84. Glycosylidene Carbenes

Part 21

Synthesis of *N*-Tosylglycono-1,4-lactone Hydrazones as Precursors of Glycofuranosylidene Carbenes

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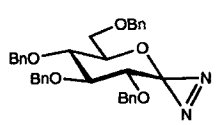
(21.IV.95)

The *N'*-(glycofuranosylidene)toluene-4-sulfonohydrazides **5** and **10** (*Scheme 1*) were prepared in good yields by oxidation (1,3-dibromo-5,5-dimethylhydantoin/Et_3N) of the *N'*-glycosyltoluene-4-sulfonohydrazides **4** and **9**, which were obtained from 2,3,5-tri-*O*-benzyl-D-ribose (**3**) and 2,3,5-tri-*O*-benzyl-D-arabinose (**8**), respectively, and toluene-4-sulfonohydrazide. The analogous naphthalene-2-sulfonohydrazides **7** and **12** were similarly prepared from **3** and **8** *via* **6** and **11**. Photolysis in the presence of phenol of the sodium salt **15** (*Scheme 2*), best generated *in situ*, yielded the anomeric glycosides **16**, some **5**, and traces of the glycosides (1*R*)/(1*S*)-**17**. Photolysis of **15** in THF gave the sulfones α-D/β-D-**18**. Photolysis of **15** (quartz filter) and dimethyl fumarate led to a single cyclopropane **19**, the sulfones α-D/β-D-**18**, and the *N*-(ribofuranosyl)-*N'*-(ribofuranosylidene)toluene-4-sulfonohydrazide **20**. Similarly, *N*-phenylmaleimide afforded the cyclopropanes **21** and **22**. Photolysis of the sodium salt of **10** and phenol afforded the anomeric glycosides α-D/β-D-**23**, the *C*-glycoside **24**, and the sulfone **25**. Photolytic glycosidation of **15** with N^6-benzyladenine gave the two nucleosides **26** and **27** (*Scheme 3*).

Introduction. – Glycopyranosylidene carbenes, known reactive intermediates [1], are best generated from diazirines, such as **1**, under mild thermal and photochemical conditions [2]. They are also formed from the alkali salts of *N'*-glycosylidenesulfonohydrazides, such as **2** [3] [4], or (in low yields) from diazides under photochemical conditions [5]. *N'*-(Glycopyranosylidene)sulfonohydrazides are more readily prepared than the corresponding diazirines and are more stable. Their salts react similarly to diazirines in forming glycosides with phenols [6–9] and cyclopropanes with electron-deficient alkenes [3] [9] [10]. Thermolysis of *N'*-(glycopyranosylidene)sulfonohydrazides, however, also generates sulfinates, and this results in the formation of additional by-products [11] [12].

Whereas pyranosylidenediazirines are sufficiently stable to be handled at ambient temperature, 1,4-anhydro-1-azi-2,3:5,6-di-*O*-isopropylidene-D-mannitol decomposes already at *ca.* −100° [6]. This high reactivity is presumably due to release of ring strain upon formation of the carbene and thought to be general for furanosylidenediazirines. Salts of



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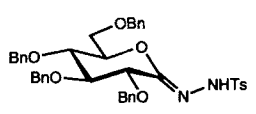

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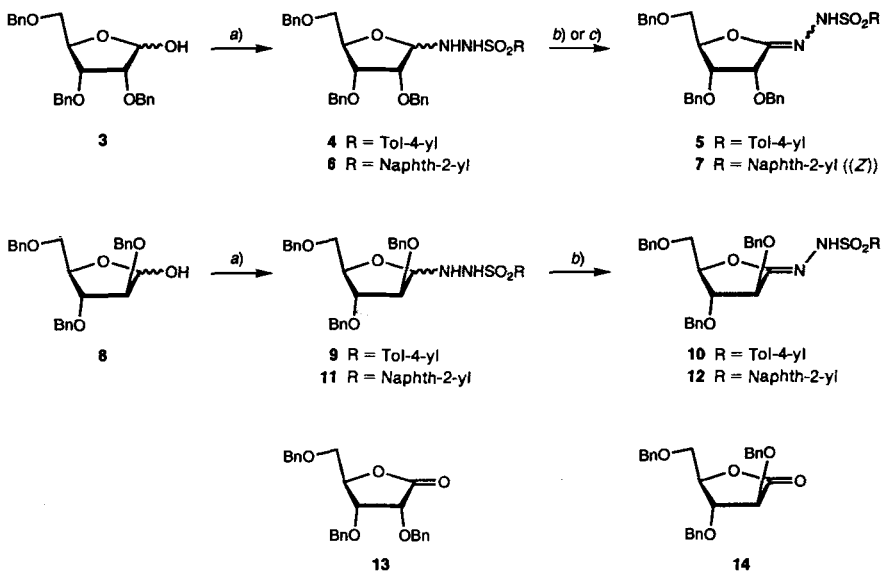
N'-furanosylidenesulfonohydrazides are thus the only practical precursors of furanosylidene carbenes accessible so far. We report the preparation and some reactions of *N'*-furanosylidenesulfonohydrazides from the known tri-*O*-benzyl-D-ribo- and -D-arabinofuranoses **3** [13] [14] and **8** [15] [16], respectively.

Results and Discussion. – Treatment of 2,3,5-tri-*O*-benzyl-D-ribofuranose (**3**, *Scheme 1*) with toluene-4-sulfonohydrazide in boiling toluene gave the anomeric *N'*-furanosyltoluene-4-sulfonohydrazides **4** (93%). The reaction is catalysed by AcOH [17]. Oxidation of **4** with 1,3-dibromo-5,5-dimethylhydantoin (dibromantin = 1,3-dibromo-5,5-dimethylimidazoline-2,4-dione) in DMF in the presence of Et_3N produced 79% of the *N'*-furanosylidenetoluene-4-sulfonohydrazide (*Z*)-**5**. A similar oxidation on a small scale in the presence of the weaker base *N*-methylmorpholine led to (*E*)/(*Z*)-**5** 1:7 (78%) and to the lactone **13** [18] [19] (9%), resulting from acid-catalysed hydrolysis of **5** during workup. The formation of **13** was suppressed by washing the crude with a hydrogen sulfite/hydrogen carbonate solution. Large-scale oxidations (up to 10 g) led to good yields of **5** when excess dibromantin was destroyed with hydrogensulfite and the acid neutralised with $NaHCO_3$. The (*E*)/(*Z*)-ratio (1:7) of a solution of **5** in $CDCl_3$ remained constant for several days at room temperature, while warming a solution of (*E*)/(*Z*)-**5** 1:7 in Et_2O/hexane to *ca.* 50° (for recrystallisation) resulted in complete transformation into (*Z*)-**5**. Similarly, **3** was transformed into the *N'*-(ribofuranosyl)naphthalene-2-sulfonohydrazide **6** and hence by oxidation with dibromantin/Et_3N into (*Z*)-isomer **7** (58% overall yield). The same sequence (treatment with toluene-4- or naphthalene-2-sulfono-

Scheme 1



a) $TsNHNH_2$ or naphthalene-2-sulfonohydrazide, MeCN, reflux; 93% of α-D/β-D-**4** 2:3, 85% of α-D/β-D-**6** 1:2, 78% of α-D/β-D-**9** 3:1, 70% of α-D/β-D-**11** 3:1. *b*) 1,3-Dibromo-5,5-dimethylhydantoin, DMF, Et_3N, −50° (for R = tol-4-yl) or 30° (for R = naphth-2-yl); 79% of (*Z*)-**5**, 68% of **7**, 81% of **10**, 65% of **12**. *c*) As *b*), but with *N*-methylmorpholine, −30°; 78% of (*E*)/(*Z*)-**5** 1:7 and 9% of **13**.

hydrazide and oxidation with dibromantin/Et_3N) was applied to the arabinofuranose **8**. It is notable that the oxidation of **9** and **11** in the presence of *N*-methylmorpholine led selectively to the (*Z*)-isomers **10** and **12**, respectively. Again, treatment of the crude product with the hydrogen sulfite/hydrogen carbonate solution prevented the formation of the lactone **14** [15] [20].

The *N'*-(pentofuranosyl)hydrazides **4**, **6**, **9**, and **11** were obtained as mixtures of α-D- and β-D-anomers. No indications for the corresponding open-chain *N'*-(pentosylidene)hydrazides could be detected in the IR and ^{1}H- and ^{13}C-NMR spectra. Upon standing in $CDCl_3$ solution, **4**, **6**, **9**, and **11** slowly equilibrated, reaching the equilibrium after 10–14 days (α-D/β-D 1:2 for **4** and **6** and 3:1 for **9** and **11**). The 1,2-*trans*-configurated anomers are more stable than the 1,2-*cis* ones. Characteristic IR bands are observed at *ca.* 3500 cm^{-1} for the amine and at 3200 cm^{-1} for the amide-type NH-stretching [21–23]. In the ^{1}H-NMR spectra, the NH–C(1) resonate at 4.74–4.18 ppm and the NH–SO_2 at 6.81–6.32 ppm [24]. Both H–N are rapidly and completely exchanged with D_2O. The assignment of the anomeric configuration is based on the chemical shifts of C(1) (upfield shift for 1,2-*cis*-substituted anomers [21] [25–28]) and on *J*(1,2) (larger values for 1,2-*cis*-substituted anomers [26]; *cf. Table*).

The lactone hydrazones **5**, **7**, **10**, and **12** show only the amide-type NH stretching at *ca.* 3250 or 3150 cm^{-1} [29]. The C=N bands appear at 1690–1650 cm^{-1} [30] [31]. The UV spectra show a characteristic absorption between 210 and 215 nm for the $\pi \rightarrow \pi^*$ transition [32]. In the ^{1}H-NMR spectra, the signals of NH–SO_2 at 7.71–7.55 ppm indicate the (*Z*)-configuration [18] [31] [33] [34]. H–N of (*E*)-**5** is shifted downfield to 8.44 ppm. In the ^{13}C-NMR

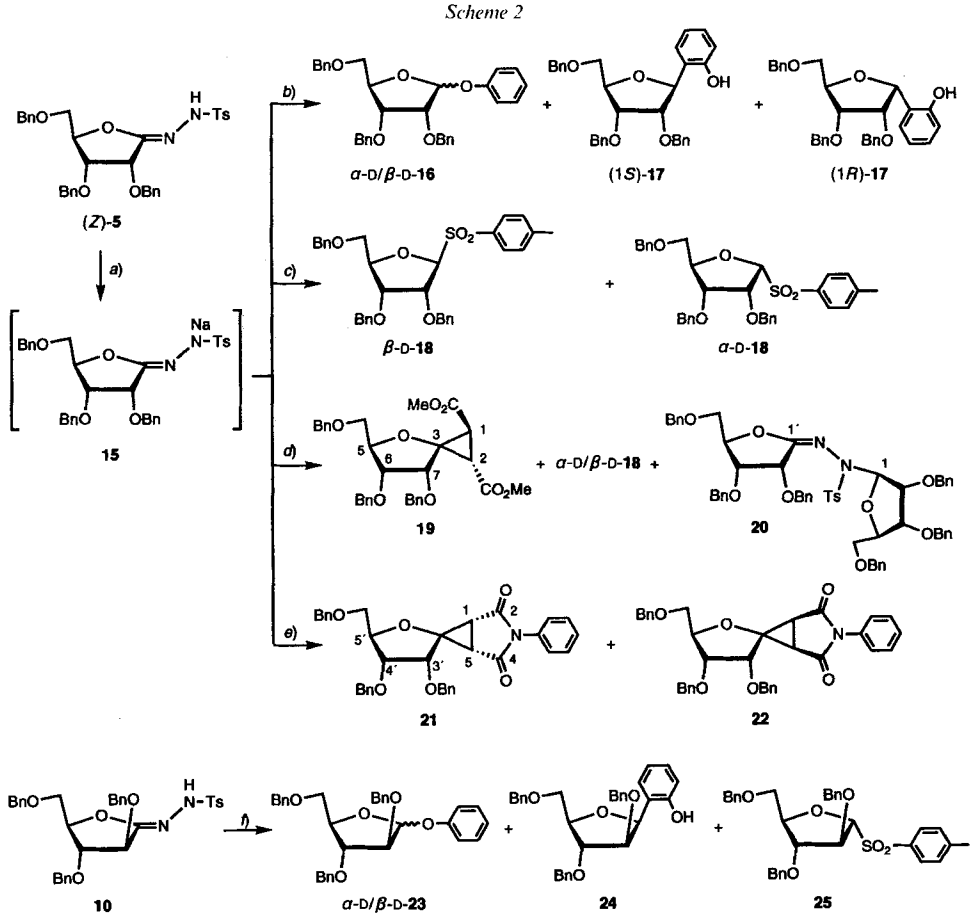
Table. *Selected Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of* **4–7**, **9–22**, *and* **23–27** *and Their Ring Conformation in $CDCl_3$ Solution*

	H–C(1)	C(1)	*J*(1,2)	*J*(2,3)	*J*(3,4)	Conformation
α-D-**4**	4.78	89.74	5.2	5.0	3.3	$^2T_3$
α-D-**6**	4.65	89.63	6.6	5.2	3.1	$^2T_3$
α-D-**16**	5.64	94.14	2.8		6.3	$^3T_2$
(1*R*)-**17**	5.07	94.16	8.3	5.7	3.0	$^2T_3$
α-D-**18**	5.01	103.42	5.0	4.8	8.2	$^3T_2$
β-D-**4**	4.68–4.65	94.06	3.1	5.3	5.6	$^3T_2$
β-D-**6**	4.66	93.95	2.7	5.6	6.0	$^3T_2$
β-D-**16**	5.71	99.80	1.0	4.6	6.7	$^3T_2$
(1*S*)-**17**	5.13	87.51	2.5	4.5	7.7	$^3T_2$
β-D-**18**	4.91	95.05	1.6	6.4	8.1	$^3T_2$
26	6.25	91.28	3.6	4.2	5.9	$^3T_2$
27	6.39	77.93	< 1	4.7	8.4	$^3T_2$
(*Z*)-**5**	–	152.58	–	5.0	8.2	$^3T_2$
(*E*)-**5**	–	169.45	–	2.0	8.9	E_2
7	–	152.75	–	5.0	8.3	$^3T_2$
15	–	96.85	–	4.5	8.1	$^3T_2$
13	–	173.64	–	5.9	2.0	$^2T_3$
20	5.90	94.16	2.0	5.2	7.3	$^3T_2$
	–	171.53	–	5.4	5.1	$^2T_3$
19	–	93.31	–	5.1	6.4	$^3T_2$
21	–	78.11	–	5.4	2.9	$^2T_3$
22	–	75.00	–	4.6	7.5	$^3T_2$
α-D-**9**	4.50–4.45	90.02			4.0	
α-D-**11**	4.18	94.28	< 1			
α-D-**23**	5.74	104.49	1.1	3.4	6.8	^0E
25	4.82	97.31	3.4	4.7	8.5	E_1
β-D-**11**	4.71	90.0	4.9			
β-D-**23**	5.57	98.96	4.3	7.0	5.6	$^3T_2$
24	5.07	88.73	6.6		5.6	
10	–	153.44	–	3.3	3.9	$^2T_3$
12	–	153.71	–	3.1	3.5	$^2T_3$
14	–	172.44	–	7.3	6.9	$^3T_2$

spectra, the chemical shifts for C(1) of (*Z*)-**5**, **7**, **10**, and **12** and the $\Delta\delta$ value for C(1) of (*E*)/(*Z*)-**5** of *ca.* 17 ppm are typical for (*E*)/(*Z*)-ketone hydrazones [35–37]. The ring conformations are deduced from $J(2,3)$ and $J(3,4)$ (*Table*). The medium $J(2,3)$ and the large $J(3,4)$ values of (*Z*)-**5** and **7** indicate a northern conformation ($^3T_2$), whereas the small value of $J(2,3)$ of (*E*)-**5** (2.0 Hz) agrees well with a E_2 conformation. $J(2,3)$ and $J(3,4)$ of the (*Z*)-configurated **10** and **12** are small and indicate a southern conformation ($^2T_3$). It is striking that the corresponding lactones prefer the opposite ring conformation, the ribonolactone **13** a southern ($^2T_3$) and the arabinolactone **14** a northern conformation ($^3T_2$).

