11), 251 (15), 217 (11), 216 (23), 198 (12), 108 (33), 91 (16). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.82, H 6.52.

Methyl 4,6-O-Benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-allopyranoside (**15**). R_f (hexane/AcOEt 3:2) 0.27. Anal. HPLC (hexane/AcOEt 3:2, 1.5 ml/min): t_R 3.34. M.p. 170° (hexane/AcOEt). $[\alpha]_D^{25} = +34.4$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3520*w* (sh), 3060*w*, 3030*w* (sh), 3000*w*, 2920*w* (br.), 2865*w*, 1500*w*, 1465*w* (sh), 1455*m*, 1405*w* (sh), 1380*w* (sh), 1365*m* (sh), 1325*w* (sh), 1315*w*, 1295*w*, 1280*w*, 1235*w*, 1180*w* (sh), 1140*m* (sh), 1105*s* (sh), 1070*s*, 1030*m*, 1010*m*, 990*m* (sh), 950*w* (sh), 915*w*, 890*w* (sh), 860*w*, 825*w* (br.), 700*s*, 670*w* (sh), 660*w*, 640*w*. ^{1}H-NMR ($CDCl_3$): 7.54–7.51 (*m*, 2 arom. H); 7.39–7.26 (*m*, 21 arom. H); 7.19–7.15 (*m*, 2 arom. H); 5.57 (*s*, PhC*H*); 5.06 (*d*, $J = 10.8$, PhC*H*); 5.00 (*d*, $J = 3.6$, H–C(1)); 4.95 (*d*, $J = 11.0$, PhC*H*); 4.83 (*d*, $J = 10.8$, PhC*H*); 4.79 (*d*, $J = 11.0$, PhC*H*); 4.74 (*d*, $J = 10.8$, PhC*H*); 4.60 (*d*, $J = 7.5$, H–C(1′)); 4.57 (*d*, $J = 12.1$, PhC*H*); 4.53 (*d*, $J = 10.9$, PhC*H*); 4.52 (*d*, $J = 12.1$, PhC*H*); (4.46 br. *td*, $J \approx 3.0, 7.5$, H–C(3)); 4.40 (*dd*, $J = 5.1, 10.3$, H_{eq}–C(6)); 4.20 (*dt*, $J = 5.2, 10.0$, H–C(5)); 3.86 (*t*, $J = 3.3$, H–C(2)); 3.77 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.70 (*dd*, $J = 2.1, 10.6$, H–C(6′)); 3.66 (*t*, $J = 9.0$, H–C(3′)); 3.64 (*dd*, $J = 5.1, 10.7$, H′–C(6′)); 3.565 (*dd*, $J = 7.6, 8.9$, H–C(2′)); 3.56 (*t*, $J = 9.3$, H–C(4′)); 3.50 (*dd*, $J = 2.6, 9.6$, H–C(4)); 3.50–3.45 (*m*, H–C(5′)); 3.47 (*s*, MeO); 3.30 (*d*, $J = 7.6$, exchangeable with D_2O, OH–C(3)). ^{13}C-NMR ($CDCl_3$): 138.59 (*s*); 138.31 (*s*); 138.01 (2 *s*); 137.20 (*s*); 129.07–126.38 (several *d*); 102.56 (*d*); 102.07 (*d*); 100.88 (*d*); 84.52 (*d*); 81.63 (*d*); 80.69 (*d*); 79.05 (*d*); 77.62 (*d*); 75.65 (*t*); 75.04 (*d*); 74.87 (*t*); 74.74 (*t*); 73.46 (*t*); 69.26 (*t*); 69.14 (*t*); 67.90 (*d*); 57.97 (*d*); 56.16 (*q*). CI-MS: 824 (15), 823 (53), 822 (100, $[M + NH_4]^+$), 108 (21). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.90, H 6.29.

