107. Glycosylidene Carbenes

Part 17

Glycosidation of Benzyl β-D- and β-L-Ribopyranosides. Further Evidence for the Effect of Stereoelectronic Control on the Regioselectivity of Glycosidation

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The H-bonds of the enantiomeric ribosides **4** and **5** and their glycosidation by the diazirine **1** are described. HO–C(2) and HO–C(4) of **4** and **5** form a 'flip-flop' H-bonding system, with HO–C(3) acting as a H-bond donor to O–C(2) or O–C(4). HO–C(2) and HO–C(4) of monomeric **4** and **5** are thus the most strongly acidic OH groups. Glycosidation of **4** and **5** by **1** depends on the solvent, the temperature, and the concentration. It yields up to 91% of a mixture of anomeric pairs of the 1,2-, 1,3-, and 1,4-linked disaccharides **8–13** and **20–25**, respectively, which were characterized as their diacetates **14–19** and **26–31** (*Scheme*). Glycosidation in CH_2Cl_2 and in dioxane yielded mostly the 1,3-linked disaccharides **10/11** and **22/23** (α/β *ca.* 4:1), while glycosidation in THF leads mostly to the 1,2- and 1,4-linked regioisomers ($\beta > \alpha$). There are small, but significant differences in the glycosidation of **4** and **5**. These, the regio-, and the stereoselectivities are rationalized as the consequences of the stereoelectronic control of both the H-transfer from HO–C(2) or HO–C(4) to the intermediate carbene and of the formation of the glycosidic C–O bond, and of the coordination of the intermediate oxycarbenium ion with THF.

Introduction. – The glycosidation of an alcohol by a glycosylidene diazirine *via* a glycosylidene carbene is stereoelectronically controlled; a proton is transferred from an OH group in the σ-plane of the carbene, and the C–O bond is formed by attack of the oxy anion in the π-plane of the thereby generated oxycarbenium cation. As a consequence, the OH group leading to the formation of the C–O bond may not correspond to the protonating OH group. Glycosidation of diols and triols depends upon their configuration and upon the nature of their H-bonds and reflects both the relative kinetic acidity of the individual OH groups and this double stereoelectronic control. We have postulated that these factors govern the glycosidation by the diazirine **1** of the diol **2** [1] and the triol **3** [2].

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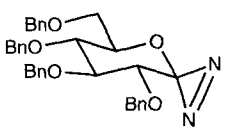
In both cases, alternative explanations of the regioselectivity cannot be rigorously excluded, and additional evidence for the consequences of the stereoelectronic control on the regioselectivity of glycosidation is required. The enantiomeric benzyl β-D- and β-L-ribopyranosides **4** and **5**, possessing three consecutive, *cis,cis*-oriented OH groups, appeared well suited for this purpose. Also, while intramolecular H-bonding in **2** and **3** reduces the kinetic acidity of the (H-bond donating) OH groups, HO–C(2) or HO–C(4) of **4** and **5** should be H-bond acceptors, show enhanced acidity, and protonate the carbene at a higher rate. The ensuing oxycarbenium cation may be attacked either by the oxy anion derived from the protonating HO–C(2) or HO–C(4), or from the vicinal HO–C(3).



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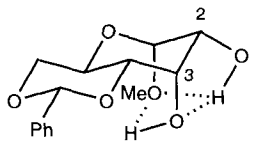

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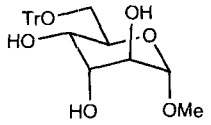

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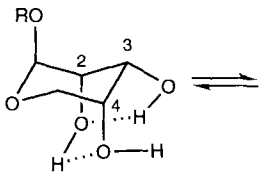

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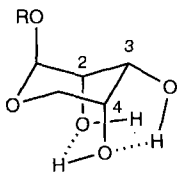
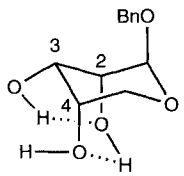
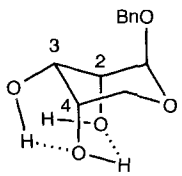
6a R = Me



4b R = Bn
6b R = Me



5a



5b

We had observed that glycosidation of hydroxy compounds by **1** either proceeds with low stereoselectivity, or – for strongly acidic hydroxy compounds – with the preferred formation of 1,2-*trans*-glycosides. Glycosidation of **2**, however, lead mostly to a 1,2-*cis*-configurated glycoside possessing an axial C–O bond. The same selectivity was observed for one anomeric pair of regioisomeric disaccharides derived from **3**. It is not clear to which extent this selectivity is conditioned by preferred formation of an axial C–O bond in an ion pair where the oxycarbenium cation rotates around the C(1)/C(4) axis, or by the energetics of the relative orientation of the carbene and/or oxycarbenium cation and the glycosyl acceptor. Glycosidation by **1** of enantiomers leads to diastereoisomeric transition states and may contribute to answer this question; *van Boeckel et al.* [3] have reported that diastereoisomeric interactions between enantiomeric glycosyl acceptors and donors affect the glycosidation.

Results and Discussion. – 1. *Hydrogen Bonds of Benzyl β-D-Ribopyranoside* (**4**). In the solid state, methyl β-D-ribopyranoside [4][5] (**6**) and analogous thio derivatives [6–8] adopt a slightly flattened $^1C_4$ conformation and possess an intramolecular H-bond between

HO–C(2) and O–C(4), similarly as in **6a**[2]). This strong intramolecular H-bond is characterised by an O···O distance of 2.761 Å, a distance between *O*–C(4) and *H*O–C(2) of 1.959 Å, and an O–H–O angle of 139°. It is part of a chair-like six-membered ring. The HO–C(4) bond is nearly perpendicular to the plane defined by O(4), C(4), and O(2); the H–O–C(4)–C(5) torsion angle is 163.9°.

The solution conformation of **4** in CD_2Cl_2, (D_8)THF, 1,4-(D_8)dioxane, and (D_6)DMSO was deduced from the ^{1}H-NMR spectra (see *Table 1*). The value of $J(1,2)$ increases with the polarity of the solvent, indicating a shift of the position of the $^1C_4/^4C_1$ equilibrium towards $^4C_1$. The $^1C_4/^4C_1$ ratio is *ca.*15:1 in CD_2Cl_2, 5:1 in (D_8)THF, 3:1 in 1,4-(D_8)dioxane, and 2:1 in (D_6)DMSO[3]). In H-bond acceptor solvents, the intramolecular H-bond between HO–C(2) and HO–C(4) has to compete with intermolecular H-bonds to the solvent with the consequence of lowered stabilization of the $^1C_4$ conformer[4]).

The coupling constants for the OH groups are compiled in *Table 1*. The $J(3,OH)$ value varies from 6.3 to 6.9 Hz, depending on the solvent, and corresponds to a dihedral angle of *ca.* 135°. This indicates that HO–C(3) is a H-donor to O(2) or O(4), forming a five-membered ring. The intramolecular O(2)–*H*···O(4) bond of methyl β-D-ribopyranoside in the

Table 1. *^{1}H-NMR* (300 MHz) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of* **4** *in CD_2Cl_2, (D_8)THF, 1,4-(D_8)Dioxane, and (D_6)DMSO*

Solvent	CD_2Cl_2	(D_8)THF	1,4-(D_8)dioxane	(D_6)DMSO
H–C(1)	4.92	4.90	4.96	4.68
H–C(2)	3.79	3.67	3.74	3.40
H–C(3)	3.81–3.86	3.77–3.82	3.92	3.69
H–C(4)	3.81–3.86	3.77–3.82	3.85	3.59–3.65
H_A–C(5)	3.90	3.90	3.95	3.59–3.65
H_B–C(5)	3.77	3.75	3.80	3.52
HO–C(2)	3.25	4.49	4.28	4.95
HO–C(3)	3.20	4.08	4.03	4.86
HO–C(4)	3.15	4.39	4.11	4.75
$J(1,2)$	2.4	3.0	3.4	4.1
$J(2,3)$			3.3	3.0
$J(3,4)$			1.1	2.8
$J(4,5_A)$	1.6		2.0	6.6
$J(4,5_B)$	2.4		4.2	2.8
$J(5_A,5_B)$	12.1		11.3	11.9
$J(2,OH)$	8.0	7.7	7.3	7.0
$J(3,OH)$	6.4	6.7	6.9	6.3
$J(4,OH)$	7.6	7.3	7.1	5.3

[2]) Denoting a strong H-bond; intermolecular H-bonds are generally preferred in the solid state [9].

[3]) Solid methyl β-D-ribopyranoside possesses a H–C(1)–C(2)–H dihedral angle of 70.5°; this angle corresponds to a $J(1,2)$ of 2.03 Hz [10][11]. A dihedral angle of 180° for H–C(1)–C(2)–H in the $^4C_1$ conformation corresponds to a theoretical $J(1,2)$ of 7.95 Hz. These values were taken as characteristic for the $^4C_1$ and $^1C_4$ conformation of **4**, respectively.

[4]) *Lemieux* and *Pavia* [12] observed and discussed a similar behaviour of methyl 3-deoxy-β-L-*erythro*-pentopyranoside and derivatives.

solid state is characterised by dihedral angles of 161° for H–O–C(2)–H and 44° for H–O–C(4)–H. A similar geometry of the O(2)–*H*···O(4) bond in **4a** and O(4)–*H*···O(2) in **4b** corresponds to coupling constants of 10.7 and 4.3 Hz for the individual tautomers [13]. The average expected *J*(2,OH) and *J*(4,OH) are *ca.* 7.5 Hz for a 1:1 equilibrium between **4a** and **4b** and correspond closely to the experimental values of 8.0 and 7.6 Hz (CD_2Cl_2), 7.7 and 7.3 Hz ((D_8)THF), and 7.3 and 7.1 Hz (1,4-(D_8)dioxane). A slight shift of the position of this equilibrium towards **4a** is expected as the consequence of a slightly higher degree of acidity for HO–C(2), due to its vicinity to the acetal function, as evidenced by the partial deuteration [14][15] of **4** in (D_6)DMSO with CD_3OD. An isotope shift is observed for all OH groups, as it is typical for an intramolecular H-bond network. It characterises HO–C(3) as a H-bond donor ($-1.5 \cdot 10^{-3}$ ppm) and HO–C(4) ($+9.63 \cdot 10^{-3}$ ppm) as a stronger H-bond acceptor than HO–C(2) ($+4.57 \cdot 10^{-3}$ ppm).

