14. A New Synthesis of Benzylidene Acetals[1])

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Aryl-halo-diazirines react under basic conditions with 1,3-*cis*-, 1,2-*cis*-, and 1,2-*trans*-diols to give acetals. Yields are high. Diastereoselectivities depend upon the diol and upon the reaction conditions. Thus, reaction of the 1,3-*cis*-diol **1** (*Scheme 1*) with **2** gave **3** as a single diastereoisomer. The 1,2-*cis*-diols **4** and **7** led to the *endo*- and *exo*-acetals **5**/**6** (93:7) and **8**/**9** (*ca.* 10:1), respectively. The 1,2-*trans*-diol **10**, **16**, and **19** reacted with **2** to afford **11**/**12** (90:10), **17**/**18** (1:1), and **20**/**21** (6:1), respectively. Reaction of the (4-nitrophenyl)diazirine **13** with **10** at higher temperatures yielded **14**/**15** (6:4). The uracil moiety, the acetamido group, and the enol-ether moiety are compatible with the reaction conditions. The diastereoselectivity is rationalized on the basis of a reaction sequence involving alkoxy-halogen exchange, which is regioselective or not, thermolysis of the ensuing alkoxydiazirine(s), protonation of the alkoxycarbene to form an (*E*)-configurated oxycarbenium ion, and attack of the neighboring oxy or hydroxy group, which is only possible for a limited range of conformers.

Introduction. – The transformation into benzylidene acetals is one of the most reliable and useful ways to protect 1,3- and 1,2-diols [1] and is usually performed by acetalation, *trans*-acetalation, or reaction with (dihalomethyl)benzene [2][2]). The first two methods require acid catalysis and are often high yielding. The third method requires base catalysis and proceeds in lower yields, especially for diols with labile groups such as the *O*-(triphenylmethyl) substituent or for 1,2-*trans*-diols. Under acidic conditions, 2-phenyl-1,3-dioxanes are formed with a very high diastereoselectivity, while 2-phenyl-1,3-dioxolanes, as a rule, are obtained as mixtures of *endo*- and *exo*-isomers. This is not only important with regard to obtain pure products, but also with hindsight to further transformations of benzylidene acetals [1c] [4].

A high-yielding method, using neutral or basic conditions for the diastereoselective preparation of 2-phenyl-1,3-dioxolanes and -dioxanes would be welcome, particularly for the selective transformation of acid-sensitive compounds, such as glycals. We have conceived of such a method, which consists in treating a diol with an aryl-halo-diazirine [5] under basic conditions, and which demonstrates the intramolecular insertion of alkoxyaryl carbenes into O–H bonds [6]. Halodiazirines are easily prepared by *Graham*'s method from amidinium salts [7] [8a] and undergo an alkoxide-halide exchange with alcohols to form alkoxy-aryl-diazirines [8a], which are thermally labile, loose N_2 *in situ* and form alkoxyaryl carbenes [8b]. For diols, insertion of these carbenes into the O–H bond of a neighboring OH group should yield benzylidene acetals.

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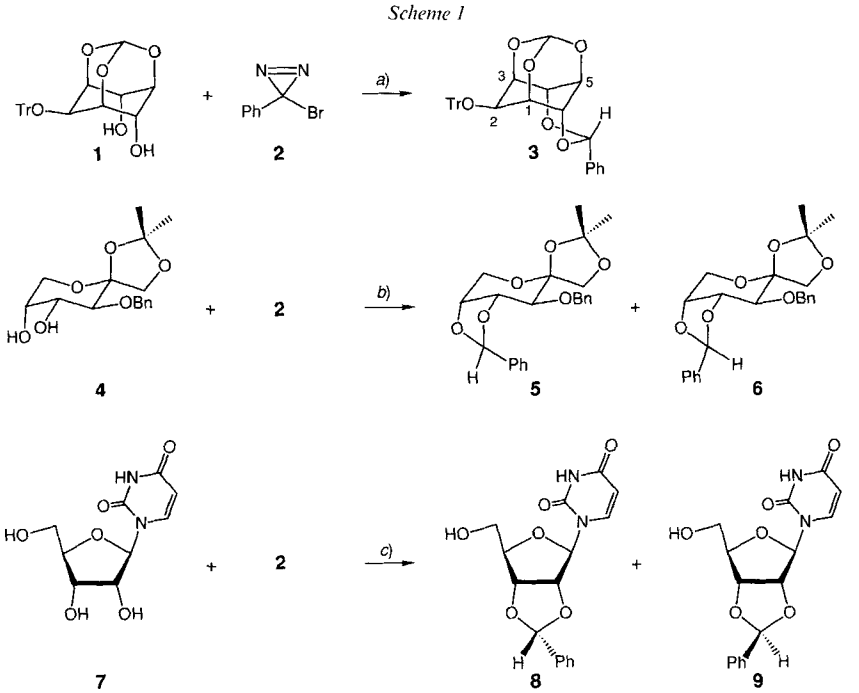
[1]) Reported in part at the 'XVIth International Carbohydrate Symposium', Paris, July 5–10, 1992.

[2]) For an oxidative 4-methoxybenzylidenation, see *e.g.* [3a], and for a reductive benzylidenation [3b].

Results and Discussion. – To study this approach to the synthesis of benzylidene acetals, we chose the 1,3-*cis* diol **1** [9][3]), the 1,2-*cis* diols **4** [13] and **7** (uridine), and the 1,2-*trans* diols **10** [14], **16** [15], and **19** [16]. Benzylidenation of these alcohols allows to check the compatibility of the reaction conditions with the presence of a heterocyclic base, an acetamido group, a trityloxy group, and an enol ether function.

The reaction of the *myo*-inositol derivative **1** (*Scheme 1*) with the bromodiazirine **2** [7] in the presence of 1 equiv. of NaH in DMSO was incomplete and led to a complex mixture of products. Simultaneous addition of concentrated aqueous KOH and a solution of **2** in hexane to a solution of **1** in DMSO, however, gave the desired acetal **3** (93%) as a single diastereoisomer. Similarly, the 1,2-*cis*-diol **4** was treated with aqueous KOH/DMSO and **2**, to yield the *endo*- and *exo*-configurated benzylidene acetals **5**/**6** (93:7), favoring the product of kinetic control. Slow addition of the solutions of KOH and **2** was important for a high yield (95%). When the solution of KOH was added in one portion, the yield decreased to 78%; it was also lower (70%), when dry DMF was used as solvent. The presence of a heterocyclic ring in uridine (**7**) did not disturb the benzylidenation. The reaction between uridine and **2** in the presence of aqueous KOH in DMSO gave **8**/**9** (10:1;

Scheme 1



a) 3 equiv. of **2**, 6 equiv. of KOH, DMSO/H_2O 20:3, r.t., 2 h; 93%. *b*) 1) 2.1 equiv. of **2**, 5 equiv. of KOH, DMF, r.t., 4 h; 70% (**5**/**6** 88:12); 2) 3.2 equiv. of **2**, 5 equiv. of KOH, DMSO/H_2O 8:1, r.t., 2 h; **5** (73%); **6** (5%); 3) 2.8 equiv. of **2**, 5 equiv. of KOH, DMSO/H_2O 20:3, r.t., 3 h; **5** (88%), **6** (7%). *c*) 5.2 equiv. of **2**, 5 equiv. of KOH, DMSO/H_2O 40:3, r.t., 1.5 h; **8**/**9** (9:1, 74%).

