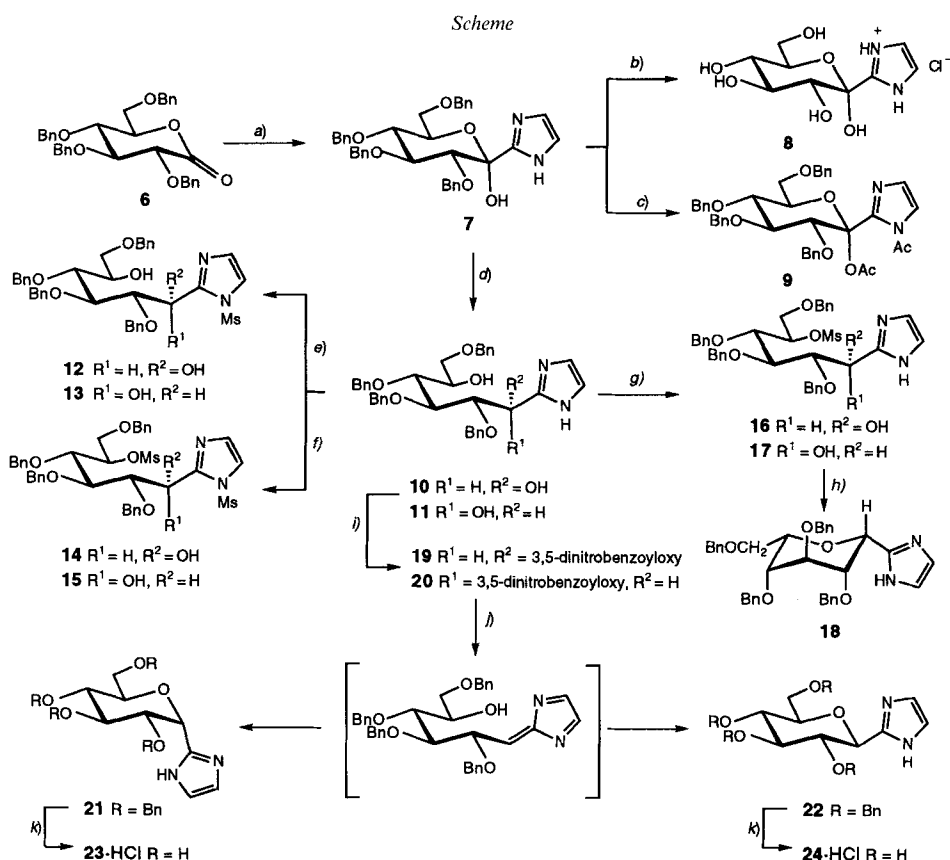


2) K_i values [μM] against sweet almond β -glucosidase [2] [3]: 1*H*-imidazole, 530; N_w -acetylhistamine, 35; L-histidine β -naphthylamide, 17; 4-phenyl-1*H*-imidazole, 0.8.

D-ribo- or L-gulono-1,4-lactones [11] [12] and of 4-lithiated *N*-sulfonylimidazoles to protected ribose- and 2-deoxyribose derivatives [13]. No (pyranos-*C*-yl)imidazoles appear to be known; the closest analogues are the anomeric *O*-benzylated (glucopyranos-1-*C*-yl)thiazoles derived from the corresponding gluconolactone [14]. (Glycopyranos-1-*C*-yl)imidazoles are of interest as potential glycosidase inhibitors. We describe the syntheses of the (glucos-1-*C*-yl)-1*H*-imidazoles **8**, **23**, and **24**, and their evaluation as inhibitors of α - and β -glucosidases.

Results. – Addition of 2-lithio 1-[(dimethylamino)methyl]-1*H*-imidazole [15] to the tetra-*O*-benzylgluconolactone **6** [16] followed by aqueous workup (where the imidazole moiety is deprotected [15]) afforded the crystalline α -D-glucopyranose **7** (68%; *Scheme*). No isomers were observed. Hydrogenolysis yielded the crystalline hydrochloride **8**.