The H-bonds of **4** in solution ((D_6)DMSO) were also characterised by the temperature dependence of the OH signals [16–20] (see *Fig.*). The $\Delta\delta/\Delta T$ values in DMSO may not reflect the H-bond structure in apolar solvents (CH_2Cl_2). Intermolecular H-bonds to DMSO will compete with weak intramolecular H-bonds. A significant amount (*ca.* 30%) of **4** adopts the $^4C_1$ conformation in DMSO, and the observed $\Delta\delta/\Delta T$ values presumably reflect the presence of the different H-bonded tautomers in the $^4C_1$ and the $^1C_4$ conformation. Similar values were observed for HO–C(2) and HO–C(4) ($\Delta\delta/\Delta T = -6.28$ and -5.94 ppb/K, resp.), while the one for HO–C(3) is smaller ($\Delta\delta/\Delta T = -8.24$ ppb/K). HOC(3) can only form a H-bond in a five-membered ring, and the $\Delta\delta/\Delta T$ value is in keeping with those found for H-bonds in five-membered rings [1][21]. HO–C(2) and HO–C(4) can form a H-bond either in a six-membered ring in the $^1C_4$ conformation, or in a five-membered ring to O(3). As a concequence, the observed $\Delta\delta/\Delta T$ values are between those typical for H-bonds in five- and in six-membered rings [22].

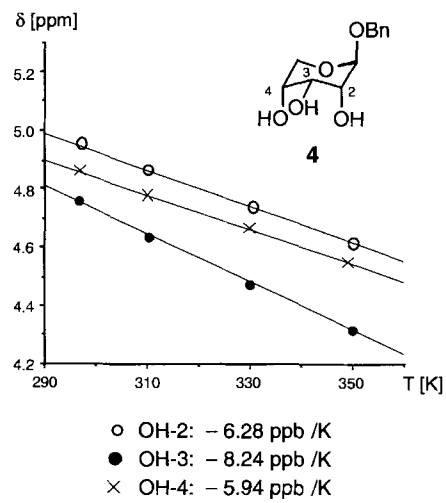


Figure. *Temperature dependence of the* ^{1}*H-NMR chemical shift* (300 MHz, (D_6)DMSO) *of the OH groups of* **4**

The FT-IR spectrum of **4** (CCl_4; 0.001M) shows OH bands at 3599, 3577, and 3521 cm^{-1}. In CH_2Cl_2[5]) (0.002M), the bands are at 3601, 3568, and 3517 cm^{-1}. The band at 3577 cm^{-1} (CCl_4) is assigned to *HO*–C(3) H-bonded in a five-membered ring to O–C(2) or to O–C(4) [24–28]. The 'flip-flop' H-bond system involving HO–C(2) and HO–C(4) is characterized by bands at 3599 and 3521 cm^{-1}, with the band at 3521 cm^{-1} corresponding to the H-donating, and the one at 3599 cm^{-1} to the H-accepting OH group[6]). The relatively low value of 3599 cm^{-1} for the H-accepting OH group is in keeping with a weak H-bond to O(3), indicating that HO–C(2), HO–C(3), and HO–C(4) form a homodromic system of H-bonds.

2. *Glycosidation of the Benzyl β-*D*- and β-*L*-Ribopyranosides* (**4** and **5**, resp.). The results of the glycosidation of the triol **4** by 1 equiv. of the diazirine **1** in CH_2Cl_2, dioxane, and THF under a variety of conditions are compiled in *Table 2*. In each case, we obtained a mixture of the anomeric pairs of the 1,2-, 1,3-, and 1,4-linked disaccharides **8**–**13** (*Scheme*). Their ratio was determined by analytical HPLC of the crude product. The individual compounds were isolated and characterized as the corresponding diacetates **14**–**19**. Their constitution and configuration were readily derived from the ^1H- and ^{13}C-NMR spectra (see *Exper. Part*).

The total yield of the disaccharides was 90% for glycosidations of **4** in CH_2Cl_2 at low concentration and at 23°; it was slightly lower at a higher concentration, at –78°, or when the reaction was performed in THF, and again lower for the glycosidation in dioxane. The 1,3-linked disaccharides are the major products in CH_2Cl_2, and by a smaller excess also in dioxane. The regioselectivity is inversely proportional to the concentration of the starting materials and to the temperature; at a concentration of 0.005M and at –78° the 1,2-, 1,3-, and 1,4-linked disaccharides were formed in a ratio of 5:81:14. The stereoselectivity of the formation of the 1,2-linked disaccharides is rather low, reaching a maximum at high dilution, where the β-D-anomer is favoured (α-D/β-D *ca.* 3:7). Conversely, the α-D-anomer is favoured for the 1,4-linked regioisomer (α-D/β-D *ca.* 7:3). The α-D-anomer of the 1,3-linked disaccharides is favoured to an extent of up to 8:2. Although qualitatively similar, the selectivities were lower for the glycosidation of **4** in dioxane. The results of the glycosidation in THF, however, are significantly different, both with regard to regio- and stereoselectivity. The 1,3-linked disaccharides were formed to a smaller extent than their regioisomers, and the β-D-anomers of both the 1,2- and the 1,4-linked disaccharides dominated to the extent of up to 8:92 and 5:95, respectively. The β-D-anomer of the 1,3-linked regioisomers was preferentially formed at low temperatures (α-D/β-D 3:7); the converse was observed for the reaction at 23° (α-D/β-D 7:3).

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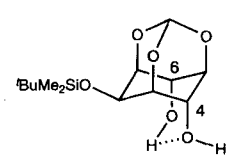
[5]) The frequencies of H-bonded OH bands depend upon the solvent [23].

[6]) The *myo*-inositol derivative **7** forms a similar flip-flop system and is characterized by IR bands (CCl_4, 0.001M) at 3618 and 3541 cm^{-1} [22].



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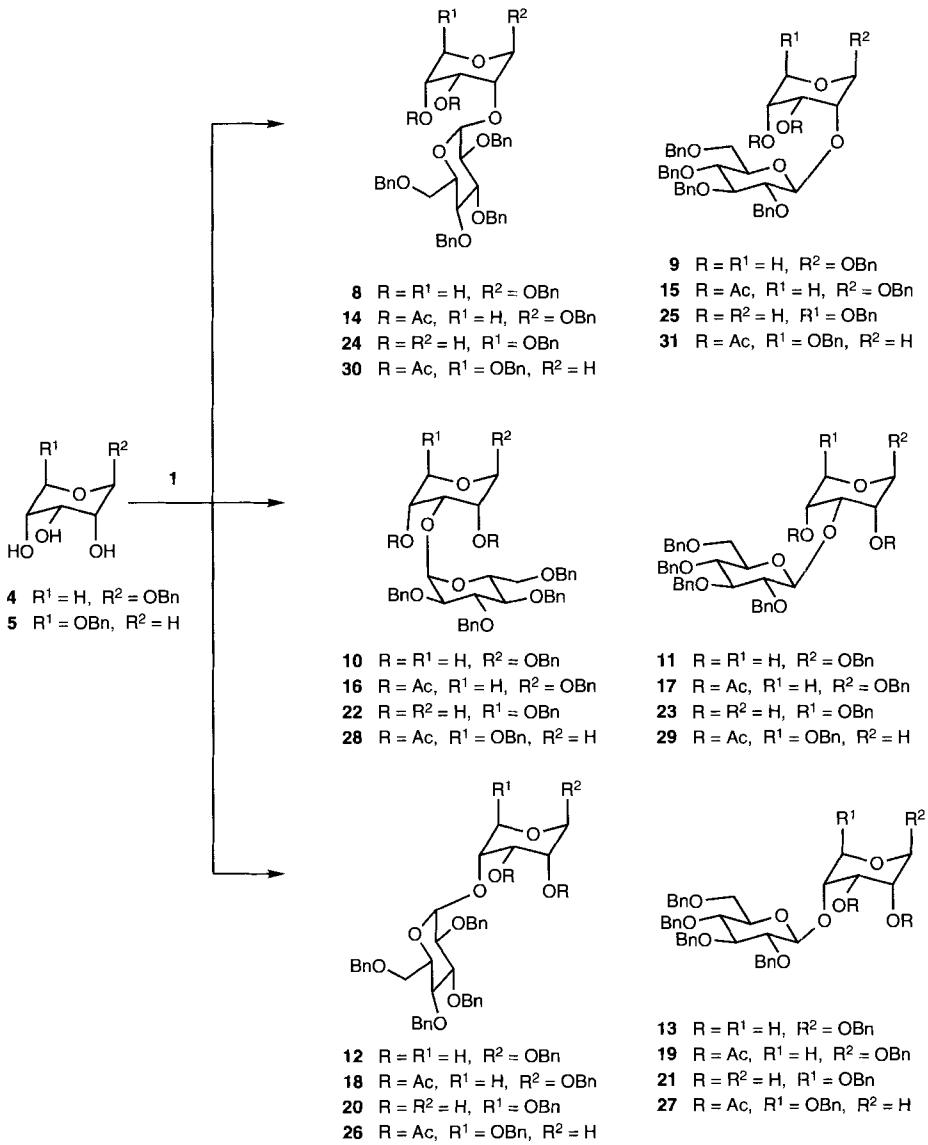
Scheme



The results of the glycosidation of benzyl β-L-ribopyranoside (**5**)[7]) by **1**, yielding the disaccharides **20**–**25** (*Scheme*) at room temperature differ only slightly, but significantly from those of its enantiomer **4**. Thus, the ratio of the regioisomeric 1,2- and 1,4-linked

[7]) The riboside **5** was prepared from L-arabinose, similarly as described for the synthesis of methyl β-L-ribopyranoside [29].

