117. Glycosylidene Carbenes

Part 7

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

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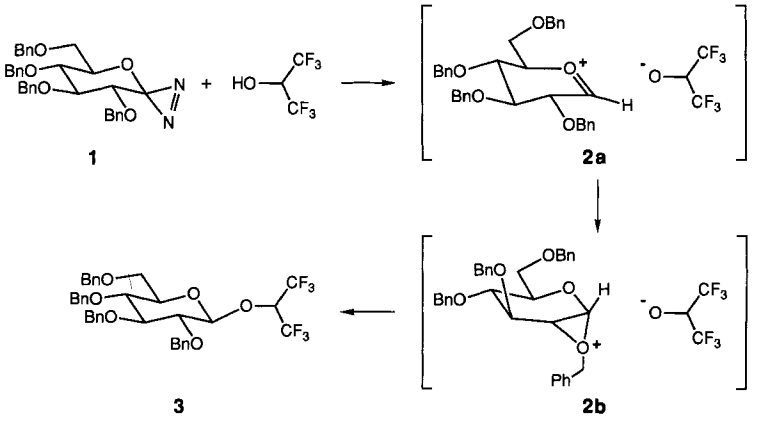
(22.V.92)

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, $(CF_3)_2CHOH$, 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*)-configurated 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 $(CF_3)_2CHOH$ and $(CF_3)_2C(Me)OH$, 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



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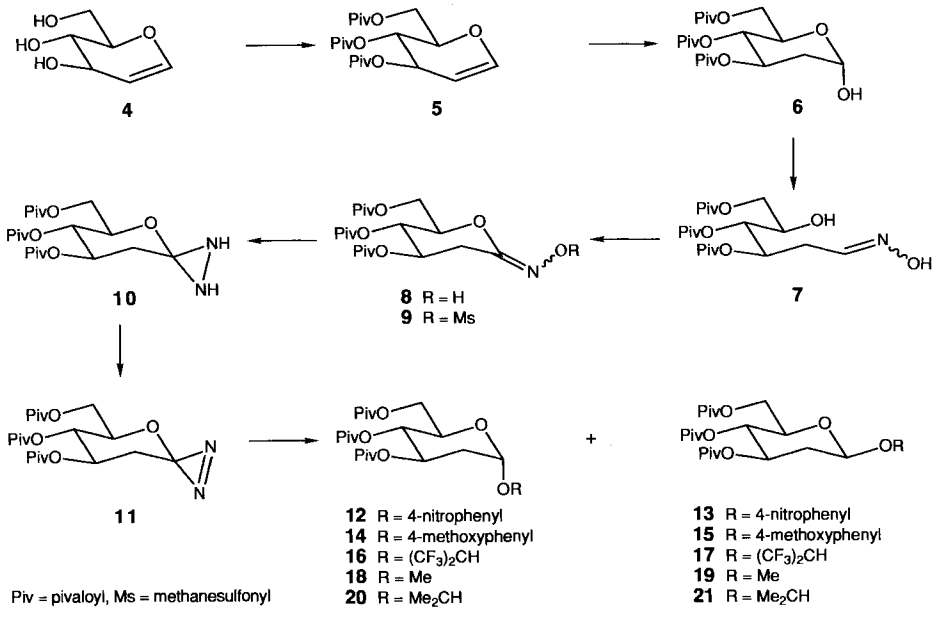
This leads to an initially non-solvated ion-pair **2a**. If the reaction is run in a non-nucleophilic solvent, the neighbouring benzyloxy group – rather than the solvent – may participate in the stabilisation of the oxycarbenium ion [3] [4] leading – in the extreme case – to an oxiranium alkoxide ion 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-configurated (*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, $(CF_3)_2CHOH$, 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

Scheme 2



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 ^{1}H-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 CH_2Cl_2 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 NH_3 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 I_2 in the presence of Et_3N. After removal of $(Et_3NH)I$, 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_2Cl_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
$(CF_3)_2CHOH$	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 $(CF_3)_2CHOH$. Glycosidation of MeOH and of i-PrOH proceeded diastereounselectively.

