

117. Glycosylidene Carbenes

Part 7

Neighbouring-Group Participation by the 2-Benzyloxy Group in the Glycosidation of Strongly Acidic Hydroxy Compounds

by Yoshikazu Takahashi¹⁾ and Andrea Vasella*

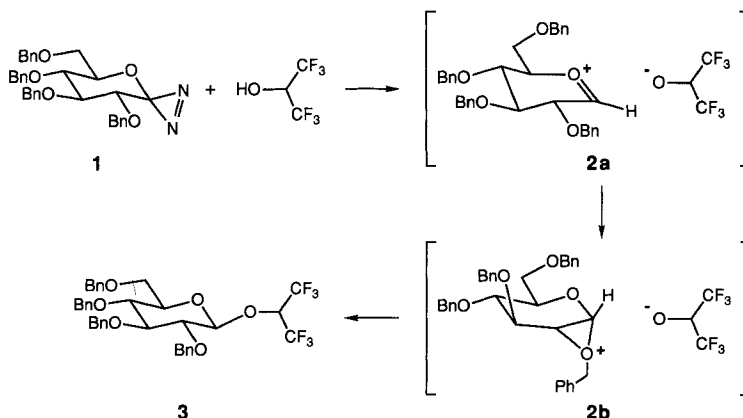
Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

(22.V.92)

To demonstrate the neighbouring-group participation of the 2-benzyloxy group in the glycosidation of phenols and of strongly acidic alcohols by the diazirine **1**, we examined the glycosidation of 4-nitrophenol, 4-methoxyphenol, $(\text{CF}_3)_2\text{CHOH}$, MeOH, and *i*-PrOH by the diazirine **11**, derived from the 2-deoxypyranose **6**. Oxidation of the oximes **7** yielded (*E*)- and (*Z*)-**8**. In solution, (*E*)-**8** isomerised to (*Z*)-**8**. Similarly, the (*E*)-configured mesylate **9**, prepared from **8**, underwent acid-catalysed isomerisation to (*Z*)-**9**. Treatment of (*Z*)-**9** with NH_3 , followed by oxidation of the resulting diaziridine **10** with I_2 , yielded the desired diazirine **11**. Glycosidation by **11** of the above mentioned hydroxy compounds yielded the glycosides **12–21**. In agreement with the postulated neighbouring-group participation, these glycosidation proceeded without, or with a very low diastereoselectivity, favouring the axial anomers.

Introduction. – Glycosidation by the diazirine **1** [1] of phenols [2] and of acidic alcohols [3], such as $(\text{CF}_3)_2\text{CHOH}$ and $(\text{CF}_3)_2\text{C}(\text{Me})\text{OH}$, in CH_2Cl_2 yields mainly 1,2-*trans*-glycosides such as **3** (Scheme 1). We rationalised this diastereoselectivity by postulating that **1** forms a glycosylidene-carbene which is protonated by the glycosyl acceptor.

Scheme 1

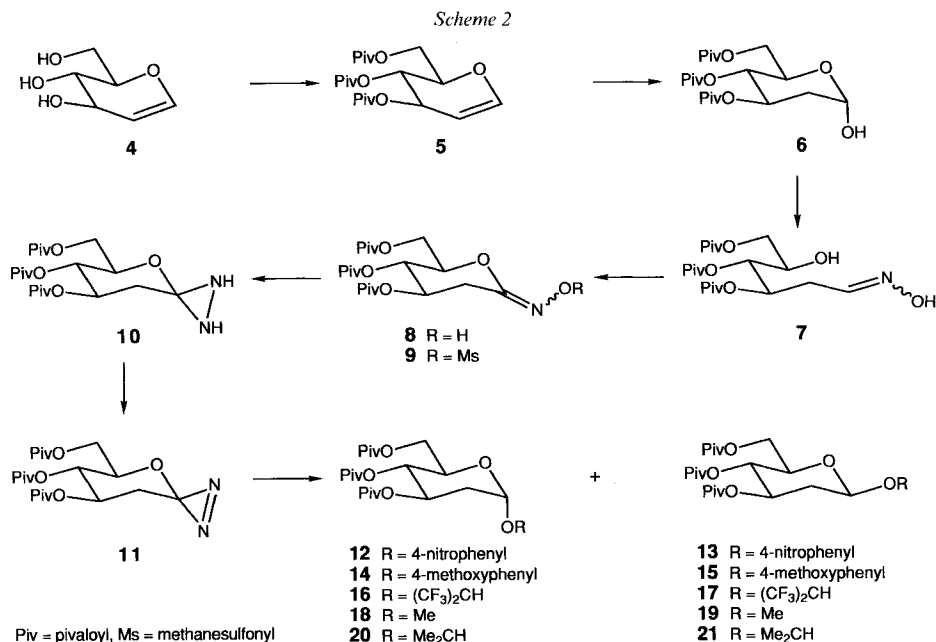


¹⁾ On leave of absence from the Institute of Microbial Chemistry, 3-14-23, Kamiosaki, Shinagawa-ku, Tokyo 141, Japan.

This leads to an initially non-solvated ion-pair **2a**. If the reaction is run in a non-nucleophilic solvent, the neighbouring benzyloxy group – rather than the solvent – may participate in the stabilisation of the oxycarbenium ion [3] [4] leading – in the extreme case – to an oxiranium alkoxide ion pair, such as **2b**, and hence to 1,2-*trans*-glycosides. Such a participation of the vicinal benzyloxy group is not observed during *Koenigs-Knorr*-type glycosidations. It may be typical only for the very reactive oxycarbenium ions which are generated by protonation of a carbene in the absence of nucleophilic solvents and of nucleophilic (weakly acidic) alcohols [3]. This hypothesis implies that analogous glycosidations with diazirines derived from 2-deoxysaccharides will not lead to 1,2-*trans*-glycosides. In our rationalisation of the behaviour of some monofunctional alcohols [3] towards diazirines, we assume that oligomeric alcohol protonates the intermediate carbene in the σ -plane, and that a H-bonded neighbour of the protonating molecule then attacks the oxycarbenium ion in the π -plane, without (at ambient temperature) discriminating between axial and equatorial attack. On the basis of this rationalisation, one expects that diazirines derived from 2-deoxyhexoses will be glycosylated by phenols and acidic alcohols in non-nucleophilic solvents to yield approximately equal amounts of α -D- and β -D-glycosides, rather than α -D-configured (*i.e.* axial) pyranosides which are expected if stereoelectronic control operates.

In the following, we report on the synthesis of the diazirine **11** (Scheme 2), and on the glycosidation of 4-methoxyphenol, 4-nitrophenol, $(\text{CF}_3)_2\text{CHOH}$, MeOH, and *i*-PrOH by **11**.