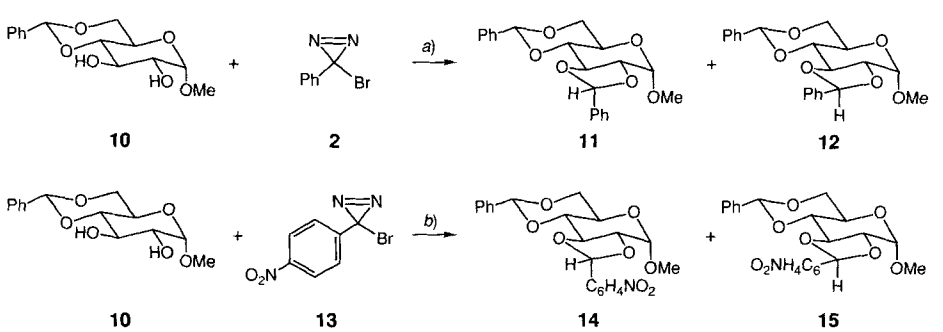
[3]) A large number of fused benzylidene acetals of 1,3-diols are known, but only a few bridged ones, namely derivatives of ribopyranosides and of δ-ribonolactone [10], of glucopyranosides [11], and of azadirachtin [12].

74%). The minor isomer was detected by ^{1}H-NMR spectroscopy of this mixture. Repeated crystallizations gave pure **8** (22%). The acetals **8**/**9** had been prepared before by the reaction of **7** with benzaldehyde in the presence of $ZnCl_2$ [17–19]. Whereas mixtures of **8**/**9** were obtained at room temperature [17] [18], the *endo*-isomer **8** was selectively formed at 5° [18]. Pure **8** and a 1:1 mixture **8**/**9** have a similar melting point (191–193°), but different $[\alpha]_D^{25}$ values (−57.9 and −92.7, respectively) [18].

In the ^{1}H-NMR spectra of **1** and **3**, H–C(2) (**1**: 5.22, **3**: 4.88 ppm) exhibits the characteristic br. *quartettoid* signal ($J \approx 1.8$ Hz) including a long-range coupling (1.1 Hz) with the methylidyne H-atom [20] [21]. H–C(5) of **1** appears at 3.91 ppm as a relatively br. *m* ($w_{20} = 11.2$ Hz). In **3**, however, it resonates at 4.23 ppm as a characteristic *tt* with vicinal couplings of 4.7 and long-range couplings to H–C(1) and H–C(3) of 1.4 Hz. The *endo*-orientation of the Ph substituent in **3** was deduced from a NOE (16%) between PhC*H* and H–C(5) (*Table*), which also evidences the boat conformation of the Ph-substituted 1,3-dioxane ring. This conformation is also indicated by the strong upfield shift (*γ* effect) of PhCH (91.90 ppm) and C(5) (**1**: 69.05 ppm, **3**: 63.30 ppm). That **5** and **6** are isomers is evidenced by the combustion analysis and the mass spectrum ($[M + 1]^+$ at *m*/*z* 399, $[M$ − acetone + $NH_4]^+$ at *m*/*z* 358, $[M$ − acetone + $1]^+$ at *m*/*z* 341). The loss of acetone is initialized by the heterolytic cleavage of the glycosidic C–O bond. The IR spectra show no bands for OH groups. In the ^{1}H-NMR spectra, *s*'s at 5.94 (**5**) and 6.12 ppm (**6**) prove the presence of a benzylidene moiety. Again, the assignment of the configuration is based upon NOE's between PhC*H*, and H–C(4) and H–C(5) in **5** and between PhC*H* and H–C(3) in **6** (*Table*). The relatively small *J*(3,4) values of **5** and **6** (7.0 and 7.5 Hz, respectively) and the relatively large *J*(4,5) values (6.2 and 5.4 Hz, respectively) suggest a flattened $^2C_5$ conformation of the tetrahydropyran ring due to the *cis*-fused dioxolane ring. As expected, the flattening is more distinct in **5** than in **6**. In agreement with these findings, calculations with the *Gandour* program [22] suggest a dihedral angle for H–C(3)–C(4)–H of 145–150° in **5** and **6**. The C=O region of the IR spectrum (KBr) of **8** is similar to the one of **7** in nujol [23]. The melting point (202–203°) of **8** is 10° higher as the reported one [18], but the $[\alpha]_D$ value in DMF and the ^{1}H-NMR spectrum in (D_6)DMF (see *Exper. Part*) correspond well to the published data [18] [19b]. In (D_6)acetone, PhC*H* of **8** resonates at 6.00 ppm, and PhC*H* of **9** at 6.16 ppm. The assignment is proven by a NOE between PhC*H*, and both H–C(2) and H–C(3) of **8** (*Table*). This is in keeping with the rule that the *exo*-H-atom of such bicyclic benzylidene acetals is more shielded than the *endo*-H-atom (see [18] [19b] [24] and ref. cited therein). In the ^{13}C-NMR spectrum, **8** exhibits the typical signals for the uracil moiety [25]. PhC*H* appears at 106.48 ppm.

Benzylidenation of **10** (*Scheme 2*) under thermodynamic conditions is at best difficult. To the best of our knowledge, no such attempt has been published. Treatment of **10** with dichlorotoluene in pyridine, however, gave the benzylidene acetals **11**/**12** in 10–20% yield [2e]. Crystallization led to an enriched sample of one diastereoisomer (m.p. 157–161°, $[\alpha]_D^{20} = +55$). The procedure was improved, leading to a purer sample (33%, 168–174°, $[\alpha]_D^{20} = +71.6$) of the crystalline diastereoisomer [26]. The configuration at the acetal

Scheme 2



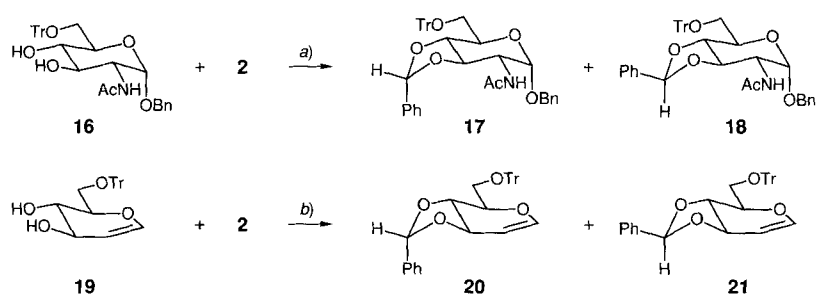
a) 1) 3 equiv. of **2**, 5 equiv. of KOH, DMF, r.t., 3 h; **11** (78%), **12** (17%); 2) 3.4 equiv. of **2**, 5 equiv. of KOH, DMSO/H_2O 20:3, r.t., 0.5 h; **11** (85%), **12** (10%). *b*) 5 equiv. of **13**, pyridine, 97–103°, 6.5 h; **14** (55%), **15** (35%).

centre was not determined. Upon treatment of **10** with **2** in the presence of KOH in DMSO/H_2O, a crystalline precipitate of **11**/**12** (9:1, 84%) was formed. Chromatographic purification of the precipitate and the supernatant gave **11** (85%, m.p. 192–193°, $[\alpha]_D^{25} = +87$) and **12** (10%, amorphous solid, $[\alpha]_D^{25} = +5$). The percentage of the minor isomer is somewhat higher (78% of **11**, 17% of **12**) with dry DMF as solvent. The use of dry DMSO led to a very sluggish reaction. The acetals **14**/**15** were obtained in low yields only, when **10** was treated with the (4-nitrophenyl)diazirine **13** at room temperature in DMSO/H_2O, DMF, DMF/H_2O, or MeCN. In pyridine at 100°, however, **10** was transformed into **14**/**15** (6:4) which were separated by flash chromatography to yield **14** (55%) and **15** (35%). This change of the conditions may indicate a change of the reaction mechanism, presumably from a S_N2' to a radical chain process [8] [27], or, less likely, to a sequence involving generation of the bromo-(4-nitrophenyl)-carbene [28].