The carbenes generated by photolysis of the *in-situ* generated sodium salts of *N'*-(glycopyranosylidene)toluene-4-sulfonohydrazides insert into O–H and C=C bonds [3]. The sodium salt **15** (*Scheme 2*) was similarly prepared from (*Z*)-**5** and NaOMe in MeOH,

Scheme 2



a) NaH, THF or 1,4-dioxane. *b*) Phenol, 1,4-dioxane, *hv*, 20° (72% of α-D/β-D-**16** 8:92 and 1% of (*R*)/(*S*)-**17** 1:1) *or* phenol, THF, *hv*, 18° (59% of α-D/β-D-**16** 1:3) *or* phenol, [15]crown-5, 1,4-dioxane, *hv*, 18° (45% of α-D/β-D-**16** 14:86 and 3% of (*R*)/(*S*)-**17** 1:2). *c*) THF, *hv*, 18° (39% of β-D-**18**) *or* 1,4-dioxane, *hv*, 24° (30% of α-D/β-D-**18** 1:4). *d*) Dimethyl fumarate, [15]crown-5, 1,4-dioxane, *hv*, 20° (28% of **19** and 45% of β-D-**18**) *or* dimethyl fumarate, 1,4-dioxane, *hv*, 20° (21% of **19**, 21% of β-D-**18**, 6% of α-D-**18**, and 13% of **20**). *e*) *N*-Phenylmaleimide, 1,4-dioxane, *hv*, 18°; 33% of **21**/**22** 10:1. *f*) NaH, phenol, 1,4-dioxane, *hv*, 20°; 58% of α-D/β-D-**23** 5:2, 2% of **24**, and 3% of **25**.

isolated by precipitation from Et_2O/hexane, and characterised by IR and ^{1}H-NMR spectra. We did not investigate if the precipitate contains crystal water, as it had been observed for the sodium salt of **2** [3] and the zwitterion obtained by deprotonation of the tosylhydrazone derived from the 3-acetyl-1-methylpyridinium ion [38]. An exploratory photolysis of isolated **15** in the presence of phenol gave poor yields of glycosides, similarly to the results in the pyranosylidene series [3]. However, *in-situ* generation of **15** with NaH, followed by irradiation in the presence of phenol yielded 72% of the known anomeric *O*-glycosides **16** [39] (α-D/β-D 8:92), besides 9% of (*Z*)-**5** and < 1% of the anomeric *C*-glycosides **17** ((1*R*)/(1*S*) 1:1). Higher concentrations of NaH increased the yield of *O*-glycosides (60% with 1.5 equiv. of NaH; 72% with 2 equiv. of NaH). Thermolysis of **15** in the presence of phenol and a large excess of [15]crown-5 at 120° in diglyme did not lead to glycosides. Above 140°, **15** decomposed. Photolysis of **15** in THF gave cleanly the sulfone β-D-**18** (39%), besides starting material (*Z*)-**5** (24%), while the use of 1,4-dioxane led to a 1:4 mixture of α-D/β-D-**18** (30%)[2]. Lactone azines, the main products of the decomposition of glycosylidenediazirines [11], were not observed. Photolysis of **15** in the presence of dimethyl fumarate in THF, using a *Vycor* filter absorbing light below 215 nm, did not lead to cyclopropanes, but again to the sulfones α-D/β-D-**18** 1:3 (46%). Use of a quartz filter, which absorbs below 180 nm, led to a poor yield of the cyclopropane **19**. Better yields were obtained in the presence of [15]crown-5 in 1,4-dioxane, leading to **19** (28%), β-D-**18** (45%), and (*Z*)-**5** (15%). In the absence of [15]crown-5, we isolated **20** (13%) as an additional product, besides **19** (21%), β-D-**18** (21%), (*Z*)-**5** (17%), and α-D-**18** (6%). The formation of **20** was enhanced by a larger excess of NaH (13% with 1.5 equiv. of NaH; 31% with 2.3 equiv. of NaH) and was only observed in the presence of dimethyl fumarate. Photolysis of **15** and *N*-phenylmaleimide in 1,4-dioxane gave the cyclopropanes **21**/**22** 10:1 (33%), besides some starting material (*Z*)-**5** (35%). The preferred formation of **19** and **21** is due to an unfavourable steric interaction between BnO–C(2) of the carbene and the ester or imide moiety of the alkene.

Photolysis of the *in-situ* generated sodium salt of **10** and phenol gave a mixture of the anomeric *O*-arabinosides **23**[3] (58%, α-D/β-D 5:2), **10** (10%), the sulfone **25** (3%), and the *C*-glycoside **24** (2%).

The structure of the *O*-glycosides **16** and **23**, the *C*-glycosides **17** and **24**, and the sulfones **18** and **25** is evidenced by the IR and ^{1}H- and ^{13}C-NMR spectra. The OH bands of **17** and **24** at 3380 cm^{-1} and the ^{1}H-NMR signals at 7.86 and 8.21 ppm indicate the presence of phenolic OH groups. The patterns of the aromatic H of **17** and **24** show the *ortho*-disubstitution of the phenol moiety. The large value of 6.6 Hz for J(1,2) of **24** (*cf. Table*) evidences the β-D-configuration. Typical SO_2 bands of **18** and **25** at 1315 and 1150 cm^{-1} indicate the presence of a sulfonyl group [41]. J(1,2) of 3.4 Hz for **25** does not allow to determine the configuration at C(1), but irradiation at H–C(1) gave a NOE (2%) for H–C(3), in keeping with the α-D-configuration. The assignment of the configuration at C(1) of **16**–**18** and **23**–**25** is based on the same criteria which were used for the *N*′-furanosyl-sulfonohydrazides (*Table*).

The configuration at C(1) and C(5) of the cyclopropanes **21** and **22** and at C(1) and C(2) of **19** was determined by NOE experiments, which had proven useful for the pyranosylidene analogues [10] [50]. Irradiation at H–C(3′) of **21** gave NOE's with both cyclopropyl H's: a NOE of 7.9% with the signal at 2.57 ppm (H–C(1)) and a weaker

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[2]) The well known pyranosyl- and furanosylsulfones are usually obtained by oxidation of thioglycosides (see *e.g.* [40–45]). Photochemical formation of sulfones by addition of alkoxycarbenes to alkali sulfinates is known [34] [46] [47]. The sulfonyl group of (1-nitro-β-D-ribofuranosyl)sulfones prefers a pseudoequatorial orientation [48].

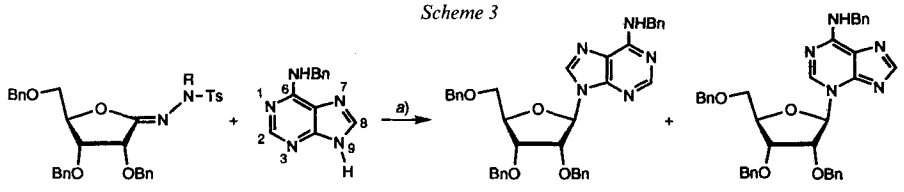
[3]) For the corresponding phenyl furanosides of L-arabinose, see [49].

one (2.3%) with the signal at 3.15 ppm (H–C(5)); irradiation at H–C(3′) of **22** gave a weak intensity increase (1.5%) with the more shielded cyclopropyl H at 2.90 ppm. $J(1,2)$ of 7.3 Hz for **19** indicates a *trans*-orientation of the methoxycarbonyl groups [10]. Irradiation of H–C(7) of **19** resulted in a NOE of 4% with the H resonating at 2.83 ppm (H–C(2)) and a 1% intensity increase for H–C(1), resonating at 2.77 ppm. These NOE's are in keeping with the (1*S*,2*S*)-configuration of **19**. IR and ^{1}H- and ^{13}C-NMR spectra of **20** indicate the presence of a ribofuranosylidene, a ribofuranosyl, and a tosyl group. The assignment of the ribofuranosylidene and ribofuranosyl H- and C-signals is based upon H,H- and C,H-COSY spectra. H–C(1) resonates at 5.90 ppm (*d* with $J(1,2) = 2.0$ Hz) and C(1) at 93.3 ppm (*cf. Table*) indicating a β-D-configuration [26] [27]. C(1′) of the furanosylidene moiety resonates at 171.53 ppm, similar to (*E*)-**5** ($\Delta\delta = 2$ ppm), but different from (*Z*)-**5** ($\Delta\delta = 19$ ppm). The analogy to ketone hydrazones strongly suggests that the large $\Delta\delta$ value is not the result of *N*,*N*-disubstitution [35] [51]; one deduces the (*E*)-configuration for **20**.

The glycosylidene carbene derived from the *N*′-pyranosylidenetoluene-4-sulfonohydrazide **2** inserts into N–H bonds [4]. Insertion of a ribofuranosylidene carbene into the H–N bond of a nucleobase should lead to nucleosides. Assuming a similar tautomeric equilibrium of N^6-benzyladenine as of adenine[4]), and glycosylation in an apolar solvent, one expects deprotonation by the carbene of H–C(9), considering the higher acidity of the purine than of the substituent N–H (pK_{HA} of adenine 9.8). Adenine and N^6,N^6-dimethyladenine are preferentially glycosylated (*Koenigs-Knorr*-type glycosylation) at N(3) and N(9) [60] [61].

Photolysis of *in-situ* generated **15** and N^6-benzyladenine produced a mixture of the two nucleosides **26** and **27** (68%; **26**/**27** 57:43) and (*Z*)-**5** (14%), which were separated by chromatography (*Scheme 3*). The formation of both isomers is in keeping with the known stereoelectronic effects in the carbene-mediated glycosylation [62–64]. Deprotonation of H–N(9) leads to a tight ion pair, where N(9) is in the σ-plane of the oxycarbenium ion; upon (partial) dissociation, N(3) may be somewhat more favourably positioned to attack in the π-plane than N(9).

Scheme 3



(*Z*)-**5** R = H
15 R = Na

26

27

a) 1,4-Dioxane, *hv*, 24°; 39% of **26** and 29% of **27**.

The structure of the nucleosides **26** and **27** is deduced from the UV and ^{1}H- and ^{13}C-NMR spectra. Both ^{1}H-NMR spectra lack purine NH signals at low field (*ca.* 11 ppm). Thus, insertion into the amine NH can be excluded. In $CDCl_3$ solution, NH of **26** resonates at 6.03 ppm and NH of **27** at 6.62 ppm, similar to NH of 9-benzyl-N^6-isopropyladenine (5.6 ppm) and 3-benzyl-N^6-isopropyladenine (6.7 ppm), but quite different from NH of 7-benzyl- N^6-isopropyladenine (4.3 ppm) [65]. The UV maximum of neutral **26** at 267 nm is only compatible with a 9-adenosine, and the one of **27** at 291 nm with a 3-adenosine[5]). This assignment is corroborated by the

[4]) Calculations show that 9*H*-adenine is the most stable tautomer in the gas phase [52–55]. In polar solvents, however, tautomeric mixtures of 9*H*- and 7*H*-adenine are observed by UV, IR, and NMR spectroscopy [56–59].

[5]) UV Maxima: 260 nm (9-adenosine [66–68] and 1-adenosine [69]), 270 nm (7-adenosine [67] [70]), 277 nm (3-adenosine [66] [71] [72]). Alkylation at N^6 leads to a bathochromic shift of *ca.* 8 nm for 9-adenosine [73] [74], of 5 nm for 7-adenine [65], and of 14 nm for 3-adenosine [60].

^{13}C-NMR spectra, where C(5) is the most shielded purine C [65] [75–78]. The chemical shift values for C(5) of **26** (119.61 ppm) and **27** (120.47 ppm) agree well with a 9- and 3-adenosine, respectively[6]). A 7-adenosine is clearly excluded. In addition, the chemical shifts of all purine C of **26** differ only slightly from those of N^6-(hydroxymethyl)-9-adenosine [77], and the values for **27** from those of 3-benzyl-N^6-isopropyladenine [65] ($\Delta\delta < 2$ ppm). The line broadening of the benzyl signals (stronger for **26** than for **27**) indicates the partial double bond character of the N–C(6) bonds [65] [81]. Characteristic shift differences between H–C(8) and H–C(2) are observed for N^6-monosubstituted 9-adenosines (0.38 ppm) [82] and 3-adenosines (0.79–0.84 ppm) [60] with, as a rule, H–C(8) resonating at higher field ($CDCl_3$ solutions) [71] [75] [82–85]. H–C(8) and H–C(2) of **26** resonate at 7.99 and 8.40 ppm ($\Delta\delta = 0.41$ ppm) and those of **27** at 7.91 and 8.65 ($\Delta\delta = 0.74$ ppm), respectively. The assignment of H–C(8) and H–C(2) is corroborated by NOE experiments (see also *Exper. Part*): irradiation of H–C(1′) of **26** led to a NOE (6.2%) with the more strongly shielded H–C(8), and irradiation of H–C(1′) of **27** led to a NOE (3.3%) with the less shielded H–C(2). The NOE's observed for H–C(2′) (3.1%) and H–C(3′) (2.8%) upon irradiation of H–C(8) of **26** and the NOE observed for H–C(3′) (3.5%) upon irradiation of H–C(2) of **27** are in keeping with the β-D-configuration, which is also suggested by the $J(1',2')$ values (**26**: 3.6 Hz; **27**: < 1 Hz).