a) BuLi, 1-(Me₂NCH₂)Im, THF; 68%. b) H₂, 10% Pd/C, 1N HCl, AcOEt; 77%. c) Ac₂O, pyridine, 25°, 17 h; 65%. d) NaBH₄, dioxane, H₂O, AcOH; > 99% (**10/11** 12:88). e) 1.6 equiv. of MsCl, pyridine, 1.2 equiv. of 4-(dimethylamino)pyridine, 5°, 2.5 h; 39%. f) 2.4 equiv. of MsCl, pyridine, 1.2 equiv. of 4-(dimethylamino)pyridine, 25°, 5.5 h; 30%. g) 2.3 equiv. of MsCl, pyridine, CH₂Cl₂, 25°, 17 h; 50% of **16/17**, 46% of **10/11**. h) **17**, NaH, DMF; 58%. i) 3,5-Dinitrobenzoyl chloride, pyridine; 73% **19/20** (15:85). j) NaH, DMF; 80% **21/22** (25:75). k) H₂, 10% Pd/C, 1N HCl, MeOH; 70%.

Reductive dehydroxylation of the hemiacetal **7** or the corresponding *O*-acetyl derivative **9** with Et_3SiH and $\text{BF}_3 \cdot \text{OEt}_2$ failed, probably due to coordination of BF_3 with the imidazole group, preventing the formation of the glycosyl cation. Therefore, the hemiacetal was reduced with NaBH_4 to yield in over 99% a 12:88 mixture of the diols **10/11**. The diols were separated by HPLC. The major isomer possesses the (*R*)-configuration at C(1). For reasons which will become clear in sequel, the following reactions were performed with the mixture of the diastereoisomers.

Attempts to selectively mesylate $\text{HO}-\text{C}(1)$ of **10/11** and to close the pyranosyl ring by an intramolecular S_N2 -type reaction failed. The imidazoles were first *N*-sulfonylated (MsCl/py) to a mixture **12/13**, isolated by preparative TLC in 39%, followed by sulfonylation of $\text{HO}-\text{C}(5)$, yielding 29% of **14/15**. Longer reaction times led to partial conversion to the *N*-desulfonylated monomesylates **16/17**. Migration of the *N*-sulfonyl group to $\text{HO}-\text{C}(1)$, however, could not be induced. The mesylate **17** was cyclized to **18** (see below).

Acylation by 3,5-dinitrobenzoyl chloride of the diols **10/11** led regioselectively to the 1-(3,5-dinitrobenzoates) **19/20**, isolated in 72% yield, and easily cyclized by treatment with NaH in DMF at -10° to a mixture of the desired anomers **21** and **22** (80%, $\alpha\text{-D}/\beta\text{-D}$ 25:75), presumably through an elimination/addition mechanism (*cf.* [17] [13])³. The anomers were separated by flash chromatography. Cyclization of the pure dinitrobenzoates **19** and **20**, obtained from the pure diols, yielded similar mixtures of **21** and **22**.

Similarly to **7**, the *C*-glucosides **21** and **22** were deprotected to give the hydrochlorides of **23** and **24**, respectively. The imidazoles **8** and **24** are rather weak competitive inhibitors of sweet-almond β -glucosidases with K_i values of 0.79 and 0.64 mM, respectively, while **23** inhibited yeast (maltase) α -glucosidase with a K_i value of 0.26 mM.

The imidazole **7** is characterized by an OH band at 3500 cm^{-1} , an NH band at 3453 cm^{-1} , and the absence of a $\text{C}=\text{O}$ absorption. The characteristic ^{13}C signal of the imidazole moiety is found at 147.6 and the one of the hemiacetal C at 94.8 ppm.

Reduction of **7** to the diols **10/11** is confirmed by the ^1H -NMR signals of $\text{H}-\text{C}(1)$ at 5.14 (*d*, $J = 2.9$) and 5.05 ppm (*d*, $J = 4.0$), for the major and the minor isomers, respectively, and by the ^{13}C -NMR spectrum, which shows 5 *d* in addition to the signals of the aromatic C-atoms. The NMR spectra of the mixture **19/20** show only two $\text{C}=\text{O}$ signals at 162.30 and 162.27 ppm, and an $\text{H}-\text{C}(1)$ *d* at 6.45 and 6.38 ppm, for the major and the minor isomers, respectively, considerably downfield from the corresponding signals of **10** and **11**. The anomeric configuration of **21** and **22** is evidenced by the $J(1,2)$ values of 5.6 and 9.5 Hz, respectively.