In the CI-MS, both **11** and **12** show $[M + 1]^+$ at m/z 371 as the base peak. The melting point and the $[\alpha]_D^{25}$ value of **11** (see above) clearly indicate that the crystalline products which were obtained in the reaction of **10** with dibromotoluene [2e] [26] correspond to impure samples of **11**. The more strongly laevorotatory $[\alpha]_D^{25}$ value of **12** is in agreement with these results. PhC*H* of **11** resonates at 5.61 ppm, PhC*H* of **12** at 5.64 ppm. These relative chemical shifts and the small $\Delta\delta$ value of 0.03 ppm are in agreement with the findings of *Garegg* and *Swahn* [2e]. The unambiguous assignment of diastereoisomers is based upon NOE's between PhC*H*, and H–C(2) (**11**) and H–C(3) (**12**), respectively (*Table*). As expected, PhC*H* of the pyranose moiety of **11** resonates at higher field ($\Delta\delta = 4$ ppm) than PhC*H* of the furanose moiety. Both **14** and **15** show similar ^{1}H- and ^{13}C-NMR spectra as **11** and **12**. PhC*H* of the furanose moiety is shifted upfield by 2 ppm. The IR spectra of **14** and **15** are characterized by the band at 1525 cm^{-1}, the CI-MS by peaks for $[M + NH_4]^+$ at m/z 433, $[M + 1]^+$ at m/z 416, and $[M - NO_2 + NH_3]^+$ (base peak) at m/z 386.

Benzylidenation of the *N*-acetylglucosamine derivative **16** [15] by **2** gave **17**/**18** (94%; *Scheme 3*). HPLC separation gave **17** and **18** in almost equal amount. Finally, the tritylated glucal **19** [16] was transformed into a mixture **20**/**21** which was separated by HPLC into **20** (51%) and **21** (8%). The yield could not be improved by variation of the conditions (solvent, ratio of **2**, and KOH). The partial decomposition of **20** and **21** on SiO_2 was prevented by treating SiO_2 with Na_2CO_3.

Scheme 3



a) 3 equiv. of **2**, 5 equiv. of KOH, DMSO/H_2O 10:1, r.t., 1.5 h; **17** (43%), **18** (39%). *b*) 2.8 equiv. of **2**, 3 equiv. of KOH, DMSO/H_2O 5:1, r.t., 2.5 h; **20** (51%), **21** (8%).

In the IR spectra, **17** and **18** show absorptions for AcNH at 1680 and 3450 cm^{-1}. The MS shows signals for $[M + 1]^+$, $[M - Ph_3C + 1 + NH_4]^+$, and $[M - Ph_3C + 2]^+$. In the ^{1}H-NMR spectra, NH resonates as a *d* at 5.82 ppm (**17**) and 5.88 ppm (**18**). The configurational assignment is again based upon NOE's (*Table*). In the ^{13}C-NMR spectra, PhC*H* appears at 104.68 ppm (**17**) and 104.99 ppm (**18**). The IR spectra of **20** and **21** are

Table. *^{13}C- (50 MHz, $CDCl_3$) and ^1H-NMR (400 MHz, $CDCl_3$) Chemical Shifts* [ppm] *of the Benzylidene C- and H-Atoms and the NOE's Observed upon Irradiation of the Benzylic H-Atoms*

Compound	PhCH	PhC*H*	NOE Observed at H-atoms on the pyranose ring upon irradiation of PhC*H* (intensity)			
3	91.90	5.47	H–C(4)/H–C(6)	(3%)	H–C(5)	(16%)
5	103.89	5.94	H–C(4)	(8%)	H–C(5)	(8%)
6	[a])	6.12	H–C(3)	(8%)		
8[b])	106.48	6.00	H–C(2′)	(3%)	H–C(3′)	(3%)
11	105.64[c])	6.14[c])	H–C(2)	(4%)		
	101.55[d])	5.61[d])				
12	[a])	6.17[c])	H–C(3)	(12%)		
		5.62[d])				
14	103.80[c])	6.21[c])	H–C(2)	(8%)		
	101.64[d])	5.61[d])				
15	103.89[c])	6.21[c])	H–C(3)	(12%)		
	101.68[d])	5.63[d])				
17	104.68	6.08	H–C(4)	(6%)		
18	104.99	6.01	H–C(3)	(7%)		
20	106.75	6.28	[e])			
21	107.04	6.21	H–C(3)	(7%)		

[a]) Not measured.
[b]) ^1H-NMR in (D_6)acetone, ^{13}C-NMR in (D_6)DMSO.
[c]) Of 1,3-dioxolane moiety.
[d]) Of 1,3-dioxane moiety.
[e]) NOE (12%) at PhC*H* upon irradiation of H–C(4), no NOE upon irradiation of H–C(3).

characterized by the enol-group absorption at 1610 cm^{-1}. The ^1H-NMR spectra show signals for olefinic H-atoms at 6.30 and 6.31 ppm (H–C(1)) and at 5.26 and 5.29 ppm (H–C(2)) for **20** and **21**, respectively. A NOE of 12% is observed for PhC*H* of **20** upon irradiation of H–C(4), whereas irradiation of PhC*H* of **21** led to a NOE of 7% for H–C(3) (*Table*). C(1) of **20** and **21** resonates at *ca.* 144, C(2) at 99, and PhCH at 107 ppm.

To explain the diastereoselectivity of the benzylidenation, we assume the reaction sequence which is described in the *Introduction* and a preferred *trans*-configuration of the intermediary alkoxycarbene and of the oxycarbenium ion, which is obtained either by intra- or by intermolecular protonation of this carbene [29]. Two (*E*)-configurated alkoxycarbene intermediates can be formed from each diol, depending upon the regioselectivity of the alkoxy-halogen exchange. The hydroxy or alkoxy group must attack the oxycarbenium ion in the π plane according to a 5-*endo-trig* mode [30]. Rotation around the C–O bond connecting the oxycarbenium moiety to the pyranose or furanose ring determines both the angle of attack onto the π system of the cationic center and the distance between the center and the attacking O-atom, independently of whether protonation of the carbene is an intra- or intermolecular process. Inspection of *Dreiding* models shows that a conformer of the oxycarbenium ion derived from a halogen-alkoxy exchange of HO–C(5) of the 1,2-*cis*-diol **4**, which has a H–C(5)–O^+=C dihedral angle of *ca.* 0° is much more easily attacked by the HO–C(4) group than a conformer with a corresponding angle of *ca.* 180°. This leads to the *endo*-isomer **5**. The same observation is valid for the regioisomeric oxycarbenium ion derived from **4**; again **5** is expected to be the major product. For the *trans*-diol **10**, the same conformation of the oxycarbenium ion is required, independently of which OH-group has reacted with the diazirine, but the

situation is different from the one in the 1,2-*cis*-diols, in that the oxycarbenium ion derived from the reaction of HO–C(2) with **2** leads to **11**, while the regioisomeric ion is expected to mostly yield **12**. Regioselective reaction with **2** is also required for uridine; in the 2′-*endo*-conformer, HO–C(2′), and in the 3′-*endo*-conformer HO–C(3′) must react preferentially to explain the preferred formation of the *endo*-product **8**. The higher reactivity of HO–C(2) in α-D-glucopyranosides is amply documented [31]. The 1:1 ratio of products derived from **16** and from **19** indicates that both OH groups react to a similar extent with **2**, while the 6:4 ratio of **14** and **15** has been obtained at a much higher temperature and may reflect partial loss of kinetic control. Regioselective halogen-alkoxy exchange must also operate in the benzylidenation of the glucal **19**, where HO–C(3) has to react preferentially.

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Experimental Part

General. All reactions, except the one for preparation of **1**, were run under Ar. Powdered KOH (*Fluka purum*, > 85%) was used throughout. The (4-nitrophenyl)amidine salt was prepared from the corresponding nitrile [32]. Diazirines were prepared by the *Graham* reaction [7]. Aliquots of a stock soln. of **2** in hexane (stored for several weeks in the refrigerator) were measured by weighing the filled syringe.