For the assignment of the ^{1}H- 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 $(CF_3)_2CHOH$, 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 $(CF_3)_2CHOH$ 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* cartriges; 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. ^{1}H- 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: 2960*m*, 2930*m*, 2910*m*, 2870*m*, 1725*s*, 1645*m*, 1475*m*, 1460*m*, 1395*w*, 1365*m*, 1275*s*, 1250–1200*m*, 1140*s*, 1100*m*, 1060*m*, 1030*m*, 965*m* (br.), 940*w*, 890*w*, 865*w* (sh). ^{1}H-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 $C_{21}H_{34}O_7$ (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 $CDCl_3/D_2O$ (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: 3600*w*, 3420*w* (br.), 2980*s*, 2940*m*, 2910*m*, 2880*m*, 1730*s*, 1480*s*, 1460*m*, 1400*m*, 1370*m*, 1280*s*, 1250–1195*m*, 1150*s* (br.), 1080*s*, 1040*m*, 1020*m*, 990*s*, 940*w*, 915*w*, 895*w*, 885*w* (sh), 870*w* (sh). ^{1}H-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 $C_{21}H_{36}O_8$ (416.51): C 60.56, H 8.71; found: C 60.80, H 8.50.

Table 2. *^{1}H-NMR* (300 MHz, $CDCl_3$) *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)	*t*-Bu	Others
5	6.46 (*dd*)	4.82 (*dd*)	–	5.33–5.30 (*m*)	5.27 (*t*)	4.30–4.25 (*m*)	4.33, 4.21 (2*dd*)	1.23, 1.19, 1.18 (3*s*)	–
6	5.42 (br. *t*)	2.28 (*ddd*)	1.77 (*dddd*)	5.37 (*ddd*)	5.10 (*t*)	4.25 (*ddd*)	4.19, 4.11 (2*dd*)	1.23, 1.17, 1.15 (3*s*)	2.75 (*dd*, exchange with D_2O, OH)
7	7.36 (*t*, (*E*)) 6.72 (‘*t*’, (*Z*))	2.76 (*ddd*, (*Z*)) 2.47–2.43 (*m*, (*E*))	2.51 (*td*, (*Z*))	5.56–5.49 (*m*)	5.11–5.05 (*m*)	3.71–3.64 (*m*)	4.18, 4.05 (2*dd*)	1.26, 1.25 (2 ×), 1.24, 1.22 (2 ×) (4*s*)	7.63 (br. *s*), 7.28 (*s*, exchange with D_2O, NOH); 3.46, 3.37 (2*d*, exchange with D_2O, OH–C(5))
(*E*)-**8**	–	3.45 (*dd*)	2.50 (*dd*)	5.20–5.08 (*m*)	5.26 (*t*)	4.11 (*td*)	4.26 (*d*)	1.23, 1.19, 1.18 (3*s*)	7.16 (*s*, NOH)
(*Z*)-**8**	–	2.90 (*dd*)	2.53 (*dd*)	5.20–5.08 (*m*)	5.20–5.08 (*m*)	4.35–4.28 (*m*)	4.35–4.28 (*m*)	1.24, 1.20, 1.19 (3*s*)	7.18 (*s*, NOH)
(*E*)-**9**	–	3.36 (*dd*)	2.84 (*dd*)	5.16 (*dt*)	5.26 (*t*)	4.36–4.27 (*m*)	4.36–4.27 (*m*)	1.24, 1.20 (2 ×) (2*s*)	3.17 (*s*, MsO)
(*Z*)-**9**	–	2.96 (*dd*)	2.73 (*ddd*)	5.16 (*q*)	5.11 (br. *dd*)	4.47–4.24 (*m*)	4.47–4.24 (*m*)	1.25, 1.22, 1.21 (3*s*)	3.12 (*s*, MsO)
12	5.77 (br. *d*)	2.53 (*ddd*)	2.01 (*ddd*)	5.49 (*ddd*)	5.19–5.11 (*m*)	4.16–3.98 (*m*)	4.16–3.98 (*m*)	1.19, 1.18, 1.12 (3*s*)	8.24–8.18, 7.24–7.19 (2*m*, each 2 H, $O_2NC_6H_4O$)
14	5.56 (br. *d*)	2.46 (br. *dd*)	1.92 (*ddd*)	5.51 (*ddd*)	5.12 (*t*)	4.17–4.02 (*m*)	4.17–4.02 (*m*)	1.185, 1.18, 1.16 (3*s*)	7.07–7.02, 6.85–6.79 (2*m*, each 2 H, $MeOC_6H_4O$); 3.77 (*s*, MeO)
16[c])	5.16 (br. *d*)	2.39 (*ddd*)	1.82 (*ddd*)	5.19 (*ddd*)	5.04 (*t*)	4.10–3.97 (*m*)	4.10–3.97 (*m*)	1.15, 1.11, 1.08 (3*s*)	4.38 (*sept.*, $(CF_3)_2CHO$)
18	4.84 (br. *d*)	2.24 (*ddd*)	1.76 (*ddd*)	5.29 (*ddd*)	5.04 (*t*)	3.99 (*ddd*)	4.18, 4.11 (2*dd*)	1.24, 1.18, 1.15 (3*s*)	3.36 (*s*, MeO)
20[d])	5.07–4.97 (*m*)	2.17 (*ddd*)	1.77 (*ddd*)	5.31 (*ddd*)	5.07–4.97 (*m*)	4.18–4.01 (*m*)	4.18–4.01 (*m*)	1.22, 1.17, 1.14 (3*s*)	3.88 (*sept.*, Me_2CH); 1.22, 1.14 (2*d*, Me_2CH)
13	5.34 (*dd*)	2.57 (*ddd*)	2.11–2.00 (*m*)	5.14 (*dt*)	5.09 (*t*)	3.89 (*ddd*)	4.28, 4.09 (2*dd*)	1.22, 1.21, 1.19 (3*s*)	8.21–8.16, 7.12–7.07 (2*m*, each 2 H, $O_2NC_6H_4O$)
15	5.14–5.02 (*m*)	2.51 (*ddd*)	2.03–1.92 (*m*)	5.14–5.02 (*m*)	5.14–5.02 (*m*)	3.81–3.75 (*m*)	4.27, 4.08 (2*dd*)	1.22, 1.19, 1.18 (3*s*)	7.02–6.96, 6.82–6.77 (2*m*, each 2 H, $MeOC_6H_4O$); 3.78 (*s*, MeO)
17[c])	4.82 (*dd*)	2.41 (*ddd*)	1.72 (*ddd*)	5.01–4.93 (*m*)	5.02 (*t*)	3.62 (*ddd*)	4.20, 3.98 (2*dd*)	1.15, 1.10, 1.08 (3*s*)	4.48 (*sept.*, $(CF_3)_2CHO$)
19	4.49 (*dd*)	2.38–2.27 (*m*)	1.75–1.61 (*m*)	5.07–4.96 (*m*)	5.07–4.96 (*m*)	3.69–3.62 (*m*)	4.23, 4.10 (2*dd*)	1.23, 1.18, 1.16 (3*s*)	3.50 (*s*, MeO)
21[d])	4.66 (*dd*)	2.31–2.22 (*m*)	1.76–1.61 (*m*)	5.08–4.93 (*m*)	5.08–4.93 (*m*)	3.64 (*ddd*)	4.22, 4.05 (2*dd*)	1.22, 1.17, 1.14 (3*s*)	3.96 (*sept.*, Me_2CH); 1.23, 1.15 (2*d*, Me_2CH)