We thank Dr. *B. Bernet* for his help in the preparation of the manuscript and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. Solvents and liquid reagents were distilled, solid reagents were recrystallised. NaH (80% NaH in white oil) was washed with dry hexane and dried. Irradiations were performed using a high-pressure Hg-lamp (*HPK 125 Philips*) equipped with a *quartz* filter. Normal workup means washing of the org. layer with H_2O and twice with brine, drying ($MgSO_4$), and evaporating below 30° in a *Büchi* rotary evaporator. Samples were dried under high vacuum (*in vacuo, i.v.*) at a pressure below 0.1 mbar. Qual. TLC: 0.25-mm precoated silica-gel plates (*Merck*, Kieselgel *60 F254*) with the solvent system indicated; detection by spraying the plates with a soln. of 5% vanillin in conc. H_2SO_4 soln. followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). M.p.: uncorrected. IR Spectra: KBr or 3% $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR Spectra: chemical shifts δ in ppm rel. to $SiMe_4$ as an internal standard, coupling constants J in Hz.

N′-(2,3,5-Tri-O-benzyl-α/β-D-ribofuranosyl)toluene-4-sulfonohydrazide (**4**). Solid toluene-4-sulfonohydrazide (5.29 g, 30 mmol) was added in portions to a soln. of **3** (12.63 g, 30 mmol) [14] [86] in MeCN (100 ml). The mixture was heated to reflux for 1 h. MeCN was distilled off at 40° *i.v.* and the residue dissolved in Et_2O. Normal workup, FC (CH_2Cl_2/MeOH 98:2), and crystallisation from Et_2O/hexane gave **4** (16.36 g, 93%; α-D/β-D 2:3). R_f (CH_2Cl_2/MeOH 98:2) 0.68. M.p. 94–95°. $[\alpha]_D^{25} = +64.7$ ($c = 0.86$, $CHCl_3$). IR (KBr): 3400*m*, 3200*m*, 3060*w*, 3030*w*, 2910*m*, 2860*m*, 1630*w*, 1595*w*, 1495*m*, 1460*w* (sh), 1450*m*, 1430*m*, 1400*w*, 1355*s*, 1330*m*, 1320*m*, 1290*m*, 1240*w*, 1205*w*, 1170*s*, 1115*m*, 1085*s*, 1035*m*, 915*m*, 810*m*, 745*m*, 695*s*, 670*m*, 605*m*. ^{1}H-NMR (400 MHz, $CDCl_3$; α-D/β-D 2:3): signals of β-D-**4**: 7.75 (*d*, $J = 8.3$, 2 arom. H); 7.38–7.20 (*m*, 17 arom. H); 6.63 (*s*, exchange with D_2O, NH); 4.68 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.68–4.65 (*m*, H–C(1)); 4.54 (*d*, $J = 12.2$, 1 H, PhCH_2); 4.48 (*d*, $J = 12,7$, 2 H, PhCH_2); 4.45 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.38 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.18 (*dd*, $J = 1.0$, 6.0, exchange with D_2O, NH); 4.11 (*td*, $J \approx 3.2$, 6.2, H–C(4)); 4.03 (*t*, $J \approx 5.6$, H–C(3)); 3.94 (*dd*, $J = 3.1$, 5.2, H–C(2)); 3.63 (*dd*, $J = 3.0$, 10.5, H–C(5)); 3.45 (*dd*, $J = 3.2$, 10.5, H–C(5)); 2.39 (*s*, Me); signals of α-D-**4**: 7.80 (*d*, $J = 8.3$, 2 arom. H); 6.32 (*s*, exchange with D_2O, NH); 4.89 (*d*, $J = 11.3$, exchange with D_2O, NH); 4.78 (*dd*, $J = 5.1$, 11.3; addn. of $D_2O \rightarrow d$, $J = 5.2$, H–C(1)); 4.69–4.66 (*m*, 1 H, PhCH_2); 4.50–4.44 (*m*, 4 H, PhCH_2); 4.49 (d, $J = 11.5$, 1 H, PhCH_2); 4.13 (*t*, $J \approx 4.1$, H–C(4)); 3.96 (*t*, $J \approx 5.2$, H–C(2)); 3.88 (*dd*, $J = 3.3$, 5.0, H–C(3)); 3.42 (*d*, $J = 4.1$, 2 HC(5)); 2.42 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$; α-D/β-D 2:3): signals of β-D-**4**: 143.59 (*s*); 137.78 (*s*); 137.59 (*s*); 137.54 (*s*); 135.23 (*s*); 129.32–127.41 (several *d*); 94.06 (*d*, C(1)); 80.19 (*d*, C(4)); 78.14 (*d*, C(2)); 77.10 (*d*, C(3)); 73.11 (*t*); 72.09 (*t*); 71.88 (*t*); 69.59 (*t*, C(5)); 21.33 (*q*, Me); signals of α-D-**4**: 143.41 (*s*); 137.66 (*s*); 137.37 (*s*); 135.38 (*s*); 89.74 (*d*, C(1)); 80.49 (*d*, C4)); *ca.* 77 (*d*); 76.77 (*d*); 73.23 (*t*); 72.69 (*t*); 72.28 (*t*); 69.98 (*t*, C(5)); 21.33 (*q*, Me). CI-MS: 435 (10), 434 (10), 433 (34, $[M - Ts]^+$), 369 (10), 325 (10), 308 (10), 307 (14), 296 (11), 295 (45), 277 (14), 247 (14), 202 (33), 187 (28), 157 (26), 139 (100). Anal. calc. for $C_{33}H_{36}N_2O_6S$ (588.73): C 67.33, H 6.16, N 4.76, S 5.45; found: C 67.41, H 6.37, N 4.90, S 5.35.

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[6]) Chemical shift values for C(5): 119.5 ppm (9-adenosine [77] [79]), 119.7 ppm (3-benzyl-N^6-isopropyladenine [65]), 110.2 ppm (7-adenosine [80]).

Oxidation of **4** *with Dibromantin. a*) A cooled (−50°) soln. of **4** (2.34 g, 4.0 mmol) in DMF (30 ml) was treated with Et_3N (700 µl, 5.0 mmol) and dibromantin (1.14 g, 4.0 mmol) in portions. The soln. was stirred for 20 min at −50°. After the addition of ice/H_2O, the mixture was extracted with Et_2O (3 ×). The org. layer was washed twice with an aq. $Na_2S_2O_5/Na_2CO_3$ soln.[7]) and with brine, dried (Na_2SO_4), and concentrated to 70 ml. After the addition of hexane, (*Z*)-**5** (1.49 g) was obtained as a crystalline solid. The mother liquor was evaporated and purified by FC (hexane/AcOEt/Et_3N 4:1:0.15→3:1:0.15). Drying of the combined crystals *i.v.* at r.t. gave (*Z*)-**5** (1.83 g, 79%).

b) A cooled (−50°) soln. of **4** (295 mg, 0.5 mmol) in DMF (10 ml) was treated with *N*-methylmorpholine (85 µl, 0.7 mmol) and dibromantin (148 mg, 0.5 mmol) in portions. The soln. was stirred for 20 min at −50°. After the addition of ice/H_2O, the mixture was extracted with Et_2O (3 ×). The org. layer was washed twice with an aq. $Na_2S_2O_5$ soln. and with brine, dried (Na_2SO_4), concentrated to *ca.* 10 ml and treated with hexane. The precipitate was filtered off, and dried *i.v.* at r.t.→(*E*)-**5**/(*Z*)-**5**/**13** 1:7:1 (256 mg; 78% of (*E*)/(*Z*)-**5**, 9% of **13**) as white crystals. A pure sample of **13** [18] [19] was prepared by oxidation of **3** with PDC (*ca.* 50% of **13**).

(Z)-N'-(2,3,5-Tri-O-benzyl-D-ribofuranosylidene)toluene-4-sulfonohydrazide ((*Z*)-**5**): R_f (hexane/AcOEt 2:1) 0.20. M.p. 99.5–101°. $[\alpha]_D^{25} = +54.2$ (*c* = 1.00, $CHCl_3$). UV (*c* = $1.19 \cdot 10^{-4}$, EtOH): 210 (22 104). IR (KBr): 3230*s*, 3060*w*, 3030*w*, 2910*m*, 2870*m*, 1690*s*, 1600*w*, 1495*m*, 1455*m*, 1410*m*, 1385*m*, 1375*w*, 1330*s*, 1290*m*, 1255*m*, 1235*m*, 1210*m*, 1185*m*, 1165*s*, 1125*s*, 1110*m* (sh), 1090*s*, 1070*m* (sh), 1030*s*, 1015*m* (sh), 980*s*, 905*m*, 890*m* (sh), 865*w*, 820*m*, 795*s*, 785*s*, 695*s*, 670*m*. IR ($CHCl_3$): 3295*w*, 3060*w*, 3020*m* (br.), 2930*w*, 2870*w*, 1690*m* (br.), 1600*w*, 1495*w*, 1455*m*, 1390*m*, 1345*m*, 1330*m* (sh), 1290*m*, 1240*w*, 1170*s*, 1125*m* (br.), 1095*s*, 1030*s*, 970*m* (sh), 910*w*, 815*w*, 700*s*, 665*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85 (*d*, *J* = 8.3, 2 arom. H); 7.58 (*s*, exchange with D_2O, NH); 7.38–7.19 (*m*, 17 arom. H); 4.60 (*ddd*, *J* = 2.0, 4.7, 8.2, H–C(4)); 4.53 (*d*, *J* = 11.6, 1 H, PhCH_2); 4.50 (*d*, *J* = 12.7, 1 H, PhCH_2); 4.48 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.47 (*d*, *J* = 11.8, 1 H, PhCH_2); 4.38 (*d*, *J* = 11.7, 1 H, PhCH_2); 4.27 (*d*, *J* = 11.7, 1 H, PhCH_2); 4.07 (*d*, *J* = 5.0, H–C(2)); 3.94 (*dd*, *J* = 5.0, 8.3, H–C(3)); 3.74 (*dd*, *J* = 2.0, 11.5, H–C(5)); 3.56 (*dd*, *J* = 4.7, 11.5, H–C(5)); 2.34 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 152.58 (*s*, C(1)); 143.95 (*s*); 137.38 (*s*); 136.80 (*s*); 136.76 (*s*); 135.16 (*s*); 129.45–127.70 (several *d*); 83.31 (*d*, C(4)); 75.39 (*d*, C(3)); 73.50 (*t*); 72.36 (*t*); 72.14 (*d*, C(2)); 70.14 (*t*); 67.85 (*t*, C(5)); 21.44 (*q*, Me). ^{15}N-NMR (400 MHz, $CDCl_3$): −144.30 (*s*, C=N); −230.51 (*d*, *J* = 83.8, NH). CI-MS: 589 (12), 588 (36), 587 (100, $[M + 1]^+$), 436 (16), 418 (10), 327 (11), 295 (27), 271 (10), 233 (11), 219 (19), 205 (15), 202 (22), 191 (10), 189 (49), 187 (22), 181 (40), 179 (12), 174 (13), 172 (44), 157 (43), 147 (47), 141 (11), 139 (20), 126 (10), 111 (14), 108 (23), 107 (64), 105 (11), 96 (11), 92 (14), 91 (54), 81 (15), 73 (10). Anal. calc. for $C_{33}H_{34}N_2O_6S$ (586.70): C 67.56, H 5.84, N 4.77, S 5.46; found: C 67.67, H 5.56, N 4.62, S 5.56.

(E)-N'-(2,3,5-Tri-O-benzyl-D-ribofuranosylidene)toluene-4-sulfonohydrazide ((*E*)-**5**): ^{1}H-NMR (400 MHz, $CDCl_3$); (*E*)-**5**/(*Z*)-**5**/**13** 1:7:1): 8.44 (br. *d*, *J* ≈ 5.9, exchange with D_2O, NH); 7.71 (*d*, *J* = 8.3, 2 arom. H); 4.19 (*d*, *J* = 2.0, H–C(2)); 3.84 (*dd*, *J* = 2.0, 8.9, H–C(3)); 3.54–3.51 (*m*, H–C(5)); 2.37 (*s*, Me). ^{13}C-NMR (150 MHz, $CDCl_3$; (*E*)-**5**/(*Z*)-**5**/**13** 1:7:1): 169.45 (*s*, C(1)); 144.54 (*s*); 137.67 (*s*); 137.44 (*s*); 136.44 (*s*); 133.58 (*s*); 80.07 (*d*, C(4)); 78.39 (*d*, C(3)); 73.42 (*t*, 2 C); 73.31 (*t*); 70.35 (*d*, C(2)); 69.18 (*t*, C(5)); 21.61 (*q*, Me).

2,3,5-Tri-O-benzyl-D-ribono-1,4-lactone (**13**): R_f (hexane/AcOEt 2:1) 0.44. M.p. 47–50° ([19]: 54–55°). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.29 (*m*, 13 arom. H); 7.21–7.17 (*m*, 2 arom. H); 4.97 (*d*, *J* = 11.9, 1 H, PhCH_2); 4.77 (*d*, *J* = 12.0, 1 H. PhCH_2); 4.72 (*d*, *J* = 11.9, 1 H, PhCH_2); 4.57 (*d*, *J* = 11.9, 1 H, PhCH_2); 4.57–4.55 (*m*, H–C(4)); 4.51 (*d*, *J* = 11.9, 1 H, PhCH_2); 4.43 (*d*, *J* = 11.3, 1 H, PhCH_2); 4.43 (*d*, *J* = 5.9, H–C(2)); 4.13 (*dd*, *J* = 2.0, 5.6, H–C(3)); 3.68 (*dd*, *J* = 2.9, 11.0, H–C(5)); 3.57 (*dd*, *J* = 2.7, 11.0, H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 173.64 (*s*, C(1)); 137.17 (*s*); 137.01 (*s*);136.89 (*s*); 128.44–126.89 (several *d*); 81.71 (*d*, C(4)); 75.32 (*d*, C(3)); 73.67 (*d*, C(2)); 73.57 (*t*); 72.65 (*t*); 72.32 (*t*); 68.68 (*t*, C(5)).