*1,3,5-*O*-Methylidyne-2-*O*-trityl*-myo-*inositol* [9] (**1**). Ph_3CCl (1.6 g, 5.8 mmol) and pyridine (5 ml) were added to a soln. of 1,3,5-*O*-methylidyne-*myo*-inositol [33] (1.00 g, 5.26 mmol) in CH_2Cl_2 (15 ml). The soln. was heated to reflux overnight, cooled, and co-evaporated with MeOH. FC (hexane/AcOEt 1:1) of the residue gave **1** (0.60 g, 26%). R_f (hexane/AcOEt 1:1) 0.38. M.p. 215–217° (AcOEt). IR (KBr): 3300*s* (br.), 3060*w*, 3020*w*, 2970*w*, 2950*w*, 2920*w*, 1600*w*, 1495*s*,1450*s*, 1395*w*, 1370*w*, 1355*w*, 1300*w*, 1275*w*, 1255*m*, 1225*w*, 1160*s*, 1095*s*, 1080*s*, 1055*s*, 1020*s*, 1000*s*, 960*m*, 930*w*, 910*w*, 900*w*, 890*w*, 830*m*, 785*m*, 765*m*, 755*m*, 705*s*, 650*w*, 630*m*, 620*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.47–7.25 (*m*, 15 arom. H); 5.52 (*d*, J = 1.1, HCO_3); 5.22 (*d*, J = 6.6, exchangeable with D_2O, 2 OH); 4.09 (br. *q*, w_{40} = 5.0; irrad. at 5.52→br. *t*, J = 1.6, H–C(2)); 4.05 (br. *q*, w_{30} = 16.5; irrad. at. 3.91→br. *t*, $J \approx 5.0$; addn. D_2O→br. *t*, $J \approx 4.0$, H–C(4), H–C(6)); 3.92–3.90 (*m*, $w_{20} \approx 11.5$, H–C(5)); 3.43 (br. *dd*, $J \approx 1.5$, 3.0, H–C(1), H–C(3)). ^{13}C-NMR (50 MHz, (D_6)DMSO): 144.14 (*s*, 3 arom. C); 128.47 (*d*, 6 arom. C); 127.92 (*d*, 6 arom. C); 127.17 (*d*, 3 arom. C); 101.40 (*d*, HCO_3); 87.06 (*s*, Ph_3C); 73.21 (*d*, 2 C); 69.05 (*d*, C(5)); 67.27 (*d*, 2 C); 61.93 (*d*, C(1)). CI-MS: 244 (20), 243 (100, $[Ph_3C]^+$). Anal. calc. for $C_{26}H_{24}O_6$ (432.45): C 72.21, H 6.04; found: C 72.21, H 5.88.

endo-*4,6-*O*-Benzylidene-1,3,5-*O*-methylidyne-2-*O*-trityl*-myo-*inositol* (**3**). A soln. of KOH (76 mg, 1.4 mmol) in H_2O/DMSO 3:10 (1.3 ml) and an aliquot of a stock soln. of **2** (20% in hexane, 579 mg, 0.69 mmol) were added dropwise to a stirred soln. of **1** (100 mg, 0.23 mmol) in DMSO (1 ml) within 2 h and 1 h, respectively. After completion of the addition, normal workup (AcOEt, brine) and FC (hexane/CH_2Cl_2 1:1) of the residue (141 mg) gave **3** (112 mg, 93%). Colorless foam. R_f (hexane/CH_2Cl_2 1:1) 0.16. IR: 3030*w*, 2940*w*, 1600*w*, 1490*w*, 1450*w*, 1380*m*, 1300*w*, 1170*s*, 1140*m*, 1110*s*, 1095*m*, 1030*s*, 1005*s*, 970*s*, 910*w*, 830*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.70–7.67 (*m*, 6 arom. H); 7.13–6.93 (*m*, irrad. at 5.47→NOE of 7%, 14 arom. H); 5.67 (*d*, J = 1.1; irrad. at 4.88→*s*, HCO_3); 5.47 (*s*, PhC*H*); 4.88 (br. *q*, w_{30} = 6.5; irrad. at 5.67→*t*, J = 2.0, H–C(2)); 4.45 (br. *t*, J = 5.0; irrad. at 4.23→br. *d*, $J \approx 4.9$; irrad. at 5.47→NOE of 3%, H–C(4), H–C(6)); 4.23 (*tt*, J = 1.4, 4.7; irrad. at 5.47→NOE of 16%, H–C(5)); 3.85 (*td*, J = 1.7, 5.3; irrad. at 4.88→*dd*, J = 1.4, 5.3; irrad. at 4.23→*dd*, J = 1.9, 5.1, H–C(1), H–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 144.11 (*s*, 3 arom. C); 136.66 (*s*, arom. C); 129.22 (*d*, arom. C); 128.90 (*d*, 6 arom. C); 128.25 (*d*, 2 arom. C); 127.94 (*d*, 6 arom. C); 127.21 (*d*, 3 arom. C); 125.91 (*d*, 2 arom. C); 102.08 (*d*, HCO_3); 91.90 (*d*, PhCH); 88.07 (*s*, Ph_3C); 71.35 (*d*, 2 C); 66.95 (*d*, 2 C); 63.30 (*d*, C(5)); 61.76 (*d*, C(2)). CI-MS: 244 (20), 243 (100, $[Ph_3C]^+$). Anal. calc. for $C_{33}H_{28}O_6$ (520.59): C 76.13, H 5.42; found: C 76.22, H 5.22.

*(R)- and (S)-3-*O*-Benzyl-4,5-*O*-benzylidene-1,2-*O*-isopropylidene-β-*D*-fructopyranose* (**5** and **6**). *a*) A mixture of **4** [13] (310 mg, 1 mmol) and powdered KOH (329 mg, 5.06 mmol) in dry DMF (10 ml) was stirred for 10 min at r.t. and then treated dropwise (within 2 h) with an aliquot of a stock soln. of **2** (26% in hexane, 1.564 g, 2.1 mmol). Stirring was continued for another 2 h, when TLC showed completion of the reaction. The soln. was poured onto ice and filtered through SiO_2 (AcOEt) to destroy the emulsion. Normal workup (AcOEt, H_2O), drying

(high vacuum/50°), and FC (hexane/AcOEt 10:1) of the red, oily residue (664 mg) gave **5**/**6** (88:12 according to ^{1}H-NMR, 280 mg, 70%).

b) A vigorously stirred soln. of **4** (155 mg, 0.5 mmol) in DMSO (4 ml) was treated with a soln. of KOH (165 mg, 2.54 mmol) in H_2O (0.5 ml) and dropwise with an aliquot of a stock soln. of **2** (26% in hexane, 782 mg, 1.0 mmol) within 20 min. After stirring for 45 min, TLC showed still the presence of **4**. After the dropwise addition of an additional aliquot of the stock soln. of **2** (391 mg, 0.52 mmol), stirring was continued for 1 h. The mixture was filtered through SiO_2 (AcOEt) to destroy the emulsion. Normal workup (AcOEt, H_2O) and 2 × FC (hexane/AcOEt 20:1) of the yellow, oily residue (400 mg) gave **5** (151 mg, 73%) and **6** (12 mg, 5%).

c) A soln. of **4** (155 mg, 0.5 mmol) in DMSO (1 ml) was treated simultaneously and dropwise with a soln. of KOH (165 mg, 2.54 mmol) in H_2O/DMSO 10:3 (1.3 ml) within 2 h, and with an aliquot of a stock soln. of **2** (26% in hexane, 1.016 g, 1.34 mmol) within 1 h. After completion of the addition, stirring was continued for 1 h. The mixture was treated with ice and AcOEt and filtered through SiO_2 (AcOEt). Normal workup (AcOEt, H_2O) and 2 × FC (hexane/AcOEt 25:1) of the yellow, oily residue (420 mg) gave **5** (176 mg, 88%) and **6** (13 mg, 7%).