Methyl 4,6-O-Benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-allopyranoside (**16**). R_f (hexane/AcOEt 3:2) 0.16. Anal. HPLC (CH_2Cl_2/AcOEt 92:8, 1.5 ml/min): t_R 6.03. $[\alpha]_D^{25} = +113.2$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3430*w* (br.), 3080*w* (sh), 3060*w*, 3030*w* (sh), 3000*w*, 2930*w* (br.), 2860*w* (br.), 1500*w*, 1465*w* (sh), 1455*m*, 1420*w* (sh), 1400*w*, 1375*w* (sh), 1365*m*, 1350*w* (sh), 1320*w* (br.), 1280*w*, 1245*w* (br.), 1185*w* (sh), 1160*m*, 1145*m*, 1125*m* (sh), 1100*s*, 1070*s*, 1060*s* (sh), 1045*s* (sh), 1030*s*, 1020*s*, 995*m* (sh), 915*w* (br.), 870*w*, 855*w* (sh), 700*s*, 670*w* (sh), 660*w*, 640*w*. ^{1}H-NMR ($CDCl_3$): 7.47–7.44 (*m*, 2 arom. H); 7.39–7.19 (*m*, 21 arom. H); 7.13–7.10 (*m*, 2 arom. H); 5.54 (*s*, PhC*H*); 4.93 (*d*, $J = 3.5$, H–C(1′)); 4.90 (*s*, $PhCH_2$); 4.88 (*d*, $J = 12.2$, PhC*H*); 4.76 (*d*, $J = 10.7$, PhC*H*); 4.72 (*d*, $J = 12.0$, PhC*H*); 4.68 (*d*, $J = 4.5$, H–C(1)); 4.50 (*d*, $J = 12.5$, exchangeable with D_2O, OH–C(2)); 4.42 (*d*, $J = 12.2$, PhC*H*); 4.41 (*d*, $J = 10.7$, PhC*H*); 4.36 (*dd*, $J = 5.2, 10.3$, H_{eq}–C(6)); 4.13 (*t*, $J \approx 3.2$, H–C(3)); 4.11 (*dd*, $J = 5.2, 10.0$, H–C(5)); 4.10 (*t*, $J = 9.4$, H–C(3′)); 4.06 (*d*, $J = 12.1$, PhC*H*); 4.00 (*td*, $J = 1.9, 10.2$, H–C(5′)); 3.71 (*ddd*, $J = 3.5, 4.5, 12.5$; after addn. of D_2O: *dd*, $J = 3.5, 4.5$, H–C(2)); 3.70 (*t*, $J = 9.7$, H–C(4′)); 3.67 (*t*, $J = 10.5$, H_{ax}–C(6)); 3.56 (*dd*, $J = 3.5, 9.5$, H–C(2′)); 3.54 (*dd*, $J = 2.9, 9.5$, H–C(4)); 3.43 (*s*, MeO); 3.31 (*dd*, $J = 2.0, 11.0$, H–C(6′)); 2.69 (*dd*, $J = 2.0, 10.9$, H′–C(6′)). ^{13}C-NMR ($CDCl_3$): 138,70 (*s*); 138.39 (*s*); 137.90 (*s*); 137.79 (*s*); 137.54 (*s*); 128.81–126.33 (several *d*); 101.40 (*d*); 100.95 (*d*); 100.08 (*d*); 82.38 (*d*); 80.22 (*d*); 79.24 (*d*); 77.60 (*d*); 77.22 (*d*); 75.41 (*t*); 74.88 (*t*); 73.93 (*t*); 73.19 (*t*); 70.51 (*d*); 69.15 (*t*); 68.63 (*d*); 67.35 (*t*); 57.60 (*d*); 56.16 (*q*). CI-MS: 825 (17), 823 (53), 822 (100, $[M + NH_4]^+$), 108 (8), 91 (5). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.61, H 6.55.