Results. – The diazirine **11** was chosen to offset the higher thermal lability, expected from the absence of an electron-withdrawing substituent at C(2) [5] by replacing the benzyloxy groups at C(3), C(4), and C(6) of **1** by more strongly electron-withdrawing



acyloxy groups. For the preparation of **11**, D-glucal (**4**) was pivaloylated to give the known **5** [6], which was treated with aqueous HCl in dioxane, yielding 88% of the crystalline hemiacetal **6**. The α -D-configuration is evidenced by $J(1,2) = 3.2$ Hz (see below). Oximation of **6** yielded a *ca.* 1:1 mixture of the (*E*)- and (*Z*)-oximes **7**, as evidenced, in the ¹H-NMR spectrum, by the H–C(1) signals at 7.36 and 6.72 ppm. These oximes were best oxidised by iodosobenzene in aqueous MeOH and in the presence of a buffer, to yield 70% of an (*E/Z*)-mixture of the hydroximolactones **8**, from which 54.5% of the (*E*)-isomer crystallised. In CH₂Cl₂ solution, (*E*)-**8** isomerised, yielding, after 24 h, a *ca.* 1:4 mixture of the (*E*)- and (*Z*)-isomers, which were transformed into the mesylates (*E*)-**9** (16%) and (*Z*)-**9** (74%). Only (*Z*)-**9** reacted with NH₃ in MeOH/dioxane to give the diaziridine **10**; similar treatment of (*E*)-**9** led to a number of compounds. Acid-catalysed isomerisation of (*E*)-**9** gave 85% of the desired (*Z*)-**9**.

The assignment of the configuration of the diastereoisomers of **8** and **9** is best based upon the differences in the chemical shift of the C(1) signals. Similarly to the (*E*)-isomers of hydroximolactones [7] [8], their *O*-phosphonoyl derivatives [7] [9], *N*-sulfonyl-lactone hydrazones [10], and *N*-sulfonyl-lactone imines [11], (*E*)-**8** and (*E*)-**9** give rise to a signal at lower field than their (*Z*)-isomers ($\Delta\delta = 8.4$ and 12.4 ppm). The differences of the chemical shifts for C(2) (γ -effect) are much smaller. The assignment is confirmed by the $\Delta\delta$ values for the H_{eq}–C(2) signals (0.55 ppm for (*E/Z*)-**8** and 0.40 ppm for (*E/Z*)-**9**). The assignment of H_{eq}/H_{ax}–C(2) is easiest for (*E*)-**8** ($J(2,3) = 9.0$ and 5.9 Hz); for the other three compounds, the differences of these coupling constants are smaller. As a rule, the (*E*)-isomers possess a higher R_f value.

The solution of the diaziridine **10** was freeze-dried and oxidised with I₂ in the presence of Et₃N. After removal of (Et₃NH)I, a solution of the diazirine **11** in dioxane or toluene was treated with 1 equiv. each of the glycosyl acceptors at 18 or 40°, as toluene and dioxane tended to give the best β -D/ α -D ratio of glycosides derived from **1** and strongly acidic hydroxy compounds [2] [3]. The glycosides were isolated by flash chromatography or by a combination of centrifugal partition and flash chromatography. The results are compiled in Table 1. Glycosidation of 4-nitrophenol proceeded without anomeric selec-

Table 1. Glycosidation of **11**: Conditions and Yields

Glycosyl acceptor	Solvent and additive ^{a)}	Temp. [°C]	Time [h]	Products	Yield [%]	Ratio α -D/ β -D
4-Nitrophenol	dioxane, 4 Å	18	4	12/13	48	51:49
	toluene ^{b)} , 4 Å	18	4		42	45:55
	CH ₂ Cl ₂ , 4 Å	18	4		34	57:43
4-Methoxyphenol	dioxane, 4 Å	18	4	14/15	43	59:41
	dioxane, –	18	4		39	62:38
	toluene, 4 Å	18	4		43	52:48
	toluene, –	18	4		39	56:44
(CF ₃) ₂ CHOH	dioxane, –	18	4	16/17	41	57:43
	toluene, –	18	4		39	60:40
MeOH	dioxane, –	18	6	18/19	28	43:57
	toluene, –	18	6		30	51:49
i-PrOH	dioxane, 3 Å	18	6	20/21	11	43:57
	dioxane, 3 Å	40	0.5		8	54:46
	toluene, 3 Å	18	6		14	46:54
	toluene, 3 Å	40	0.5		26	49:51

^{a)} Molecular sieves 3 Å or 4 Å. ^{b)} 1.0 ml of solvent.

tivity. A slight excess of the α -D-anomer was obtained from 4-methoxyphenol and similarly from $(\text{CF}_3)_2\text{CHOH}$. Glycosidation of MeOH and of i-PrOH proceeded diastereounselectively.

For the assignment of the ^1H - and ^{13}C -NMR data, see *Tables 2–4*. The anomeric configurations were determined using the specific rotation (see *Exper. Part*), $J(1,2)$ (*Table 3*), and the chemical shift for C(1) (*Table 4*). In all cases, the specific rotations follow *Hudson's rule*. All β -D-anomers, with the exception of **15**, where the H–C(1) signal overlaps with those for H–C(3) and H–C(4), show a typical, large $J(1,2)$ coupling constant. The differences of the chemical-shift values for C(1) are as expected, but small for the aryl glycosides. The fluorinated anomers **16** and **17** are an exception, in that C(1) of the α -D-anomer **16** resonates at lower field than C(1) of β -D-anomer **17**.

These results, and particularly the ones realised with 4-methoxyphenol and $(\text{CF}_3)_2\text{CHOH}$, are clearly different from those obtained with the diazirine **1** and in keeping with a participation of the 2-benzyloxy group in the glycosidation of phenols and strongly acidic alcohols by **1**. The slight excess of the α -D-anomers observed for the glycosides of 4-methoxyphenol and of $(\text{CF}_3)_2\text{CHOH}$ indicates that the stereoelectronic control is operative to a small extent only.

Y. T. thanks for a grant-in-aid from the *Ciba-Geigy Foundation* (Japan) for the promotion of science.

Experimental Part

General. Normal workup means extraction with the indicated solvents, washing of the org. phase with sat. aq. NaHCO_3 soln. and/or H_2O , drying (Na_2SO_4), evaporation, and drying of the residue under high vacuum. Qual. TLC: 0.25-mm precoated silica gel plates (*Merck*, Kieselgel 60 F_{254}) with the indicated solvent systems; detection by spraying the plates with a soln. of 5% vanillin in conc. H_2SO_4 followed by heating at ca. 200°. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). Centrifugal partition chromatography (CPC): model *LLN* (*Sanki Engineering*, Kyoto, Japan) with six type-250W cartridges; solvent system MeCN/hexane. M.p.: uncorrected. Optical rotations: 1-dm cell at 25° and 365, 436, 546, 578, and 589 nm; values at 589 nm were determined from a regression curve. IR Spectra: 3% CHCl_3 soln. ^1H - and ^{13}C -NMR Spectra: chemical shifts in ppm rel. to TMS as internal standard.

1,5-Anhydro-2-deoxy-3,4,6-tri-O-pivaloyl-D-arabino-hex-1-enitol [**6**] (**5**). A soln. of 3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol (*Fluka*; 11.08 g, 40 mmol) and NaOMe (40 mg, 0.74 mmol) in MeOH (200 ml) was stirred for 5 h. After evaporation, the crystalline residue (**4**) was dissolved in pyridine (50 ml) and treated with pivaloyl chloride (17.7 ml, 144 mmol). The mixture was stirred at r.t. for 24 h, treated with H_2O (1 ml), and stirred for further 2 h. Normal workup (AcOEt/hexane 1:1) and washing of the crystalline residue with MeOH (10 ml) gave 15.35 g (95%) of **5**. R_f (AcOEt/hexane 1:4) 0.66. M.p. 106–107°. $[\alpha]_D^{20} = -30.7$ ($c = 1.05$, CHCl_3). IR: 2960m, 2930m, 2910m, 2870m, 1725s, 1645m, 1475m, 1460m, 1395w, 1365m, 1275s, 1250–1200m, 1140s, 1100m, 1060m, 1030m, 965m (br.), 940w, 890w, 865w (sh). ^1H -NMR (300 MHz, CDCl_3): *Tables 2 and 3*. ^{13}C -NMR (50.6 MHz, CDCl_3): *Table 4*. EI-MS: 399 ($[M + 1]^+$). Anal. calc. for $\text{C}_{21}\text{H}_{34}\text{O}_7$ (398.50): C 63.30, H 8.60; found: C 63.08, H 8.38.