[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. *^{1}H-NMR* ($CDCl_3$) *Coupling Constants* [Hz] *of Compounds* **5–9** *and* **12–21**

	$J(1,2)$[a])	$J(1,2')$[b])	$J(2,2')$	$J(2,3)$[a])	$J(2',3)$[b])	$J(3,4)$	$J(4,5)$	$J(5,6)$	$J(5,6')$	$J(6,6')$	Others
5	6.2	–	–	3.1	–	5.9	5.9	5.2	2.3	11.1	$J(1,3) = 1.2$
6	1.1	3.2	12.9	5.2	11.5	9.8	9.8	2.0	4.3	12.3	$J(1,OH) = 3.3$, $J(2ax,OH) = 2.2$
(*E*/*Z*)-**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	$J(5,OH) = 5.4$
(*E*)-**8**	–	–	16.1	5.9	9.0	8.2	8.7	3.5	3.5	c)	
(*Z*)-**8**	–	–	15.5	4.9	6.7	c)	c)	c)	c)	c)	
(*E*)-**9**	–	–	17.3	5.8	7.5	7.4	7.4	c)	c)	c)	
(*Z*)-**9**	–	–	16.2	4.4	5.1	4.7	7.7	c)	c)	c)	$J(2',4) = 0.7$
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)	$J(H,F) = 5.8$
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)	$J(Me_2CH, Me_2CH) = 6.3$
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	$J(H,F) = 5.8$
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	$J(Me_2CH, Me_2CH) = 6.3$