N'-(2,3,5-Tri-O-benzyl-α/β-D-ribofuranosyl)naphthalene-2-sulfonohydrazide (**6**). As described for **4**, with naphthalene-2-sulfonohydrazide (2.65 g, 11.9 mmol), **3** (5.00 g, 11.9 mmol), and MeCN (50 ml; 15 min). The residue was dissolved in CH_2Cl_2 and the soln. filtered through SiO_2 and evaporated. FC (hexane/Et_2O 1:1) gave **6** (6.35 g, 85%; α-D/β-D 36:64). R_f (hexane/Et_2O 1:1) 0.03. $[\alpha]_D^{25} = +52.0$ (*c* = 1.65, $CHCl_3$). IR (KBr): 3440*m* (br.), 3240*w* (br.), 3060*w*, 3030*w*, 2920*w*, 2870*w*, 1625*w*, 1590*w*, 1495*m*, 1455*m*, 1330*m*, 1270*w*, 1210*w*, 1165*s*, 1130*s*, 1075*s*, 1030*m*, 905*m*, 860*m*, 820*m*, 740*s* (br.), 700*s*, 660*m*, 615*m*. ^{1}H-NMR (400 MHz, $CDCl_3$; α-D/β-D 36:64): signals of β-D-**6**: 8.50 (*d*, *J* = 10.5, 1 arom. H); 7.96–7.85 (*m*, 4 arom. H); 7.82–7.79 (*m*, 1 arom. H); 7.67–7.54 (*m*, 2 arom. H); 7.38–7.15 (*m*, 14 arom. H); 6.80 (*s*, exchange with D_2O, NH); 4.66 (*dd*, *J* = 2.4, 5.3, addn. of D_2O→*d*, *J* = 2.4, H–C(1)); 4.65 (*d*, *J* = 11.7, 1 H, PhCH_2); 4.52 (*d*, *J* = 11.9, 1 H, PhCH_2); 4.49–4.36 (*m*, 4 H, PhCH_2, NH (exchange with D_2O)); 4.33 (*d*, *J* = 11.6, 1 H, PhCH_2); 4.12–4.08 (*m*, addn. of D_2O→*td*, *J* ≈ 3.0, 6.0, H–C(4)); 4.03 (*t*, *J* ≈ 5.6, H–C(3)); 3.92–3.90 (*m*, addn. of D_2O→*dd*, *J* = 2.1, 5.2, H–C(2)); 3.65 (*dd*, *J* = 2.7, 10.5, H–C(5));

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[7]) Prepared from 0.37 g (2.0 mmol) of $Na_2S_2O_5$ and 1.00 g (4.0 mmol) of $Na_2CO_3 \cdot 10\ H_2O$ in 200 ml of H_2O.

3.45 (*dd*, J = 2.9, 10.5, H–C(5)); signals of α-D-**6**: 6.43 (*s*, exchange with D_2O, NH); 4.97 (*d*, J = 11.3, exchange with D_2O, NH); 4.74 (*dd*, J = 5,6. 10.9, addn. of $D_2O \rightarrow d$, J = 5.6, H–C(1)); 4.12–4.08 (*m*, H–C(4)); 3.92–3.90 (*m*, addn. of $D_2O \rightarrow$3.91, *dd*, J = 5.2, 6.6, H–C(2)); 3.87–3.83 (*m*, addn. of $D_2O \rightarrow$3.85, *dd*, J = 3.1, 4.9, H–C(3)); 3.39 (*d*, J = 4.1, 2 H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$; α-D/β-D 36:64): signals of β-D-**6**: 137.58 (*s*); 137.50 (*s*); 137.43 (*s*); 135.05 (*s*); 134.81 (*s*, 2 C); 129.96–127.24 (several *d*); 123.08–122.62 (several *d*); 93.95 (*d*, C(1)); 80.26 (*d*, C(4)); 78.14 (*d*, C(2)); 76.94 (*d*, C(3)); 73.23 (*t*); 72.13 (*t*); 71.91 (*t*); 69.40 (*t*, C(5)); signals of α-D-**6**: 137.27 (*s*); 135.14 (*s*); 131.88 (*s*, 2 C); 89.63 (*d*, C(1)); 80.37 (*d*, C(4)); 78.05 (*d*, C(2)); 76.94 (*d*, C(3)); 72.80 (*t*); 72.22 (*t*); 69.94 (*t*, C(5)). ESI-MS: 625 ([M + 1]$^+$). Anal. calc. for $C_{36}H_{36}N_2O_6S$ (624.75): C 69.21, H 5.81, N 4.48, S 5.13; found: C 69.33, H 5.83, N 4.49, S 5.31.

(Z)-N'-(2,3,5-Tri-O-benzyl-D-ribofuranosylidene)naphthalene-2-sulfonohydrazide (**7**). As described for (*Z*)-**5** (*Exper. a*), with **6** (2.18 g, 3.5 mmol), DMF (20 ml), Et_3N (1 ml, 7.2 mmol), and dibromantin (1.00 g, 3.5 mmol; 45 min): **7** (1.18 g). Concentration of the mother liquor and FC (hexane/AcOEt/Et_3N 4:1:0.15→3:1:0.15) gave additional 7 (0.29 g, total yield 68%). R_f (hexane/AcOEt 1:1) 0.56. M.p. 104°. $[\alpha]_D^{25}$ = +28.4 (c = 1.08, $CHCl_3$). UV ($c = 7.62 \cdot 10^{-5}$, EtOH): 229 (44514). IR (KBr): 3235*m*, 3060*w*, 3030*w*, 2940*w* (br.), 2885*w* (br.), 1695*m*, 1495*w*, 1455*m*, 1395*m*, 1365*m*, 1340*m*, 1330*m*, 1315*m*, 1255*m*, 1205*w*, 1170*s*, 1135*s*, 1110*s*, 1075*m*, 1030*s*, 890*w*, 825*w*, 735*m*, 695*s*, 680*m*, 665*m*, 635*w*, 615*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.58 (br. *s*, 1 arom. H); 7.95–7.85 (*m*, 4 arom. H); 7.71 (*s*, exchange with D_2O, NH); 7.65–7.55 (*m*, 2 arom. H); 7.38–7.16 (*m*, 13 arom. H); 7.01–6.99 (*m*, 2 arom. H); 4.58 (*ddd*, J = 2.0, 4.7, 8.2, H–C(4)); 4.52 (*d*, J = 12.0, 1 H, PhCH_2); 4.50 (*d*, J = 11.5, 1 H, PhCH_2); 4.47 (*d*, J = 11.8, 1 H, PhCH_2); 4.36 (*d*, J = 11.7, 1 H, PhCH_2); 4.33 (*d*, J = 11.7, 1 H, PhCH_2); 4.20 (*d*, J = 11.7, 1 H, PhCH_2); 4.06 (*d*, J = 5.0, H–C(2)); 3.92 (*dd*, J = 5.0, 8.3, H–C(3)); 3.73 (*dd*, J = 2.0, 11.5, H–C(5)); 3.55 (*dd*, J = 4.7, 11.5, H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 152.75 (*s*, C(1)); 137.29 (*s*); 136.66 (*s*); 136.52 (*s*); 134.87 (*s*, 2 C); 131.89 (*s*); 129.55–127.36 (several *d*); 122.79 (*d*); 83.28 (*d*, C(4)); 75.30 (*d*, C(3)); 72.12 (*d*, C(2)); 73.32 (*t*); 72.21 (*t*); 70.07 (*t*); 67.72 (*t*, C(5)). CI-MS: 625 (14), 624 (42), 623 (100, [M + 1]$^+$), 515 (11), 436 (12), 433 (16), 325 (16), 308 (31), 225 (71), 191 (18), 175 (32), 108 (28). Anal. calc. for $C_{36}H_{34}N_2O_6S$ (622.74): C 69.43, H 5.50, S 5.15; found: C 69.22, H 5.61, S 5.31.

N'-(2,3,5-Tri-O-benzyl-α/β-D-arabinofuranosyl)toluene-4-sulfonohydrazide (**9**). As described for **4**, with toluene-4-sulfonohydrazide (8.54 g, 45.9 mmol), **8** (19.29 g, 45.9 mmol), and MeCN (200 ml; 2 h). Normal workup and crystallisation from Et_2O/hexane gave **9** (20.42 g, 78%; α-D/β-D 5:1). R_f (CH_2Cl_2/MeOH 98:2) 0.48. M.p. 117°. $[\alpha]_D^{25}$ = +23.3 (c = 0.98, $CHCl_3$). IR (KBr): 3320*m*, 3250*s*, 3060*w*, 3030*m*, 2910*m*, 2860*m*, 2800*w* (sh), 1595*m*, 1495*m*, 1455*s*, 1410*w*, 1380*m*, 1365*m*, 1325*s*, 1305*m* (sh), 1290*m* (sh), 1255*w*, 1205*m*, 1155*s*, 1085*s*, 1045*s*, 1030*m*, 960*m*, 905*m*, 880*w*, 810*m*, 755*m*, 745*s*, 695*s*, 670*m* (sh), 645*w*. ^{1}H-NMR (400 MHz, $CDCl_3$; α-D/β-D 5:1): signals of α-D-**9**: 7.85 (*d*, J = 8.2, 2 arom. H); 7.35–7.19 (*m*, 17 arom. H); 6.45 (*s*, exchange with D_2O, NH); 4.55–4.50 (*m*, exchange with D_2O, NH); 4.52 (*d*, J = 12.0, 1 H, PhCH_2); 4.50 (*d*, J = 12.8, 1 H, PhCH_2); 4.50–4.45 (*m*, H–C(1)); 4.47 (*d*, J = 12.1, 1 H, PhCH_2); 4.44 (*d*, J = 11.8, 1 H, PhCH_2); 4.35 (*d*, J = 11.8, 1 H, PhCH_2); 4.26 (*d*, J = 11.8, 1 H, PhCH_2); 4.18 (br. *q*, $J \approx$ 5.1, irrad. at 3.48→br. *d*, $J \approx$ 4.0, irrad. at 3.84→*t*, J = 5.3, H–C(4)); 3.85–3.83 (*m*, 2 H, irrad. at 4.18→3.84, *s*, H–C(2), H–C(3)); 3.50 (*dd*, J = 6.0, 10.0, H–C(5)); 3.46 (*dd*, J = 5.2, 10.0, H–C(5)); 2.38 (*s*, Me); signals of β-D-**9**: 7.76 (*d*, J = 8.2, 2 arom. H); 6.22 (*s*, exchange with D_2O, NH); 4.00–3.90 (*m*, 3 H); 2.41 (*s*, Me). ^{13}C-NMR (50,6 MHz, $CDCl_3$; α-D/β-D 5:1): signals of α-D-**9**: 143.81 (*s*); 137.72 (*s*); 137.41 (*s*); 137.27 (*s*); 135.52 (*s*); 129.46–127.63 (several *d*); 94.16 (*d*, C(1)); 83.88 (*d*, C(4)); 82.51 (*d*, C(2)); 80.76 (*d*, C(3)); 73.30 (*t*); 71.91 (*t*); 71.60 (*t*); 70.45 (*t*, C(5)); 21.44 (*q*, Me); signals of β-D-**9**: 137.61 (*s*); 135.44 (*s*); 90.02 (*d*, C(1)); 81.93 (*d*, C(4)); 81.83 (*d*, C(2)); 79.90 (*d*, C(3)); 73.40 (*t*); 71.91 (*t*); 71.84 (*t*); 70.53 (*t*, C(5)); 21.56 (*q*, Me). CI-MS (NH_3): 423 (30), 422 (100), 405 (16), 204 (54), 174 (85), 173 (21), 156 (32), 139 (67), 108 (19). Anal. calc. for $C_{33}H_{36}N_2O_6S$ (588.73): C 67.33, H 6.16, N 4.76, S 5.45; found: C 67.30, H 6.30, N 4.57, S 5.55.

Oxidation of **9** *with Dibromantin. a*) As described for (*Z*)-**5** (*Exper. a*), with **9** (2.00 g, 3.4 mmol) in DMF (20 ml; −60°), Et_3N (700 µl, 5.0 mmol), and dibromantin (0.96 g, 3.3 mmol; 80 min at −60°). Addition of hexane to the concentrated soln. (*ca.* 50 ml) gave crystalline **10** (1.31 g). Concentration of the mother liquor and FC (hexane/AcOEt/Et_3N 4:1:0.15→3:1:0.15) gave additional **10** (0.3 g, total yield 81%). R_f (hexane/AcOEt 2:1) 0.30. M.p. 88°. $[\alpha]_D^{25}$ = +26.0 (c = 1.23, $CHCl_3$).

b) An analogous reaction omitting washing with aq. $Na_2S_2O_5/Na_2CO_3$ soln. led to **10** (1.30 mg, 65%) and **14** [15] [20] (0.14 g, 10%).