Some information about the conformations of the diols **10/11** and of the esters **19/20** is derived from the values of the vicinal coupling constants. Qualitatively, the conformation of **10** and **11** appears to be quite similar to other open-chain glucose derivatives [18]. The $J(1,2)$ value of **11** ($J(1,2) = 2.9\text{ Hz}$) changes upon acylation of $\text{HO}-\text{C}(1)$ to **20** ($J(1,2) = 8.4$) in agreement with the disappearance of a H-bond between $\text{HO}-\text{C}(1)$ and $\text{BnO}-\text{C}(3)$ and a preferred ${}_1G^+$ conformation of **20**. The analogous *O*-acylation of **10**, however, does not affect $J(1,2)$ but $J(2,3)$ which changes from 3.8 in **10** to 7.1 in **19**, evidencing a conformational change, leading to a ${}_2G^-$ sickle conformation.

A comparison of the CD spectra of **7**, **21**, and **22** shows similar negative *Cotton* effects at 220 nm for **7** and **22**, and a positive *Cotton* effect for **21**, further evidencing their configuration at C(1). To determine the C(1) configuration of the diols, a pure sample of **11** was mesylated to **17** and cyclized to the *L*-ido-derivative **18** which adopts a 1C_4 conformation. An NOE effect between $\text{H}-\text{C}(1)$ and $\text{H}-\text{C}(5)$ is a strong evidence for the (1*R*)-configuration of **18** and consequently also for **11**. The structure of **22** was estab-

³) A range of conditions (NaH in DMF, KH in DMF, KF in THF, BuLi in THF) did not lead to equilibration of either the $\alpha\text{-D}$ -anomer **21** or the $\beta\text{-D}$ -anomer **22**.

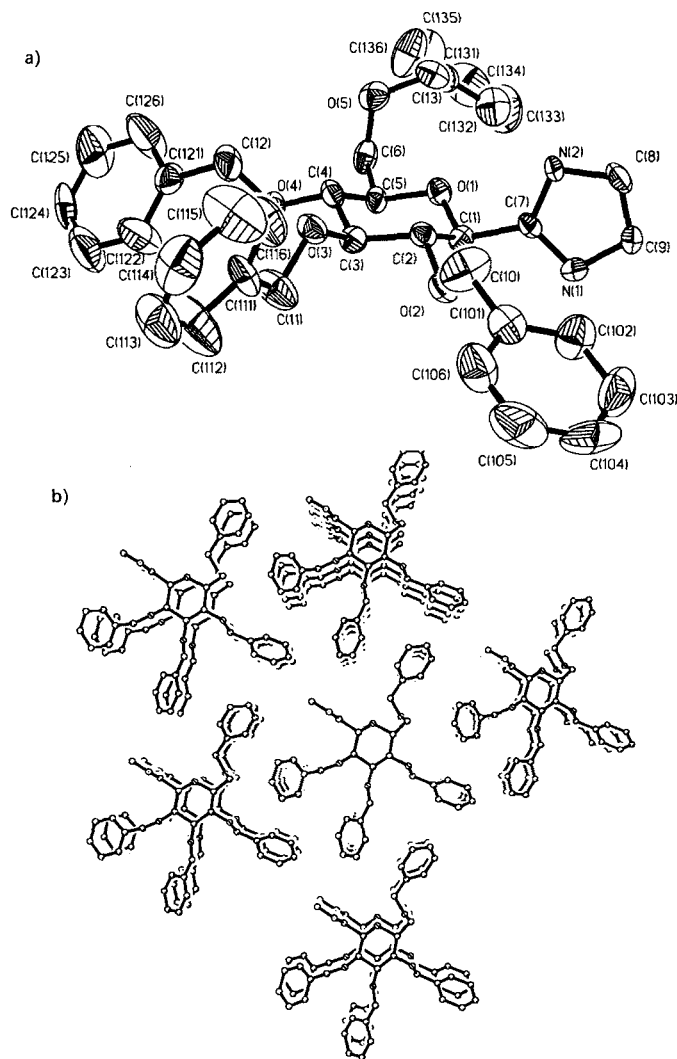


Figure. a) ORTEP Representation and b) X-ray structure of **22** (projection on the *x*-axis)

lished by X-ray analysis, which shows that the plane of the imidazole ring is perpendicular to the one of the pyranose ring. The torsional angle O(1)–C(1)–C(7)–N(1) (*cf.* Fig.) is -129° and the torsional angle C(2)–C(1)–C(7)–N(1) is 111° . The crystals are stabilized by intermolecular H-bonds between the imidazole rings (N–H $\cdots$ N: 1.69 Å)⁴.