Data of **5**: R_f (hexane/AcOEt 25:1) 0.08. M.p. 205–206° (AcOEt). $[\alpha]_D^{25} = -77.7$ ($c = 1$, $CHCl_3$). IR: 3030*w*, 2940*s*, 2880*s*, 1450*m*, 1370*m*, 1090*s*, 980*s*, 900*s*, 880*s*, 840*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55–7.19 (*m*, irrad. at 5.94→NOE of 6%, 10 arom. H); 5.94 (*s*, PhC*H*); 4.89 (*d*, $J = 12.0$), 4.57 (*d*, $J = 12.0$, PhCH_2); 4.53 (*t*, $J \approx 6.6$; irrad. at 3.53→*d*, $J = 6.3$; irrad. at 5.94→NOE of 8%, H–C(4)); 4.32 (*ddd*, $J = 0.8$, 2.6, 6.2; irrad. at 4.53→*dd*, $J = 1.0$. 2.7; irrad. at 5.94→NOE of 8%, H–C(5)); 4.23 (*dd*, $J = 2.7$, 13.5, H–C(6)); 4.17 (br. *d*, $J \approx 13.5$, H′–C(6)); 4.04 (*d*, $J = 8.6$, H–C(1)); 3.85 (*d*, $J = 8.6$, H′–C(1)); 3.53 (*d*, $J = 7.0$; irrad. at 4.53→*s*, H–C(3)); 1.52 (*s*, Me); 1.44 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.98 (*s*, arom. C); 137.42 (*s*, arom. C); 129.32 (*d*, arom. C); 128.42 (*d*, 2 arom. C); 128.23 (*d*, 2 arom. C); 127.88 (*d*, 2 arom. C); 127.55 (*d*, arom. C); 126.67 (*d*, 2 arom. C); 112.25 (*s*, Me_2C); 104.30 (*s*, C(2)); 103.89 (*d*, PhCH); 77.49, 76.32, 76.23 (3*d*, C(3), C(4), C(5)); 72.73, 71.91 (2*t*, C(1), PhCH_2); 60.09 (*t*, C(6)); 26.89, 26.05 (2*q*, 2 Me). CI-MS: 399 (20, $[M + 1]^+$), 359 (20), 358 (100, $[M$ – acetone + $NH_4]^+$), 342 (11), 341 (54, $[M$ – acetone + $1]^+$). Anal. calc. for $C_{23}H_{26}O_6$ (398.46): C 69.33, H 6.58; found: C 69.33, H 6.67.

Data of **6**: amorphous precipitate (Et_2O/pentane at –20°, melting range 92–96°). R_f (hexane/AcOEt 25:1) 0.16. $[\alpha]_D^{25} = -43.4$ ($c = 1$, $CHCl_3$). IR: 3030*w*, 3000*m*, 2920*s*, 2900*m*, 1370*m*, 1090*s*, 970*m*, 900*w*, 880*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.48–7.30 (*m*, irrad. at 6.12→NOE of 4%, 10 arom. H); 6.12 (*s*, PhC*H*); 5.03 (*d*, $J = 12.0$), 4.78 (*d*, $J = 12.0$, PhCH_2); 4.71 (*dd*, $J = 5.4$, 7.4, H–C(4)); 4.23–4.21 (*m*, H–C(5)); 4.16 (*d*, $J = 8.5$, H–C(1)); 4.14 (*dd*, $J = 2.4$, 13.4, H–C(6)); 4.06 (*d*, $J = 13.4$, H′–C(6)); 3.93 (*d*, $J = 8.5$, H′–C(1)); 3.64 (*d*, $J = 7.5$; irrad. at 5.94→NOE of 8%, H–C(3)); 1.52 (*s*, Me); 1.46 (*s*, Me). CI-MS: 399 (30, $[M + 1]^+$), 359 (16), 358 (100, $[M$ – acetone + $NH_4]^+$), 341 (17, $[M$ – acetone + $1]^+$). Anal. calc. for $C_{23}H_{26}O_6$ (398.46): C 69.33, H 6.58; found: C 69.59, H 6.84.

(R)- and (S)-2′,3′-O-Benzylideneuridine (**8** and **9**) [17–19]. At r.t., a soln. of **7** (100 mg, 0.41 mmol) in DMSO (2 ml) was treated with a soln. of KOH (133 mg, 2 mmol) in H_2O (0.3 ml) at r.t. and then dropwise (within 0.5 h) with an aliquot of a stock soln. of **2** (30% in hexane, 807 mg, 1.2 mmol). Crystallized uridine was redissolved by evaporation of hexane and addition of DMSO (2 ml). TLC showed still the presence of **7**. After the dropwise addition of an additional aliquot of the stock soln. of **2** (600 mg, 0.91 mmol), stirring was continued for 1 h. Normal workup (AcOEt, brine and aq. NH_4Cl) and FC (Et_2O and AcOEt) of the residue (240 mg) gave **8**/**9** (10:1 according to ^{1}H-NMR, 101 mg, 74%). Several recrystallizations (2 × in AcOEt, 2 × in AcOEt/hexane/acetone, 2 × in EtOH/toluene/hexane, 2 × in EtOH/toluene) gave pure **8** (32 mg, 22%).

Data of **8**: fine needles. R_f (AcOEt) 0.40. M.p. 202–203° (AcOEt; [18]: 191–191.5°). $[\alpha]_D^{25} = -91.4$ ($c = 1$, acetone), –94.3 ($c = 0.6$, DMF; [18]: –93.3 ($c \approx 8$, DMF)). IR (KBr): 3470*m*, 3140*w*, 3030*w*, 2890*w*, 1775*w*, 1700*s*, 1680*s*, 1620*w*, 1465*m*, 1410*m*, 1370*w*, 1340*w*, 1280*m*, 1265*m*, 1225*w*, 1115*s*, 1095*s*, 1070*s*, 1050*w*, 1030*w*, 980*m*, 940*w*, 920*w*, 850*m*, 810*w*, 755*m*, 700*m*, 640*w*. ^{1}H-NMR (400 MHz, (D_6)acetone): 10.05 (br. *s*, exchangeable with D_2O, NH); 7.85 (*d*, $J = 8,1$, H–C(6)); 7.58–7.55 (*m*, irrad. at 6.00→NOE of 6%, 2 arom. H); 7.49–7.40 (*m*, 3 arom. H); 6.04 (*d*, $J = 2.9$, H–C(1′)); 6.00 (*s*, PhC*H*); 5.60 (*d*, $J = 8.1$, H–C(5)); 5.09 (*dd*, $J = 2.9$, 6.7; irrad. at 6.04→*d*, $J = 6.7$; irrad. at 6.00→NOE of 3%, H–C(2′)); 5.00 (*dd*, $J = 3.2$, 6.7; irrad. at 4.36→*d*, $J = 6.7$, irrad. at 6.00→NOE of 3%, H–C(3′)); 4.36 (br. *q*, $J \approx 3.6$, H–C(4′)); 4.26 (*t*, $J = 5.2$, exchangeable with D_2O, OH); 3.86–3.78 (*m*, addn. D_2O→3.80, *dd*, $J = 4.0$, 11.9, 3.76, *dd*, $J = 4.0$, 11.9; irrad. at 4.36→*AB*, $J = 11.9$, 2 H–C(5′)). ^{1}H-NMR (400 MHz, (D_6)DMF): 11.04 (br. *s*, NH); 8.00 (*d*, $J = 8.0$, H–C(6)); 7.61–7.59 (*m*, 2 arom. H); 7.48–7.46 (*m*, 3 arom. H); 6.12 (*d*, $J = 2.7$, H–C(1′)); 6.05 (*s*, PhC*H*); 5.69 (*d*, $J = 8.0$, H–C(5)); 5.33 (*t*, $J = 5.2$, OH); 5.15 (*dd*, $J = 2.7$, 6.6, H–C(2′)); 5.01 (*dd*, $J = 2.9$, 6.7, H–C(3′)); 4.39 (br. *q*, $J \approx 4.0$, H–C(4′)); 3.79–3.73 (*m*, 2 H–C(5′)). ^{13}C-NMR (50 MHz, (D_6)DMSO): 163.20 (*s*, C(4)); 150.35 (*s*, C(2)); 142.09 (*d*, C(6)); 136.21 (*s*, arom. C); 129.72 (*d*, arom. C); 128.38 (*d*, 2 arom. C); 126.87 (*d*, 2 arom. C); 106.48 (*d*, PhCH); 101.72 (*d*, C(5)); 91.33 (*d*, C(1′)); 86.35, 84.44, 81.87 (3*d*, C(2′), C(3′), C(4′)); 61.33 (*t*, C(5′)). CI-MS: 351 (18), 350 (100, $[M + NH_4]^+$), 334

(14), 333 (69, $[M + 1]^+$), 332 (18), 238 (26), 221 (17), 130 (9), 113 (6). Anal. calc. for $C_{16}H_{16}N_2O_6$ (332.32): C 57.82, H 4.85, N 8.43; found: C 57.87, H 4.93, N 8.43.