Table 2. *Glycosidation of the Triols* **4** *and* **5** *with* **1**

Triol	Solvent	Conc.	Temp.	Yield	Regioselectivity [%]			Diastereoselectivity (α/β)		
		[M]	[°C]	[%]	O–C(2)	O–C(3)	O–C(4)	O–C(2)	O–C(3)	O–C(4)
4	dioxane	0.05	27	69	30	40	30	33:67	75:25	60:40
5	dioxane	0.05	27	65	29	41	30	49:51	68:32	43:57
4	CH_2Cl_2	0.05	23	85	19	58	23	47:53	74:26	59:41
5	CH_2Cl_2	0.05	23	86	29	47	24	55:45	64:36	49:51
4	CH_2Cl_2	0.025	23	86	17	61	22	45:55	77:23	61:39
4	CH_2Cl_2	0.005	23	91	14	65	21	31:69	80:20	70:30
5	CH_2Cl_2	0.005	23	90	31	51	18	54:46	65:35	45:55
4	THF	0.05	23	80	34	29	37	29:71	69:31	32:68
5	THF	0.05	23	83	39	25	36	29:71	54:46	36:64
4	CH_2Cl_2	0.05	–78	66	12	62	26	42:58	74:26	69:31
5	CH_2Cl_2	0.05	–78	64	21	58	21	62:38	79:21	47:53
4	CH_2Cl_2	0.005	–78	81	5	81	14	40:60	77:23	64:36
5	CH_2Cl_2	0.005	–78	87	16	74	10	66:34	79:21	58:42
4	THF	0.05	–78	83	42	19	39	8:92	28:72	5:95
5	THF	0.05	–78	80	35	21	44	13:87	41:59	12:88

disaccharides **20/21** and **24/25** is inverted. In CH_2Cl_2, the relative amount of 1,2-linked products decreases for the glycosidation of both **4** and **5** on lowering the temperature from 23 to –78°, and the ratio of the 1,2- to 1,4-linked products drops from 0.83:1 to 0.46:1 (**4**; 0.05M), from 0.67:1 to 0.36:1 (**4**; 0.005M), from 1.21:1 to 1:1 (**5**; 0.05M), and from 1.72:1 to 1.60:1 (**5**; 0.005M). The ratio of the anomers of the 1,3-linked products is quite similar for the glycosidation of **4** and **5** in CH_2Cl_2 at –78°, but consistently lower for the glycosidation of **5** at 23°.

The ratio of the 1,2- and 1,4- *vs.* the 1,3-linked disaccharides resulting from the glycosidation of **4** or **5** in CH_2Cl_2 and in dioxane is consistent with the hypothesis that the carbene is preferentially protonated by the most strongly acidic OH group, *i.e.* by HO–C(2) or by HO–C(4), and that the ensuing oxycarbenium ion is intercepted by the favourably oriented neighbouring HO–C(3). The dependence upon concentration and temperature reflects the presence of intermolecular H-bonds[8]). The association of two or more molecules of the triols is favoured at low temperature and high concentration and leads to an interception of the oxycarbenium ion by HO–C(2) or HO–C(4) of a second molecule, implying that the triols associate by H-bonds involving HO–C(2) and HO–C(4). The rate of interception of the oxycarbenium cation by HO–C(3) is increased at low temperature due to the lower dissociation rate of the ion pair.

The ratio in which the 1,2- and 1,4-linked disaccharides are formed reflects the nature of the intermolecular H-bonding, the position of the equilibrium between the tautomers **4a/4b**, the rate of interception by HO–C(3) of the oxycarbenium ion derived from protonation

[8]) Dimeric and oligomeric alcohols protonate alkoxyalkyl carbenes more rapidly than monomeric alcohols [30][31].

of the carbene by either HO–C(2) or HO–C(4) (due both to differences of intra- and intermolecular interactions), and the influence of the solvent. Intermolecular H-bonding is minimal for glycosidations at high dilutions, where the regioselectivity of the glycosidations of **4** and **5** in CH_2Cl_2 is increased. It is further increased for the glycosidation of **4** in CH_2Cl_2 at low temperatures, favouring the 1,4- over the 1,2-linked disaccharides, while glycosidation of **5** gave more of the 1,2- than of the 1,4-linked products. As **4** and **5** are enantiomers, this difference must be due to the different diastereoisomeric interactions of the carbene with HO–C(2) and HO–C(4) in **4** and in **5**. The regioselectivities suggest that the carbene derived from **1** interacts more favourably with **4a** than with **4b**, but more favourably with **5b** than with **5a**. The decrease at low temperatures of the relative amount of the 1,2-linked products derived from both **4** and **5** suggests that **4a** and **5a** are favoured in the temperature-dependent equilibria **4a/b** and **5a/b**.

The doubly complementary anomeric selectivitiy in which the 1,2- and the 1,4-linked products of **4** and **5** are formed indicate a (slight) bias for a sterically defined and complementary interaction of the carbene or oxycarbenium ion with HO–C(2) and HO–C(4); in the absence of the BnO–C(1) substituent these groups are enantiotopic[9]). Considering that the 1,3-linked disaccharides are derived from the oxycarbenium ion formed by protonation by either HO–C(2) and HO–C(4) (and thus originally in a different orientation), it is significant that the α-D-anomers **10** and **22** are clearly the dominating products of the glycosidation of both **4** and **5** in CH_2Cl_2 and in dioxane. This shows that the BnO group at C(2) of the oxycarbenium cation competes at best to a minor extent with HO–C(3) in coordinating with the cationic center of the oxycarbenium ion, and also that the oxycarbenium ion is capable of reorienting itself, at the least to some extent, possibly by rotation around the C(1),C(4) axis. The influence of THF – competition with HO–C(3) in the interaction with the oxycarbenium ion (and with the carbene?) – is well precedented [1][30] and expressed both in the regio- and stereoselectivity of the glycosidation of **4** and **5**.

We thank Dr. *D. Nanz* and Mr. *Th. Plüss* 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 [22].

General Procedure for the Glycosidation with **1** *under Thermal Conditions.* A mixture of the aglycone in the indicated solvent (0.05–0.005M) under Ar, was treated with 1 equiv. of **1**. The mixture was stirred at r.t. for 4 h, and evaporation gave the crude product.

General Procedure for the Glycosidation with **1** *under Photolytic Conditions.* A mixture of the aglycone and dried, powdered 4-Å molecular sieves (10 mg/ml) in the indicated solvent (0.05–0.005M) was stirred for 1 h at r.t. under Ar. The mixture was cooled to –78°, treated with 1.1 equiv. of **1**, and irradiated (*HPK-125 Philips* high-pressure Hg lamp, quarz-glass filter) for 1 h. Filtration through *Celite* and evaporation gave the crude product.

Glycosidation of **4** *with* **1**. The reaction of **1** (412 mg, 0.75 mmol) with **4** (180 mg, 0.75 mmol) in 1,4-dioxane (15 ml) for 4 h at 27° and FC (hexane/AcOEt 2:1) of the crude product gave 356 mg (62%) of **8/9/10/11/12/13** 10:20:30:10:18:12. Partial separation by prep. HPLC (hexane/AcOEt 2:1) gave fractions of **9**, **12**, **13**, and **8/10/11**.

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[9]) For an example of glycosidation of enantiotopic OH groups, see [32]; a diastereoselectivity of 16.6:1 was observed by glycosylating a *meso*-dihydroxydecalin.

Acetylation (Ac_2O, Et_3N, 4-(dimethylamino)pyridine, CH_2Cl_2) of these fractions and prep. HPLC (hexane/Et_2O 1:1) gave pure samples of **14–19**. Deacetylation (MeOH/MeONa) afforded pure samples of **8–13**.

Benzyl 2-O-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl)-β-D-ribopyranoside (**8**). R_f (hexane/AcOEt 1:1) 0.29. t_R (hexane/AcOEt 2:1) 5.38. $[\alpha]_D^{25} = +19.3$ (*c* = 1.08, EtOH). FT-IR (CCl_4): 3868*w*, 3510*w*, 3090*w*, 3067*w*, 3032*w*, 2928*m*, 2870*m*, 1497*w*, 1455*m*, 1398*w*, 1362*w*, 1261*w*, 1209*w*, 1130*m*, 1089*s*, 1073*s*, 1029*s*, 910*w*, 820*w*, 726*m*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 3*; additionally, 7.33–7.03 (*m*, 25 arom. H); 4.92 (*d*, *J* = 11.5, 1H, PhCH_2); 4.89 (*d*, *J* = 11.3, 1H, PhCH_2); 4.76 (*d*, *J* = 11.4, 1H, PhCH_2); 4.59 (*d*, *J* = 12.0, 1H, PhCH_2); 4.58 (*d*, *J* = 11.2, 1H, PhCH_2); 4.45 (*d*, *J* = 11.7, 1H, PhCH_2); 4.40 (*d*, *J* = 10.5, 1H, PhCH_2); 4.38 (*d*, *J* = 11.9, 1H, PhCH_2); 4.27 (*d*, *J* = 11.3, 1H, PhCH_2); 4.25 (*d*, *J* = 11.7, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.61 (*s*); 138.08 (*s*); 137.89 (2*s*); 137.67 (*s*); 128.46–127.57 (*m*); 75.72 (*t*); 75.07 (*t*); 73.48 (*t*); 72.94 (*t*); 69.65 (*t*). ESI-MS: 785 (100, $[M + 23]^+$).

Benzyl 2-O-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)-β-D-ribopyranoside (**9**). R_f (hexane/AcOEt 1:1) 0.33. t_R (hexane/AcOEt 2:1) 4.65. M.p. 160°. $[\alpha]_D^{25} = -106.9$ (*c* = 0.022, EtOH). FT-IR (CCl_4): 3559*w*, 3090*w*, 3067*w*, 3032*w*, 2930*w*, 2871*w*, 1497*w*, 1454*m*, 1369*w*, 1261*w*, 1071*s*, 1028*m*, 726*m*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 3*; additionally, 7.50–7.03 (*m*, 25 arom. H); 4.85 (*d*, *J* = 11.3, 1H, PhCH_2); 4.81 (*d*, *J* = 10.6, 1H, PhCH_2); 4.80 (*d*, *J* = 11.3, 2H, PhCH_2); 4.73 (*d*, *J* = 10.7, 1H, PhCH_2); 4.57 (*d*, *J* = 11.2, 1H, PhCH_2); 4.54 (*d*, *J* = 12.0, 1H, PhCH_2); 4.36 (*d*, *J* = 12.2, 1H, PhCH_2); 4.31 (*d*, *J* = 12.1, 1H, PhCH_2); 4.24 (*d*, *J* = 12.0, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.36 (*s*); 138.18 (*s*); 138.04 (*s*); 137.73 (*s*); 137.35 (*s*); 128.56–127.74 (*m*); 75.62 (*t*); 75.43 (*t*); 75.05 (*t*); 73.51 (*t*); 69.33 (*t*). CI-MS: 780 (100, $[M + 18]^+$).