The ^{13}C -NMR spectrum of **8** shows the expected characteristic C(1) *s* at 96.93 ppm. The ^1H -NMR spectra of **23**·HCl and **24**·HCl exhibit the expected characteristic H–C(1) *d* (**24**·HCl in CD_3OD : 4.63 ppm, $J = 8.8$ Hz; **23**·HCl in D_2O : 5.47 ppm, $J = 6.2$ Hz).

⁴) Crystallographic data have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, England.

The chemical shift of H–C(3) and H–C(5) of **23**·HCl, possessing an axial imidazolium substituent, changes upon deprotonation of the imidazolium moiety. Neutralization of **23**·HCl in D₂O by Et₃N induces a downfield shift of 0.5 ppm for H–C(3) and 0.3 ppm for H–C(5). At the same time, the signal of H–C(1) is shifted upfield ($\Delta\delta = 0.3$ ppm). The values of the coupling constants do not change noticeably. The pyranose ring thus remains in a flattened ⁴C₁ conformation. The chemical-shift differences, however, indicate a change of the torsion angle between the imidazole and the pyranose rings. In the neutral compound, the torsional angles O(1)–C(1)–C(7)–N(1) and C(2)–C(1)–C(7)–N(1) appears to be close to 120°, similarly to solid **22** (Fig.), exposing H–C(3) and H–C(5) to the shielding effect of the imidazole ring, while the protonated imidazole ring appears to rotate by ca. 90° around the C(1)–C(7) bond, exposing H–C(3) and H–C(5) to its deshielding effect. Neutralization of **24**·HCl, possessing an equatorial imidazolium substituent, does not lead to any similar change of the chemical shift of the pyranose ring protons, except for H–C(1), which is shifted upfield ($\Delta\delta \approx 0.2$ ppm).

We thank A. Martelletti for determining the X-ray structure, and the Swiss National Science Foundation and F. Hoffmann-La Roche AG, Basel, for generous support.

Experimental Part

General. See [19]. Prep. HPLC: Merck LiChrosorb NH2 (7 μ m) 250 $\times$ 25 mm column. UV Spectra ($\lambda_{\max}$ in nm (log ϵ)): 1-cm quartz cell. CD Spectra ($\lambda_{\max}$ in nm (molar ellipticity [θ] in deg·cm²·decimol^{–1})): JASCO-J-710 spectropolarimeter. IR Spectra: KBr or 3% CHCl₃ soln. K_i Determinations were performed at pH 6.8, 37° with 4-nitrophenyl β -D-glucopyranoside (Fluka Biochemica) as substrate for **8** and **24**, and 4-nitrophenyl α -D-glucopyranoside (Fluka Biochemica) as substrate for **23** [20].