Data of **9**: ^{1}H-NMR (from **8**/**9** 10:1, 400 MHz, (D_6)acetone): 7.76 (*d*, *J* = 8.1, H–C(6)); 6.16 (*s*, PhC*H*); 5.99 (*d*, *J* = 2.7, H–C(1′)); 5.61 (*d*, *J* = 8.1, H–C(5)); 4.27 (*dd*, *J* = 4.0, 8.1, H–C(4′)).

*Methyl (2*R*,4*R*)- and (2*S*,4*R*)-2,3:4,6-Di-*O*-benzylidene-α-*D*-glucopyranoside* (**11** *and* **12**). *a*) A mixture of **10** [14] (200 mg, 0.71 mmol) and powered KOH (230 mg, 3.54 mmol) in DMF (10 ml) was stirred for 7 min at r.t., leading to a viscous soln. After the dropwise addition (within 0.5 h) of an aliquot of a stock soln. of **2** (26% in hexane, 782 mg, 1.0 mmol), stirring was continued for 1 h. TLC showed still the presence of **10**. After the dropwise addition (within 0.5 h) of an additional aliquot of the stock soln. of **2** (1.0 ml, 1.1 mmol) and stirring for 1 h, TLC showed completion of the reaction. Normal workup (brine, CH_2Cl_2) and FC (hexane/AcOEt 10:0.8) gave **11** (205 mg, 78%) and **12** (45 mg, 17%).

b) At r.t., a vigorously stirred soln. of **10** (100 mg, 0.35 mmol) in DMSO (2 ml) was treated with a soln. of KOH (115 mg, 1.77 mmol) in H_2O (0.3 ml) and dropwise (within 15 min) with an aliquot of a stock soln. of **2** (26% in hexane, 782 mg, 1.0 mmol). After stirring for further 15 min, the crystalline precipitate was separated by filtration, washed with H_2O and hexane, and dried *in vacuo* to yield **11**/**12** (9:1, 110 mg, 84%). FC (hexane/AcOEt 10:0.8) gave **11** (95 mg) and **12** (12 mg). Normal workup of the filtrate (Et_2O, H_2O) and FC (hexane/AcOEt 10:0.8) of the residue (40 mg) gave **11** (17 mg, combined yield 85%) and **12** (1 mg, combined yield 10%).

Data of **11**: R_f (hexane/AcOEt 10:0.8) 0.1. M.p. 192–193° (hexane/CH_2Cl_2). $[\alpha]_D^{25} = +87.0$ (*c* = 1, $CHCl_3$). IR: 3020*w*, 2920*m*, 1450*m*, 1370*m*, 1310*w*, 1110*s*, 1050*s*, 1020*s*, 1000*s*, 960*m*, 910*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.52–7.33 (*m*, irrad. at 6.14→NOE of 4%, 10 arom. H); 6.14 (*s*, PhC*H* of dioxolane moiety); 5.61 (*s*, PhC*H* of dioxane moiety); 5.23 (*d*, *J* = 3.0, H–C(1)); 4.35 (*dd*, *J* = 4.6, 10.2, H_{eq}–C(6)); 4.29 (*t*, *J* = 9.5, H–C(3)); 3.95 (*t*, *J* = 9.3, H–C(4)); 3.89 (*t*, *J* = 10.3, H_{ax}–C(6)); 3.78 (*m*, H–C(5)); 3.75 (*dd*, *J* = 3.1, 9.3; irrad. at 6.14→NOE of 4%, H–C(2)); 3.54 (*s*, MeO). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.98 (*s*, arom. C); 136.87 (*s*, arom. C); 129.31, 129.09, 128.35, 128.30, 128.18, 126,64 (several *d*, 10 arom. C); 105.64 (*d*, PhCH of dioxolane moiety); 101.55 (*d*, PhCH of dioxane moiety); 98.85 (*d*, C(1)); 81.49 (*d*, C(4)); 78.59 (*d*, C(2)); 72.81 (*d*, C(3)); 68.84 (*t*, C(6)); 64.25 (*d*, C(5)); 55.75 (*q*, MeO). CI-MS: 372 (22), 371 (100, $[M + 1]^+$). Anal. calc. for $C_{21}H_{22}O_6$ (370.41): C 68.09, H 5.98; found: C 67.93, H 5.78.

Data of **12**: R_f (hexane/AcOEt 10:0.8) 0.16. $[\alpha]_D^{25} = +5.0$ (*c* = 1, $CHCl_3$). IR: 3020*w*, 2930*w*, 1450*w*, 1380*m*, 1310*w*, 1110*s*, 1090*s*, 1050*s*, 1020*m*, 995*w*, 970*w*, 910*w*, 900*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55–7.33 (*m*, irrad. at 6.17→NOE of 4%, 10 arom. H); 6.17 (*s*, PhC*H* of dioxolane moiety); 5.62 (*s*, PhC*H* of dioxane moiety); 5.18 (*d*, *J* = 3.1, H–C(1)); 4.38 (*t*, *J* = 9.3; irrad. at 6.17→NOE of 12%, H–C(3)); 4.36 (*dd*, *J* = 4.4, 10.0, H_{eq}–C(6)); 4.03 (*t*, *J* ≈ 9.3, H–C(4)); 3.90 (*t*, *J* = 10.3, H_{ax}–C(6)); 3.81 (*ddd*, *J* = 4.4, 8.7, 10.3, H–C(5)); 3.68 (*dd*, *J* = 3.1, 9.3, H–C(2)); 3.55 (*s*, MeO). CI-MS: 372 (20), 371 (100, $[M + 1]^+$). Anal. calc. for $C_{21}H_{22}O_6$ (370.41): C 68.09, H 5.98; found: C 68.16, H 5.75.

*Methyl (2*R*,4*R*)- and (2*S*,4*R*)-4,6-O-Benzylidene-2,3-O-(4-nitrobenzylidene)-α-*D*-glucopyranoside* (**14** and **15**). A soln. **13** (858 mg, 3.6 mmol) in 1,4-dioxane (1.2 ml) was added dropwise (within 3 h) to a hot (oil bath 97–103°) soln. of **10** (203 mg, 0.72 mmol) in dry pyridine (10 ml). Stirring was continued for 3.5 h, when TLC showed complete disappearance of **10**, and the color of the soln. had changed from red to purple. The viscous soln. was filtered through alumina (*Woelm BIII*, acetone/hexane 2:1). FC (hexane/AcOEt 10:1.5) of the purple residue (505 mg) gave **14** (163 mg, 55%) and **15** (103 mg, 35%).