Table 3. *Selected ^{1}H-NMR* (400 MHz, C_6D_6) *Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Glycosides* **8–13**

	8	**9**	**10**	**11**	**12**	**13**
H–C(1)	5.02	5.39	5.02	5.01	5.05	5.06
H–C(2)	4.06	3.99	4.04	4.06	3.93	3.97–4.09
H–C(3)	3.61–3.68	3.89	3.80	3.87	3.85	3.97–4.09
H–C(4)	4.02	3.58–3.62	3.85	3.77	3.85	3.97–4.09
H_A–C(5)	3.71	3.68–3.72	3.73	3.54–3.72	3.57–3.69	3.66
H_B–C(5)	3.59	3.58–3.62	3.66	3.54–3.72	3.57–3.69	3.46–3.59
H–C(1')	4.98	4.49	4.95	4.37	5.07	4.17
H–C(2')	3.49	3.35	3.52	3.54–3.72	3.50	3.31
H–C(3')	4.14	3.54	4.24	3.54–3.72	4.06	3.46–3.59
H–C(4')	3.70	3.68–3.72	3.57	3.54–3.72	3.57–3.69	3.46–3.59
H–C(5')	4.34	3.17	4.36	3.26	4.20	3.40
H_2C(6')	3.61–3.68	3.47–3.62	3.59/3.68	3.45/3.52	3.57–3.69	3.46–3.63
OH	3.54	3.40	4.54	3.54–3.72	3.57–3.69	3.46–3.59
OH	3.47	3.08	4.28	3.54–3.72	3.46	3.33
J(1,2)	2.8	1.8	3.2	3.2	1.9	2.3
J(2,3)	3.0	3.5	3.1		4.0	
J(3,4)		3.5	3.1			
$J(4,5_A)$	3.4		3.9			2.9
$J(4,5_B)$	2.2		2.3			
$J(5_A,5_B)$	11.7		11.7			12.2
J(1',2')	3.8	7.7	3.9	7.3	3.8	7.8
J(2',3')	9.4	8.9	9.6		9.6	8.8
J(3',4')	9.2	9.1	9.1		9.0	
J(4',5')	10.1	9.6	10.2		10.0	9.6
$J(5',6'_A)$	3.2	4.4	1.8	2.0	1.9	1.9
$J(5',6'_B)$	3.2	1.9	5.8	5.2	4.3	5.4
$J(6'_A,6'_B)$		11.0	10.4	10.6		10.6

Table 4. *Selected* ^{13}C*-NMR* (50 MHz, $CDCl_3$) *Chemical-Shift Values* [ppm] *of the Glycosides* **8–19**

	8	**9**[a])	**10**	**11**	**12**	**13**	**14**	**15**	**16**[a])	**17**	**18**	**19**
C(1)	95.87[b])	99.00	99.92[b])	99.65	100.31[b])	100.49	98.68[b])	99.42	95.55	97.59	97.60[b])	97.77
C(2)	74.55	80.51	68.30	67.79	71.06[c])	71.41	74.08	76.58[b])	69.02	70.01[b])	69.06[c])	69.16[b])
C(3)	65.71	65.38	76.37	77.64[b])	65.55	65.54	67.12[c])	66.26[c])	69.19	69.82[b])	67.02[c])	67.87[b])
C(4)	69.33	69.71	69.40	69.85	78.98	80.81	68.21[c])	67.70[c])	68.32	66.75[b])	71.55[c])	71.70[b])
C(5)	64.30	63.83	63.72	63.94	62.26	62.09	61.29	60.99	61.28	61.24	62.54	61.53
C(1')	94.47[b])	104.99	97.10[b])	102.16	100.08[b])	103.58	97.96[b])	105.64	97.72	101.76	96.57[b])	102.27
C(2')	79.33	81.79	79.68	81.65	79.23	81.83	79.19	82.47	79.84	81.82	79.81	82.20
C(3')	81.87	85.20	81.76	84.82	82.27	84.56	81.62	84.44	81.43	84.57	81.59	84.51
C(4')	77.21	77.91	77.64	77.71[b])	77.63	77.61	77.41	77.61	77.60	77.34	77.19	77.42
C(5')	70.78	75.05	70.99	74.78	71.01[c])	74.97	70.87	74.70[b])	71.03	74.82	70.82	74.84
C(6')	68.34	68.78	68.46	68.73	68.40	68.70	68.31	69.12	68.51	68.52	68.41	68.61
CH_3O							20.92	21.29	21.01	20.95	20.87	20.88
CH_3O							20.92	20.73	20.82	20.95	20.69	20.88
CO							170.30	170.73	170.11	170.34	170.22	170.03
CO							170.07	170.11	169.78	170.22	170.05	169.97

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

*Benzyl 3-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**10**). R_f (hexane/AcOEt 1:1) 0.29. t_R (hexane/AcOEt 2:1) 5.57. $[\alpha]_D^{25}$ = +10.1 (*c* = 0.98, EtOH). FT-IR (CCl_4): 3502*w* (br.), 3090*w*, 3067*w*, 3032*w*, 2925*m*, 2870*w*, 1497*m*, 1455*m*, 1362*m*, 1261*w*, 1209*w*, 1072*s*, 1028*s*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 3*; additionally, 7.37–7.01 (*m*, 25 arom. H); 4.94 (*d*, *J* = 11.4, 1H, PhCH_2); 4.89 (*d*, *J* = 11.2, 1H, PhCH_2); 4.81 (*d*, *J* = 11.4, 1H, PhCH_2); 4.61 (*d*, *J* = 11.9, 1H, PhCH_2); 4.54 (*d*, *J* = 11.2, 1H, PhCH_2); 4.51 (*d*, *J* = 11.6, 1H, PhCH_2); 4.46 (*d*, *J* = 11.6, 1H, PhCH_2); 4.37 (*d*, *J* = 12.2, 1H, PhCH_2); 4.28 (*d*, *J* = 11.9, 1H, PhCH_2); 4.27 (*d*, *J* = 11.8, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.46 (*s*); 137.78 (*s*); 137.47 (*s*); 137.37 (*s*); 137.26 (*s*); 128.22–127.37 (*m*); 75.50 (*t*); 74.93 (*t*); 73.59 (*t*); 73.30 (*t*); 69.40 (*t*). ESI-MS: 785 (100, $[M + 23]^+$). Anal. calc. for $C_{46}H_{50}O_{10}$ (762.91): C 72.42, H 6.61; found: C 72.61, H 6.34.

*Benzyl 3-*O*-(2,3,4,6-Tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**11**). R_f (hexane/AcOEt 1:1) 0.28. t_R (hexane/AcOEt 2:1) 6.88. $[\alpha]_D^{25}$ = –38.8 (*c* = 0.99, EtOH). FT-IR (CCl_4): 3533*w* (br.), 3090*w*, 3067*w*, 3033*w*, 2922*w*, 2871*w*, 1497*w*, 1454*m*, 1360*w*, 1210*w*, 1070*s*, 1029*m*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 3*; additionally, 7.40–7.04 (*m*, 25 arom. H); 4.99 (*d*, *J* = 11.5, 1H, PhCH_2); 4.95 (*d*, *J* = 11.4, 1H, PhCH_2); 4.82 (*d*, *J* = 11.3, 1H, PhCH_2); 4.80 (*d*, *J* = 11.5, PhCH_2); 4.63 (*d*, *J* = 11.8, 1H, PhCH_2); 4.49 (*d*, *J* = 11.4, 1H, PhCH_2); 4.35 (*d*, *J* ≈ 11, 1H, PhCH_2); 4.31 (*d*, *J* = 10.7, 1H, PhCH_2); 4.29 (*d*, *J* = 12.1, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.26 (*s*); 137.91 (*s*); 137.82 (*s*); 137.72 (*s*); 137.19 (*s*); 128.43–127.66 (*m*); 75.58 (*t*); 75.09 (*t*); 74.96 (*t*); 73.45 (*t*); 69.60 (*t*). CI-MS: 780 (100, $[M + 18]^+$), 540 (14), 324 (16), 216 (13).

*Benzyl 4-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-ribopyranoside.* (**12**). R_f (hexane/AcOEt 1:1) 0.46. t_R (hexane/AcOEt 2:1) 3.16. $[\alpha]_D^{25}$ = +6.9 (*c* = 1.03, EtOH). FT-IR (CCl_4): 3545*w* (br., sh), 3090*w*, 3067*w*, 3033*w*, 2924*m*, 2870*w*, 1497*w*, 1362*w*, 1261*w*, 1209*w*, 1131*m*, 1071*s*, 1028*s*, 726*m*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 3*; additionally, 7.34–7.03 (*m*, 25 arom. H); 4.87 (*d*, *J* = 11.2, 1H, PhCH_2); 4.76 (*d*, *J* = 11.4, 1H, PhCH_2); 4.64 (*d*, *J* = 11.4, 1H, PhCH_2); 4.57 (*s*, PhCH_2); 4.55 (*d*, *J* ≈ 10, 1H, PhCH_2); 4.49 (*d*, *J* = 11.9, 1H, PhCH_2); 4.41 (*d*, *J* = 12.2, 1H, PhCH_2); 4.35 (*d*, *J* = 12.2, 1H, PhCH_2); 4.20 (*d*, *J* = 12.0, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.41 (*s*); 138.00 (*s*); 137.80 (*s*); 137.50 (*s*); 137.15 (*s*); 128.55–127.54 (*m*); 75.71 (*t*); 75.13 (*t*); 73.92 (*t*); 73.47 (*t*); 69.37 (*t*). ESI-MS: 780 (100, $[M + 18]^+$).