(Z)-N'-(2,3,5-Tri-O-benzyl-D-arabinofuranosylidene)toluene-4-sulfonohydrazide (**10**): R_f (hexane/AcOEt 1:1) 0.57. UV ($c = 1.45 \cdot 10^{-4}$, EtOH): 215 (21140). IR (KBr): 3210*s*, 3060*w*, 3030*m*, 2920*m*, 2870*m*, 1695*s*, 1595*m*, 1545*w*, 1500*m*, 1455*s*, 1395*s*, 1370*s*, 1350*s*, 1335*s* (sh), 1320*m* (sh), 1240*m*, 1215*m*, 1185*m*, 1170*s*, 1135*s*, 1090*s* (br.), 1020*s* (br.), 930*w*, 915*w*, 865*w*, 815*m*, 795*w*, 740*s* (br.), 700*s*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.84 (*d*, J = 8.3, 2 arom. H); 7.55 (*s*, exchange with D_2O, NH); 7.37–7.18 (*m*, 17 arom. H); 4.67 (*d*, J = 11.6, 1 H, PhCH_2); 4.58–4.50

(*m*, H–C(4)); 4.53 (*d*, J = 11.9, 1 H, PhCH_2); 4.49 (*s*, 2 H, PhCH_2); 4.48 (*d*, J = 10.1, 1 H, PhCH_2); 4.45 (*d*, J = 11.3, 1 H, PhCH_2); 4.33 (*d*, J = 3.1, H–C(2)); 4.02 (*t*, $J \approx$ 3.5, H–C(3)); 3.56 (*d*, J = 5.6, 2 H–C(5)); 2.35 (*s*, Me). ^{1}H-NMR (400 MHz, C_6D_6): 7.97 (*d*, J = 8.3, 2 arom. H); 7.85 (*s*, exchange with D_2O, NH); 7.20–7.01 (*m*, 15 arom. H); 6.70 (*d*, J = 8.1, 2 arom. H); 4.72 (*d*, J = 11.5, 1 H, PhCH_2); 4.38 (*d*, J = 11.5, 1 H, PhCH_2); 4.24 (*dt*, J = 3.9, 5.7, H–C(4)); 4.22 (*d*, J = 12.2, 1 H, PhCH_2); 4.16 (*d*, J = 3.3, H–C(2)); 4.12 (*d*, J = 12.0, 1 H, PhCH_2); 4.12 (*s*, 2 H, PhCH_2); 3.94 (*t*, $J \approx$ 3.6, H–C(3)); 3.26 (*dd*, J = 5.6, 10.6, H–C(5)); 3.22 (*dd*, J = 5.8, 10.6, H–C(5)); 1.79 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 153.44 (*s*, C(1)); 143.75 (*s*); 137.29 (*s*); 136.83 (*s*); 136.70 (*s*); 135.18 (*s*); 129.34 (*d*, 2 C); 128.35–127.61 (several *d*); 84.79 (*d*, C(4)); 80.88 (*d*, C(3)); 78.19 (*d*, C(2)); 73.29 (*t*); 71.86 (*t*); 71.07 (*t*); 68.71 (*t*, C(5)); 21.39 (*q*, Me). CI-MS: (NH_3): 604 (13, $[M + NH_4]^+$), 588 (26), 587 (100, $[M + 1]^+$). Anal. calc. for $C_{33}H_{34}N_2O_6S$ (586.70): C 67.56, H 5.84, N 4.77, S 5.46; found: C 67.79, H 5.76, N 4.70, S 5.72.

*2,3,5-Tri-O-benzyl-*D*-arabinono-1,4-lactone* (**14**): R_f (hexane/AcOEt 1:1) 0.64. M.p. 66–68° ([15]: 63–65°; [20]: 67.5–68.5°). ^{1}H- and ^{13}C-NMR ($CDCl_3$): see [20]. ^{1}H-NMR (400 MHz, C_6D_6): 7.29 (*d*, J = 7.0, 2 arom. H); 7.15–7.04 (*m*, 13 arom. H); 5.05 (*d*, J = 11.6, 1 H, PhCH_2); 4.60 (*d*, J = 11.6, 1 H, PhCH_2); 4.42 (*d*, J = 11.9, 1 H, PhCH_2); 4.27 (*d*, J = 11.9, 1 H, PhCH_2); 4.21 (*d*, J = 12.3, 1 H, PhCH_2); 4.19 (*t*, $J \approx$ 7.4, irrad. at 4.00→*s*, H–C(3)); 4.15 (*d*, J = 12.5, 1 H, PhCH_2); 4.01 (*ddd*, J = 3.0, 4.5, 6.9, H–C(4)); 3.99 (*d*, J = 7.3, H–C(2)); 3.33 (*dd*, J = 3.0, 11.3, irrad. at 4.00→*d*, J = 11.2, H–C(5)); 3.17 (*dd*, J = 4.6, 11.3, irrad. at 4.00→*d*, J = 11.1, H–C(5)).

N′*-(2,3,5-Tri-O-benzyl-α/β-*D*-arabinofuranosyl)naphthalene-2-sulfonohydrazide* (**11**). As described for **6**, with naphthalene-4-sulfonohydrazide (4.32 g, 19.4 mmol), **8** (8.17 g, 19.4 mmol), and MeCN (80 ml; 4 h): **11** (8.43 g, 70%; α-D/β-D 4:1). R_f (hexane/AcOEt 1:1) 0.49. M.p. 121°. $[\alpha]_D^{25}$ = +19.7 (c = 0.93, $CHCl_3$). IR (KBr): 3320*m*, 3245*s*, 3050*w*, 3030*w*, 2900*w*, 2850*w*, 1625*w*, 1605*w*, 1590*w*, 1485*m*, 1470*w*, 1380*m*, 1365*m*, 1345*m*, 1325*s*, 1265*w*, 1245*w*, 1205*w*, 1155*s*, 1145*s*, 1130*s*, 1095*m*, 1070*s*, 1050*s*, 1020*m*, 995*m*, 950*m*, 865*w*, 810*m*, 735*s*, 695*s*, 660*m*, 640*m*, 620*w*. ^{1}H-NMR (400 MHz, $CDCl_3$; α-D/β-D 4:1): signals of α-D-**11**: 8.55 (*s*, 1 arom. H); 7.98–7.82 (*m*, 4 arom. H); 7.67–7.57 (*m*, 2 arom. H); 7.32–7.21 (*m*, 12 arom. H); 7.18–7.13 (*m*, 2 arom. H); 7.01–6.99 (*m*, 1 arom. H); 6.58 (*s*, exchange with D_2O, NH); 4.59 (*d*, J = 10.1, exchange with D_2O, NH); 4.49 (*d*, J = 11.9, 1 H, PhCH_2); 4.47 (*d*, J = 11.0, 1 H, PhCH_2); 4.44 (*d*, J = 11.0, 1 H, PhCH_2); 4.41 (*d*, J = 11.8, 1 H, PhCH_2); 4.18 (*d*, J = 9.6, addn. of D_2O→*s*, H–C(1)); 4.17 (*d*, J = 11.6, 1 H, PhCH_2); 4.11 (*d*, J = 11.8, 1 H, PhCH_2); 3.97–3.91 (*m*, H–C(4)); 3.81–3.78 (*m*, H–C(2), H–C(3)); 3.46 (*dd*, J = 6.3, 10.1, H–C(5)); 3.42 (*dd*, J = 5.5, 10.1, H–C(5)); signals of β-D-**11**: 8.48 (*s*, 1 arom. H); 6.35 (*s*, exchange with D_2O, NH); 4.71 (*dd*, J = 4.9, 11.5, addn. of D_2O→*d*, J = 4.7, H–C(1)); 4.40 (*d*, J = 11.9, 1 H, PhCH_2); 4.33 (*d*, J = 11.4, 1 H, PhCH_2); 3.52 (*dd*, J = 3.9, 10.2, H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$; α-D/β-D 4:1): signals of α-D-**11**: 137.58 (*s*); 137.21 (*s*, 2 C); 135.29 (*s*); 134.89 (*s*); 131.96 (*s*); 129.97–123.01 (several *d*); 94.28 (*d*, C(1)); 83.85 (*d*, C(4)); 82.47 (*d*, C(2)); 80.60 (*d*, C(3)); 73.24 (*t*); 71.85 (*t*); 71.49 (*t*); 70.52 (*t*, C(5)); signals of β-D-**11**: 90.0 (*d*, C(1)); 81.77 (*d*, C(4)); 80.57 (*d*); 80.53 (*d*, C(2), C(3)); 73.34 (*t*); 71.77 (*t*); 69.8 (*t*, C(5)). ESI-MS: 625 ($[M + 1]^+$). Anal. calc. for $C_{36}H_{36}N_2O_6S$ (624.75): C 69.21, H 5.81, N 4.48, S 5.13; found: C 69.20, H 5.70, N 4.52, S 5.35.

*(Z)-N′-(2,3,5-Tri-O-benzyl-*D*-arabinofuranosylidene)naphthalene-2-sulfonohydrazide* (**12**). As described for (*Z*)-**5** (*Exper. a*), with **11** (2.04 g, 3.3 mmol), DMF (20 ml), Et_3N (1 ml, 7.2 mmol), and dibromantin (0.93 g, 3.2 mmol; 30 min): **12** (0.98 g). Concentration of the mother liquor and FC (hexane/AcOEt/Et_3N 3:1:0.15) gave additional **12** (0.33 g, total yield 65%). R_f (hexane/AcOEt 1:1) 0.60. M.p. 101.5–102°. $[\alpha]_D^{25}$ = +35.6 (c = 1.00, $CHCl_3$). UV ($c = 1.00 \cdot 10^{-4}$, EtOH): 230 (36391). IR (KBr): 3240*m*, 3060*m*, 3030*m*, 2970*m*, 2920*m*, 2880*m*, 1690*m*, 1625*w*, 1590*w*, 1500*m*, 1470*w*, 1455*m*, 1395*m* (sh) 1380*s*, 1370*s* (sh), 1345*s*, 1335*m*, 1320*m*, 1280*w*, 1240*m*, 1220*m*, 1170*s*, 1135*s*, 1115*m*, 1090*s*, 1075*s*, 1065*s* (sh), 1015*s*, 1000*m* (sh), 915*w*, 870*m*, 825*m*, 755*s*, 740*s*, 700*s*, 660*m*, 640*m*, 620*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.56 (br. *s*, 1 arom. H); 7.94–7.85 (*m*, 4 arom. H); 7.65 (*s*, exchange with D_2O, NH); 7.65–7.55 (*m*, 2 arom. H); 7.34–7.15 (*m*, 13 arom. H); 7.06–7.04 (*m*, 2 arom. H); 4.60 (*d*, J = 11.5, 1 H, PhCH_2); 4.51–4.47 (*m*, H–C(4)); 4.49 (*d*, J = 11.8, 1 H. PhCH_2); 4.46 (*s*, 2 H, PhCH_2); 4.42 (*d*, J = 11.5, 1 H, PhCH_2); 4.41 (*d*, J = 11.8, 1 H, PhCH_2); 4.30 (*d*, J = 3.1, H–C(2)); 3.97 (*t*, $J \approx$ 3.5, H–C(3)); 3.52 (*d*, J = 5.6, 2 H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 153.71 (*s*, C(1)); 137.28 (*s*); 136.71 (*s*, 2 C); 135.10 (*s*); 135.00 (*s*); 132.04 (*s*); 129.64–127.42 (several *d*); 122.98 (*d*); 84.89 (*d*, C(4)); 80.90 (*d*, C(3)); 78.17 (*d*, C(2)); 73.36 (*t*); 71.95 (*t*); 71.20 (*t*); 68.76 (*t*, C(5)). CI-MS (NH_3): 625 (13), 624 (41), 623 (100, $[M + 1]^+$), 433 (10), 327 (19), 325 (13), 175 (23), 108 (11). Anal. calc. for $C_{36}H_{34}N_2O_6S \cdot H_2O$ (640.74): C 67.48, H 5.66, N 4.37; found: C 67.51, H 5.56, N 4.51.

*(Z)-N-Sodio-N′-(2,3,5-tri-O-benzyl-*D*-ribofuranosylidene)toluene-4-sulfonohydrazide* (**15**). A suspension of (*Z*)-**5** (150 mg, 0.34 mmol) in abs. MeOH (5 ml) was treated with 4.35M Na in abs. MeOH (60 µl) and stirred for 10 min. The clear soln. was concentrated to *ca.* 20% of the volume. Addition of Et_2O/hexane gave **15** (135 mg, 91%). R_f (hexane/AcOEt 1:1) 0.56. M.p. 112°. IR (KBr): 3060*w*, 3030*m*, 2920*m*, 2870*m*, 1665*m*, 1600*w*, 1495*m*, 1455*m*, 1395*w*, 1365*w*, 1235*m*, 1210*m* (sh), 1130*s*, 1085*s*, 1025*s*, 910*w*, 815*w*, 735*m*, 700*s*, 660*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.74 (*d*, J = 8.1, 2 arom. H); 7.33–6.97 (*m*, 17 arom. H); 4.34 (*d*, J = 11.8, 1 H, PhCH_2); 4.36–4.28 (*m*,

H–C(4)); 4.27 (*d*, *J* = 11.6, 1 H, PhCH_2); 4.20 (*d*, *J* = 11.9, 2 H, PhCH_2); 4.13 (*d*, *J* = 13.2, 1 H, PhCH_2); 4.09 (*d*, *J* = 4.5, H–C(2)); 4.08 (*d*, *J* = 13.1, 1 H, PhCH_2); 3.76 (*dd*, *J* = 4.9, 8.1, H–C(3)); 3.48 (br. *d*, *J* ≈ 9.1, H–C(5)); 3.32 (*dd*, *J* = 5.4, 10.9, H–C(5)); 2.06 (*s*, Me).

*Reaction of (Z)-***5** *with Phenol. a*) A suspension of NaH (28 mg, 1.17 mmol) and (*Z*)-**5** (538 mg, 0.92 mmol) in 1,4-dioxane (25 ml) was stirred in a quartz vessel under N_2 for 10 min. The clear soln. was treated with phenol (445 mg, 4.73 mmol) and irradiated at *ca.* 20°. After 3 h, the mixture was treated again with NaH (15 mg, 0.63 mmol). Irradiation at *ca.* 20° was continued for 2 h. After evaporation, the residue was dissolved in Et_2O, washed with 2M NaOH (2 ×), and worked up as usual. Several FC's (hexane/Et_2O 4:1) and HPLC (*Spherisorb* silica (5 μm) 250 × 20 mm column, flow 16 ml/min, detection with UV (280 nm), hexane/Et_2O 4:1) gave β-D-**16** [39] (301 mg, 67%), α-D-**16** [39] (25 mg, 5%), (1*R*)/(1*S*)-**17** (2 mg, 0.5%), and (*Z*)-**5** (50 mg, 9%).

b) A suspension of NaH (24 mg, 1.00 mmol) and (*Z*)-**5** (500 mg, 0.85 mmol) in 1,4-dioxane (25 ml) was stirred in a quartz vessel under N_2 for 10 min. The clear soln. was treated with phenol (445 mg, 4.73 mmol) and irradiated at *ca.* 20° for 2.5 h. Workup as described for *a*) gave β-D-**16** (212 mg, 52%), α-D-**16** (40 mg, 8%), (1*R*)-**17** (12 mg, 3 %), (1*S*)-**17** (6 mg, 2%), and (*Z*)-**5** (93 mg, 19%).

c) A suspension of NaH (24 mg, 1.0 mmol) and (*Z*)-**5** (500 mg, 0.85 mmol) in THF (25 ml) was stirred under N_2 for 10 min. The clear soln. was treated with phenol (445 mg, 4.73 mmol) and irradiated at *ca.* 18° for 2.5 h. Workup as described for *a*) gave α-D/β-D-**16** (248 mg, 59%; α-D/β-D 1:3) and (*Z*)-**5** (21 mg, 4%).