2-Deoxy-3,4,6-tri-O-pivaloyl- α -D-arabino-hexopyranose (**6**). A soln. of **5** (4.00 g, 10 mmol) in dioxane (100 ml) was treated with 8N HCl (36 ml, 288 mmol) for 48 h at r.t. After neutralisation of the mixture with NaHCO_3 (24.2 g, 288 mmol), dioxane was evaporated. Normal workup (AcOEt/hexane 1:1) and washing of the crystalline residue with hexane gave 3.71 g (93%) of pure **6**. Partial anomerisation of the NMR sample occurred upon standing in $\text{CDCl}_3/\text{D}_2\text{O}$ (after 2 d, α -D/ β -D ca. 4:1). R_f (AcOEt/hexane 1:2) 0.46. M.p. 118–119°. $[\alpha]_D^{20} = +67.3$ ($c = 1.03$, CHCl_3). IR: 3600w, 3420w (br.), 2980s, 2940m, 2910m, 2880m, 1730s, 1480s, 1460m, 1400m, 1370m, 1280s, 1250–1195m, 1150s (br.), 1080s, 1040m, 1020m, 990s, 940w, 915w, 895w, 885w (sh), 870w (sh). ^1H -NMR (300 MHz, CDCl_3): *Tables 2 and 3*; 5.42 (after addn. of D_2O : 5.41, br. d, $J \approx 3.1$); 1.77 (after addn. of D_2O : ddd, $J = 3.5, 11.5, 12.9$). ^{13}C -NMR (50.6 MHz, CDCl_3): *Table 4*. CI-MS: 417 ($[M + 1]^+$). Anal. calc. for $\text{C}_{21}\text{H}_{36}\text{O}_8$ (416.51): C 60.56, H 8.71; found: C 60.80, H 8.50.

Table 2. ¹H-NMR (300 MHz, CDCl₃) Chemical Shifts [ppm] of Compounds **5-9** and **12-21**

	H-C(1)	H-C(2) ^{a)}	H'-C(2) ^{b)}	H-C(3)	H-C(4)	H-C(5)	H-C(6), H'-C(6)	<i>t</i> -Bu	Others
5	6.46 (<i>dd</i>)	4.82 (<i>dd</i>)	–	5.33–5.30 (<i>m</i>)	5.27 (<i>t</i>)	4.30–4.25 (<i>m</i>)	4.33, 4.21 (2 <i>dd</i>)	1.23, 1.19, 1.18 (3 <i>s</i>)	–
6	5.42 (<i>br. t</i>)	2.28 (<i>ddd</i>)	1.77 (<i>dddd</i>)	5.37 (<i>ddd</i>)	5.10 (<i>t</i>)	4.25 (<i>ddd</i>)	4.19, 4.11 (2 <i>dd</i>)	1.23, 1.17, 1.15 (3 <i>s</i>)	2.75 (<i>dd</i> , exchange with D ₂ O, OH)
7	7.36 (<i>dd</i> , <i>Z</i>)	2.76 (<i>ddd</i> , <i>Z</i>)	2.51 (<i>td</i> , <i>Z</i>)	5.56–5.49 (<i>m</i>)	5.11–5.05 (<i>m</i>)	3.71–3.64 (<i>m</i>)	4.18, 4.05 (2 <i>dd</i>)	1.26, 1.25 (2 ×), 1.24, 1.22 (2 ×) (4 <i>s</i>)	7.63 (<i>br. s</i>), 7.28 (<i>s</i> , exchange with D ₂ O, NOH); 3.46, 3.37 (2 <i>d</i> , exchange with D ₂ O, OH–C(5))
(<i>E</i>)- 8	–	3.45 (<i>dd</i>)	2.50 (<i>dd</i>)	5.20–5.08 (<i>m</i>)	5.26 (<i>t</i>)	4.11 (<i>td</i>)	4.26 (<i>d</i>)	1.23, 1.19, 1.18 (3 <i>s</i>)	7.16 (<i>s</i> , NOH)
(<i>Z</i>)- 8	–	2.90 (<i>dd</i>)	2.53 (<i>dd</i>)	5.20–5.08 (<i>m</i>)	5.20–5.08 (<i>m</i>)	4.35–4.28 (<i>m</i>)	4.35–4.28 (<i>m</i>)	1.24, 1.20, 1.19 (3 <i>s</i>)	7.18 (<i>s</i> , NOH)
(<i>E</i>)- 9	–	3.36 (<i>dd</i>)	2.84 (<i>dd</i>)	5.16 (<i>di</i>)	5.26 (<i>t</i>)	4.36–4.27 (<i>m</i>)	4.36–4.27 (<i>m</i>)	1.24, 1.20 (2 ×) (2 <i>s</i>)	3.17 (<i>s</i> , MsO)
(<i>Z</i>)- 9	–	2.96 (<i>dd</i>)	2.73 (<i>ddd</i>)	5.16 (<i>q</i>)	5.11 (<i>br. dd</i>)	4.47–4.24 (<i>m</i>)	4.47–4.24 (<i>m</i>)	1.25, 1.22, 1.21 (3 <i>s</i>)	3.12 (<i>s</i> , MsO)
12	5.77 (<i>br. d</i>)	2.53 (<i>ddd</i>)	2.01 (<i>ddd</i>)	5.49 (<i>ddd</i>)	5.19–5.11 (<i>m</i>)	4.16–3.98 (<i>m</i>)	4.16–3.98 (<i>m</i>)	1.19, 1.18, 1.12 (3 <i>s</i>)	8.24–8.18, 7.24–7.19 (2 <i>m</i> , each 2 H, O ₂ NC ₆ H ₄ O)
14	5.56 (<i>br. d</i>)	2.46 (<i>br. dd</i>)	1.92 (<i>ddd</i>)	5.51 (<i>ddd</i>)	5.12 (<i>t</i>)	4.17–4.02 (<i>m</i>)	4.17–4.02 (<i>m</i>)	1.185, 1.18, 1.16 (3 <i>s</i>)	7.07–7.02, 6.85–6.79 (2 <i>m</i> , each 2 H, MeOC ₆ H ₄ O); 3.77 (<i>s</i> , MeO)
16^{c)}	5.16 (<i>br. d</i>)	2.39 (<i>ddd</i>)	1.82 (<i>ddd</i>)	5.19 (<i>ddd</i>)	5.04 (<i>t</i>)	4.10–3.97 (<i>m</i>)	4.10–3.97 (<i>m</i>)	1.15, 1.11, 1.08 (3 <i>s</i>)	4.38 (<i>sept.</i> , (CF ₃) ₂ CHO)
18	4.84 (<i>br. d</i>)	2.24 (<i>ddd</i>)	1.76 (<i>ddd</i>)	5.29 (<i>ddd</i>)	5.04 (<i>t</i>)	3.99 (<i>m</i>)	4.18, 4.11 (<i>m</i>)	1.24, 1.18, 1.15 (3 <i>s</i>)	3.36 (<i>s</i> , MeO)
20^{d)}	5.07–4.97 (<i>m</i>)	2.17 (<i>ddd</i>)	1.77 (<i>ddd</i>)	5.31 (<i>ddd</i>)	5.07–4.97 (<i>m</i>)	4.18–4.01 (<i>m</i>)	4.18–4.01 (<i>m</i>)	1.22, 1.17, 1.14 (3 <i>s</i>)	3.88 (<i>sept.</i> , Me ₂ CH); 1.22, 1.14 (2 <i>d</i> , Me ₂ CH)
13	5.34 (<i>dd</i>)	2.57 (<i>ddd</i>)	2.11–2.00 (<i>m</i>)	5.14 (<i>di</i>)	5.09 (<i>m</i>)	3.89 (<i>ddd</i>)	4.28, 4.09 (2 <i>dd</i>)	1.22, 1.21, 1.19 (3 <i>s</i>)	8.21–8.16, 7.12–7.07 (2 <i>m</i> , each 2 H, O ₂ NC ₆ H ₄ O)
15	5.14–5.02 (<i>m</i>)	2.51 (<i>ddd</i>)	2.03–1.92 (<i>m</i>)	5.14–5.02 (<i>m</i>)	5.14–5.02 (<i>m</i>)	3.81–3.75 (<i>m</i>)	4.27, 4.08 (2 <i>dd</i>)	1.22, 1.19, 1.18 (3 <i>s</i>)	7.02–6.96, 6.82–6.77 (2 <i>m</i> , each 2 H, MeOC ₆ H ₄ O); 3.78 (<i>s</i> , MeO)
17^{e)}	4.82 (<i>dd</i>)	2.41 (<i>ddd</i>)	1.72 (<i>ddd</i>)	5.01–4.93 (<i>m</i>)	5.02 (<i>t</i>)	3.62 (<i>ddd</i>)	4.20, 3.98 (2 <i>dd</i>)	1.15, 1.10, 1.08 (3 <i>s</i>)	4.48 (<i>sept.</i> , (CF ₃) ₂ CHO)
19	4.49 (<i>dd</i>)	2.38–2.27 (<i>m</i>)	1.75–1.61 (<i>m</i>)	5.07–4.96 (<i>m</i>)	5.07–4.96 (<i>m</i>)	3.69–3.62 (<i>m</i>)	4.23, 4.10 (2 <i>dd</i>)	1.23, 1.18, 1.16 (3 <i>s</i>)	3.50 (<i>s</i> , MeO)
21^{d)}	4.66 (<i>dd</i>)	2.31–2.22 (<i>m</i>)	1.76–1.61 (<i>m</i>)	5.08–4.93 (<i>m</i>)	5.08–4.93 (<i>m</i>)	3.64 (<i>ddd</i>)	4.22, 4.05 (2 <i>dd</i>)	1.22, 1.17, 1.14 (3 <i>s</i>)	3.96 (<i>sept.</i> , Me ₂ CH); 1.23, 1.15 (2 <i>d</i> , Me ₂ CH)