*Benzyl 4-*O*-(2,3,4,6-Tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**13**). R_f (hexane/AcOEt 1:1) 0.38. t_R (hexane/AcOEt 2:1) 4.23. $[\alpha]_D^{25}$ = –36.9 (*c* = 0.93, EtOH). FT-IR (CCl_4): 3552*w*, 3495*w*, 3090*w*, 3068*w*, 3032*w*, 2925*m*, 2870*w*, 1497*w*, 1455*m*, 1400*w*, 1358*m*, 1304*w*, 1260*w*, 1209*w*, 1123*s*, 1070*s*, 1050*s*, 1029*s*, 726*m*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 3*; additionally, 7.42–7.06 (*m*, 25 arom. H); 4.94 (*d*, *J* = 11.4, 1H, PhCH_2); 4.92 (*d*, *J* = 11.2, 1H, PhCH_2); 4.80 (*d*, *J* = 11.3, 1H, PhCH_2); 4.78 (*d*, *J* = 11.4, 1H, PhCH_2); 4.65 (*d*, *J* = 11.2, 1H, PhCH_2); 4.55 (*d*, *J* = 12.0, 1H, PhCH_2); 4.49 (*d*, *J* = 11.5, 1H, PhCH_2); 4.46 (*d*, *J* ≈ 13, 1H, PhCH_2); 4.42 (*d*, *J* = 12.3, 1H, PhCH_2); 4.24 (*d*, *J* = 12.0, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4;* additionally, 138.36 (*s*); 137.90 (*s*); 137.78 (2*s*); 137.24 (*s*); 128.45–127.67 (*m*); 75.63 (*t*); 75.14 (*t*); 75.03 (*t*); 73.56 (*t*); 69.59 (*t*). ESI-MS: 780 (100, $[M + 18]^+$).

*Benzyl 3,4-Di-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**14**). R_f (hexane/AcOEt 2:1) 0.32. t_R (hexane/Et_2O 1:1) 2.95. $[\alpha]_D^{25}$ = +25.1 (*c* = 1.08, EtOH). FT-IR (CCl_4): 3090*w*, 3066*w*, 3032*w*, 2928*w*, 2874*w*, 1752*s*, 1497*w*, 1454*m*, 1366*m*, 1240*s*, 1152*m*, 1082*s*, 1028*s*, 910*w*, 726*m*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 5;* additionally, 7.35–7.03 (*m*, 25 arom. H); 5.03 (*d*, *J* ≈ 11.6, 1H, PhCH_2); 4.95 (*d*, *J* = 11.4, 1H, PhCH_2); 4.85 (*d*, *J* = 11.3, 1H, PhCH_2); 4.68 (*d*, *J* = 12.0, 1H, PhCH_2); 4.66 (*d*, *J* = 11.4, 1H, PhCH_2); 4.45 (*d*, *J* = 12.1, 2H, PhCH_2); 4.38 (*d*, *J* = 12.0, 1H, PhCH_2); 4.35 (*d*, *J* = 12.1, 1H, PhCH_2); 4.32 (*d*, *J* ≈ 10, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.75 (*s*); 138.61 (*s*); 138.26 (*s*); 137.85 (*s*); 137.05 (*s*); 128.67–127.11 (*m*); 75.45 (*t*); 74.65 (*t*); 73.48 (*t*); 72.11 (*t*); 70.01 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 217 (32), 108 (17), 91 (13).

*Benzyl 3,4-Di-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**15**). R_f (hexane/AcOEt 2:1) 0.31. t_R (hexane/Et_2O 1:1) 3.11. $[\alpha]_D^{25}$ = –19.6 (*c* = 1.06, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3033*w*, 2922*w*, 2870*w*, 1747*s*, 1494*w*, 1454*m*, 1365*m*, 1242*s*, 1225*s*, 1070*s*, 1028*m*, 912*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 5;* additionally, 7.44–7.04 (*m*, 25 arom. H); 5.36 (*d*, *J* = 11.4, 1H, PhCH_2); 4.99 (*d*, *J* = 11.3, 1H, PhCH_2); 4.84 (*d*, *J* = 11.4, 1H, PhCH_2); 4.80 (*d*, *J* = 11.3, 1H, PhCH_2); 4.73 (*d*, *J* = 11.4, 1H, PhCH_2); 4.59 (*d*, *J* = 11.7, 1H, PhCH_2); 4.56 (*d*, *J* = 10.7, 1H, PhCH_2); 4.38 (*d*, *J* = 12.3, 1H, PhCH_2); 4.36 (*d*, *J* = 12.3, 1H, PhCH_2); 4.30 (*d*, *J* = 12.3, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.71 (*s*); 138.51 (*s*); 138.10 (*s*); 138.04 (*s*); 137.15 (*s*); 128.33–127.27 (*m*); 75.69 (*t*); 74.97 (*t*); 74.45 (*t*); 73.36 (*t*); 69.58 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 217 (22), 108 (13).

*Benzyl 2,4-Di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**16**). R_f (hexane/AcOEt 2:1) 0.30. t_R (hexane/Et_2O 1:1) 3.34. $[\alpha]_D^{25}$ = +12.8 (*c* = 1.07, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3033*w*, 2925*w*, 2870*w*, 1743*s*, 1497*w*, 1454*m*, 1367*m*, 1228*s*, 1136*m*, 1075*s*, 1028*s*, 909*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 5;* additionally, 7.35–7.02 (*m*, 25 arom. H); 5.03 (*d*, *J* = 11.4, 1H, PhCH_2); 4.96 (*d*, *J* = 11.4,

Table 5. *Selected ^{1}H-NMR* (400 MHz, C_6D_6) *Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Glycosides* **14–19**

	14	**15**	**16**	**17**	**18**	**19**
H–C(1)	5.01	5.44	5.09	5.08	4.90	4.93
H–C(2)	3.97	4.14	5.41	5.38	5.34	5.33
H–C(3)	5.75	5.54	4.38	4.45	5.61	5.74
H–C(4)	5.16	5.17	5.15	5.18	3.79	3.90
H_A–C(5)	3.69	3.73	3.84	3.71–3.76	4.02	3.72–3.77
H_B–C(5)	3.64	3.73	3.79	3.71–3.76	3.82	3.72–3.77
H–C(1')	5.08	4.43	5.19	4.44	4.76	4.14
H–C(2')	3.49	3.59–3.70	3.52	3.52	3.49	3.53
H–C(3')	4.23	3.59–3.70	4.21	3.60	4.19	3.62
H–C(4')	3.83	3.59–3.70	3.76	3.71–3.76	3.73	3.78
H–C(5')	4.28	3.22	4.26	3.21	4.22	3.20
H_2C(6')	3.72/3.79	3.43–3.70	3.71/3.76	3.63	3.68/3.74	3.65–3.71
CH_3	1.82	1.72	1.77	1.89	1.85	1.84
CH_3	1.79	1.71	1.66	1.77	1.71	1.76
J(1,2)	4.8	2.5	4.4	3.6	4.7	5.3
J(2,3)	3.3	3.8	3.1	3.5	3.3	3.0
J(3,4)	3.3	3.8	3.2	3.5	2.9	3.2
$J(4,5_A)$	3.8		4.9		5.7	5.8
$J(4,5_B)$	6.3		3.4		3.1	3.8
$J(5_A,5_B)$	12.2		11.7		11.6	
J(1',2')	3.5	7.2	3.6	7.6	3.5	7.7
J(2',3')	9.6		9.7	8.8	9.6	9.1
J(3',4')	9.1		9.2	8.8	8.9	8.7
J(4',5')	9.9	9.6	10.0	9.9	9.9	9.7
$J(5',6_A')$	3.8	4.5	4.3	3.4	4.5	2.7
$J(5',6_B')$	1.9	1.6	1.9	2.2	1.9	2.7
$J(6'_A,6'_B)$	10.7	11.0	10.7		10.7	

1H, PhCH_2); 4.87 (*d*, *J* = 11.3, 1H, PhCH_2); 4.65 (*d*, *J* = 11.4, 1H, PhCH_2); 4.60 (*d*, *J* = 12.5, 1H, PhCH_2); 4.56 (*d*, *J* = 11.8, 1H, PhCH_2); 4.46 (*d*, *J* = 12.1, 1H, PhCH_2); 4.45 (*d*, *J* = 11.6, 1H, PhCH_2); 4.37 (*d*, *J* = 12.3, 1H, PhCH_2); 4.25 (*d*, *J* = 12.1, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.78 (*s*); 138.39 (2*s*); 137.93 (*s*); 137.06 (*s*); 128.54–127.12 (*m*), 75.50 (*t*); 74.85 (*t*); 73.51 (*t*); 72.79 (*t*); 70.07 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 774 (15), 325 (10), 307 (12), 217 (43), 108 (13). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.98): C 70.90, H 6.43; found: C 71.14, H 6.59.

*Benzyl 2,4-Di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**17**). R_f (hexane/AcOEt 2:1) 0.29. t_R (hexane/Et_2O 1:1) 3.62. $[\alpha]_D^{25} = -22.7$ (*c* = 1.01, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3033*w*, 2925*w*, 2872*w*, 1741*s*, 1497*w*, 1454*m*, 1368*m*, 1231*s*, 1070*s*, 1028*s*, 910*w*, 726*m*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 5*; additionally, 7.44–7.04 (*m*, 25 arom. H); 5.03 (*d*, *J* = 11.5, 1H, PhCH_2); 4.92 (*d*, *J* = 11.4, 1H, PhCH_2); 4.81 (*d*, *J* = 11.4, 1H, PhCH_2); 4.75 (*d*, *J* = 11.4, 1H, PhCH_2); 4.70 (*d*, *J* = 11.5, 1H, PhCH_2); 4.57 (*d*, *J* = 12.0, 1H, PhCH_2); 4.54 (*d*, *J* = 11.4, 1H, PhCH_2); 4.46 (*d*, *J* = 12.1, 1H, PhCH_2); 4.33 (*d*, *J* = 10.5, 1H, PhCH_2); 4.30 (*d*, *J* ≈ 10.5, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.58 (*s*); 138.52 (*s*); 138.16 (*s*); 137.99 (*s*); 136.82 (*s*); 129.63–127.43 (*m*); 175.44 (*t*); 74.82 (*t*) 74.24 (*t*); 73.29 (*t*); 70.01 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 217 (32), 198 (15).