Methyl 4,6-O-Benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-allopyranoside (**17**). R_f (hexane/AcOEt 3:2) 0.15. Anal. HPLC (CH_2Cl_2/AcOEt 92:8, 1.5 ml/min): t_R 8.52. $[\alpha]_D^{25} = +59.6$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3550*w* (br.), 3430*w* (br.), 3080*w* (sh), 3060*w*, 3030*w* (sh), 3000*w*, 2930*m*, 2910*m*, 2860*m*, 1610*w*, 1500*w*, 1465*w* (sh), 1455*m*, 1400*w* (br.), 1380*w* (sh), 1360*m*, 1330*w*, 1310*w*, 1280*w*, 1265*w* (sh), 1240*w* (br.), 1205*w* (sh), 1195*w* (sh), 1180*w* (sh), 1150*m* (sh), 1120*s* (sh), 1095*s* (br.), 1060*s* (br.), 1030*m* (sh), 1005*s*, 990*m* (sh), 965*w* (sh), 940*w* (sh), 915*w* (br.), 885*w* (sh), 860*w*, 825*w* (br.), 675*s*, 665*w* (sh), 640*w*, 615*w*. ^{1}H-NMR ($CDCl_3$): 7.55–7.51 (*m*, 2 arom. H); 7.39–7.16 (*m*, 23 arom. H); 5.55 (*s*, PhC*H*); 5.13 (*d*, $J = 11.5$, PhC*H*); 4.92 (*d*, $J = 11.0$, PhC*H*); 4.82 (*d*, $J = 11.1$, PhC*H*); 4.79 (*d*, $J = 11.9$, PhC*H*); 4.755 (*d*, $J = 7.1$, H–C(1′)); 4.75 (*d*, $J = 4.2$, H–C(1)); 4.75 (*d*, $J = 11.6$, PhC*H*); 4.65 (*d*, $J = 12.3$, PhC*H*); 4.57 (*d*, $J = 12.3$, PhC*H*); 4.54 (*d*, $J = 10.8$, PhC*H*); 4.51 (*t*, $J \approx 3.0$, H–C(3)); 4.30 (*dd*, $J = 5.2, 9.9$, H_{eq}–C(6)); 4.26 (*dt*, $J = 5.3, 9.8$, H–C(5)); 3.78 (*td*, $J \approx 3.7, 11.3$, H–C(2)); 3.75–3.55 (*m*, 8 H); 3.50–3.46 (*m*, H–C(5′)); 3.42 (*s*, MeO). ^{13}C-NMR ($CDCl_3$): 138.67 (2 *s*); 138.14 (*s*); 138.08 (*s*); 137.31 (*s*); 128.98–126.36 (several *d*); 103.07 (*d*); 102.13 (*d*); 100.25 (*d*); 84.38 (*d*); 81.61 (*d*); 78.58 (*d*); 77.51 (*d*); 75.45 (*d*); 75.21 (*t*); 74.83 (*t*); 74.67 (*d*); 74.05 (*t*); 73.39 (*t*); 69.29 (*t*); 68.70 (*t*); 67.80 (*d*); 57.82 (*d*); 54.05 (*q*). CI-MS: 825 (3), 824 (16), 823 (54), 822 (100, $[M + NH_4]^+$), 324 (5), 216 (5), 108 (10). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.87, H 6.46.

Glycosidation of **12** *with* **1**. The reaction of **1** (120 mg, 0.22 mmol) with **12** (47.3 mg, 0.17 mmol) in 1,4-dioxane (3 ml) for 5 h at r.t. and FC (hexane/AcOEt 8:2 → 7:3) gave **18**/**19** (55 mg, 41%) and **20**/**21** (52 mg, 39%). Acetylation of **18**/**19** in pyridine/Ac_2O 1:1 (2 ml) gave **22**/**23** (56 mg, 97%) which upon FC (CH_2Cl_2/AcOEt 99:1) afforded **22** (18 mg, 31%) and **23** (38 mg, 66%). Treatment of **22** and **23** separately with NaOMe/MeOH gave crystalline **18** and **19**. FC (hexane/Et_2O 1:1) of **20**/**21** gave **20** (21 mg, 15%) as a colourless oil and **21** (32 mg, 24%) as a crystalline solid.