Data of **14**: R_f (hexane/AcOEt 10:1.5) 0.16. $[\alpha]_D^{25} = +150.4$ (*c* = 1, $CHCl_3$). IR: 3030*w*, 2940*w*, 1610*w*, 1525*w*, 1380*w*, 1350*s*, 1110*s*, 1090*s*, 1060*s*, 1025*m*, 965*m*, 920*w*, 865*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.25–8.23 (*m*, 2 arom. H); 7.71–7.68 (*m*, irrad. at 6.21→NOE of 8%, 2 arom. H); 7.50–7.34 (*m*, 5 arom. H); 6.21 (*s*, PhC*H* of dioxolane moiety); 5.61 (*s*, PhC*H* of dioxane moiety); 5.24 (*d*, *J* = 3.0, H–C(1)); 4.35 (*dd*, *J* = 4.6, 10.2, H_{eq}–C(6)); 4.19 (*t*, *J* ≈ 9.5, H–C(3)); 3.96 (*t*, *J* ≈ 9.8; irrad. at 4.19→br. *d*, *J* = 9.5, H–C(4)); 3.89 (*t*, *J* = 10.4; irrad. at 4.35→*d*, *J* = 10.3, H_{ax}–C(6)); 3.77 (*dd*, *J* = 3.0, 9.2; irrad. at 5.24→*d*, *J* = 9.2; irrad. at 4.19→*d*, *J* = 3.0; irrad. at 6.21→NOE Of 8%, H–C(2)); 3.75 (*m*, irrad. at 4.35→less complex signals, H–C(5)); 3.54 (*s*, MeO). ^{13}C-NMR (50 MHz, $CDCl_3$): 144.73 (*s*, arom. C); 136.73 (*s*, arom. C); 129.23, 128.25, 127.59, 126.25, 123.59 (several *d*, 9 arom. C); 103.80 (*d*, PhCH of dioxolane moiety); 101.64 (*d*, PhCH of dioxane moiety); 98.68 (*d*, C(1)); 81.20 (*d*, C(4)); 78.62 (*d*, C(2)); 72.97 (*d*, C(3)); 68.77 (*t*, C(6)); 64.26 (*d*, C(5)); 55.80 (*q*, MeO). CI-MS: 433 (11, $[M + NH_4]^+$), 416 (17, $[M + 1]^+$), 387 (20), 386 (100, $[M - NO_2 + NH_3]^+$). Anal. calc. for $C_{21}H_{21}NO_8$ (415.40): C 60.72, H 5.10, N 3.37; found: C 61.00, H 4.97, N 3.40.

Data of **15**: R_f (hexane/AcOEt 10:1.5) 0.26. $[\alpha]_D^{25} = -40.0$ (*c* = 1, $CHCl_3$). IR: 3030*w*, 2940*m*, 1610*w*, 1525*s*, 1450*w*, 1380*w*, 1350*s*, 1110*s*, 1090*s*, 1060*s*, 1020*s*, 1000*s*, 970*m*, 920*w*, 855*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.27–8.24 (*m*, 2 arom. H); 7.71–7.68 (*m*, irrad. at 6.21→NOE of 6%, 2 arom. H); 7.53–7.51 (*m*, 2 arom. H); 7.39–7.36 (*m*, 3 arom. H); 6.21 (*s*, PhC*H* of dioxolane moiety); 5.63 (*s*, PhC*H* of dioxane moiety); 5.20 (*d*, *J* = 3.0;

irrad. at 3.61→*s*, H–C(1)); 4.41 (*t*, *J* = 9.2; irrad. at 3.61→*d*, *J* = 9.8; irrad. at 6.21→NOE of 12%, H–C(3)); 4.36 (*dd*, *J* = 4.5, 10.2, H_{eq}–C(6)); 4.00 (*t*, *J* = 8.8, H–C(4)); 3.90 (*t*, *J* = 10.3, H_{ax}–C(6)); 3.81 (*ddd*, *J* = 4.3, 8.6, 10.3, H–C(5)); 3.61 (*dd*, *J* = 3.0, 9.2, H–C(2)); 3.57 (*s*, MeO). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.49 (*s*, arom. C); 144.49 (*s*, arom. C); 136.71, 128.28, 127.23, 126.26, 123.63 (several *d*, 9 arom. C); 103.89 (*d*, PhCH of dioxolane moiety); 101.64 (*d*, PhCH of dioxane moiety); 98.77 (*d*, C(1)); 80.69 (*d*, C(4)); 76.36, 76.06 (2*d*, C(2), C(3)); 68.78 (*t*, C(6)); 64.14 (*d*, C(5)); 55.88 (*q*, MeO). CI-MS: 433 (8, $[M + NH_4]^+$), 417 (11), 416 (55, $[M + 1]^+$), 387 (20), 386 (100, $[M - NO_2 + NH_3]^+$). Anal. calc. for $C_{21}H_{21}NO_8$ (415.40): C 60.72, H 5.10, N 3.37; found: C 60.51, H 5.31, N 3.59.

*Benzyl (*S*)- and (*R*)-2-Acetamido-3,4-*O*-benzylidene-2-deoxy-6-*O*-trityl-α-*D*-glucopyranoside* (**17** and **18**). At r.t., a soln. of **16** [15] (120 mg, 0.22 mmol) in DMSO (1 ml) was treated first with a soln. of KOH (58 mg, 1.04 mmol) in H_2O (0.1 ml) and then dropwise (within 45 min) with an aliquot of a stock soln. of **2** (38% in hexane, 390 mg, 0.73 mmol). Stirring was continued for 45 min. Filtration through SiO_2 (AcOEt), drying (high vacuum/50°), and FC (hexane/AcOEt 2:3) of the residue (170 mg) gave **17**/**18** (130 mg, 94%). HPLC (CH_2Cl_2/MeCN 10:1.5) of an aliquot of this mixture (85 mg) gave **17** (43 mg, 31%) and **18** (35 mg, 25%).

Data of **17**: R_f (CH_2Cl_2/MeCN 10:1.5) 0.50. t_R (CH_2Cl_2/MeCN 10:1.5) 7.1 min. M.p. 181° (hexane/Et_2O). $[\alpha]_D^{25} = +54.8$ (*c* = 1, $CHCl_3$). IR: 3450*m*, 3070*w*, 3010*m*, 2930*w*, 2890*w*, 1680*s*, 1600*w*, 1510*m*, 1450*m*, 1370*w*, 1315*w*, 1290*w*, 1110*m*, 1040*s*, 940*w*, 900*w*, 845*w*, 695*m*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54–7.23 (*m*, irrad. at 6.08→NOE of 6%, 25 arom. H); 6.08 (*s*, PhC*H*); 5.82 (*d*, *J* = 9.2, NH); 5.12 (*d*, *J* = 3.8, H–C(1)); 4.88 (*d*, *J* = 11.7), 4.59 (*d*, *J* = 11.7, PhCH_2); 4.54 (*ddd*, *J* = 3.8, 9.2, 11.2, H–C(2)); 4.18 (*ddd*, *J* = 3.1, 5.7, 9.3, H–C(5)); 3.85 (*dd*, *J* = 8.9, 11.2, H–C(3)); 3.63 (*t*, *J* = 9.1; irrad. at 4.18→*d*, *J* = 8.8; irrad. at 6.08→NOE of 6%, H–C(4)); 3.47 (*dd*, *J* = 5.8, 10.0; irrad. at 4.18→*d*, *J* = 10.0, H–C(6)); 3.43 (*dd*, *J* = 3.0, 10.0; irrad. at 4.18→*d*, *J* = 10.0, H–C(6)); 1.98 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.78 (*s*, C=O); 143.83 (*s*, 3 arom. C); 138.22 (*s*, arom. C); 136.90 (*s*, arom. C); 129.16–126.39 (*m*, arom. C); 104.68 (*d*, PhCH); 96.84 (*d*, C(1)); 86.67 (*s*, Ph_3C); 76.46, 76.37, 71.85 (3*d*, C(3), C(4), C(5)); 69.75 (*t*, PhCH_2); 63.67 (*t*, C(6)); 52.79 (*d*, C(2)); 23.24 (*q*, Me). CI-MS: 659 (35), 643 (28), 642 (70, $[M + 1]^+$), 417 (31, $[M - Ph_3C + 1 + NH_4]^+$), 401 (21), 400 (100, $[M - Ph_3C + 2]^+$), 354 (12). Anal. calc. for $C_{41}H_{39}NO_6$ (641.77): C 76.73, H 6.13, N 2.18; found: C 76.70, H 6.28, N 2.38.