*Benzyl 2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**18**). R_f (hexane/AcOEt 2:1) 0.38. t_R (hexane/Et_2O 1:1) 2.74. $[\alpha]_D^{25} = -1.9$ (*c* = 1.13, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3033*w*, 2926*w*, 2869*w*, 1749*s*, 1497*w*, 1454*m*, 1368*m*, 1244*s*, 1224*s*, 1135*m*, 1087*s*, 1028*s*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 5*; additionally, 7.35–7.04 (*m*, 25 arom. H); 5.00 (*d*, *J* = 11.3, 1H, PhCH_2); 4.93 (*d*, *J* = 11.2, 1H, PhCH_2); 4.82 (*d*, *J* = 11.3, 1H, PhCH_2); 4.65 (*d*, *J* = 12.1, 1H, PhCH_2); 4.60 (*d*, *J* = 11.2, 1H, PhCH_2); 4.49–

4.41 (*m*, 3H, PhCH_2); 4.36 (*d*, *J* = 12.1, 1H, PhCH_2); 4.34 (*d*, *J* = 12.1, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.67 (*s*); 138.22 (2*s*); 137.88 (*s*); 137.02 (*s*); 128.34–127.36 (*m*); 75.46 (*t*); 75.09 (*t*); 73.49 (*t*); 72.72 (*t*); 69.99 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 217 (27), 108 (14).

*Benzyl 2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-ribopyranoside* (**19**). R_f (hexane/AcOEt 2:1) 0.37. t_R (hexane/Et_2O 1:1) 2.94. $[\alpha]_D^{25} = -41.1$ (*c* = 1.07, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3032*w*, 2925*w*, 2870*w*, 1751*s*, 1497*w*, 1454*m*, 1370*m*, 1305*w*, 1244*s*, 1227*s*, 1071*s*, 1028*m*, 899*w*, 726*m*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 5*; additionally, 7.43–7.05 (*m*, 25 arom. H); 5.10 (*d*, *J* = 11.0, 1H, PhCH_2); 5.00 (*d*, *J* = 11.4, 1H, PhCH_2); 4.85 (*d*, *J* = 11.3, PhCH_2); 4.71 (*d*, *J* = 12.1, 1H, PhCH_2); 4.67 (*d*, *J* = 11.0, 1H, PhCH_2); 4.61 (*d*, *J* = 11.3, 1H, PhCH_2); 4.53 (*d*, *J* = 12.1, 1H, PhCH_2); 4.41 (*d*, *J* = 12.1, 1H, PhCH_2); 4.40 (*d*, *J* = 12.3, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 4*; additionally, 138.66 (*s*); 138.33 (*s*); 138.12 (2*s*); 137.09 (*s*); 128.42–127.60 (*m*); 75.59 (*t*); 75.01 (*t*); 74.94 (*t*); 73.44 (*t*); 70.13 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 217 (26), 108 (15).

Glycosidation of **5** *with* **1**. The reaction of **1** (247 mg, 0.45 mmol) with **5** (109 mg, 0.45 mmol) in 1,4-dioxane (9 ml) for 4 h at 27° and FC (hexane/AcOEt 3:1) of the crude product gave 216 mg (62%) of **20/21/22/23/24/25** 14:15:28:13:13:17. Partial separation by prep. HPLC (hexane/AcOEt 2:1) gave fractions of **20**, **24**, **25**, and **21/22/23**. Acetylation (Ac_2O, Et_3N, 4-(dimethylamino)pyridine, CH_2Cl_2) of these fractions and prep. HPLC (hexane/Et_2O 1:1) gave pure samples of **26–31**. Deacetylation (MeOH, MeONa) afforded pure samples of **20–25**.

*Benzyl 2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**20**). R_f (hexane/AcOEt 1:1) 0.29. t_R (hexane/AcOEt 2:1) 5.69. M.p. 114°. $[\alpha]_D^{25} = +110.2$ (*c* = 0.90, EtOH). FT-IR (CCl_4): 3554*w* (br.), 3090*w*, 3066*w*, 3033*w*, 2928*m*, 2872*w*, 1497*w*, 1455*w*, 1361*w*, 1240*m*, 1131*m*, 1072*s*, 1050*s*, 1029*m*, 726*w*, 697*m*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 6*; additionally, 7.34–6.94 (*m*, 25 arom. H); 4.86 (*d*, *J* = 11.2, 1H, PhCH_2); 4.77 (*d*, *J* = 11.4, 1H, PhCH_2); 4.65 (*d*, *J* = 11.4, 1H, PhCH_2); 4.57–4.49 (*m*, 4H, PhCH_2); 4.39 (*d*, *J* = 12.1, 1H, PhCH_2);

Table 6. *Selected ^{1}H-NMR* (400 MHz, C_6D_6) *Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Glycosides* **20–25**

	20	**21**	**22**	**23**	**24**	**25**
H–C(1)	5.18	4.98	4.96	4.98	4.98	5.01
H–C(2)	3.89–3.92	3.83	4.04	3.71–3.92	3.87–3.90	3.87
H–C(3)	3.89–3.92	4.01	3.79	3.71–3.92	3.94	3.91
H–C(4)	3.59–3.65	3.74–3.78	3.76	3.71–3.92	3.81	3.56–3.69
H_A–C(5)	3.74	3.74–3.78	3.79	3.71–3.92	3.61–3.68	4.07
H_B–C(5)	3.59–3.65	3.66	3.68	3.71–3.92	3.61–3.68	3.56–3.69
H–C(1')	5.03	4.15	4.93	4.26–4.33	5.02	4.46
H–C(2')	3.46	3.27–3.35	3.52	3.52–3.63	3.54	3.38
H–C(3')	4.05	3.48–3.52	4.23	3.52–3.63	4.12	3.56–3.69
H–C(4')	3.59–3.65	3.48–3.52	3.67	3.52–3.63	3.72	3.56–3.69
H–C(5')	4.16	3.27–3.35	4.33	3.27	4.23	3.25–3.30
H_2C(6')	3.52–3.65	3.48–3.58	3.59–3.62	3.42–3.63	3.40–3.68	3.56–3.69
OH	3.51	4.01	4.22	3.71–3.92	3.81	3.25–3.30
OH	3.43	3.13	4.11	3.52–3.63	3.28	3.08
J(1,2)	2.2	3.0	3.2	3.5	1.8	2.1
J(2,3)		2.4	3.2		3.3	
J(3,4)		2.4	3.2		3.3	
$J(4,5_A)$	3.0		3.8			2.7
$J(4,5_B)$		2.5	2.0			
$J(5_A,5_B)$	12.2	11.9	11.2			12.3
J(1',2')	3.8	7.8	3.7		3.9	7.8
J(2',3')	9.6		9.6		9.4	8.8
J(3',4')	9.0		9.0		9.0	
J(4',5')			10.4		10.2	
$J(5',6'_A)$		2.0	3.3		1.9	
$J(5',6'_B)$	1.7		3.3	5.5	4.3	
$J(6'_A,6'_B)$	10.7	10.8		10.6		

Table 7. *Selected* ^{13}C*-NMR* (50 MHz, $CDCl_3$) *Chemical-Shift Values* [ppm] *of the Glycosides* **20–31**

	20	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**
C(1)	100.28[b])	98.37	99.92[b])	100.15	100.33	99.92	98.44[b])	99.12	97.26[b])	97.69	97.65[b])	97.47
C(2)	79.81[c])	81.67[b])	67.36	68.28	70.66	70.99	73.38	73.34	68.35[c])	68.40[b])	69.08[c])	69.38[b])
C(3)	65.29	65.47	76.06	76.89	65.69	65.79	66.36[c])	67.03[b])	69.46[c])	70.54[b])	68.33[c])	67.49[b])
C(4)	69.49	69.69	70.25	70.04	72.77	79.14	67.00[c])	68.14[b])	66.89[c])	68.31[b])	71.92[c])	73.75[b])
C(5)	63.87	64.50	63.82	63.04	57.42	62.52	61.21	61.36	60.99	61.37	61.31	63.45
C(1')	98.16[b])	103.84	97.24[b])	103.12	92.27	104.36	95.94[b])	102.49	94.79[b])	102.42	97.20[b])	104.31
C(2')	79.11[c])	81.79[b])	79.63	81.68	79.21	81.76	79.51	82.24	79.72	81.70	79.82	82.19
C(3')	82.18	84.47	81.93	84.61	82.00	85.17	81.69	84.45	81.23	84.51	81.80	84.45
C(4')	77.45	77.53	77.77	77.64	77.21	77.93	77.61	77.47	77.45	77.29	77.43	77.62
C(5')	70.94	74.88	71.04	74.65	71.06	74.97	70.29	74.75	70.83	74.68	70.89	74.68
C(6')	68.17	68.62	68.41	68.88	68.31	68.83	68.09	68.59	68.23	68.61	68.24	68.92
CH_3O							20.84	20.86	20.75	21.05	20.86	20.96
CH_3O							20.61	20.78	20.65	20.88	20.78	20.72
CO							170.21	170.06	169.88	170.41	170.02	170.07
CO							170.21	169.88	169.63	170.01	169.96	170.01

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

4.29 (*d*, *J* = 12.2, 1H, PhC*H*$_2$); 4.21 (*d*, *J* = 12.0, 1H, PhC*H*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.35 (*s*); 137.94 (*s*); 137.72 (*s*); 137.43 (*s*); 136.97 (*s*); 128.50–127.42 (*m*); 75.65 (*t*); 75.05 (*t*); 73.89 (*t*); 73.39 (*t*); 69.17 (*t*). CI-MS: 780 (100, $[M + 18]^+$).