[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**). $NH_2OH \cdot HCl$ (1.04 g, 15 mmol) was added to a mixture of **6** (2.00 g, 4.8 mmol) and $NaHCO_3$ (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*. ^{1}H-NMR (300 MHz, $CDCl_3$, (*E*)/(*Z*) 1:1): *Tables 2* and *3*. ^{13}C-NMR (50.6 MHz, $CDCl_3$): *Table 4*. CI-MS: 432 ($[M + 1]^+$). Anal. calc. for $C_{21}H_{35}NO_8$ (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 K_2HPO_4 (404 mg, 2.32 mmol) in H_2O (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 (CH_2Cl_2/MeOH 150:1) gave further 154 mg of (*E*/*Z*)-**8** (total yield: 70%). In soln., (*E*)-**8** slowly isomerised to (*Z*)-**8**. In $CDCl_3$ 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 ($CHCl_3$/MeOH 50:1) 0.37 ((*E*)-**8**), 0.35 ((*Z*)-**8**). M.p. 129–130° ((*E*)-**8**). $[\alpha]_D^{20} = +25.1 \rightarrow +14.7$ ($c = 1.04$, $CHCl_3$). 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). ^{1}H-NMR (300 MHz, $CDCl_3$; (*E*)/(*Z*) 1:1): *Tables 2* and *3*. ^{13}C-NMR (50.6 MHz, $CDCl_3$, 0°; (*E*)/(*Z*) 1:2): *Table 4*. CI-MS: 430 ($[M + 1]^+$). Anal. calc. for $C_{21}H_{35}NO_8$ (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 CH_2Cl_2 was left for 24 h at 0° ($\rightarrow$(*E*/*Z*) = 2:8 to 1:9), treated with methanesulfonyl chloride (0.22 ml, 2.80 mmol) and Et_3N (0.49 ml, 3.50 mmol), and stirred at 0° for 5 min. After the addition of H_2O, stirring was continued for 1 h. Dilution with CH_2Cl_2 (25 ml), normal workup (CH_2Cl_2), 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.). $[\alpha]_D^{20} = +41.7$ ($c = 1.08$, $CHCl_3$). 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*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*. ^{13}C-NMR (50.6 MHz, (D_6)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 (*d*)	99.05 (*d*)	74.12, 67.50, 66.62 (3*d*)	61.30 (*t*)	–	178.10, 177.77, 176.54 (3*s*, 3 CO); 38.84 (*s*, Me_3C); 38.71 (*s*, 2 Me_3C); 27.09, 27.03, 26.97 (3*q*, 3 *Me_3*C)
6	91.60 (*d*)	35.28 (*t*)	68.63, 68.60, 68.36 (3*d*)	62.17 (*t*)	–	178.31, 177.53, 176.70 (3*s*, CO); 38.87, 38.73, 38.64 (3*s*, 3 Me_3C); 27.05 (*q*, 3 *Me_3*C)
(*E*/*Z*)-**7**	146.80 (*d*) 146.70 (*d*)	31.83 (*t*) 26.04 (*t*)	71.83 (2C), 68.94, 68.71, 67.76, 67.69 (5*d*)	64.35 (*t*)	–	179.13, 178.66, 177.05, 177.02 (4*s*, CO); 39.08, 39.04, 38.95, 38.84 (4*s*, Me_3C); 27.21, 27.04, 26.93 (3*q*, *Me_3*C)
(*E*)-**8**	158.61 (*s*)	25.48 (*t*)	68.21, 67.19, 76.28[a]) (3*d*)	61.74 (*t*)	–	177.94 (*s*, CO); 177.25 (*s*, CO, (*E*)-**8**); 177.14 (*s*, CO, (*Z*)-**8**); 176.45 (*s*, CO); 38.87, 38.76, 38.71 (3*s*, 3 Me_3C); 27.06, 26.95 (*q*, 3 *Me_3*C)
(*Z*)-**8**	150.23 (*s*)	29.19 (*t*)	68.63, 67.69, 76.15[a]) (3*d*)	61.74 (*t*)	–	