^{a)} H_{eq}–C(2) of **6** and **12-21**. ^{b)} H_{ax}–C(2) of **6** and **12-21**. ^{c)} At 400 MHz. ^{d)} At 270 MHz.

Table 3. ¹H-NMR (CDCl₃) Coupling Constants [Hz] of Compounds **5–9** and **12–21**

	<i>J</i> (1,2) ^a	<i>J</i> (1,2') ^b	<i>J</i> (2,2')	<i>J</i> (2,3) ^a	<i>J</i> (2',3) ^b	<i>J</i> (3,4)	<i>J</i> (4,5)	<i>J</i> (5,6)	<i>J</i> (5,6')	<i>J</i> (6,6')	Others
5	6.2	–	–	3.1	–	5.9	5.9	5.2	2.3	11.1	<i>J</i> (1,3) = 1.2
6	1.1	3.2	12.9	5.2	11.5	9.8	9.8	2.0	4.3	12.3	<i>J</i> (1,OH) = 3.3, <i>J</i> (2ax,OH) = 2.2 <i>J</i> (5,OH) = 5.4
(<i>E/Z</i>)- 7	5.7, 5.8	5.7, 4.9	^c , 16.0	^c , 9.0	^c , 4.9	^c	^c	2.2	4.8	12.0	
(<i>E</i>)- 8	–	–	16.1	5.9	9.0	8.2	8.7	3.5	3.5	^c	
(<i>Z</i>)- 8	–	–	15.5	4.9	6.7	^c	^c	^c	^c	^c	
(<i>E</i>)- 9	–	–	17.3	5.8	7.5	7.4	7.4	^c	^c	^c	
(<i>Z</i>)- 9	–	–	16.2	4.4	5.1	4.7	7.7	^c	^c	^c	<i>J</i> (2',4) = 0.7
12	1.1	3.6	13.2	5.3	11.5	9.6	^c	^c	^c	^c	
14	< 1.5	3.5	12.9	5.3	11.5	9.6	9.6	^c	^c	^c	
16	1.0	4.0	13.6	5.4	11.4	9.6	9.6	^c	^c	^c	<i>J</i> (H,F) = 5.8
18	1.1	3.6	12.9	5.3	11.6	9.5	10.0	2.2	5.4	12.1	
20	1.0	3.7	12.9	5.3	11.6	9.6	^c	^c	^c	^c	<i>J</i> (Me ₂ CH, Me ₂ CH) = 6.3
13	2.3	9.2	12.7	4.8	9.1	9.2	9.1	2.1	7.1	12.1	
15	2.1	^c	12.6	4.8	^c	^c	^c	2.0	7.0	12.0	
17	2.0	9.4	12.4	5.0	11.0	9.6	9.6	2.0	5.6	12.0	<i>J</i> (H,F) = 5.8
19	2.0	9.6	^c	^c	^c	^c	^c	2.1	6.2	12.1	
21	2.0	9.6	^c	^c	^c	^c	9.2	2.0	6.6	11.9	<i>J</i> (Me ₂ CH, Me ₂ CH) = 6.3

^a) *J*(1,2eq) and *J*(2eq,3) of **6** and **12–21**, respectively. ^b) *J*(1,2ax) and *J*(2ax,3) of **6** and **12–21**, respectively.^c) Not determined.

(*E/Z*)-2-Deoxy-3,4,6-tri-*O*-pivaloyl-D-arabino-hexose Oximes (**7**). NH₂OH·HCl (1.04 g, 15 mmol) was added to a mixture of **6** (2.00 g, 4.8 mmol) and NaHCO₃ (1.26 g, 15 mmol) in 60% aq. dioxane (25 ml). The mixture was stirred at r.t. for 12 h. After evaporation, normal workup (AcOEt/hexane 3:1) and FC (AcOEt/hexane 1:3) gave 1.83 g (91%) of **7**. Oil. *R*_f (AcOEt/hexane 1:2) 0.40, 0.32. IR: 3590*m*, 3450*w* (br.), 2980*s*, 2940*m*, 2910*m*, 2880*m*, 1730*s*, 1480*s*, 1460*m*, 1400*m*, 1370*m*, 1280*s*, 1250–1190*m*, 1145*s* (br.), 1080*m* (br.), 1035*m*, 995*w*, 940*m*, 920*m* (sh), 885*m*. ¹H-NMR (300 MHz, CDCl₃, (*E*)/(*Z*) 1:1): *Tables 2* and *3*. ¹³C-NMR (50.6 MHz, CDCl₃): *Table 4*. CI-MS: 432 ([*M* + 1]⁺). Anal. calc. for C₂₁H₃₃NO₈ (431.53): C 58.45, H 8.64, N 3.24; found: C 58.56, H 8.38, N 3.09.