*Benzyl 2-O-(2,3,4,6-Tetra-O-benzyl-β-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**21**). R_f (hexane/AcOEt 1:1) 0.23. t_R (hexane/AcOEt 2:1) 8.20. $[\alpha]_D^{25}$ = +46.6 (*c* = 0.79, EtOH). FT-IR (CCl_4): 3565*w*, 3502*w*, 3090*w*, 3067*w*, 3032*w*, 2927*m*, 2870*w*, 1497*w*, 1455*w*, 1397*w*, 1301*w*, 1261*w*, 1226*w*, 1209*w*, 1148*m*, 1071*s*, 1028*m*, 726*w*, 698*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 6*; additionally, 7.39–7.05 (*m*, 25 arom. H); 4.93 (*d*, *J* = 11.1, 1H, PhC*H*$_2$); 4.92 (*d*, *J* = 11.4, 1H, PhC*H*$_2$); 4.79 (*d*, *J* = 11.0, 1H, PhC*H*$_2$); 4.76 (*d*, *J* = 11.1, 1H, PhC*H*$_2$); 4.64 (*d*, *J* = 11.1, 1H, PhC*H*$_2$); 4.57 (*d*, *J* = 11.8, 1H, PhC*H*$_2$); 4.49 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.44 (*d*, *J* = 12.2, 1H, PhC*H*$_2$); 4.38 (*d*, *J* = 12.2, 1H, PhC*H*$_2$); 4.23 (*d*, *J* = 11.8, 1H, PhC*H*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.34 (*s*); 137.84 (*s*); 137.75 (2*s*); 136.95 (*s*); 128.40–127.69 (*m*); 75.66 (*t*); 75.11 (*t*); 75.06 (*t*); 73.54 (*t*); 69.55 (*t*). CI-MS: 780 (100, $[M + 18]^+$).

*Benzyl 3-O-(2,3,4,6-Tetra-O-benzyl-α-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**22**). R_f (hexane/AcOEt 1:1) 0.23. t_R (hexane/AcOEt 2:1) 7.55. M.p. 106°. $[\alpha]_D^{25}$ = +121.0 (*c* = 0.45, EtOH). FT-IR (CCl_4): 3502*w* (br.), 3090*w*, 3067*w*, 3033*w*, 2927*m*, 2869*w*, 1497*w*, 1455*m*, 1362*w*, 1324*w*, 1240*w*, 1209*w*, 1072*s*, 1028*m*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 6*; additionally, 7.33–7.03 (*m*, 25 arom. H); 4.89 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.88 (*d*, *J* = 11.5, 1H, PhC*H*$_2$); 4.79 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.60 (*d*, *J* ≈ 10.5, 1H, PhC*H*$_2$); 4.57 (*d*, *J* ≈ 10.9, 1H, PhC*H*$_2$); 4.52 (*d*, *J* = 11.6, 1H, PhC*H*$_2$); 4.43 (*d*, *J* = 11.7, 1H, PhC*H*$_2$); 4.36 (*d*, *J* = 12.1, 1H, PhC*H*$_2$); 4.27 (*d*, *J* = 11.9, 1H, PhC*H*$_2$); 4.25 (*d*, *J* = 12.3, 1H, PhC*H*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.52 (*s*); 137.99 (*s*); 137.55 (*s*); 137.47 (*s*); 136.26 (*s*); 128.69–127.63 (*m*); 75.60 (*t*); 75.04 (*t*); 73.95 (*t*); 73.49 (*t*); 69.65 (*t*). CI-MS: 780 (100, $[M + 18]^+$), 540 (15), 324 (11), 258 (14). Anal. calc. for $C_{46}H_{50}O_{10}$ (762.91): C 72.42, H 6.61; found: C 72.53, H 6.76.

*Benzyl 3-O-(2,3,4,6-Tetra-O-benzyl-β-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**23**). R_f (hexane/AcOEt 1:1) 0.23. t_R (hexane/AcOEt 2:1) 8.24. $[\alpha]_D^{25}$ = +57.2 (*c* = 0.42, EtOH). FT-IR (CCl_4): 3524*w* (br.), 3090*w*, 3067*w*, 3033*w*, 2926*m*, 2870*w*, 1497*w*, 1455*m*, 1358*w*, 1261*w*, 1209*w*, 1070*s*, 1029*m*, 909*w*, 726*w*, 698*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 6*; additionally, 7.43–7.03 (*m*, 25 arom. H); 5.02 (*d*, *J* = 11.6, 1H, PhC*H*$_2$); 4.99 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.82 (*d*, *J* = 11.4, 1H, PhC*H*$_2$); 4.81 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.75 (*d*, *J* = 11.2, 1H, PhC*H*$_2$); 4.61 (*d*, *J* = 11.8, 1H, PhC*H*$_2$); 4.49 (*d*, *J* = 11.4, 1H, PhC*H*$_2$); 4.33–4.26 (*m*, 3H, PhC*H*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.33 (*s*); 138.04 (*s*); 137.81 (*s*); 137.72 (*s*); 137.13 (*s*); 128.39–127.62 (*m*); 75.61 (*t*); 74.98 (2*t*); 73.47 (*t*); 69.67 (*t*). CI-MS: 780 (100, $[M + 18]^+$), 258 (61), 108 (36).

*Benzyl 4-O-(2,3,4,6-Tetra-O-benzyl-α-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**24**). R_f (hexane/AcOEt 1:1) 0.44. t_R (hexane/AcOEt 2:1) 3.49. $[\alpha]_D^{25}$ = +102.9 (*c* = 0.75, EtOH). FT-IR (CCl_4): 3577*w*, 3489*w*, 3090*w*, 3067*w*, 3033*w*, 2926*m*, 2870*w*, 1497*w*, 1455*m*, 1362*w*, 1262*w*, 1208*w*, 1093*s*, 1028*m*, 918*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 6*; additionally, 7.35–7.05 (*m*, 25 arom. H); 4.92 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.90 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.74 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.60 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.54 (*d*, *J* = 11.7, 1H, PhC*H*$_2$); 4.50 (*d*, *J* = 12.0, 1H, PhC*H*$_2$); 4.45 (*d*, *J* = 11.7, 1H, PhC*H*$_2$); 4.41 (*d*, *J* = 12.1, 1H, PhC*H*$_2$); 4.33 (*d*, *J* = 12.1, 1H, PhC*H*$_2$); 4.20 (*d*, *J* = 12.0, 1H, PhC*H*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.57 (*s*); 138.08 (*s*); 137.77 (*s*); 137.66 (*s*); 137.17 (*s*); 128.44–127.56 (*m*); 75.71 (*t*); 75.04 (*t*); 73.44 (*t*); 73.04 (*t*); 69.36 (*t*). CI-MS: 780 (100, $[M + 18]^+$), 558 (28), 258 (25), 108 (18).

*Benzyl 4-O-(2,3,4,6-Tetra-O-benzyl-β-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**25**). R_f (hexane/AcOEt 1:1) 0.38. t_R (hexane/AcOEt 2:1) 4.77. M.p. 116°. $[\alpha]_D^{25}$ = +67 (*c* = 0.82, EtOH). FT-IR (CCl_4): 3546*w*, 3090*w*, 3067*w*, 3033*w*, 2923*w*, 2869*w*, 1497*w*, 1455*m*, 1360*w*, 1307*w*, 1262*w*, 1209*w*, 1096*s*, 1029*m*, 977*w*, 927*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 6*; additionally, 7.47–7.03 (*m*, 25 arom. H); 4.87 (*d*, *J* = 11.5, 1H, PhC*H*$_2$); 4.83 (*d*, *J* = 10.8, 1H, PhC*H*$_2$); 4.81 (*d*, *J* = 11.5, PhC*H*$_2$); 4.73 (*d*, *J* = 10.7, 1H, PhC*H*$_2$); 4.56 (*d*, *J* = 11.2, 1H, PhC*H*$_2$); 4.53 (*d*, *J* = 12.0, 1H, PhC*H*$_2$); 4.43 (*d*, *J* = 12.3, 1H, PhC*H*$_2$); 4.39 (*d*, *J* = 12.3, 1H, PhC*H*$_2$); 4.22 (*d*, *J* = 11.9, 1H, PhC*H*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.28 (*s*); 138.08 (*s*); 137.88 (*s*); 137.64 (*s*); 137.18 (*s*); 128.45–127.65 (*m*); 75.55 (*t*); 75.32 (*t*); 74.97 (*t*); 73.43 (*t*); 69.52 (*t*). CI-MS: 780 (100, $[M + 18]^+$).

*Benzyl 3,4-Di-O-acetyl-2-O-(2,3,4,6-tetra-O-benzyl-α-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**26**). R_f (hexane/AcOEt 2:1) 0.26. t_R (hexane/Et_2O 1:1) 3.05. $[\alpha]_D^{25}$ = +83.5 (*c* = 1.15, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3033*w*, 2924*w*, 2870*w*, 1750*s*, 1497*w*, 1454*m*, 1367*m*, 1241*s*, 1220*s*, 1157*m*, 1083*s*, 1048*s*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 8*; additionally, 7.37–7.01 (*m*, 25 arom. H); 5.00 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.92 (*d*, *J* = 11.2, 1H, PhC*H*$_2$); 4.85 (*d*, *J* = 11.3, 1H, PhC*H*$_2$); 4.73 (*d*, *J* = 11.7, 1H, PhC*H*$_2$); 4.61 (*d*, *J* = 11.2, 1H, PhC*H*$_2$); 4.54 (*d*, *J* = 11.7, 1H, PhC*H*$_2$); 4.46 (*d*, *J* = 12.1, 1H, PhC*H*$_2$); 4.42 (*d*, *J* = 11.7, 1H, PhC*H*$_2$); 4.36 (*d*, *J* = 11.7, 1H, PhC*H*$_2$); 4.30 (*d*, *J* = 12.1, 1H, PhC*H*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.69 (*s*); 138.43 (*s*); 138.17 (*s*); 137.85 (*s*); 136.89 (*s*); 128.33–127.22 (*m*); 75.43 (*t*); 74.81 (*t*); 73.24 (*t*); 72.47 (*t*); 70.25 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 656 (42), 432 (45).