Table 5. *Selected ^{1}H-NMR* (400 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Disaccharides Derived from the Diols* **9** *and* **12**

H or *J*	**14**[a])	**15**[a])	**16**[a])	**17**	**18**[a])	**19**	**20**[a])	**21**[a])[b])
H–C(1)	4.845	5.00	4.68	4.75	4.85	4.77	4.49	4.55
H–C(2)	3.60	3.86	3.71	3.78	3.605	3.76	3.53	3.45
H–C(3)	4.44–4.40	4.46	4.13	4.51	4.41	4.48	4.21	4.49
H–C(4)	3.45	3.50	3.54	3.75–3.55	3.52	3.55–3.51	3.58	3.77
H–C(5)	4.16	4.20	4.11	4.26	4.06	4.07	3.84	4.03
H_{eq}–C(6)	4.38	4.40	4.36	4.30	4.30	4.41	4.38	4.27
H_{ax}–C(6)	3.74	3.77	3.67	3.75–3.55	3.74	3.74	3.72	3.72
MeO	3.47	3.47	3.43	3.42	3.52	3.52	3.56	3.44
PhC*H*	5.54	5.57	5.54	5.55	5.52	5.54	5.53	5.64
OH	3.27	3.30	4.50	3.75–3.55	2.50	2.63	4.28	3.93
H–C(1′)	4.91	4.60	4.93	4.75	5.35	4.64	4.90	4.76
H–C(2′)	3.59	3.565	3.56	3.75–3.55	3.605	3.55–3.51	3.585	3.52
H–C(3′)	4.08	3.66	4.10	3.75–3.55	4.01	3.67	3.98	3.67–3.57
H–C(4′)	3.67	3.56	3.70	3.75–3.55	3.57	3.61	3.70	3.67–3.57
H–C(5′)	4.13	3.50–3.45	4.00	3.50–3.46	3.96	3.47	3.94	3.67–3.57
H–C(6′)	3.74	3.70	3.31	3.75–3.55	3.70–3.66	3.73	3.35	3.72
H′–C(6′)	3.67	3.64	2.69	3.75–3.66	3.70–3.66	3.67	2.80	3.70
J(1,2)	3.2	3.6	4.5	4.2	7.9	7.7	7.9	8.1
J(2,3)	3.5	3.0	3.5	3.3	2.5	2.8	3.1	3.0
J(3,4)	2.5	2.6	2.9	2.8	2.4	[c])	2.9	2.3
J(4,5)	9.7	9.6	9.5	9.8	9.7	9.8	9.6	9.7
J(OH,H)	7.2	7.6	12.5	11.3	< 0.5	0.5	10.8	8.5
J(1′,2′)	3.7	7.5	3.5	7.1	3.8	7.8	3.7	7.5
J(2′,3′)	9.6	8.9	9.5	[c])	9.4	9.0	9.5	8.7
J(3′,4′)	9.0	9.0	9.3	[c])	9.0	9.1	9.2	[c])
J(4′,5′)	10.1	9.6	10.1	[c])	9.8	9.4	10.0	[c])

[a]) Assignments corroborated by selective irradiations. [b]) In (D_6)acetone. [c]) Not determined.

Table 6. *Selected ^{13}C-NMR* (50.6 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of the Disaccharides Derived from the Diols* **9** *and* **12**

	9[a])	**14**	**15**	**16**	**17**	**12**	**18**	**19**	**20**	**21**[b])
C(1)	100.66	99.23	100.88	100.95[c])	100.25	102.35	101.64[c])	100.75	103.25	103.95
C(2)	68.13	75.60	80.69	68.63	67.80	68.85	76.88	76.35	72.00	71.03
C(3)	69.47	69.46	67.90	77.22	75.45	71.20	69.40	66.63	77.53[c])	78.91[c])
C(4)	78.36	78.87	79.05	79.24	78.58	78.76	78.62	78.52	79.01	79.54
C(5)	57.21	57.90	57.37	57.60	57.82	63.13	62.71	62.51	63.69	64.51
C(6)	69.18	69.14	69.26[c])	67.35	69.29[c])	69.07	68.71[d])	68.74[c])	67.29	69.61[d])
MeO	56.31	55.94	56.16	56.16	56.05	57.42	56.34	57.09	56.32	56.84
PhC*H*	101.94	102.01	102.07	101.40	102.13	101.91	101.82[c])	101.82	101.45	102.57
C(1′)	–	98.08	102.56	100.08[c])	103.07	–	97.99	99.81	100.79	104.19
C(2′)	–	80.10	81.63	80.22	81.61	–	79.38	81.53	79.44	83.31
C(3′)	–	81.62	84.52	82.38	84.38	–	81.66	84.96	82.41	85.18
C(4′)	–	77.63	77.62	77.60	77.51	–	77.64	77.74	77.77[c])	78.50[c])
C(5′)	–	70.86	75.04	70.51	74.67	–	70.96	75.24	70.59	75.36
C(6′)	–	68.51	69.14[c])	69.15	68.70[c])	–	69.18[d])	69.14[c])	69.05	69.87[d])