*Phenyl 2,3,5-Tri-*O*-benzyl-*β*-*D*-ribofuranoside* (β-D-**16**): See [39], R_f (hexane/AcOEt 2:1) 0.61. M.p. 75–76° ([39]: 76–77°). $[\alpha]_D^{25} = -19.1$ (*c* = 0.70, $CHCl_3$, [39]: –20.3).

*Phenyl 2,3,5-Tri-*O*-benzyl-*α*-*D*-ribofuranoside* (α-D-**16**): See [39], R_f (hexane/AcOEt 2:1) 0.55. $[\alpha]_D^{25} = +68.2$ (*c* = 0.54, $CHCl_3$, [39]: +124.6).

*(1*R*)-1,4-Anhydro-2,3,5-tri-*O*-benzyl-1-*C*-(2-hydroxyphenyl)-*D*-ribitol* ((1*R*)-**17**): R_f (hexane/AcOEt 2:1) 0.45. $[\alpha]_D^{25} = -1.9$ (*c* = 0.37, $CHCl_3$). IR ($CHCl_3$): 3380*m*, 3050*w*, 3030*w* (sh), 3000*w*, 2960*m*, 2920*m*, 2870*m*, 1585*w*, 1490*m*, 1455*m*, 1360*m*, 1260*s*, 1100*s*, 1050*s*, 1030*s*, 915*w*, 865*w*, 700*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.86 (*s*, exchange with D_2O, OH); 7.37–7.16 (*m*, 17 arom. H); 6.89 (*dd*, *J* = 1.2, 7.8, 1 arom. H); 6.86 (*dd*, *J* = 1.2, 7.5, 1 arom. H); 5.07 (*d*, *J* = 8.3, H–C(1)); 4.66 (*d*, *J* = 12.1, 2 H, PhCH_2); 4.53 (*d*, *J* = 11.9, 1 H, PhCH_2);4.47 (*d*, *J* = 12.8, 1 H, PhCH_2); 4.45 (*s*, 2 H, PhCH_2); 4.27 (*q*, *J* ≈ 2.8, H–C(4)); 4.10 (*dd*, *J* = 5.7, 8.3, H–C(2)); 4.00 (*dd*, *J* = 3.0, 5.7, H–C(3)); 3.65 (*dd*, *J* = 3.1, 10.2, H–C(5)); 3.45 (*dd*, *J* = 2.3, 10.3, H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 155.50 (*s*); 137.75 (*s*); 137.48 (*s*); 137.24 (*s*); 129.44 (*d*); 128.77 (*d*); 128.48–127.77 (several *d*); 122.97 (*s*); 119.70 (*d*); 117.34 (*d*); 94.14 (*d*, C(1)); 83.74 (*d*, C(4)); 83.03 (*d*, C(2)); 81.65 (*d*, C(3)); 73.41 (*t*); 72.77 (*t*); 72.38 (*t*); 68.89 (*t*, C(5)). CI-MS (NH_3): 515 (36), 514 (100, $[M + NH_4]^+$), 436 (11), 371 (29), 330 (21), 281 (17), 108 (18), 91 (21). Anal. calc. for $C_{32}H_{32}O_5$ (496.60): C 77.40, H 6.49; found: C 77.68, H 6.71.

*(1*S*)-1,4-Anhydro-2,3,5-tri-*O*-benzyl-1-*C*-(2-hydroxyphenyl)-*D*-ribitol* ((1*S*)-**17**): R_f (hexane/AcOEt 2:1) 0.42. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.21 (*s*, exchange with D_2O, OH); 7.36–7.19 (*m*, 14 arom. H); 7.08–7.05 (*m*, 2 arom. H); 6.96 (*dd*, *J* = 1.5, 7.7, 1 arom. H); 6.91 (*dd*, *J* = 1.0, 8.2, 1 arom. H); 6.83 (*td*, *J* = 1.1, 7.5, 1 arom. H); 5.13 (*d*, *J* = 2.5, H–C(1)); 4.60 (*d*, *J* = 12.1, 1 H, PhCH_2); 4.55 (*d*, *J* = 11.9, 1 H, PhCH_2); 4.51 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.46–4.41 (*m*, H–C(4)); 4.40 (*d*, *J* = 12.2, 1 H, PhCH_2); 4.37 (*d*, *J* = 12.6, 1 H, PhCH_2); 4.35 (*dd*, *J* ≈ 4.5, 7.7, H–C(3)); 4.28 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.14 (*t*, *J* ≈ 3.3, H–C(2)); 3.78 (*dd*, *J* = 2.7, 11.0, H–C(5)); 3.64 (*dd*, *J* = 3.3, 11.0, H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 157.09 (*s*); 138.14 (*s*); 137.61 (*s*, 2 C); 129.35 (*d*); 128.57–127.63 (several *d*); 120.56 (*s*); 119.27 (*d*); 117.39 (*d*); 94.16 (*d*, C(1)); 85.08 (*d*, C(4)); 79.85 (*d*, C(2)); 79.45 (*d*, C(3)); 73.57 (*t*); 73.27 (*t*); 72.59 (*t*); 69.75 (*t*, C(5)). CI-MS (NH_3): 515 (29), 514 (100, $[M + NH_4]^+$).

*Photolysis of (Z)-***5** *in the Presence of NaH. a*) A suspension of NaH (27 mg, 1.13 mmol) and (*Z*)-**5** (527 mg, 1.13 mmol) in THF (25 ml) was stirred in a quartz vessel under N_2 for 10 min. The clear soln. was irradiated at *ca.* 18° for 6 h and evaporated. The residue was dissolved in AcOEt, worked up as usual, and filtered through silica gel (hexane/AcOEt 2:1). FC (hexane/AcOEt 7:1) gave β-D-**18** (195 mg, 39%) and (*Z*)-**5** (141 mg, 24%).

b) As *a*), but in 1,4-dioxane. FC gave β-D-**18** (120 mg, 24%) and α-D-**18** (31 mg, 6%).

*2,3,5-Tri-*O*-benzyl-1-deoxy-1-[(tol-4-yl)sulfonyl]-*β*-*D*-ribofuranose* (β-D-**18**): R_f (hexane/AcOEt 2:1) 0.37. M.p. 74°. $[\alpha]_D^{25} = +8.2$ (*c* = 0.61, $CHCl_3$). IR (KBr): 3440*m*, 3060*w*, 3020*m*, 2950*w*, 2930*m*, 2890*m*, 2870*m*, 1595*w*, 1495*w*, 1455*m*, 1465*m* (sh), 1415*w*, 1360*m*, 1330*m*, 1315*s*, 1290*s*, 1260*w*, 1210*m*, 1150*s*, 1130*s*, 1080*s*, 1060*s*,1025*m*, 1005*m*, 1000*m* (sh), 975*w*, 930*w*, 815*m*, 760*m*, 735*s*, 695*m*, 665*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.73 (*d*, *J* = 8.3, 2 arom. H); 7.43–7.23 (*m*, 17 arom. H); 4.91 (*d*, *J* = 1.6, H–C(1)); 4.74 (*d*, *J* = 11,9, 1 H, PhCH_2); 4.61 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.57 (*dd*, *J* ≈ 1.6, 5.3 (partially hidden), H–C(2)); 4.57 (*d*, *J* = 12.2, 1 H, PhCH_2); 4.51 (*d*, *J* = 12.8, 2 H, PhCH_2); 4.38 (*ddd*, *J* = 3.4, 6.2, 8.0, H–C(4)); 4.40 (*d*, *J* = 11.6, 1 H, PhCH_2); 3.99 (*dd*, *J* = 5.3, 8.1, H–C(3)); 3.67 (*dd*, *J* = 3.4, 10.9, H–C(5)); 3.62 (*dd*, *J* = 6.2, 10.9, H–C(5)); 2.42 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 145.17 (*s*); 138.06 (*s*); 137.26 (*s*); 136.77 (*s*); 133.17 (*s*); 129.64 (*d*); 129.44 (*d*); 128.50–127.64 (several *d*); 96.85 (*d*, C(1)); 82.48 (*d*, C(4)); 78.23 (*d*, C(2)); 75.90 (*d*, C(3)); 73.29 (*t*); 72.48 (*t*); 72.25 (*t*); 70.20 (*t*, C(5)); 21.65 (*q*, Me).

CI-MS (NH_3): 578 (11), 577 (38), 576 (100, $[M + NH_4]^+$), 108 (13), 91 (5). Anal. calc. for $C_{33}H_{34}O_6S \cdot 0.5\ H_2O$ (567.69): C 69.82, H 6.21, N 5.65; found: C 69.96, H 6.13, N 5.97.

*2,3,5-Tri-*O*-benzyl-1-deoxy-1-[(tol-4-yl)sulfonyl]-α-*D*-ribofuranose* (α-D-**18**): R_f (hexane/AcOEt 2:1) 0.27. M.p. 100–103°. $[\alpha]_D^{25} = +116.0$ ($c = 0.50$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3020*w* (br.), 2930*w*, 2870*w*, 1600*w*, 1495*w*, 1455*m*, 1405*w*, 1360*w* (sh), 1330*m*, 1315*m*, 1305*m*, 1260*w*, 1150*s* (br.), 1070*s*, 1030*m*, 1020*m*, 910*w*, 815*m*, 700*s*, 655*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.77 (*d*, $J = 8.3$, 2 arom. H); 7.42–7.12 (*m*, 17 arom. H); 5.01 (*d*, $J = 5.0$, H–C(1)); 4.93 (*d*, $J = 11.2$, 1 H, PhCH_2); 4.74 (*d*, $J = 11.2$, 1 H, PhCH_2); 4.52 (*t*, $J = 4.9$, H–C(2)); 4.50 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.48 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.42 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.35 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.27 (*ddd*, $J = 2.5$, 3.0, 8.0, H–C(4)); 3.96 (*dd*, $J = 4.8$, 8.2, H–C(3)); 3.69 (*dd*, $J = 2.3$, 11.4, H–C(5)); 3.49 (*dd*, $J = 3.4$, 11.4, H–C(5)); 2.35 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 144.14 (*s*); 137.80 (*s*); 137.48 (*s*); 137.35 (*s*); 135.75 (*s*); 129.47 (*d*); 128.25 (*d*); 128.12–127.46 (several *d*); 95.05 (*d*, C(1)); 81.46 (*d*, C(4)); 77.56 (*d*, C(2)); 76.95 (*d*, C(3)); 74.52 (*t*); 73.26 (*t*); 72.75 (*t*); 68.10 (*t*, C(5)); 21.48 (*q*, Me). CI-MS (NH_3): 578 (12), 577 (37), 576 (100, $[M + NH_4]^+$), 552 (13), 420 (11), 295 (21), 108 (13). Anal. calc. for $C_{33}H_{34}O_6S$ (558.69): C 70.94, H 6.13; found: C 70.87, H 5.93.

*Reaction of (*Z*)-***5*** with Dimethyl Fumarate. a)* A suspension of NaH (30 mg, 1.25 mmol) and (*Z*)-**5** (501 mg, 0.85 mmol) in 1,4-dioxane (25 ml) was stirred in a quartz vessel under N_2 for 10 min. The clear soln. was treated with [15]crown-5 (0.42 ml, 2.12 mmol) and dimethyl fumarate (371 g, 2.57 mmol) and irradiated at *ca.* 18° for 4 h. Evaporation, normal workup (AcOEt), filtration through silica gel (hexane/AcOEt 2:1) and several FC's (hexane/Et_2O 4:1) gave **19** (132 mg, 28%), β-D-**18** (213 mg, 45%), and (*Z*)-**5** (75 mg, 15%).

b) As *a)* but without [15]crown-5: **19** (96 mg, 21%), β-D-**18** (97 mg, 21%), α-D-**18** (29 mg, 6%), **20** (53 mg, 13%), and (*Z*)-**5** (85 mg, 17%).

*Dimethyl (1*S*,2*S*,5*R*,6*R*,7*R*)-6,7-Bis(benzyloxy)-5-[(benzyloxy)methyl]-4-oxaspiro[2,4]heptane-1,2-dicarboxylate* (**19**): R_f (hexane/AcOEt 2:1) 0.32. $[\alpha]_D^{25} = +52.7$ ($c = 0.73$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3030*w* (sh), 3000*w*, 2950*m*, 2920*w*, 2860*w*, 1725*s*, 1495*w*, 1455*m*, 1440*m*, 1400*w*, 1350*m* (sh), 1330*m*, 1300*m*, 1260*s*, 1240*m* (sh), 1195*m*, 1170*m* (sh), 1150*s*, 1100*s* (br.), 1030*s*, 905*m*, 870*w*, 810*m*, 700*m*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.26 (*m*, 15 arom. H); 4.72 (*s*, 2 H, PhCH_2); 4.59 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.59 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.49 (*d*, $J = 11.8$, 2 H, PhCH_2); 4.28 (*ddd*, $J = 3.2$, 3.3, 6.5, H–C(5)); 4.19 (*d*, $J = 5.0$, irrad. at 2.83→NOE (2.7%), irrad. at 2.77→NOE (1.1%), H–C(7)); 4.14 (*dd*, $J = 5.2$, 6.4, H–C(6)); 3.74 (*s*, MeO); 3.69 (*dd*, $J = 3.1$, 11.1, 1 H, CH_2–C(5)); 3.62 (*s*, MeO); 3.57 (*dd*, $J = 3.5$, 11.1, 1 H, CH_2–C(5)); 2.83 (*d*, $J = 7.3$, irrad. at 4.19→NOE (4.1%), irrad. at 2.77→NOE (3.4%), H–C(1)); 2.77 (*d*, $J = 7.3$, irrad. at 4.19→NOE (1.4%), irrad. at 2.83→NOE (3.9%), H–C(2)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 169.59 (*s*); 167.77 (*s*); 138.14 (*s*); 138.09 (*s*); 137.68 (*s*); 128.48–127.56 (several *d*); 81.12 (*d*, C(5)); 78.04 (*d*, C(7)); 76.02 (*d*, C(6)); 75.00 (*s*, C(3)); 73.37 (*t*); 72.65 (*t*); 72.32 (*t*); 69.18 (*t*, CH_2–C(5)); 52.30 (*q*, MeO); 52.08 (*q*, MeO); 30.39 (*d*); 29.24 (*d*, C(1), C(2)). CI-MS (NH_3): 565 (36), 564 (100, $[M + NH_4]^+$), 330 (11), 108 (9). Anal. calc. for $C_{32}H_{34}O_8$ (546.29): C 70.36, H 6.27; found: C 70.56, H 6.23.