Benzyl 3,4-Di-O-acetyl-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-L-ribopyranoside (**27**). R_f (hexane/AcOEt 2:1) 0.26. t_R (hexane/Et_2O 1:1) 2.78. $[\alpha]_D^{25}$ = +41.5 (*c* = 1.00, EtOH). FT-IR (CCl_4): 3090*w*, 3066*w*, 3032*w*, 2915*w*, 2874*w*, 1752*s*, 1497*w*, 1454*w*, 1366*m*, 1241*s*, 1152*m*, 1072*s*, 1028*m*, 962*w*, 910*w*, 726*w*, 697*m*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 8*; additionally, 7.44–7.02 (*m*, 25 arom. H); 5.23 (*d*, *J* = 10.9, 1H, PhCH_2); 4.99 (*d*, *J* = 11.4, 1H, PhCH_2); 4.84 (*d*, *J* = 11.3, 1H, PhCH_2); 4.80 (*d*, *J* = 11.4, 1H, PhCH_2); 4.70 (*d*, *J* = 11.1, PhCH_2); 4.58 (*d*, *J* = 11.4, 1H, PhCH_2); 4.51–4.48 (*m*, 1H, PhCH_2); 4.38 (*d*, *J* = 12.3, 1H, PhCH_2); 4.37 (*d*, *J* = 11.6, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.69 (*s*); 138.51 (*s*); 138.16 (*s*); 138.10 (*s*); 136.90 (*s*); 128.51–127.44 (*m*); 75.44 (*t*); 74.90 (*t*); 74.64 (*t*); 73.36 (*t*); 70.58 (*t*). CI-MS: 864 (100, $[M + 18]^+$).

Benzyl 2,4-Di-O-acetyl-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-L-ribopyranoside (**28**). R_f (hexane/AcOEt 2:1) 0.21. t_R (hexane/Et_2O 1:1) 3.53. $[\alpha]_D^{25}$ = +114.8 (*c* = 1.20, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3032*w*, 2922*w*, 2870*w*, 1754*s*, 1739*s*, 1497*w*, 1455*m*, 1368*m*, 1246*s*, 1228*s*, 1136*m*, 1083*s*, 1028*s*, 981*w*, 862*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 8*; additionally, 7.35–7.03 (*m*, 25 arom. H); 5.03 (*d*, *J* = 11.0, 1H, PhCH_2); 4.94 (*d*, *J* = 11.4, 1H, PhCH_2); 4.89 (*d*, *J* = 11.3, 1H, PhCH_2); 4.63 (*d*, *J* = 11.4, 1H, PhCH_2); 4.59 (*d*, *J* = 11.5, 1H, PhCH_2); 4.56 (*d*, *J* = 10.8, 1H, PhCH_2); 4.51 (*d*, *J* = 11.9, 1H, PhCH_2); 4.44 (*d*, *J* = 12.2, 1H, PhCH_2); 4.34 (*d*, *J* = 12.2, 1H, PhCH_2); 4.25 (*d*, *J* = 11.5, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.61 (*s*); 138.24 (2*s*); 137.74 (*s*); 136.78 (*s*); 128.23–127.30 (*m*); 75.32 (*t*); 74.65 (*t*); 73.26 (*t*); 72.65 (*t*); 69.68 (*t*). CI-MS: 864 (100, $[M + 18]^+$). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.98): C 70.90, H 6.43; found: C 70.76, H 6.42.

Table 8. *Selected ^{1}H-NMR* (400 MHz, C_6D_6) *Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Glycosides* **26–31**

	26	**27**	**28**	**29**	**30**	**31**
H–C(1)	5.13	5.02	5.02	5.01	4.93	4.98
H–C(2)	3.95	4.10	5.44	5.52	5.36	5.30
H–C(3)	5.71	5.73	4.38	4.51	5.74	5.86
H–C(4)	5.07	5.10	5.12	5.20	3.68–3.78	3.83
H_A–C(5)	3.73	3.71	3.81	3.86	3.81	4.12
H_B–C(5)	3.62	3.66	3.66–3.73	3.69	3.68–3.78	4.05
H–C(1')	4.95	4.48–4.51	5.24	4.42	4.72	4.25
H–C(2')	3.50	3.55–3.60	3.54	3.52–3.65	3.51	3.54
H–C(3')	4.27	3.55–3.60	4.24	3.52–3.65	4.19	3.63–3.68
H–C(4')	3.80	3.78	3.76	3.76	3.88	3.36–3.68
H–C(5')	4.44	3.11	4.22	3.16	4.13	3.25
H_2C(6')	3.53/3.65	3.61/3.64	3.66–3.73	3.52–3.65	3.68–3.78	3.55/3.59
CH_3	1.77	1.88	1.84	1.88	1.82	1.73
CH_3	1.69	1.72	1.62	1.78	1.79	1.70
J(1,2)	5.4	5.3	4.0	3.0	4.9	5.9
J(2,3)	3.3	3.6	3.2	3.4	3.3	3.3
J(3,4)	3.3	3.0	3.4	3.6	2.7	3.3
J(4,5$_A$)	4.0	4.2	4.8	4.2	3.7	4.3
J(4,5$_B$)	7.2	6.9	2.2	2.6		7.5
J(5$_A$,5$_B$)	11.7	11.8	12.1	12.5	10.7	11.6
J(1',2')	3.5		3.5	7.1	3.5	7.6
J(2',3')	9.7		9.7		9.6	8.8
J(3',4')	9.8		9.3	9.2	9.1	
J(4',5')	9.3	9.8	9.9	9.2	9.9	9.2
J(5',6'$_A$)	4.1	3.4			3.3	4.5
J(5',6'$_B$)	1.7	2.0			1.7	2.1
J(6'$_A$,6'$_B$)	11.0	10.5				10.8

*Benzyl 2,4-Di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-O-benzyl-β-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**29**): R_f (hexane/AcOEt 2:1) 0.24. t_R (hexane/Et_2O 1:1) 3.21. $[\alpha]_D^{25}$ = +56.1 (*c* = 1.10, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3033*w*, 2923*w*, 2872*w*, 1741*s*, 1497*w*, 1454*w*, 1368*m*, 1232*m*, 1133*m*, 1082*s*, 1028*m*, 978*w*, 910*w*, 836*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 8*; additionally, 7.43–7.03 (*m*, 25 arom. H); 5.03 (*d*, *J* = 10.8, 1H, PhCH_2); 4.91 (*d*, *J* = 11.4, 1H, PhCH_2); 4.82 (*d*, *J* = 11.4, 1H, PhCH_2); 4.74 (*d*, *J* = 11.4, 1H, PhCH_2); 4.68 (*d*, *J* = 11.4, 1H, PhCH_2); 4.55 (*d*, *J* = 11.2, 1H, PhCH_2); 4.54 (*d*, *J* = 12.3, 1H, PhCH_2); 4.44 (*d*, *J* = 11.9, 1H, PhCH_2); 4.33 (*d*, *J* = 12.0, 1H, PhCH_2); 4.24 (*d*, *J* = 11.9, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.59 (*s*); 138.42 (*s*); 138.15 (*s*); 138.01 (*s*); 136.69 (*s*); 128.40–127.40 (*m*); 75.38 (*t*); 74.82 (*t*); 74.24 (*t*); 73.30 (*t*); 69.91 (*t*). CI-MS: 864 (100, $[M + 18]^+$). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.98): C 70.90, H 6.43; found: C 70.80, H 6.44.

*Benzyl 2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**30**). R_f (hexane/AcOEt 2:1) 0.28. t_R (hexane/Et_2O 1:1) 2.96. $[\alpha]_D^{25}$ = +107.6 (*c* = 0.94, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3032*w*, 2926*w*, 2868*w*, 1751*s*, 1497*w*, 1455*m*, 1368*m*, 1330*w*, 1243*s*, 1224*s*, 1136*m*, 1074*s*, 1050*s*, 1028*s*, 900*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 8*; additionally, 7.35–7.04 (*m*, 25 arom. H); 4.99 (*d*, *J* = 11.0, 1H, PhCH_2); 4.96 (*d*, *J* = 11.0, 1H, PhCH_2); 4.83 (*d*, *J* = 11.3, 1H, PhCH_2); 4.68 (*d*, *J* = 11.3, 1H, PhCH_2); 4.66 (*d*, *J* = 12.0, 1H, PhCH_2); 4.47 (*d*, *J* = 11.6, 1H, PhCH_2); 4.45 (*d*, *J* = 12.0, 1H, PhCH_2); 4.38 (*d*, *J* = 11.8, 1H, PhCH_2); 4.35 (*d*, *J* = 12.2, 1H, PhCH_2); 4.34 (*d*, *J* = 12.2, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.75–137.10 (5*s*); 128.43–127.46 (*m*); 75.48 (*t*); 74.75 (*t*); 73.49 (*t*); 73.02 (*t*); 70.06 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 600 (14).

*Benzyl 2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*L*-ribopyranoside* (**31**). R_f (hexane/AcOEt 2:1) 0.29. t_R (hexane/Et_2O 1:1) 2.73. $[\alpha]_D^{25}$ = +50.4 (*c* = 0.93, EtOH). FT-IR (CCl_4): 3090*w*, 3067*w*, 3032*w*, 2912*w*, 2869*w*, 1751*s*, 1497*w*, 1454*w*, 1370*m*, 1306*w*, 1242*m*, 1222*m*, 1071*s*, 1028*m*, 911*w*, 726*w*, 697*s*. ^{1}H-NMR (400 MHz, C_6D_6): see *Table 8*; additionally, 7.47–7.04 (*m*, 25 arom. H); 5.12 (*d*, *J* = 11.4, 1H, PhCH_2); 5.00 (*d*, *J* = 11.3, 1H, PhCH_2); 4.84 (*d*, *J* = 11.4, 1H, PhCH_2); 4.81 (*d*, *J* = 11.4, 1H, PhCH_2); 4.76 (*d*, *J* = 12.1, 1H, PhCH_2); 4.68 (*d*, *J* = 11.4, 1H, PhCH_2); 4.54 (*d*, *J* = 11.4, 1H, PhCH_2); 4.42 (*d*, *J* = 12.1, 1H, PhCH_2); 4.41 (*d*, *J* = 12.2, 1H, PhCH_2); 4.34 (*d*, *J* = 12.2, 1H, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 7*; additionally, 138.50 (2*s*); 138.04 (2*s*); 137.01 (*s*); 128.58–127.32 (*m*); 75.69 (*t*); 74.97 (*t*); 74.47 (*t*); 73.42 (*t*); 70.01 (*t*). CI-MS: 864 (100, $[M + 18]^+$), 508 (12), 303 (14), 243 (13).

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