(*E*)- and (*Z*)-2-Deoxy-3,4,6-tri-*O*-pivaloyl-D-arabino-hexonhydroximo-1,5-lactone (**8**). A soln. of K₂HPO₄ (404 mg, 2.32 mmol) in H₂O (12.9 ml) was added dropwise to a soln. of **7** (1.0 g, 2.32 mmol) in MeOH (64.3 ml). The mixture was heated to 60°, treated with PhIO (974 mg, 4.43 mmol), and stirred at 60° for 15 min. After evaporation, normal workup (AcOEt) gave a pale yellow oil which crystallised from hexane (15 ml): 540 mg of pure (*E*)-**8**. FC of the mother liquor (CH₂Cl₂/MeOH 150:1) gave further 154 mg of (*E/Z*)-**8** (total yield: 70%). In soln., (*E*)-**8** slowly isomerised to (*Z*)-**8**. In CDCl₃ soln., pure (*E*)-**8** gave a 1:1 (*E/Z*)-mixture after 3 h at r.t. and a 1:2 (*E/Z*)-mixture after 20 h at 0°. *R*_f (CHCl₃/MeOH 50:1) 0.37 ((*E*)-**8**), 0.35 ((*Z*)-**8**). M.p. 129–130° ((*E*)-**8**). [*α*]_D²⁰ = +25.1 → +14.7 (*c* = 1.04, CHCl₃). IR: 3590*w*, 3430*w* (sh), 3310*w* (br.), 3140*w* (sh), 2980*s*, 2940*m*, 2920*m*, 2880*m*, 1735*s*, 1675*m*, 1480*m*, 1460*m*, 1400*m*, 1370*m*, 1335*w*, 1280*s*, 1260*m* (sh), 1245–1200*m*, 1140*s* (br.), 1095*m*, 1040*m*, 1015*m* (sh), 1000*m*, 945*m*, 895*w*, 870*w* (sh). ¹H-NMR (300 MHz, CDCl₃, (*E*)/(*Z*) 1:1): *Tables 2* and *3*. ¹³C-NMR (50.6 MHz, CDCl₃, 0°; (*E*)/(*Z*) 1:2): *Table 4*. CI-MS: 430 ([*M* + 1]⁺). Anal. calc. for C₂₁H₃₃NO₈ (429.51): C 58.73, H 8.21, N 3.26; found: C 58.82, H 8.00, N 3.05.

(2-Deoxy-3,4,6-tri-*O*-pivaloyl-D-arabino-hexopyranosylidene)amino Methanesulfonate (**9**). A soln. of (*E*)-**8** (1.0 g, 2.33 mmol) in CH₂Cl₂ was left for 24 h at 0° (→(*E/Z*) = 2:8 to 1:9), treated with methanesulfonyl chloride (0.22 ml, 2.80 mmol) and Et₃N (0.49 ml, 3.50 mmol), and stirred at 0° for 5 min. After the addition of H₂O, stirring was continued for 1 h. Dilution with CH₂Cl₂ (25 ml), normal workup (CH₂Cl₂), and FC (AcOEt/hexane 1:3) gave crystalline (*E*)-**9** (184 mg, 16%) and crystalline (*Z*)-**9** (877 mg, 74%).

Data of (*E*)-**9**: *R*_f (AcOEt/hexane 1:2) 0.47. M.p. 178–179° (dec.). [*α*]_D²⁰ = +41.7 (*c* = 1.08, CHCl₃). IR: 3030*w* (br.), 2980*s*, 2940*m*, 2920*w*, 2880*w*, 1740*s*, 1660*m*, 1480*m*, 1460*m*, 1400*m*, 1370*s*, 1330*m*, 1280*s*, 1245–1195*m*, 1180*s*, 1165*s* (sh), 1135*s* (br.), 1090*m*, 1040*m*, 1020*w*, 1000*w*, 970*m*, 940*w*, 890*w* (sh), 860*m*, 850*m*, 830*m*, 790–740*m*, 710*m*, 665*m*. ¹H-NMR (300 MHz, CDCl₃): *Tables 2* and *3*. ¹³C-NMR (50.6 MHz, (D₆)acetone): *Table 4*. FAB-MS: 508

Table 4. ^{13}C -NMR (50.6 MHz, CDCl_3) Chemical Shifts [ppm] of Compounds **5-9** and **12-21**