(*E*)-**9**[b])	168.99 (*s*)	27.57 (*t*)	68.68, 67.90, 77.36[a]) (3*d*)	62.12 (*t*)	36.29 (*q*)	177.75, 177.25, 176.74 (3*s*, 3 CO); 39.36, 39.28, 39.19 (3*s*, Me_3C); 27.30 (*q*, *Me_3*C); 27.18 (*q*, 2 *Me_3*C)
(*Z*)-**9**	157.44 (*s*)	28.18 (*t*)	67.67, 67.56, 77.20[a]) (3*d*)	61.40 (*t*)	35.93 (*q*)	177.76, 176.82, 176.42 (3*s*, 3 CO); 38.85 (*s*, Me_3C); 38.75 (*s*, 2 Me_3C); 26.99 (*q*, *Me_3*C); 26.88 (*q*, 2 *Me_3*C)
12	95.44 (*d*)	34.76 (*t*)	69.89, 68.11, 68.07 (3*d*)	62.10 (*t*)	160.98 (*s*); 142.62 (*s*); 125.73 (*d*, 2 C); 116.32 (*d*, 2 C)	177.87, 177.53, 176.73 (3*s*, 3 CO); 38.78 (*s*, Me_3C); 38.70 (*s*, 2 Me_3C); 27.04 (*q*, 2 *Me_3*C); 29.96 (*q*, *Me_3*C)
13	96.48(*d*)	35.36 (*t*)	73.05, 69.44, 67.90 (3*d*)	62.58 (*t*)	161.41 (*s*); 142.80 (*s*); 125.67 (*d*, 2 C); 116.35 (*d*, 2 C)	177.91, 177.47, 176.79 (3*s*, 3 CO); 38.81, 38.78, 38.71 (3*s*, 3 Me_3C); 27.08 (*q*, *Me_3*C); 27.02 (*q*, 2 *Me_3*C)
14[c])	96.03 (*d*)	35.27 (*t*)	69.04, 68.68, 68.59 (3*d*)	62.48 (*t*)	154.97 (*s*); 150.46 (*s*); 117.59 (*d*, 2 C); 114.63 (*d*, 2 C); 55.70 (*q*, MeO)	178.13, 177.59, 176.89 (3*s*, 3 CO); 38.81 (*s*, 2 Me_3C); 38.74 (*s*, Me_3C); 27.10 (*q*, 3 *Me_3*C)
15	98.31 (*d*)	35.99 (*t*)	72.62, 70.08, 68.33 (3*d*)	62.75 (*t*)	155.30 (*s*); 150.96 (*s*); 118.18 (*d*, 2 C); 114.45 (*d*, 2 C); 55.62 (*q*, MeO)	178.07, 177.54, 176.84 (3*s*, 3 CO); 38.80 (*s*, 2 Me_3C); 38.71 (*s*, Me_3C); 27.11 (*q*, *Me_3*C); 27.05 (*q*, 2 *Me_3*C)
16[c])	98.99 (*d*)	34.27 (*t*)	70.03, 67.85, 67.75 (3*d*)	61.87 (*t*)	72.31 (*sept.*, $J = 33$); 121.57 (*q*, $J = 282$); 121.07 (*q*, $J = 284$)	177.99, 177.38, 176.68 (3*s*, 3 CO); 38.85, 38.82, 38.69 (3*s*, 3 Me_3C); 27.05 (*q*, 3 *Me_3*C)
17[c])	98.65 (*d*)	35.55 (*t*)	72.81, 69.51, 67.82 (3*d*)	61.69 (*t*)	71.70 (*sept.*, $J = 33$); 121.54 (*q*, $J = 284$); 120.57 (*q*, $J = 287$)	177.97, 177.50, 176.60 (3*s*, 3 CO); 38.82, 38.78, 38.69 (3*s*, 3 Me_3C); 27.01 (*q*, *Me_3*C); 26.97 (*q*, 2 *Me_3*C)
18[c])	97.97 (*d*)	35.01 (*t*)	68.77, 68.72, 68.23 (3*d*)	62.54 (*t*)	54.81 (*q*)	178.11, 177.38, 176.84 (3*s*, 3 CO); 38.85, 38.76, 38.64 (3*s*, 3 Me_3C); 27.15 (*q*, *Me_3*C); 27.06 (*q*, 2 *Me_3*C)
19[c])	100.45 (*d*)	36.05 (*t*)	72.36, 70.32, 68.57 (3*d*)	62.57 (*t*)	56.71 (*q*)	178.17, 177.61, 176.80 (3*s*, 3 CO); 38.83, 38.78, 38.67 (3*s*, 3 Me_3C); 27.10, 27.05, 27.01 (3*q*, 3 *Me_3*C)
20[c])	94.72 (*d*)	35.64 (*t*)	69.00, 68.97, 68.36 (3*d*)	62.73 (*t*)	69.06[d]) (*d*); 23.33, 21.28 (2*q*)	178.15, 177.48, 176.89 (3*s*, 3 CO); 38.83, 38.76, 38.64 (3*s*, 3 Me_3C); 27.12 (*q*, *Me_3*C); 27.08 (*q*, 2 *Me_3*C)
21[c])	97.54 (*d*)	36.70 (*t*)	72.27, 70.55, 68.68 (3*d*)	62.75 (*t*)	71.39[e]) (*d*); 23.42, 21.76 (2*q*)	178.15, 177.65, 176.85 (3*s*, 3 CO); 38.80 (*s*, 2 Me_3C); 38.67 (*s*, Me_3C); 27.08, 27.05, 26.99 (3*q*, 3 *Me_3*C)