2,3,4,6-Tetra-O-benzyl-1-C-(1H-imidazol-2-yl)- α -D-glucopyranose (7). At –78°, a soln. of 1-[(dimethylamino)methyl]-1H-imidazole (764 mg, 6.87 mmol) in THF (40 ml) was treated dropwise with BuLi (1.6M in hexane, 4.24 ml) and stirred at –78° for 1 h. A soln. of **6** (3.320 g, 6.15 mmol) in THF (30 ml) was added dropwise within 35 min at –78°. The yellow soln. was then stirred at –78° for 5 h and neutralized with a sat. soln. of NH₄Cl. Normal workup afforded 3.8 g of a white foam which was crystallized from CHCl₃/Et₂O 15:85 (82 ml) to give 2.52 g of **7** (67.5%). White, slightly hygroscopic crystals. M.p. 141°. *R*_f (AcOEt/hexane 4:1) 0.39. $[\alpha]_D^{25} = +31.3$ (*c* = 0.93, CHCl₃). UV (MeOH): 208 (4.6). CD (MeOH): 220 (–15400). IR (CHCl₃): 3500w, 3453m, 3191w, 3090w, 3067w, 3043w, 3008m, 2928m, 2870m, 1603w, 1497m, 1454s, 1403m, 1361m, 1263m, 1152s, 1067s, 1028s, 949m, 913w, 823w, 646w, 608w, 532w. ¹H-NMR (CDCl₃): 3.59 (dd, *J* = 2.1, 10.2, H–C(6)); 3.68 (dd, *J* = 4.2, 10.5, H'–C(6)); 3.74 (t, *J* $\approx$ 9.9, H–C(4)); 3.99 (d, *J* = 9.3, H–C(2)); 4.13 (t, *J* = 9.1, H–C(3)); 4.12–4.20 (m, H–C(5)); 4.22 (d, *J* = 10.3, PhCH); 4.36 (s, PhCH₂); 4.47 (d, *J* = 10.2, PhCH); 4.52 (d, *J* = 10.4, PhCH); 4.84 (d, *J* = 11.1, PhCH); 4.85 (d, *J* = 11.0, PhCH); 4.95 (d, *J* = 11.1, PhCH); 6.91 (s, NCH=CHN); 7.36–7.00 (m, 20 arom. H). ¹H-NMR (C₆D₆): 3.58 (dd, *J* = 1.3, 10.0, irradi. at 3.71 $\rightarrow$ br. s, irradi. at 4.47 $\rightarrow$ d, *J* $\approx$ 10.0, H–C(6)); 3.71 (dd, *J* = 3.9, 10.6, irradi. at 4.47 $\rightarrow$ d, *J* $\approx$ 10.0, H'–C(6)); 4.00 (t, *J* = 9.4, H–C(4)); 4.23–4.33 (m, H–C(2), PhCH₂); 4.36 (d, *J* = 10.3, PhCH); 4.43 (t, *J* = 9.3, H–C(3)); 4.45–4.50 (m, irradi. at 3.71 $\rightarrow$ br. d, *J* $\approx$ 10.5, irradi. at 4.00 $\rightarrow$ br. s, H–C(5)); 4.57–4.62 (m, PhCH₂); 4.84 (d, *J* = 11.4, PhCH); 4.96 (d, *J* = 11.5, PhCH); 5.00 (d, *J* = 11.5, PhCH); 6.5 (br. s, OH); 6.9–7.4 (m, 22 arom. H); 10.5 (br. s, NH). ¹³C-NMR (CDCl₃): 68.79 (t); 71.23 (d); 73.67 (t); 74.80 (t); 74.94 (t); 75.74 (t); 77.49 (d); 82.80 (d); 83.44 (d); 94.77 (s); 127.6–128.6 (several d); 136.96 (s); 137.68 (s); 138.25 (s); 138.65 (s); 147.62 (s). FAB-MS: 607 (100, [*M* + 1]⁺), 589 (36, [*M* – H₂O]⁺). Anal. calc. for C₃₇H₃₈N₂O₆ (606.72): C 73.25, H 6.31, N 4.62; found: C 72.99, H 6.58, N 4.60.

1-C-(1H-Imidazol-2-yl)- α -D-glucopyranose Hydrochloride (8). At 25°, a suspension of Pd/C (10%, 70 mg) in 1N HCl (5 ml) was activated for 2 h under H₂ (7 bar). After the addition of a soln. of **7** (69 mg, 0.114 mmol) in AcOEt (2 ml), the suspension was stirred at 7 bar and 25° for 24 h, diluted with MeOH, and filtered through Celite. The filtrate was concentrated to ca. 0.5 ml. Crystallization was induced by addition of acetone (15 ml) affording 25 mg of **8** (77%). White crystals. M.p. 205°. *R*_f (AcOEt/MeOH/AcOH 7:5:1) 0.125. $[\alpha]_D^{25} = +51.4$ (*c* = 0.52, H₂O). UV (H₂O): 214 (3.7). IR (KBr): 3487s, 3349s, 3290s, 3160s, 3092s, 3003s, 2964m, 2910m, 1618m, 1567w, 1518w, 1423m, 1384m, 1356m, 1332m, 1276s, 1259m, 1195m, 1169m, 1151m, 1111s, 1092m, 1068s, 1051s, 1032s, 1018s, 938m, 912m, 894m, 878w, 851w, 814m, 785s, 622m, 574m, 553m, 530m. ¹H-NMR (D₂O): 3.50 (d, *J* = 9.3, H–C(2)); 3.63 (t, *J* = 9.0, H–C(4)); 3.83–4.05 (m, irradi. at 3.50 $\rightarrow$ change, H–C(5), 2 H–C(6), H–C(3)); 7.50 (s, NCH=CHN). ¹³C-NMR (D₂O): 62.87 (t); 71.72 (d); 75.56 (d); 75.91 (d); 77.15 (d); 96.93 (s); 122.11 (d); 122.25 (d); 148.18 (s). FAB-MS: 247 (100, [*M* – Cl]⁺), 229 (13, [*M* – H₂O – Cl]⁺). Anal. calc. for C₉H₁₅ClN₂O₆ (282.68): C 38.24, H 5.35, Cl 12.54, N 9.91; found: C 38.42, H 5.15, Cl 12.57, N 9.79.