*N′-[(*E*)-2′,3′,5′-Tri-*O*-benzyl-*D*-ribofuranosylidene]-*N*-(2,3,5-tri-*O*-benzyl-β-*D*-ribofuranosyl)toluene-4-sulfonohydrazide* (**20**): R_f (hexane/AcOEt 1:1) 0.52. $[\alpha]_D^{25} = +12.6$ ($c = 0.67$, $CHCl_3$). IR ($CHCl_3$): 3070*m*, 3030*m* (sh), 3010*m*, 2930*m*, 2870*s*, 1960*w*, 1880*w*, 1815*w*, 1660*s*, 1600*m*, 1500*m*, 1455*m*, 1405*m*, 1355*s*, 1310*m*, 1290*m*, 1260*m*, 1240*m* (sh), 1170*s*, 1090*s* (br.), 1040*s* (sh), 1030*s*, 915*m*, 815*m*, 700*s*, 665*m*. ^{1}H-NMR (400 MHz. $CDCl_3$): 7.84 (*d*, $J = 8.3$, 2 arom. H); 7.33–7.11 (*m*, 32 arom. H); 5.90 (*d*, $J = 2.0$, H–C(1)); 4.85 (*d*, $J = 11.8$ 1 H, PhCH_2); 4.71 (*dt*, $J = 2.6$, 5.1, H–C(4)); 4.63 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.59 (*d*, $J = 11.3$, 1 H, PhCH_2); 4.56 (*d*, $J = 11,4$, 1 H, PhCH_2); 4.49 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.48 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.46 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.39 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.34 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.27 (*d*, $J = 5.4$, H–C(2′)); 4.23 (*d*, $J = 12.2$, 1 H, PhCH_2); 4.20 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.19 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.15–4.11 (*m*, H–C(4), H–C(3′)); 3.94 (*dd*, $J = 2.1$, 5.2, H–C(2)); 3.73 (*dd*, $J = 5.2$, 7.3, H–C(3)); 3.70 (*dd*, $J = 2.5$, 11.3, H–C(5′)); 3.56 (*dd*, $J = 2.7$, 11.3, H–C(5′)); 3.45 (*dd*, $J = 3.9$, 11.1, H–C(5′)), 3.40 (*dd*, $J = 6.0$, 11.1, H–C(5)); 2.28 (*s*, Me). ^{13}C-NMR (150 MHz, $CDCl_3$): 171.53 (*s*, C(1′)); 143.34 (*s*); 138.65 (*s*); 138.02 (*s*); 137.84 (*s*); 137.22 (*s*); 137.17 (*s*); 137.11 (*s*); 135.57 (*s*); 129.17 (*d*); 128.75 (*d*); 128.64–127.19 (several *d*); 93.31 (*d*, C(1′)); 85.26 (*d*, C(4′)); 80.45 (*d*, C(4)); 78.79 (*d*, C(2)); 77.72 (*d*, C(3)); 75.27 (*d*, C(3′)); 74.65 (*d*, C(2′)); 73.43 (*t*); 72.96 (*t*); 72.21 (*t*); 72.03 (*t*); 71.92 (*t*); 71.69 (*t*); 70.80 (*t*, C(5)); 67.64 (*t*, C(5′)); 21.44 (*q*, Me). CI-MS (NH_3): 995 (22), 994 (54, $[M + NH_4]^+$), 993 (85), 901 (17), 885 (11), 682 (14), 681 (31), 593 (11), 592 (37), 591 (100), 576 (16), 418 (14), 374 (15), 308 (15), 295 (15). Anal. calc. for $C_{59}H_{60}O_{11}S \cdot 0.5\ H_2O$ (986.18): C 71.86, H 6.23; found: C 71.99, H 6.41.

*Reaction of (*Z*)-***5*** with N-Phenylmaleimide.* A suspension of NaH (29 mg, 1.22 mmol) and (*Z*)-**5** (604 mg, 1.02 mmol) in 1,4-dioxane (40 ml) was stirred in a quartz vessel under N_2 for 10 min. The clear soln. was treated with *N*-phenylmaleimide (1.81 g, 10.45 mmol) and irradiated at *ca.* 18° for 4 h. Evaporation, usual workup (AcOEt), filtration through silica gel (hexane/AcOEt 2:1), and several FC's (hexane/Et_2O 4:1) gave **21** (176 mg, 30%), **22** (17 mg, 3%), and (*Z*)-**5** (208 mg, 35%).

(1R,3'R,4'R,5S,5'R)-3',4'-Bis(benzyloxy)-5'-[(benzyloxy)methyl]-4',5'-dihydro-3-phenylspiro[3-azabicyclo[3.1.0]hexane-6,2'(3'H)-furan]-2,4-dione (**21**): R_f (hexane/AcOEt 2:1) 0.21. $[\alpha]_D^{25} = +15.3$ ($c = 0.96$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3030*w* (sh), 3000*w*, 2920*w*, 2860*m*, 1775*m*, 1715*s*, 1600*w*, 1500*m*, 1455*m*, 1390*s*, 1360*m*, 1330*w* (sh), 1250*m* (br.), 1180*m*, 1165*m*, 1120*s* (br.), 1090*m*, 1045*m*, 1030*m*, 990*m* (sh), 940*w*, 910*w*, 860*w*, 815*w*, 695*s*, 665*w*, 615*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.43–7.23 (*m*, 20 arom. H); 4.69 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.65 (*d*, $J = 12.1$, 1 H, PhCH_2); 461 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.52 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.47 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.43 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.37 (br. *q*, $J \approx 3.6$, H–C(5')); 4.17 (*d*, $J = 5.4$, irrad. at 2.57→NOE (4%), H–C(3')); 4.13 (*dd*, $J = 2.9$, 5.4, H–C(4')); 3.50 (*d*, $J = 4.0$, CH_2–C(5')); 3.15 (*d*, $J = 5.5$, irrad. at 2.57→NOE (8%), irrad. at 4.17→NOE (2.3%), H–C(5)); 2.57 (*d*, $J = 5.5$, irrad. at 4.17→NOE (8%), H–C(1)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 171.55 (*s*); 171.21 (*s*); 137.72 (*s*); 137.54 (*s*); 137.10 (*s*); 132.18 (*s*); 129.45–126.91 (several *d*); 83.14 (*d*, C(5)); 77.93 (*s*, C(6); 77.19 (*d*, C(3')); 76.54 (*d*, C(4')); 73.48 (*t*); 72.48 (*t*); 71.92 (*t*); 69.84 (*t*, CH_2–C(5')); 29.13 (*d*); 28.89 (*d*, C(1), C(5)). CI-MS (NH_3): 594 (28), 593 (72, $[M + NH_4]^+$), 577 (40), 576 (100, $[M + 1]^+$), 108 (15), 91 (18). Anal. calc. for $C_{36}H_{33}NO_6 \cdot 0.5\ H_2O$ (584.66): C 73.96, H 5.86, N 2.40; found: C 74.17, H 5.84, N 2.19.

(1S,3'R,4'R,5R,5'R)-3',4'-Bis(benzyloxy)-5-[(benzyloxy)methyl]-4',5'-dihydro-3-phenylspiro[3-azabicyclo[3.1.0]hexane-6,2'(3'H)-furan]-2,4-dione (**22**): R_f (hexane/AcOEt 2:1) 0.24. $[\alpha]_D^{25} = -14.5$ ($c = 0.75$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3030*w* (sh), 3000*m*, 2920*m*, 2865*m*, 1775*m*, 1710*s*, 1600*w*, 1500*s*, 1455*s*, 1385*s*, 1330*w*, 1310*w*, 1265*m*, 1235*m*, 1170*s*, 1120*s*, 1090*s*, 1050*m*, 1030*m*, 995*m*, 910*w*, 860*w*, 695*s*, 680*w*, 615*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.13 (*m*, 20 arom. H); 4.73 (*d*, $J = 10.8$, 1 H, PhCH_2); 4.65 (*d*, $J = 11.6$, 1 H, PhCH_2); 4.57 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.57 (*d*, $J = 11.5$, 1 H, PhCH_2); 4.53–4.40 (*m*, 1 H, PhCH_2); 4.50 (*d*, $J = 10.7$, 1 H, PhCH_2); 4.43–4.36 (*m*, irrad. at 2.99→NOE (1.7%), H–C(5')); 4.30 (*dd*, $J = 4.6$, 7.5, irrad. at 4.16→NOE (8.7%), H–C(4')); 4.16 (*d*, $J = 4.6$, irrad. at 2.90→NOE (1.4%), H–C(3')); 3.65 (*dd*, $J = 2.7$, 11.0, 1 H, CH_2–C(5')); 3.53 (*dd*, $J = 4.2$, 11.0, 1 H, CH_2–C(5')); 2.99 (*d*, $J = 6.2$, irrad. at 2.90→NOE (6.8%), H–C(5)); 2.90 (*d*, $J = 6.1$, irrad. at 4.16→NOE (1.5%), irrad. at 2.99→NOE (7.1%), H–C(1)). ^{13}C-NMR (101.2 MHz, $CDCl_3$): 170.68 (*s*, 2 C); 137.75 (*s*); 137.25 (*s*); 137.07 (*s*); 131.65 (*s*); 129.60–125.99 (several *d*); 81.04 (*d*, C(5')); 79,10 (*d*, C(3')); 78.11 (*s*, C(6)); 76.38 (*d*, C(4')); 73.46 (*t*); 73.18 (*t*); 72.68 (*t*); 68.85 (*t*, CH_2–C(5')); 31.59 (*d*); 29.75 (*d*, C(1), C(5)). CI-MS (NH_3): 595 (10), 594 (41), 593 (100, $[M + NH_4]^+$), 274 (12), 214 (12), 168 (14), 108 (23), 106 (22), 91 (7). Anal. calc. for $C_{36}H_{33}NO_6$ (575.65): C 75.11, N 2.43; found: C 75.21, N 2.63.

Reaction of **10** *with Phenol.* A suspension of NaH (34 mg, 1.42 mmol) and **10** (505 mg, 0.86 mmol) in 1,4-dioxane (30 ml) was stirred in a quartz vessel under N_2 for 10 min. The clear soln. was treated with phenol (453 mg, 4.81 mmol) and irradiated at *ca.* 20° for 3 h. The mixture was treated again with NaH (11 mg, 0.46 mmol) and irradiated at *ca.* 20° for 2 h. The residue obtained by evaporation was dissolved in Et_2O, washed with 2M NaOH (2 ×) and worked up as usual. Several FC (hexane/Et_2O 4:1) and HPLC (*Spherisorb* silica (5 μm) 250 × 20 mm column, flow 16 ml/min, detection with UV (280 nm), hexane/Et_2O 4:1) gave α-D/β-D-**23** (249 mg, 58%; α-D/β-D 5:2), **24** (7 mg, 2%), **25** (16 mg, 3%), and **10** (48 mg, 10%).

*Phenyl 2,3,5-Tri-*O*-benzyl-α-*D*-arabinofuranoside* (α-D-**23**): R_f (hexane/AcOEt 2:1) 0.64. $[\alpha]_D^{25} = +72.4$ ($c = 0.92$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3030*w* (sh), 3000*m*, 2920*m*, 2870*m*, 1600*m*, 1590*m*, 1495*s*, 1455*m*, 1365*m*, 1310*w*, 1235*m*, 1195*w*, 1175*w*, 1080*s* (br.), 1040*s*, 1030*s*, 1010*s*, 990*s*, 910*m*, 865*w*, 815*w*, 700*s*, 640*w* (br.), 605*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.24 (*m*, 18 arom. H); 7.08–7.00 (*m*, 2 arom. H); 5.74 (*d*, $J = 0.8$, H–C(1)); 4.62 (*d*, $J = 11.7$, 2 H, PhCH_2); 4.61 (*d*, $J = 12.2$, 2 H, PhCH_2); 4.56 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.54 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.37–4.33 (*m*, H–C(4)); 4.33 (*dd*, $J = 1.1$, 3.4, H–C(2)); 4.12 (*dd*, $J = 3.4$, 6.8, H–C(3)); 3.69 (*dd*, $J = 3.9$, 11.0, H–C(5)); 3.64 (*dd*, $J = 4.6$, 10.9, H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 156.55 (*s*); 138.02 (*s*); 137.80 (*s*); 137.27 (*s*); 129.34 (*d*, 2 C); 128.38–127.53 (several *d*); 121.96 (*d*); 116.68 (*d*, 2 C); 104.49 (*d*, C(1)); 88.39 (*d*, C(4)); 83.12 (*d*, C(2)); 81.48 (*d*, C(3)); 73.30 (*t*); 72.16 (*t*); 72.03 (*t*); 69.22 (*t*, C(5)). CI-MS (NH_3): 515 (29), 514 (100, $[M + NH_4]^+$), 420 (25). Anal. calc. for $C_{32}H_{32}O_5$ (496.60, data from α-D/β-D-**23** 1:3): C 77.40, H 6.49; found: C 77.61, H 6.50.

*Phenyl 2,3,5-Tri-*O*-benzyl-β-*D*-arabinofuranoside* (β-D-**23**): R_f (hexane/AcOEt 2:1) 0.61. $[\alpha]_D^{25} = -73.0$ ($c = 0.20$, $CHCl_3$). IR ($CHCl_3$): 3060*w*, 3020*w* (br.), 2960*w*, 2940*w*, 2910*w* (sh), 2860*w*, 1600*m*, 1590*m* (sh), 1495*s*, 1455*m*, 1365*w*, 1260*s*, 1235*w*, 1170*w* (sh), 1090*s* (br.), 1030*s*, 1015*s* (sh), 915*w* (br.), 860*m*, 810*m*, 700*s*, 670*w* (br.). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.18 (*m*, 16 arom. H); 7.09–7.02 (*m*, 4 arom. H); 5.57 (*d*, $J = 4.2$, H–C(1)); 4.74 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.68 (*d*, $J = 11.7$, 1 H, PhCH_2); 4.68 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.63 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.48 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.43 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.31 (*dd*, $J = 5.6$, 7.0, H–C(3)); 4.25 (*dd*, $J = 4.3$, 6.9, H–C(2)); 4.23 (*q*, $J \approx 5.8$, H–C(4)); 3.57 (*d*, $J = 6.0$, 2 H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$, α-D/β-D-**23** 1:3): 156.96 (*s*); 138.05 (*s*); 137.98 (*s*); 137.43 (*s*); 129.34 (*d*, 2 C); 128.37–127.39 (several *d*); 122.13 (*d*); 116.90 (*d*, 2 C); 98.96 (*d*, C(1)); 84.02 (*d*, C(4)); 82.98 (*d*, C(2)); 81.14 (*d*, C(3)); 73.23 (*t*); 72.51 (*t*); 72.36 (*t*); 72.14 (*t*, C(5)). CI-MS (NH_3): 515 (37), 514 (100, $[M + NH_4]^+$), 420 (12), 295 (28), 108 (14).