Data of **18**: R_f (CH_2Cl_2/MeCN 10:1.5) 0.64. t_R (CH_2Cl_2/MeCN 10:1.5) 6.2 min. $[\alpha]_D^{25} = +87.5$ (*c* = 1, $CHCl_3$). IR: 3450*m*, 3070*w*, 3010*m*, 2930*w*, 2890*w*, 1680*s*, 1600*w*, 1505*m*, 1450*m*, 1370*w*, 1315*w*, 1110*m*, 1040*s*, 940*w*, 900*w*, 845*w*, 695*m*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.48–7.20 (*m*, irrad. at 6.01→NOE of 7%, 25 arom. H); 6.01 (*s*, PhC*H*); 5.88 (*d*, *J* = 9.1; irrad. at 4.62→*s*, NH); 5.14 (*d*, *J* = 3.7; irrad. at 4.62→*s*, H–C(1)); 4.88 (*d*, *J* = 11.7), 4.59 (*d*, *J* = 11.7, PhCH_2); 4.62 (*ddd*, *J* = 3.8, 9.2, 11.3, H–C(2)); 4.13 (*td*, *J* = 4.2, 9.2, H–C(5)); 3.94 (*dd*, *J* = 8.9, 11.2; irrad. at 4.62→*d*, *J* = 8.8; irrad. at 6.01→NOE of 7%, H–C(3)); 3.58 (*t*, *J* ≈ 9.4; irrad. at 4.13→*d*, *J* = 8.8, H–C(4)); 3.34 (*d*, *J* = 4.6; irrad. at 4.13→*s*, 2 H–C(6)); 2.00 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.79 (*s*, C=O); 143.80 (*s*, 3 arom. C); 137.84 (*s*, arom. C); 137.00 (*s*, arom. C); 129.37–126.58 (*m*, arom. C); 104.99 (*d*, PhCH); 96.71 (*d*, C(1)); 86.52 (*s*, Ph_3C); 78.77, 75.10, 72.24 (3*d*, C(3), C(4), C(5)); 69.75 (*t*, PhCH_2); 63.62 (*t*, C(6)); 52.50 (*d*, C(2)); 23.31 (*q*, Me). CI-MS: 659 (23), 642 (27, $[M + 1]^+$), 417 (51, $[M - CPh_3 + 1 + NH_4]^+$), 401 (22), 400 (100, $[M - CPh_3 + 2]^+$), 384 (13). Anal. calc. for $C_{41}H_{39}NO_6$ (641.77): C 76.73, H 6.13, N 2.18; found: C 76.64, H 5.90, N 2.38.

*(*S*)- and (*R*)-1,5-Anhydro-3,4-*O*-benzylidene-2-deoxy-6-*O*-trityl-*D*-arabino-hex-1-enitol* (**20** and **21**). At r.t., a soln. of **19** [16] (500 mg, 1.3 mmol) in DMSO (3.5 ml) was treated simultaneously and dropwise with a soln. of KOH (250 mg, 3.85 mmol) in H_2O (0.7 ml) within 42 min and with an aliquot of a stock soln. of **2** (50% in hexane, 1.44 g, 3.65 mmol) within 1.5 h. After stirring for further 15 min, normal workup (Et_2O, H_2O) and FC (SiO_2 treated with a soln. of Na_2CO_3 (5%) in H_2O and dried for 24 h at 120°, hexane/Et_2O/Et_3N 200:10:1) of the residue (798 mg) gave **20**/**21** (236 mg). HPLC (hexane/Et_2O/Et_3N 100:10:1) yielded **20** (213 mg) and a fraction of **20**/**21** (196 mg) which, upon a second HPLC, gave **20** (102 mg, combined yield 51%) and **21** (53 mg, 8%).

Data of **20**: R_f (hexane/Et_2O/Et_3N 100:10:1) 0.19. t_R (hexane/Et_2O/Et_3N 100:10:1) 9.4 min. $[\alpha]_D^{25} = +67.5$ (*c* = 1, $CHCl_3$): IR: 3030*w*, 2920*w*, 1610*m*, 1490*m*, 1450*m*, 1150*w*, 1110*s*, 1030*s*, 900*m*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.52–7.22 (*m*, 20 arom. H); 6.30 (*dd*, *J* = 2.5, 6.0; irrad. at 5.26→*d*, *J* = 2.4, H–C(1)); 6.28 (*s*; irrad. at 4.38→NOE of 1%; irrad. at 4.02→NOE of 12%, PhC*H*); 5.26 (*dd*, *J* = 1.3, 6.0; irrad. at 4.38→NOE of 5%, H–C(2)); 4.55 (*ddd*, *J* = 2.9, 5.4, 10.8; irrad. at 4.38→NOE of 10%, H–C(5)); 4.38 (*ddd*, *J* = 1.5, 2.3, 8.4; irrad. at 5.26→*dd*, *J* = 2.4, 8.4, H–C(3)); 4.02 (*dd*, *J* = 8.4, 10.8, H–C(4)); 3.52 (*dd*, *J* = 2.8, 10.5, H–C(6)); 3.43 (*dd*, *J* = 5.4, 10.5, H′–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 144.04 (*d*, C(1)); 143.79 (*s*, 3 arom. C); 138.65 (*s*, arom. C); 129.12 (*d*, arom. C); 128.79 (*d*, 6 arom. C); 128.38 (*d*, 2 arom. C); 127.81 (*d*, 6 arom. C); 127.04 (*d*, 3 arom. C); 126.14 (*d*, 2 arom. C); 106.75 (*d*, PhCH); 99.48 (*d*, C(2)); 86.71 (*s*, Ph_3C); 78.17, 78.13, 73.34 (3*d*, C(3), C(4), C(5)); 64.10 (*t*, C(6)). CI-MS: 244 (18), 243 (100, $[Ph_3C]^+$). Anal. calc. for $C_{33}H_{28}O_4$ (476.58): C 80.64, H 5.92; found: C 80.78, H 5.95.

Data of **21**: R_f (hexane/Et_2O/Et_3N 100:10:1) 0.15. t_R (hexane/Et_2O/Et_3N 100:10:1) 11.4 min. $[\alpha]_D^{25} = -29.5$ (c = 1, $CHCl_3$). IR: 3060*w*, 3010*w*, 2920*w*, 1610*m*, 1490*w*, 1450*m*, 1370*w*, 1300*w*, 1050*m*, 1110*s*, 1020*s*, 900*m*, 695*w*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.51–7.20 (*m*, irrad. at 6.21→NOE of 12%, 20 arom. H); 6.31 (*dd*, J = 2.4, 6.0, H–C(1)); 6.21 (*s*, PhC*H*); 5.29 (*dd*, J = 1.3, 6.0, H–C(2)); 4.57–4.51 (*m*; irrad. at 6.21→NOE of 7%, H–C(3), H–C(5)); 4.08 (*dd*, J = 8.4, 10.7, H–C(4)); 3.46 (*dd*, J = 2.8, 10.5, H–C(6)); 3.36 (*dd*, J = 5.2, 10.4, H′–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 144.46 (*d*, C(1)); 143.71 (*s*, 3 arom. C); 138.16 (*s*, arom. C); 129.22 (*d*, arom. C); 128.70 (*d*, 6 arom. C); 128.38 (*d*, 2 arom. C); 127.74 (*d*, 6 arom. C); 126.95 (*d*, 3 arom. C); 126.38 (*d*, 2 arom. C); 107.04 (*d*, Ph*C*H); 98.92 (*d*, C(2)); 86.53 (*s*, Ph_3C); 78.58, 77.65, 76.17 (3*d*, C(3), C(4), C(5)); 63.95 (*t*, C(6)). CI-MS: 244 (17), 243 (100, $[Ph_3C]^+$). Anal. calc. for $C_{33}H_{28}O_4$ (476.58): C 80.64, H 5.92; found: C 80.81, H 6.18.

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