	C(1)	C(2)	C(3), C(4), C(5)	C(6)	MsO or aglycone	Pivaloyl groups
5	145.59 (<i>d</i>)	99.05 (<i>d</i>)	74.12, 67.50, 66.62 (3 <i>d</i>)	61.30 (<i>t</i>)	–	178.10, 177.77, 176.54 (3 <i>s</i> , 3 CO); 38.84 (<i>s</i> , Me_3C); 38.71 (<i>s</i> , 2 Me_3C); 27.09, 27.03, 26.97 (3 <i>q</i> , 3 Me_3C)
6	91.60 (<i>d</i>)	35.28 (<i>t</i>)	68.63, 68.60, 68.36 (3 <i>d</i>)	62.17 (<i>t</i>)	–	178.31, 177.53, 176.70 (3 <i>s</i> , CO); 38.87, 38.73, 38.64 (3 <i>s</i> , 3 Me_3C); 27.05 (<i>q</i> , 3 Me_3C)
(<i>E/Z</i>)- 7	146.80 (<i>d</i>) 146.70 (<i>d</i>)	31.83 (<i>t</i>) 26.04 (<i>t</i>)	71.83 (2 <i>C</i>), 68.94, 68.71, 67.76, 67.69 (5 <i>d</i>)	64.35 (<i>t</i>)	–	179.13, 178.66, 177.05, 177.02 (4 <i>s</i> , CO); 39.08, 39.04, 38.95, 38.84 (4 <i>s</i> , Me_3C); 27.21, 27.04, 26.93 (3 <i>q</i> , Me_3C)
(<i>E</i>)- 8	158.61 (<i>s</i>)	23.48 (<i>t</i>)	68.21, 67.19, 76.28 ^a (3 <i>d</i>)	61.74 (<i>t</i>)	–	177.94 (<i>s</i> , CO); 177.25 (<i>s</i> , CO, (<i>E</i>)- 8); 177.14 (<i>s</i> , CO, (<i>Z</i>)- 8); 176.45 (<i>s</i> , CO); 38.87, 38.76, 38.71 (3 <i>s</i> , 3 Me_3C); 27.06, 26.95 (<i>q</i> , 3 Me_3C)
(<i>Z</i>)- 8	150.23 (<i>s</i>)	29.19 (<i>t</i>)	68.63, 67.69, 76.15 ^b (3 <i>d</i>)	61.74 (<i>t</i>)	–	177.75, 177.25, 176.74 (3 <i>s</i> , 3 CO); 39.36, 39.28, 39.19 (3 <i>s</i> , Me_3C); 27.30 (<i>q</i> , Me_3C); 27.18 (<i>q</i> , 2 Me_3C)
(<i>E</i>)- 9 ^c	168.99 (<i>s</i>)	27.57 (<i>t</i>)	68.68, 67.90, 77.36 ^d (3 <i>d</i>)	62.12 (<i>t</i>)	36.29 (<i>q</i>)	177.76, 176.82, 176.42 (3 <i>s</i> , 3 CO); 38.85 (<i>s</i> , Me_3C); 38.75 (<i>s</i> , 2 Me_3C); 26.99 (<i>q</i> , Me_3C); 26.88 (<i>q</i> , 2 Me_3C)
(<i>Z</i>)- 9	157.44 (<i>s</i>)	28.18 (<i>t</i>)	67.67, 67.56, 77.20 ^b (3 <i>d</i>)	61.40 (<i>t</i>)	35.93 (<i>q</i>)	177.87, 177.53, 176.73 (3 <i>s</i> , 3 CO); 38.78 (<i>s</i> , Me_3C); 38.70 (<i>s</i> , 2 Me_3C); 27.04 (<i>q</i> , 2 Me_3C); 29.96 (<i>q</i> , Me_3C)
12	95.44 (<i>d</i>)	34.76 (<i>t</i>)	69.89, 68.11, 68.07 (3 <i>d</i>)	62.10 (<i>t</i>)	160.98 (<i>s</i>); 142.62 (<i>s</i>); 125.73 (<i>d</i> , 2 C); 116.32 (<i>d</i> , 2 C)	177.91, 177.47, 176.79 (3 <i>s</i> , 3 CO); 38.81, 38.78, 38.71 (3 <i>s</i> , 3 Me_3C); 27.08 (<i>q</i> , Me_3C); 27.02 (<i>q</i> , 2 Me_3C)
13	96.48 (<i>d</i>)	35.36 (<i>t</i>)	73.05, 69.44, 67.90 (3 <i>d</i>)	62.58 (<i>t</i>)	161.41 (<i>s</i>); 142.80 (<i>s</i>); 125.67 (<i>d</i> , 2 C); 116.35 (<i>d</i> , 2 C)	178.13, 177.59, 176.89 (3 <i>s</i> , 3 CO); 38.81 (<i>s</i> , 2 Me_3C); 38.74 (<i>s</i> , Me_3C); 27.10 (<i>q</i> , 3 Me_3C)
14 ^c	96.03 (<i>d</i>)	35.27 (<i>t</i>)	69.04, 68.68, 68.59 (3 <i>d</i>)	62.48 (<i>t</i>)	154.97 (<i>s</i>); 150.46 (<i>s</i>); 117.59 (<i>d</i> , 2 C); 114.63 (<i>d</i> , 2 C); 55.70 (<i>q</i> , MeO)	178.07, 177.54, 176.84 (3 <i>s</i> , 3 CO); 38.80 (<i>s</i> , 2 Me_3C); 38.71 (<i>s</i> , Me_3C); 27.11 (<i>q</i> , Me_3C); 27.05 (<i>q</i> , 2 Me_3C)
15	98.31 (<i>d</i>)	35.99 (<i>t</i>)	72.62, 70.08, 68.33 (3 <i>d</i>)	62.75 (<i>t</i>)	155.30 (<i>s</i>); 150.96 (<i>s</i>); 118.18 (<i>d</i> , 2 C); 114.45 (<i>d</i> , 2 C); 55.62 (<i>q</i> , MeO)	177.99, 177.38, 176.68 (3 <i>s</i> , 3 CO); 38.85, 38.82, 38.69 (3 <i>s</i> , 3 Me_3C); 27.05 (<i>q</i> , 3 Me_3C)
16 ^c	98.99 (<i>d</i>)	34.27 (<i>t</i>)	70.03, 67.85, 67.75 (3 <i>d</i>)	61.87 (<i>t</i>)	72.31 (<i>sept.</i> , <i>J</i> = 33); 121.57 (<i>q</i> , <i>J</i> = 282); 121.07 (<i>q</i> , <i>J</i> = 284)	177.97, 177.50, 176.60 (3 <i>s</i> , 3 CO); 38.82, 38.78, 38.69 (3 <i>s</i> , 3 Me_3C); 27.01 (<i>q</i> , Me_3C); 26.97 (<i>q</i> , 2 Me_3C)
17 ^c	98.65 (<i>d</i>)	35.55 (<i>t</i>)	72.81, 69.51, 67.82 (3 <i>d</i>)	61.69 (<i>t</i>)	71.70 (<i>sept.</i> , <i>J</i> = 33); 121.54 (<i>q</i> , <i>J</i> = 284); 120.57 (<i>q</i> , <i>J</i> = 287)	178.11, 177.38, 176.84 (3 <i>s</i> , 3 CO); 38.85, 38.76, 38.64 (3 <i>s</i> , 3 Me_3C); 27.15 (<i>q</i> , Me_3C); 27.06 (<i>q</i> , 2 Me_3C)
18 ^c	97.97 (<i>d</i>)	35.01 (<i>t</i>)	68.77, 68.72, 68.23 (3 <i>d</i>)	62.54 (<i>t</i>)	54.81 (<i>q</i>)	178.17, 177.61, 176.80 (3 <i>s</i> , 3 CO); 38.83, 38.78, 38.67 (3 <i>s</i> , 3 Me_3C); 27.10, 27.05, 27.01 (3 <i>q</i> , 3 Me_3C)
19 ^c	100.45 (<i>d</i>)	36.05 (<i>t</i>)	72.36, 70.32, 68.57 (3 <i>d</i>)	62.57 (<i>t</i>)	56.71 (<i>q</i>)	178.15, 177.48, 176.89 (3 <i>s</i> , 3 CO); 38.83, 38.76, 38.64 (3 <i>s</i> , 3 Me_3C); 27.12 (<i>q</i> , Me_3C); 27.08 (<i>q</i> , 2 Me_3C)
20 ^c	94.72 (<i>d</i>)	35.64 (<i>t</i>)	69.00, 68.97, 68.36 (3 <i>d</i>)	62.73 (<i>t</i>)	69.06 ^d (<i>d</i>); 23.33, 21.28 (2 <i>q</i>)	178.15, 177.65, 176.85 (3 <i>s</i> , 3 CO); 38.80 (<i>s</i> , 2 Me_3C); 38.67 (<i>s</i> , Me_3C); 27.08, 27.05, 26.99 (3 <i>q</i> , 3 Me_3C)
21 ^c	97.54 (<i>d</i>)	36.70 (<i>t</i>)	72.27, 70.55, 68.68 (3 <i>d</i>)	62.75 (<i>t</i>)	71.39 ^e (<i>d</i>); 23.42, 21.76 (2 <i>q</i>)	

^a) Assigned to C(5). ^b) In (D_6)acetone. ^c) At 68 MHz. ^d) Assignment based upon a ^1H , ^{13}C -COSY spectrum. ^e) Assignment may be interchanged with a value for C(3), C(4), C(5).

($[M + 1]^+$). Anal. calc. for $C_{22}H_{37}NO_{10}S$ (507.60): C 52.06, H 7.35, N 2.76, S 6.32; found: C 52.20, H 7.29, N 2.74, S 6.08.