*(S)-1,4-Anhydro-2,3,5-tri-*O*-benzyl-1-*C*-(2-hydroxyphenyl)-*D*-arabinitol* (**24**): R_f (hexane/AcOEt 2:1) 0.50. $[\alpha]_D^{25} = +22.7$ ($c = 0.15$, $CHCl_3$). IR ($CHCl_3$): 3360*m* (br.), 3060*w*, 3010*w*, 2940*m*, 2920*m*, 2870*m*, 1620*w*, 1590*m*, 1495*m*, 1470*w* (sh), 1365*m*, 1310*m* (br.), 1245*m*, 1170*m* (sh), 1150*m* (sh), 1120*s* (sh), 1100*s* (br.), 1075*s* (sh), 1030*m*, 990*m* (sh), 910*w*, 820*w*, 700*s*, 660*w*, 640*w* (br.), 610*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.69 (*s*, exchange with D_2O, OH); 7.35–7.17 (*m*, 17 arom. H); 6.91–6.84 (*m*, 2 arom. H); 5.07 (*d*, $J = 6.6$, H–C(1)); 4.60 (*s*, 2 H, PhCH_2); 4.58 (*d*, $J = 12.2$, 1 H, PhCH_2); 4.53 (*d*, $J = 11.9$, 1 H, PhCH_2); 4.50 (*s*, 2 H, PhCH_2); 4.44 (*dt*, $J = 3.3$, 5.6, H–C(4)); 4.26–4.22 (*m*, H–C(2), H–C(3)); 3.69 (*dd*, $J = 5.7$, 10.2, H–C(5)); 3.66 (*dd*, $J = 5.8$, 10.2, H–C(5)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 155.06 (*s*); 137.74 (*s*); 137.36 (*s*); 137.17 (*s*); 129.38 (*d*); 128.44–127.63 (several *d*); 123.38 (*s*); 119.84 (*d*); 117.21 (*d*); 88.73 (*d*, C(1)); 84.40 (*d*, C(4)); 83.35 (*d*, C(2)); 81.94 (*d*, C(3)); 73.47 (*t*); 72.62 (*t*); 71.87 (*t*); 69.33 (*t*, C(5)). Anal. calc. for $C_{32}H_{32}O_5$ (496.60): C 77.40, H 6.49; found: C 76.95, H 6.55.

*2,3,5-Tri-*O*-benzyl-1-deoxy-1-[(tol-4-yl)sulfonyl]-α-*D*-arabinofuranose* (**25**): R_f (hexane/AcOEt 2:1) 0.50. M.p. 76°. $[\alpha]_D^{25} = +42.5$ ($c = 0.20$, $CHCl_3$). IR ($CHCl_3$): 3080*w* (sh), 3060*w* (sh), 3020*w* (br.), 2980*w* (sh), 2920*w*, 2870*w*, 1600*w*, 1495*m*, 1455*m*, 1400*w*, 1360*m*, 1320*m*, 1305*m*, 1290*m*, 1260*m*, 1235w (sh), 1150*s*, 1090*s*, 1070*s*, 1030*m*, 1020*m* (sh), 910*w*, 860*w*, 810*m*, 700*m*, 660*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.83 (*d*, $J = 8.2$, 2 arom. H); 7.43–7.21 (*m*, 17 arom. H); 4.86 (*dd*, $J = 3.6$, 4.7, H–C(2)); 4.82 (*d*, $J = 3.4$, H–C(1)); 4.80 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.64 (*d*, $J = 11.7$, 1 H, PhCH_2); 4.57 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.52 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.47 (*d*, $J = 11.5$, 1 H, PhCH_2); 4.44 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.49–4.45 (*m*, H–C(4)); 4.17 (*dd*, $J = 4.7$, 8.5, H–C(3)); 3.67 (*dd*, $J = 2.7$, 11.4, H–C(5)); 3.52 (*dd*, $J = 4.8$, 11.4, H–C(5)); 2.44 (*s*, Me). ^{1}H-NMR (400 MHz, C_6D_6): 7.83 (*d*, $J = 8.2$, irrad. at 4.89→NOE (3.1%), 2 arom. H); 7.38–7.34 (*m*, 2 arom. H); 7.19–7.04 (*m*, 13 arom. H); 6.75 (*d*, $J = 8.0$, 2 arom. H); 5.17 (*dd*, $J = 3.6$, 4.8, H–C(2)); 4.89 (*d*, $J = 3.6$, irrad. at 4.32→NOE (1.3%), H–C(1)); 4.81 (*d*, $J = 11.9$, 1 H, irrad. at 4.89→NOE (1.8%), PhCH_2); 4.79 (*ddd*, $J = 2.8$, 5.0, 8.6, H–C(4)); 4.59 (*d*, $J = 11.8$, 1 H, irrad. at 4.89→NOE (1.8%), PhCH_2); 4.51 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.38 (*d*, $J = 11.9$, 1 H, PhCH); 4.32 (*dd*, $J = 4.8$, 8.6, irrad. at 4.89→NOE (2.0%), H–C(3)); 4.25 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.17 (*d*, $J = 12.2$, 1 H, PhCH_2); 3.51 (*dd*, $J = 2.7$, 11.3, H–C(5)); 3.36 (*dd*, $J = 4.9$, 11.3, H–C(5)); 1.84 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 145.17 (*s*); 137.84 (*s*); 137.50 (*s*); 137.13 (*s*); 133.51 (*s*); 129.75 (*d*, 2 C); 129.39 (*d*, 2 C); 128.47–127.62 (several *d*); 97.31 (*d*, C(1)); 83.24 (*d*, 2 C); 82.15 (*d*, C(2), C(3), C(4)); 73.21 (*t*); 72.61 (*t*); 72.38 (*t*); 68.32 (*t*, C(5)); 21.69 (*q*, Me). CI-MS (NH_3): 578 (10), 577 (31), 576 (100, $[M + NH_4]^+$). Anal. calc. for $C_{33}H_{34}O_6S$ (558.69): C 70.94, H 6.13; found: C 71.20, H 6.38.

*Reaction of (Z)-***5** *with* N^6*-Benzyladenine.* A suspension of NaH (26 mg, 1.06 mmol), and (*Z*)-**5** (504 mg, 0.86 mmol) in 1,4-dioxane (80 ml) was stirred in a quartz vessel under N_2 for 10 min. The clear soln. was treated with N^6-benzyladenine (421 mg, 1.87 mmol) and irradiated at *ca.* 24° for 3 h. The mixture was again treated with NaH (22 mg, 0.92 mmol) and irradiated at *ca.* 24° for 3 h. The residue obtained by evaporation was dissolved in AcOEt and the soln. worked up as usual and filtered through silica gel (AcOEt→MeOH). FC (hexane/AcOEt 4:1→MeOH) and FC (AcOEt/MeOH 6:1) gave **26** (21 mg, 39%), **27** (157 mg, 29%), and (*Z*)-**5** (73 mg, 14%).

N^6*-Benzyl-9-(2,3,5-tri-*O*-benzyl-β-*D*-ribofuranosyl)adenine* (**26**): R_f (hexane/AcOEt 1:1) 0.24. $[\alpha]_D^{25} = +17.1$ ($c = 1.04$, $CHCl_3$). UV ($c = 1.75 \cdot 10^{-4}$, EtOH): 218 (2.26), 267 (2.58). IR ($CHCl_3$): 3420*m*, 3320*w* (br.), 3060*w*, 3000*m*, 2960*m*, 2930*m*, 2870*m*, 1620*s*, 1585*m*, 1525*w*, 1495*m*, 1480*m*, 1455*s*, 1405*s*, 1355*m*, 1330*m*, 1295*m*, 1260*s*, 1120*s* (sh), 1090*s* (br.), 1050*s*, 1030*s*, 910*m*, 885*w*, 865*w*, 815*m*, 695*s*, 660*w*, 645*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.40 (*s*, H–C(2)); 7.99 (*s*, irrad. at 6.25→NOE (6.2%), irrad. at 4.50→NOE (4.9%), H–C(8)); 7.41–7.19 (*m*, 20 arom. H); 6.25 (*d*, $J = 3.6$, irrad. at 4.50→*s*, irrad. at 7.99→NOE (5.7%), irrad. at 4.50→NOE (2.9%), H–C(1′)); 6.03 (*t*, $J \approx 5.5$, exchange with D_2O, irrad. at 4.89→*s*, NH); 4.94–4.84 (br. *s*, addn. of D_2O→4.89, *s*, 2 H, PhCH_2N); 4.76 (*d*, $J = 12.2$, 1 H, PhCH_2); 4.71 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.59 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.55 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.52 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.50 (*t*, $J \approx 4.2$, irrad. at 6.25→NOE (2.8%), irrad. at 7.99→NOE (3.1%), H–C(2′)); 4.44 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.43–4.40 (*m*, H–C(4′)); 4.26 (*t*, $J \approx 5.5$, irad. at 4.52→*d*, $J = 5.9$, irrad. at 7.99→NOE (2.8%), irrad. at 4.50→NOE (6.2%), H–C(3′)); 3.85 (*dd*, $J = 3.2$, 10.8, H–C(5′)); 3.65 (*dd*, $J = 3.4$, 10.8, H–C(5′)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 154.55 (*s*, C(6)); 153.03 (*s*, C(4)); 153.03 (*d*, C(2)); 138.59 (*d*, C(8)); 138.51 (*s*); 137.61 (*s*); 137.47 (*s*); 137.16 (*s*); 128.62–127.33 (several *d*); 119.61 (*s*, C(5)); 87.51 (*d*, C(1′)); 81.65 (*d*, C(4′)); 79.15 (*d*, C(2′)); 75.64 (*d*, C(3′)); 73.45 (*t*); 72.21 (*t*, 2 C); 68.72 (*t*, C(5′)); 44.35 (*t*). CI-MS (NH_3): 630 (13), 629 (44), 628 (100, $[M + 1]^+$). Anal. calc. for $C_{38}H_{37}N_5O_4$ (627.74): C 72.21, H 5.94, N 11.16; found: C 72.54, H 6.13, N 10.93.

N^6*-Benzyl-3-(2,3,5-tri-*O*-benzyl-β-*D*-ribofuranosyl)adenine* (**27**): R_f (hexane/AcOEt 1:1) 0.01. M.p. 140–142°. $[\alpha]_D^{25} = +64.7$ ($c = 0.62$, $CHCl_3$). UV ($c = 1.43 \cdot 10^{-4}$, EtOH): 218 (2.455), 291 (2.193). IR ($CHCl_3$): 3420*w*, 3230*m* (br.), 3170*m* (br.), 3090*m* (sh), 3060*m*, 3030*m*, 2920*m*, 2860*m*, 1645*s*, 1630*s* (sh), 1590*w*, 1530*m*, 1500*m*, 1485*w*, 1470*m*, 1455*m*, 1430*m* (sh), 1410*m*, 1360*m*, 1330*w*, 1275*m*, 1260*m* (sh), 1210*m*, 1165*m*, 1145*s*, 1130*s*, 1085*s* (sh), 1075*s*, 1055*m*, 1035*m*, 1030*m*, 1015*m*, 990*m*, 960*w*, 945*w*, 885*w*, 815*w*, 785*w*, 755*m* (sh), 735*s*, 700*s*, 660*m*, 605*w*. ^{1}H-NMR (400 MHz, C_6D_6): 8.65 (*s*, irrad. at 4.02→NOE (3.6%), irrad. at 6.39→NOE (3.3%), irrad. at

4.36→NOE (1.4%), H–C(2)); 7.91 (*s*, H–C(8)); 7.32 (*d*, J = 6.5, 2 arom. H); 7.18–7.01 (*m*, 18 arom. H); 6.62 (*s*, exchange with D_2O, NH); 6.39 (*s*, irrad. at 4.36→NOE (3.1%), irrad. at 8.65→NOE (3.6%), H–C(1′)); 4.96 (*d*, J = 12.2, 1 H, PhCH_2N); 4.87 (*d*, J = 12.2, 1 H, PhCH_2N); 4.70 (*s*, 2 H, PhCH_2); 4.36 (*td*, J = 2.3, 8.5, irrad. at 6.39→NOE (1.4%), H–C(4′)); 4.33 (*d*, J = 12.1, 1 H, PhCH_2); 4.25 (br. *d*, $J \approx 4.5$, irrad. at 4.02→NOE (5.4%), irrad. at 6.39→NOE (3.2%), H–C(2′)); 4.20 (*d*, J = 11.8, 1 H, PhCH_2); 4.13 (*d*, J = 11.7, 1 H, PhCH_2); 4.02 (*dd*, J = 4.7, 8.4, irrad. at 4.36→NOE (4.0%), irrad. at 8.65→NOE (3.5%), H–C(3′)); 3.92 (*d*, J = 11.6, 1 H, PhCH_2); 3.75 (*dd*, J = 2.3, 11.1, H–C(5′)); 3.46 (*dd*, J = 2.2, 11.1, H–C(5′)). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 153.46 (*s*, C(6)); 152.85 (*d*, C(8)); 147.87 (*s*, C(4)); 140.46 (*d*, C(2)); 138.24 (*s*); 138.17 (*s*, 2 C); 137.54 (*s*); 129.22–127.27 (several *d*); 120.47 (*s*, C(5)); 91.28 (*d*, C(1′)); 81.67 (*d*, C(4′)); 78.67 (*d*, C(2′)); 74.30 (*d*, C(3′)); 73.53 (*t*); 72.14 (*t*); 71.77 (*t*); 67.55 (*t*, C(5′)); 44.45 (*t*). CI-MS (NH_3): 630 (10), 629 (44), 628 (100, $[M + 1]^+$), 538 (18). Anal. calc. for $C_{38}H_{37}N_5O_4$ (627.74): C 72.71, H 5.94, N 11.16; found: C 72.54, H 5.74, N 11.15.

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