[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: 3030*w* (br.), 2980*s*, 2940*m*, 2920*m*, 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* (sh), 1040*m*, 1020*w*, 1000*w*, 970*m*, 940*w*, 895*w* (sh), 860*m*, 850*m*, 830*m*, 810–710*m*, 665*w*. ^{1}H-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: 3030*w* (sh), 2980*s*, 2940*m*, 2920*w*, 2880*w*, 1730*s*, 1615*m*, 1600*s*, 1520*m*, 1510*m* (sh), 1495*m*, 1480*m*, 1460*m*, 1400*w*, 1370*m*, 1350*s*, 1330*m* (sh), 1310*m*, 1280*s*, 1245–1200*m*, 1150*s*, 1125*s* (sh), 1115*s*, 1095*m*, 1040*m*, 1020*m*, 1000*m* (sh), 975*s*, 940*w*, 900*w* (sh), 885*w*, 870*m*, 850*m*. ^{1}H-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: 3030*w* (sh), 2980*m*, 2940*m*, 2910*w*, 2880*m*, 1730*s*, 1615*m*, 1600*m*, 1520*m*, 1510*m* (sh), 1495*m*, 1480*m*, 1460*m*, 1395*m*, 1370*m*, 1350*s*, 1330*m* (sh), 1280*s*, 1250–1200*s*, 1140*s* (br.), 1115*s*, 1070*s*, 1040*m*, 1020*w* (sh), 1000*m*, 970*w*, 945*w*, 915*w*, 900*w*, 865*m*, 850*m*. ^{1}H-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: 3030*w*, 2970*m*, 2940*w*, 2910*w*, 2870*w*, 2830*w*, 1730*s*, 1505*s*, 1480*m*, 1460*m*, 1440*w*, 1370*w*, 1350*w*, 1280*m*, 1220*m*, 1195*m*, 1150*s*, 1120*m*, 1095*m*, 1040*m*, 1020*w*, 1005*w*, 980*m*, 960*w*, 910*w*, 895*w*, 880*w*, 860*w*, 830*w*. ^{1}H-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: 3020*w*, 2970*m*, 2940*w*, 2910*w*, 2870*w*, 2830*w*, 1725*s*, 1505*s*, 1480*m*, 1460*m*, 1440*w*, 1400*w*, 1370*w*, 1320*w*, 1280*m*, 1225*m*, 1155*s*, 1065*s*, 1040*m*, 990*w*, 965*w*, 940*w*, 910*w*, 895*w*, 865*w*, 830*w*. ^{1}H-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 $C_{21}H_{42}O_9$ (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: 3030*w*, 2970*m*, 2940*w*, 2910*w*, 2880*w*, 1735*s*, 1480*m*, 1460*w*, 1400*w*, 1370*m*, 1290*s*, 1265*m*, 1225*m*, 1195*s*, 1155*s*, 1140*s*, 1105*s*, 1090*s*, 1040*w*, 1020*w*, 1000*w*, 975*m*, 940*w*, 900*w*, 885*w*, 685*w*. ^{1}H-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: 3030*w*, 2980*m*, 2940*w*, 2920*w*, 2880*w*, 1730*s*, 1480*m*, 1460*w*, 1415*w*, 1400*w*, 1375*m*, 1290*s*, 1270*m*, 1230*m*, 1195*s*, 1140*s*, 1120*s*,