Data of (Z)-9: R_f (AcOEt/hexane 1:2) 0.34. M.p. 111–112°. $[\alpha]_D^{20} = -4.2$ ($c = 0.81$, $CHCl_3$). IR: 3030w (br.), 2980s, 2940m, 2920m, 2880w, 1740s, 1660m, 1480m, 1460m, 1400m, 1370s, 1330m, 1280s, 1245–1195m, 1180s, 1165s(sh), 1135s (br.), 1090m (sh), 1040m, 1020w, 1000w, 970m, 940w, 895w (sh), 860m, 850m, 830m, 810–710m, 665w. 1H -NMR (300 MHz, $CDCl_3$): *Tables 2 and 3*. ^{13}C -NMR (50.6 MHz, $CDCl_3$): *Table 4*. CI-MS: 508 ($[M + 1]^+$). Anal. calc. for $C_{22}H_{37}NO_{10}S$ (507.60): C 52.06, H 7.35, N 2.76, S 6.32; found: C 52.16, H 7.41, N 2.58, S 6.06.

Isomerisation of (E)-9 to (Z)-9. A soln. of (*E*)-9 (100 mg, 0.20 mmol) in CH_2Cl_2 (20 ml) was treated with 10% HCl/MeOH (0.1 ml) for 3 h at r.t. Normal workup (CH_2Cl_2) and FC (AcOEt/hexane 1:3) gave 85 mg (85%) of spontaneously crystallising (*Z*)-9.

Transformation of (Z)-9 into 11 and Glycosidations with Phenols and Alcohols. A soln. of (*Z*)-9 (50 mg, 0.099 mmol) in dioxane (5 ml) was treated with 5M NH_3 in MeOH (3 ml) and stirred at 0° for 48 h. After evaporation of half of the solvent, the remaining soln. was lyophilised at –15 to –10° for 1.5 h. The residue was treated with cyclohexane (5 ml). The precipitate (NH_4OMs) was filtered off and the filtrate lyophilised for 1.5 h at –15 to –10°. A cooled (–25°) soln. of the residue (**10**) in pentane (5 ml) was treated with a soln. of I_2 (25 mg, 0.099 mmol) in Et_2O (1 ml) and with Et_3N (0.11 ml, 0.79 mmol) and stirred for 20 min at –25°. Precipitated (Et_3NH)I was filtered off and the filtrate evaporated at –40 to –30° *in vacuo*. The residue (**11**) was dried at –15 to –10°/high vacuum for 1.5 h, dissolved in dioxane and/or toluene (0.5 ml), treated with 1 equiv. of the glycosyl acceptor (4-nitrophenol, 4-methoxyphenol, $(CF_3)_2CHOH$, MeOH, or *i*-PrOH), and stirred for the mentioned period at 18° or 40° (*Table 1*).

4-Nitrophenyl 2-Deoxy-3,4,6-tri-O-pivaloyl- α - and - β -D-arabino-hexopyranoside (12 and 13). After evaporation of the solvent, the products were separated by FC (AcOEt/hexane 1:3) and dried under high vacuum.

Data of 12: R_f (AcOEt/hexane 1:6) 0.35. M.p. 108–109°. $[\alpha]_D^{20} = +161.3$ ($c = 0.3$, $CHCl_3$). IR: 3030w (sh), 2980s, 2940m, 2920w, 2880w, 1730s, 1615m, 1600s, 1520m, 1510m (sh), 1495m, 1480m, 1460m, 1400w, 1370m, 1350s, 1330m (sh), 1310m, 1280s, 1245–1200m, 1150s, 1125s (sh), 1115s, 1095m, 1040m, 1020m, 1000m (sh), 975s, 940w, 900w (sh), 885w, 870m, 850m. 1H -NMR (300 MHz, $CDCl_3$): *Tables 2 and 3*. ^{13}C -NMR (50.6 MHz, $CDCl_3$): *Table 4*. FAB-MS: 538 ($[M + 1]^+$). Anal. calc. for $C_{27}H_{39}NO_{10}$ (537.61): C 60.32, H 7.31, N 2.61; found: C 60.53, H 7.22, N 2.57.

Data of 13: R_f (AcOEt/hexane 1:6) 0.31. M.p. 158–159°. $[\alpha]_D^{20} = -59.7$ ($c = 0.32$, $CHCl_3$). IR: 3030w (sh), 2980m, 2940m, 2910w, 2880m, 1730s, 1615m, 1600m, 1520m, 1510m (sh), 1495m, 1480m, 1460m, 1395m, 1370m, 1350s, 1330m (sh), 1280s, 1250–1200s, 1140s (br.), 1115s, 1070s, 1040m, 1020w (sh), 1000m, 970w, 945w, 915w, 900w, 865m, 850m. 1H -NMR (300 MHz, $CDCl_3$): *Tables 2 and 3*. ^{13}C -NMR (50.6 MHz, $CDCl_3$): *Table 4*. FAB-MS: 538 ($[M + 1]^+$). Anal. calc. for $C_{27}H_{39}NO_{10}$ (537.61): C 60.32, H 7.31, N 2.61; found: C 60.52, H 7.50, N 2.63.

4-Methoxyphenyl 2-Deoxy-3,4,6-tri-O-pivaloyl- α - and - β -D-arabino-hexopyranoside (14 and 15). After evaporation of the solvent, the products were separated by FC (Et_2O /hexane 1:10→1:8) and dried under high vacuum.

Data of 14: R_f (AcOEt/hexane 1:6) 0.43. M.p. 79–83°. $[\alpha]_D^{20} = +124.0$ ($c = 0.2$, $CHCl_3$). IR: 3030w, 2970m, 2940w, 2910w, 2870w, 2830w, 1730s, 1505s, 1480m, 1460m, 1440w, 1370w, 1350w, 1280m, 1220m, 1195m, 1150s, 1120m, 1095m, 1040m, 1020w, 1005w, 980m, 960w, 910w, 895w, 880w, 860w, 830w. 1H -NMR (300 MHz, $CDCl_3$): *Tables 2 and 3*. ^{13}C -NMR (68 MHz, $CDCl_3$): *Table 4*. FAB-MS: 522 (M^+). Anal. calc. for $C_{28}H_{42}O_9$ (522.63): C 64.10, H 8.25; found: C 64.35, H 8.10.

Data of 15: R_f (AcOEt/hexane 1:6) 0.36. M.p. 113–114°. $[\alpha]_D^{20} = -34.5$ ($c = 0.2$, $CHCl_3$). IR: 3020w, 2970m, 2940w, 2910w, 2870w, 2830w, 1725s, 1505s, 1480m, 1460m, 1440w, 1400w, 1370w, 1320w, 1280m, 1225m, 1155s, 1065s, 1040m, 990w, 965w, 940w, 910w, 895w, 865w, 830w. 1H -NMR (300 MHz, $CDCl_3$): *Tables 2 and 3*. ^{13}C -NMR (50.6 MHz, $CDCl_3$): *Table 4*. FAB-MS: 522 (M^+). Anal. calc. for $C_{27}H_{42}O_9$ (522.63): C 64.10, H 8.25; found: C 64.12, H 8.11.