[a]) Similar to published data [28]. [b]) In (D_6)acetone. [c]) [d]) Assignments may be reversed.

Glycosidation of **12** *with* **2**. A mixture of **12** (30 mg, 0.11 mmol) and powdered 4-Å molecular sieves (50 mg) in CH_2Cl_2 (2 ml) was stirred for 30 min at r.t. under Ar and cooled to $-30°$. A soln. of **2** (80.1 mg, 0.12 mmol) in CH_2Cl_2 (2 ml) followed by a soln. of $BF_3 \cdot Et_2O$ (14 µl, 0.12 mmol) in CH_2Cl_2 (1 ml) was injected into the mixture. After stirring for 30 min at $-30°$, addition of Et_3N (0.1 ml), and filtration through *Celite*, the filtrate was evaporated. Purification as described above gave **18** (3.9 mg, 4%), **19** (31.5 mg, 37%), **20** (12.9 mg, 15%), and **21** (28.7 mg, 34%).

*Methyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-allopyranoside* (**18**). R_f (CH_2Cl_2/MeOH 99:1) 0.25. Anal. HPLC (CH_2Cl_2/MeOH 99.5:0.5, 1.5 ml/min): t_R 6.23. $[\alpha]_D^{25} = +33.6$ ($c = 0.3$, $CHCl_3$). M.p. 211° (hexane/AcOEt). IR ($CHCl_3$): 3580*w*, 3460*w* (br.), 3060*w* (sh), 3030*w* (sh), 2910*w*, 2860*w*, 1495*w*, 1465*w* (sh), 1450*w* (sh), 1390*w*, 1360*w*, 1300*w*, 1275*w* (sh), 1260*w*, 1240*w* (sh), 1195*w*, 1160*m* (sh), 1135*m* (sh), 1100*s*, 1080*s*, 1070*s*, 1035*s* (sh), 1025*s*, 1000*s*, 910*w*, 700*s*, 665*w*. ^{1}H-NMR ($CDCl_3$): 7.50–7.48 (*m*, 2 arom. H); 7.40–7.21 (*m*, 21 arom. H); 7.17–7.15 (*m*, 2 arom. H); 5.52 (*s*, PhC*H*); 5.35 (*d*, $J = 3.8$, H–C(1′)); 5.00 (*d*, $J = 10.8$, PhC*H*); 4.85 (*d*, $J = 7.9$, H–C(1)); 4.84 (*d*, $J = 11.4$, PhC*H*); 4.815 (*d*, $J = 12.3$, PhC*H*); 4.805 (*d*, $J = 10.8$, PhC*H*); 4.68 (*d*, $J = 11.8$, PhC*H*); 4.57 (*d*, $J = 12.0$, PhC*H*); 4.50 (*d*, $J = 11.0$, PhC*H*); 4.48 (*d*, $J = 12.0$, PhC*H*); 4.41 (*t*, $J \approx 2.5$, H–C(3)); 4.30 (*dd*, $J = 5.1$, 10.2, H_{eq}–C(6)); 4.06 (*dt*, $J = 5.1$, 10.1, H–C(5)); 4.01 (*t*, $J = 9.3$, H–C(3′)); 3.96 (*ddd*, $J = 2.0$, 4.7, 9.8, H–C(5′)); 3.74 (*t*, $J = 10.4$, H_{ax}–C(6)); 3.70–3.66 (*m*, 2 H–C(6′)); 3.605 (*dd*, $J = 3.9$, 9.4, H–C(2′)); 3.605 (*dd*, $J = 2.4$, 8.1, H–C(2)); 3.57 (*dd*, $J = 9.0$, 9.8, H–C(4′)); 3.52 (*dd*, $J = 2.4$, 9.7, H–C(4)); 3.52 (*s*, MeO); 2.50 (br. *s*, exchangeable with D_2O, OH–C(3)). ^{13}C-NMR ($CDCl_3$): 138.73 (*s*); 138.14 (2 *s*); 137.85 (*s*); 137.17 (*s*); 129.12–126.23 (several *d*); 101.82 (*d*); 101.64 (*d*); 97.99 (*d*); 81.66 (*d*); 79.38 (*d*); 78.62 (*d*); 77.64 (*d*); 76.88 (*d*); 75.65 (*t*); 75.01 (*t*); 73.51 (*t*); 71.89 (*t*); 70.96 (*d*); 69.40 (*d*); 69.18 (*t*); 68.71 (*t*); 62.71 (*d*); 57.38 (*q*). CI-MS: 824 (16), 823 (51), 822 (100, $[M + NH_4]^+$), 732 (8), 610 (10), 466 (10), 328 (7), 300 (19), 283 (6), 247 (14), 108 (15), 106 (14).

*Methyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-allopyranoside* (**19**). R_f (CH_2Cl_2/MeOH 99:1) 0.29. Anal. HPLC (CH_2Cl_2/MeOH 99.5:0.5, 1.5 ml/min): t_R 4.50. $[\alpha]_D^{25} = -22.3$ ($c = 0.4$, $CHCl_3$). M.p. 154° (hexane/AcOEt). IR ($CHCl_3$): 3600–3400*w* (br.), 3060*w* (sh), 3030*w* (sh), 2970*w* (sh), 2930*w* (sh), 2910*w*, 2860*w*, 1495*w*, 1465*w* (sh), 1450*w*, 1390*w*, 1355*w*, 1305*w*, 1275*w*, 1235*w*, 1195*w*, 1175*w* (sh), 1145*m* (sh), 1120*m* (sh), 1100*s*, 1080*s*, 1065*s*, 1025*m*, 1000*m*, 910*w*, 700*s*, 670*w*. ^{1}H-NMR ($CDCl_3$): 7.51–7.48 (*m*, 2 arom. H); 7.40–7.26 (*m*, 21 arom. H); 7.19–7.17 (*m*, 2 arom. H); 5.54 (*s*, PhC*H*); 4.96 (*d*, $J = 11.2$, PhC*H*); 4.91 (*d*, $J = 11.0$, PhC*H*); 4.815 (*d*, $J = 11.6$, PhC*H*); 4.81 (*d*, $J = 10.6$, PhC*H*); 4.79 (*d*, $J = 10.7$, PhC*H*); 4.77 (*d*, $J = 7.7$, H–C(1)); 4.64 (*d*, $J = 7.8$, H–C(1′)); 4.61 (*d*, $J = 11.2$, PhC*H*); 4.56 (*d*, $J = 10.1$, 2 PhC*H*); 4.48 (br. *t*, H–C(3)); 4.41 (*dd*, $J = 5.1$, 10.2, H_{eq}–C(6)); 4.07 (*dt*, $J = 5.3$, 10.0, H–C(5)); 3.76 (*dd*, $J = 2.8$, 7.8, H–C(2)); 3.74 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.73 (*dd*, $J = 2.1$, 10.8, H–C(6′)); 3.67 (*dd*, $J = 4.8$, 10.8, H′–C(6′)); 3.67 (*t*, $J = 9.0$, H–C(3′)); 3.61 (*t*, $J \approx 9.1$, H–C(4′)); 3.55–3.51 (*m*, H–C(4), H–C(2′)); 3.52 (*s*, MeO); 3.47 (*ddd*, $J = 2.2$, 4.8, 9.4, H–C(5′)); 2.63 (*d*, $J = 0.5$, exchangeable with D_2O, OH–C(3)). ^{13}C-NMR ($CDCl_3$): 138.40 (*s*); 138.13 (*s*); 138.10 (*s*); 137.94 (*s*); 137.06 (*s*); 129.04–126.17 (several *d*); 101.82 (*d*); 100.75 (*d*); 99.81 (*d*); 84.96 (*d*); 81.53 (*d*); 78.52 (*d*); 77.74 (*d*); 76.35 (*d*); 75.54 (*t*); 75.24 (*d*); 74.93 (*t*); 74.82 (*t*); 73.43 (*t*); 69.14 (*t*); 68.74 (*t*); 66.63 (*d*); 62.51 (*d*); 57.09 (*q*). CI-MS: 824 (15), 823 (54), 822 (100, $[M + NH_4]^+$), 732 (7), 610 (7), 558 (6), 556 (8), 466 (16), 300 (19), 283 (7), 282 (10), 265 (8), 247 (19), 108 (17), 106 (17).

*Methyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-allopyranoside* (**20**). R_f (hexane/Et_2O 15:85) 0.34. Anal. HPLC (hexane/Et_2O 30:70, 1.5 ml/min): t_R 5.41. $[\alpha]_D^{25} = +44.1$ ($c = 0.4$, $CHCl_3$). IR ($CHCl_3$): 3410*w* (br.), 3090*w* (sh), 3070*w* (sh), 3030*w* (sh), 3000*w*, 2940*m*, 2870*m*, 1500*w*, 1460*w* (sh), 1455*m*, 1405*w* (sh), 1385*w* (sh), 1365*w* (sh), 1325*w*, 1315*w*, 1155*m*, 1140*m*, 1105*s*, 1085*s*, 1065*s*, 1045*s*, 1030*s* (sh), 1010*s*, 960*w*, 870*w*, 860*w*, 695*m*. ^{1}H-NMR ($CDCl_3$): 7.48–7.46 (*m*, 2 arom. H); 7.39–7.19 (*m*, 21 arom. H); 7.09–7.07 (*m*, 2 arom. H); 5.53 (*s*, PhC*H*); 4.92 (*s*, PhCH_2); 4.90 (*d*, $J = 3.7$, H–C(1′)); 4.85 (*d*, $J = 11.9$, PhC*H*); 4.74 (*d*, $J = 10.6$, PhC*H*); 4.73 (*d*, $J = 11.8$, PhC*H*); 4.49 (*d*, $J = 7.9$, H–C(1)); 4.43 (*d*, $J = 12.3$, PhC*H*); 4.40 (*d*, $J = 11.6$, PhC*H*); 4.38 (*dd*, $J = 4.9$, 10.3, H_{eq}–C(6)); 4.28 (*d*, $J = 10.8$, exchangeable with D_2O, OH–C(2)); 4.21 (*t*, $J \approx 3.0$, H–C(3)); 4.05 (*d*, $J = 12.1$, PhC*H*); 3.98 (*t*, $J = 9.3$, H–C(3′)); 3.94 (*td*, $J = 1.9$, 10.0, H–C(5′)); 3.84 (*dt*, $J = 4.9$, 10.1, H–C(5)); 3.72 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.71 (*dd*, $J = 9.2$, 10.0, H–C(4′)); 3.585 (*dd*, $J = 3.7$, 9.5, H–C(2′)); 3.58 (*dd*, $J = 2.9$, 9.6, H–C(4)); 3.56 (*s*, MeO); 3.53 (*ddd*, $J = 3.1$, 7.8, 10.8; after addn. of D_2O: *dd*, $J = 3.1$, 7.8, H–C(2)); 3.35 (*dd*, $J = 2.1$, 10.9, H–C(6′)); 2.80 (*dd*, $J = 2.1$, 10.9, H′–C(6′)). ^{13}C-NMR ($CDCl_3$): 138.54 (*s*); 138.21 (*s*); 137.79 (*s*); 137.37 (*s*); 137.28 (*s*); 128.91–126.32 (several *d*); 103.25 (*d*); 101.45 (*d*); 100.79 (*d*); 82.41 (*d*); 79.44 (*d*); 79.01 (*d*); 77.77 (*d*); 77.53 (*d*); 75.41 (*t*); 74.94 (*t*); 73.99 (*t*); 73.27 (*t*); 72.00 (*d*); 70.59 (*d*); 69.04 (*t*); 67.29 (*t*); 63.69 (*d*); 57.32 (*q*). MS: 827 (100, $[M + Na]^+$).

*Methyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-allopyranoside* (**21**). R_f (hexane/Et_2O 15:85) 0.29. Anal. HPLC (hexane/Et_2O 3:7, 1.5 ml/min): t_R 7.98. $[\alpha]_D^{25} = +11.5$ ($c = 0.4$, $CHCl_3$). M.p. 131° (hexane/AcOEt). IR ($CHCl_3$): 3420*w* (br.), 3060*w* (sh), 2970*w*, 2910*w*, 2860*w*, 1450*w* (br.), 1380*w*,

1350*w*, 1240*m* (sh), 1200*s*, 1100*s* (sh), 1060*s*, 1000*w*, 780*w*, 710*m*. ^{1}H-NMR ((D$_6$)acetone): 7.51–7.48 (*m*, 2 arom. H); 7.40–7.13 (*m*, 23 arom. H); 5.64 (*s*, PhC*H*); 5.14 (*d*, *J* = 11.6, PhC*H*); 4.86 (*d*, *J* = 11.1, PhC*H*); 4.81 (*d*, *J* = 11.1, PhC*H*); 4.76 (*d*, *J* = 7.5, H–C(1′)); 4.74 (*d*, *J* = 11.1, PhC*H*); 4.72 (*d*, *J* = 11.6, PhC*H*); 4.60 (*d*, *J* = 12.3, PhC*H*); 4.59 (*d*, *J* = 12.3, PhC*H*); 4.55 (*d*, *J* = 8.1, H–C(1)); 4.54 (*d*, *J* = 12.2, PhC*H*); 4.49 (*t*, *J* = 2.6, H–C(3)); 4.27 (*dd*, *J* = 5.1, 10.1, H$_{eq}$–C(6)); 4.03 (*dt*, *J* = 5.2, 10.0, H–C(5)); 3.93 (*d*, *J* = 8.5, exchangeable with D$_2$O, OH–C(2)); 3.77 (*dd*, *J* = 2.2, 9.6, H–C(4)); 3.75 (*dd*, *J* = 1.6, 10.8, H–C(6′)); 3.72 (*t*, *J* = 10.3, H$_{ax}$–C(6)); 3.70 (*dd*, *J* ≈ 4.5, 10.7, H′–C(6′)); 3.67–3.57 (*m*, H–C(3′), H–C(4′), H–C(5′)); 3.52 (*dd*, *J* = 7.6, 8.7, H–C(2′)); 3.45 (*ddd*, *J* = 3.0, 7.5, 8.3; after addn. of D$_2$O: *dd*, *J* = 3.0, 8.3, H–C(2)); 3.44 (*s*, MeO). ^{13}C-NMR ((D$_6$)acetone): 139.87 (*s*); 139.54 (*s*); 139.47 (*s*); 138.89 (2 *s*); 129.77–127.38 (several *d*); 104.19 (*d*); 103.95 (*d*); 102.57 (*d*); 85.18 (*d*); 83.31 (*d*); 79.54 (*d*); 78.91 (*d*); 78.50 (*d*); 75.79 (*t*); 75.36 (*d*); 75.27 (2*t*); 73.87 (*t*); 71.03 (*d*); 69.87 (*t*); 69.61 (*t*); 64.51 (*d*); 56.84 (*q*). CI-MS: 824 (17), 823 (54), 822 (100, $[M + NH_4]^+$), 733 (5), 732 (13), 300 (11), 108 (9), 106 (10).

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