1105*s*, 1080*m*, 1045*w*, 1000*w*, 970*w*, 940*w*, 900*w*, 885*w*, 690*w*. ^{1}H-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 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. $[\alpha]_D^{20} = +89.6$ ($c = 0.27$, $CHCl_3$). IR: 3030*w*, 2980*m*, 2940*m*, 2910*w*, 2880*w*, 2840*w*, 1730*s*, 1480*m*, 1465*w*, 1450*w*, 1400*w*, 1370*w*, 1305*w*, 1285*m*, 1230*w*, 1160*s*, 1130*s*, 1095*w*, 1045*m*, 1020*w*, 1005*w*, 970*w*, 945*w*, 920*w*, 900*w*, 870*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*. ^{13}C-NMR (68 MHz, $CDCl_3$): *Table 4*. FAB-MS: 431 ($[M + 1]^+$). Anal. calc. for $C_{22}H_{38}O_8$ (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°. $[\alpha]_D^{20} = -10.8$ ($c = 0.24$, $CHCl_3$). IR: 3030*w*, 2980*m*, 2950*w*, 2920*w*, 2890*w*, 2850*w*, 1730*s*, 1480*m*, 1465*w*, 1455*w*, 1400*w*, 1375*w*, 1325*w*, 1285*m*, 1220*w* (br.), 1150*s*, 1110*w*, 1090*w*, 1045*m*, 1020*w*, 1010*w*, 990*w*, 960*w*, 945*w*, 915*w*, 895*w*, 870*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*. ^{13}C-NMR (68 MHz, $CDCl_3$): *Table 4*. FAB-MS: 431 ($[M + 1]^+$). Anal. calc. for $C_{22}H_{38}O_8$ (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°. $[\alpha]_D^{20} = +97.0$ ($c = 0.3$, $CHCl_3$). IR: 3040*w*, 2980*s*, 2950*m*, 2920*w*, 2880*w*, 1730*s*, 1485*m*, 1465*m*, 1400*w*, 1390*w*, 1375*m*, 1340*w*, 1305*m*, 1285*s*, 1235*w*, 1160*s*, 1130*s* (sh), 1090*m*, 1045*m*, 1020*m*, 1005*s*, 980*w*, 970*w*, 920*w*, 900*w*, 870*w*, 850*w*, 835*w*. ^{1}H-NMR (270 MHz, $CDCl_3$): *Tables 2* and *3*. ^{13}C-NMR (68 MHz, $CDCl_3$): *Table 4*. FAB-MS: 459 ($[M + 1]^+$). Anal. calc. for $C_{24}H_{42}O_8$ (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°. $[\alpha]_D^{20} = -17.7$ ($c = 0.3$, $CHCl_3$). IR: 3030*w*, 2980*m*, 2940*m*, 2910*w*, 2880*w*, 1730*s*, 1480*m*, 1465*w*, 1400*w*, 1385*w*, 1370*w*, 1320*w*, 1285*m*, 1230*w*, 1160*s*, 1145*s*, 1090*w*, 1065*m*, 1040*w*, 1020*w*, 990*w*, 965*w*, 940*w*, 920*w*, 900*w*. ^{1}H-NMR (270 MHz, $CDCl_3$): *Tables 2* and *3*. ^{13}C-NMR (68 MHz, $CDCl_3$): *Table 4*. FAB-MS: 459 ($[M + 1]^+$). Anal. calc. for $C_{24}H_{42}O_8$ (458.59): C 62.86, H 9.23; found: C 63.02, H 9.19.

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