1-O-Acetyl-1-C-(1-acetyl-1H-imidazol-2-yl)-2,3,4,6-tetra-O-benzyl- α -D-glucopyranose (9). A soln. of **7** (110 mg, 0.18 mmol) in pyridine (2 ml) and Ac₂O (1 ml) was stirred at 25° for 14 h. Normal workup and FC (AcOEt/hexane 1:1) afforded 82 mg (65%) of **9**. *R_f* (AcOEt) 0.57. IR (CHCl₃): 3066w, 3043w, 3008m, 2927m, 2867m, 1758s, 1604w, 1497m, 1454m, 1389m, 1366m, 1265s, 1156s, 1085s, 1028m, 1013m, 948m. ¹H-NMR (CDCl₃): 2.2t (s, Ac); 2.39 (s, Ac); 3.69 (dd, *J* = 1.0, 10.8, irradi. at 3.87 → *d*, *J* ≈ 10.6, H-C(6)); 3.77 (dd, *J* = 3.2, 10.8, irradi. at 3.87 → *d*, *J* ≈ 10.0, H'-C(6)); 3.83–3.92 (*m*, H-C(5)); 3.92 (*t*, *J* = 9.9, H-C(4)); 4.12 (*t*, *J* = 9.1, 10.0, irradi. at 4.54 → *d*, *J* ≈ 8.7, H-C(3)); 4.43–4.51 (*m*, 2 PhCH); 4.54 (*d*, *J* = 9.3, H-C(2)); 4.55–4.64 (*m*, 3 PhCH); 4.88 (*d*, *J* = 10.8, PhCH); 4.90 (*d*, *J* = 10.7, PhCH); 4.98 (*d*, *J* = 11.1, PhCH); 7.00 (*d*, *J* = 1.7, NCH=C); 7.11 (*d*, *J* = 1.7, NCH=C); 7.14–7.37 (*m*, 20 arom. H). ¹³C-NMR (CDCl₃, 50 MHz): 22.17 (*q*); 25.28 (*q*); 68.71 (*t*); 73.35 (*t*); 73.93 (*d*); 74.88 (*t*); 75.60 (*t*); 75.93 (*t*); 77.49 (*d*); 79.86 (*d*); 83.87 (*d*); 100.55 (*s*); 120.14 (*d*); 127.69–129.04 (several *d*); 138.35 (*s*); 138.43 (*s*); 138.68 (*s*); 139.07 (*s*); 144.93 (*s*); 167.33 (*s*); 168.68 (*s*).

(1S)- and (1R)-2,3,4,6-Tetra-O-benzyl-1-C-(1H-imidazol-2-yl)-D-glucitol (10 and 11, resp.). A soln. of **7** (1.2 g, 1.98 mmol) in dioxane/H₂O 4:1 (90 ml) and AcOH (0.3 ml) was treated at 0° within 3 min with NaBH₄ (1.2 g). The suspension was stirred at 0° for 40 min and at 25° for 1 h. Neutralization by addition of a sat. NH₄Cl soln. (200 ml) and normal workup afforded 1.2 g (99%) of **10/11** 12:88 (¹H-NMR). White foam. FC (AcOEt) and HPLC (THF/hexane 1:10) of the crude material from a different batch provided pure samples of **10** and **11**.