2,2,2-Trifluoro-1-(trifluoromethyl)ethyl 2-Deoxy-3,4,6-tri-O-pivaloyl- α - and - β -D-arabino-hexopyranoside (16 and 17). After evaporation of the solvent, the products were separated by FC (AcOEt/hexane 1:30→1:20) and dried under high vacuum.

Data of 16: R_f (AcOEt/hexane 1:6) 0.52. M.p. 102–103°. $[\alpha]_D^{20} = +101.0$ ($c = 0.2$, $CHCl_3$). IR: 3030w, 2970m, 2940w, 2910w, 2880w, 1735s, 1480m, 1460w, 1400w, 1370m, 1290s, 1265m, 1225m, 1195s, 1155s, 1140s, 1105s, 1090s, 1040w, 1020w, 1000w, 975m, 940w, 900w, 885w, 685w. 1H -NMR (400 MHz, $CDCl_3$): *Tables 2 and 3*. ^{13}C -NMR (68 MHz, $CDCl_3$): *Table 4*. FAB-MS: 567 ($[M + 1]^+$). Anal. calc. for $C_{24}H_{36}F_6O_8$ (566.53): C 50.88, H 6.40, F 20.12; found: C 51.12, H 6.58, F 20.09.

Data of 17: R_f (AcOEt/hexane 1:6) 0.42. M.p. 157–158°. $[\alpha]_D^{20} = -15.0$ ($c = 0.2$, $CHCl_3$). IR: 3030w, 2980m, 2940w, 2920w, 2880w, 1730s, 1480m, 1460w, 1415w, 1400w, 1375m, 1290s, 1270m, 1230m, 1195s, 1140s, 1120s,

1105s, 1080m, 1045w, 1000w, 970w, 940w, 900w, 885w, 690w. ¹H-NMR (400 MHz, CDCl₃): *Tables 2 and 3*. ¹³C-NMR (68 MHz, CDCl₃): *Table 4*. FAB-MS: 567 ([*M* + 1]⁺). Anal. calc. for C₂₄H₃₆F₆O₈ (566.53): C 50.88, H 6.40, F 20.12; found: C 50.66, H 6.64, F 20.41.

Methyl 2-Deoxy-3,4,6-tri-O-pivaloyl-α- and -β-D-arabino-hexopyranoside (18 and 19). After evaporation of the solvent, the products were purified by CPC and then by FC (AcOEt/hexane 1:20). Removal of solvents and drying under high vacuum gave oily **18** and crystalline **19**.

Data of 18: *R*_f (AcOEt/hexane 1:6) 0.41. [α]_D²⁰ = +89.6 (*c* = 0.27, CHCl₃). IR: 3030w, 2980m, 2940m, 2910w, 2880w, 2840w, 1730s, 1480m, 1465w, 1450w, 1400w, 1370w, 1305w, 1285m, 1230w, 1160s, 1130s, 1095w, 1045m, 1020w, 1005w, 970w, 945w, 920w, 900w, 870w. ¹H-NMR (300 MHz, CDCl₃): *Tables 2 and 3*. ¹³C-NMR (68 MHz, CDCl₃): *Table 4*. FAB-MS: 431 ([*M* + 1]⁺). Anal. calc. for C₂₂H₃₈O₈ (430.54): C 61.37, H 8.90; found: C 61.68, H 8.93.

Data of 19: *R*_f (AcOEt/hexane 1:6) 0.33. M.p. 124–145°. [α]_D²⁰ = –10.8 (*c* = 0.24, CHCl₃). IR: 3030w, 2980m, 2950w, 2920w, 2890w, 2850w, 1730s, 1480m, 1465w, 1455w, 1400w, 1375w, 1325w, 1285m, 1220w (br.), 1150s, 1110w, 1090w, 1045m, 1020w, 1010w, 990w, 960w, 945w, 915w, 895w, 870w. ¹H-NMR (300 MHz, CDCl₃): *Tables 2 and 3*. ¹³C-NMR (68 MHz, CDCl₃): *Table 4*. FAB-MS: 431 ([*M* + 1]⁺). Anal. calc. for C₂₂H₃₈O₈ (430.54): C 61.37, H 8.90; found: C 61.25, H 8.93.

Isopropyl 2-Deoxy-3,4,6-tri-O-pivaloyl-α- and -β-D-arabino-hexopyranoside (20 and 21). After evaporation of the solvent, the products were purified by CPC and then by FC (AcOEt/hexane 1:30). Removal of solvent and drying gave crystalline **20** and **21**.

Data of 20: *R*_f (AcOEt/hexane 1:6) 0.52. M.p. 87–88°. [α]_D²⁰ = +97.0 (*c* = 0.3, CHCl₃). IR: 3040w, 2980s, 2950w, 2920w, 2880w, 1730s, 1485m, 1465m, 1400w, 1390w, 1375m, 1340w, 1305m, 1285s, 1235w, 1160s, 1130s (sh), 1090m, 1045m, 1020m, 1005s, 980w, 970w, 920w, 900w, 870w, 850w, 835w. ¹H-NMR (270 MHz, CDCl₃): *Tables 2 and 3*. ¹³C-NMR (68 MHz, CDCl₃): *Table 4*. FAB-MS: 459 ([*M* + 1]⁺). Anal. calc. for C₂₄H₄₂O₈ (458.59): C 62.86, H 9.23; found: C 62.56, H 9.23.

Data of 21: *R*_f (AcOEt/hexane 1:6) 0.49. M.p. 111–113°. [α]_D²⁰ = –17.7 (*c* = 0.3, CHCl₃). IR: 3030w, 2980m, 2940m, 2910w, 2880w, 1730s, 1480m, 1465w, 1400w, 1385w, 1370w, 1320w, 1285m, 1230w, 1160s, 1145s, 1090w, 1065m, 1040w, 1020w, 990w, 965w, 940w, 920w, 900w. ¹H-NMR (270 MHz, CDCl₃): *Tables 2 and 3*. ¹³C-NMR (68 MHz, CDCl₃): *Table 4*. FAB-MS: 459 ([*M* + 1]⁺). Anal. calc. for C₂₄H₄₂O₈ (458.59): C 62.86, H 9.23; found: C 63.02, H 9.19.

REFERENCES

- [1] K. Briner, A. Vasella, *Helv. Chim. Acta* **1989**, *72*, 1371.
- [2] K. Briner, A. Vasella, *Helv. Chim. Acta* **1990**, *73*, 1364.
- [3] K. Briner, A. Vasella, *Helv. Chim. Acta* **1992**, *75*, 621.
- [4] A. Vasella, *Pure Appl. Chem.* **1991**, *63*, 507.
- [5] H. Paulsen, *Angew. Chem.* **1982**, *94*, 184.
- [6] S. J. Danishefsky, D. M. Armistead, F. E. Wincott, H. G. Selnick, R. Hungate, *J. Am. Chem. Soc.* **1989**, *111*, 2967.
- [7] D. Beer, A. Vasella, *Helv. Chim. Acta* **1985**, *68*, 2254.
- [8] B. Bernet, A. Vasella, unpublished results.
- [9] R. Meuwly, A. Vasella, *Helv. Chim. Acta* **1985**, *68*, 997.
- [10] S. E. Mangholz, A. Vasella, *Helv. Chim. Acta* **1991**, *74*, 2100.
- [11] S. Fritsch, A. Vasella, *Helv. Chim. Acta* **1991**, *74*, 2024.