Data of 10/11 12:88: *R_f* (AcOEt) 0.13. UV (MeOH): 258 (2.9), 219 (3.9). CD (MeOH): 220 (–1800). IR (CHCl₃): 3456m, 3090w, 3067w, 3043w, 3007m, 2926m, 2869m, 1603w, 1545w, 1497w, 1454s, 1401m, 1358m, 1257m, 1075s, 1028s, 920w, 850w, 648w, 604w, 534w. FAB-MS: 609 (100, [*M* + 1]⁺).

Data of 10: UV (MeOH): 258 (3.0), 218 (4.1). CD (MeOH): 223 (–10200). IR (CH₂Cl₂): 3546w, 3446m, 3089w, 3033m, 2927m, 2860m, 1616w, 1576w, 1540w, 1497m, 1456m, 1395m, 1362w, 1210w, 1098s, 1028s, 920w. ¹H-NMR (CDCl₃): 3.60–3.64 (*m*, irradi. at 3.95 → change, 2 H-C(6)); 3.78 (dd, *J* = 3.8, 4.4, H-C(3)); 3.86 (dd, *J* = 4.9, 7.1, irradi. at 3.78 → *d*, *J* ≈ 7.1, H-C(4)); 3.90–4.00 (*m*, irradi. at 3.86 → change, H-C(5)); 4.22 (*t*, *J* = 3.9, irradi. at 5.05 → *d*, *J* ≈ 3.8, irradi. at 3.78 → *d*, *J* ≈ 4.0, H-C(2)); 4.38 (*d*, *J* = 11.2, PhCH); 4.49 (*d*, *J* = 11.9, PhCH); 4.51 (*d*, *J* = 11.9, PhCH); 4.54 (*d*, *J* = 11.3, PhCH); 4.55 (*d*, *J* = 10.9, PhCH); 4.59 (*d*, *J* = 11.8, PhCH); 4.62 (*s*, 2 PhCH); 4.66 (*d*, *J* = 11.2, PhCH); 5.05 (*d*, *J* = 4.0, irradi. at 4.36 → *s*, H-C(1)); 6.93 (*s*, NCH=CHN); 7.17–7.36 (*m*, 20 arom. H). ¹³C-NMR (CDCl₃): 68.32 (*d*); 71.19 (*d*); 71.30 (*t*); 73.45 (*t*); 73.62 (*t*); 74.03 (*t*); 74.44 (*t*); 77.25 (*d*); 79.06 (*d*); 80.73 (*d*); 127.69–128.55 (several *d*); 137.60 (*s*); 137.75 (*s*); 138.03 (*s*); 138.08; 147.83 (*s*).

Data of 11: UV (MeOH): 258 (3.0), 215 (4.4). CD (MeOH): 228 (–1800). IR (CH₂Cl₂): 3554w, 3447m, 3089w, 3033m, 2914m, 2869m, 1605w, 1586w, 1543w, 1497m, 1454m, 1399m, 1358m, 1213m, 1074s, 1028s, 920w. ¹H-NMR (CDCl₃): 3.62 (dd, *J* = 5.0, 9.9, H-C(6)); 3.66 (dd, *J* = 3.5, 9.9, H'-C(6)); 3.87 (dd, *J* = 4.0, 7.2, irradi. at 4.10 → *s*, H-C(4)); 4.04–4.17 (*m*, irradi. at 3.6 or 3.87 → change, H-C(3), H-C(5)); 4.22 (*d*, *J* = 11.0, PhCH); 4.36 (dd, *J* = 2.9, 6.1, irradi. at 4.10 → *d*, *J* ≈ 2.7, H-C(2)); 4.49 (*d*, *J* = 11.9, PhCH); 4.51 (*d*, *J* = 11.3, PhCH); 4.55 (*d*, *J* = 12.0, PhCH); 4.56 (*d*, *J* = 11.4, PhCH); 4.57–4.63 (*m*, 2 PhCH); 5.14 (*d*, *J* = 2.9, irradi. at 4.36 → *s*, H-C(1)); 6.92 (*s*, NCH=CHN); 7.10–7.50 (*m*, 20 arom. H). ¹³C-NMR (CDCl₃): 68.21 (*d*); 71.12 (*d*); 71.36 (*t*); 73.46 (*t*, 2 C); 74.39 (*t*); 74.80 (*t*); 77.19 (*d*); 79.59 (*d*); 80.85 (*d*); 127.00–129.00 (several *d*); 137.67 (*s*); 137.79 (*s*); 137.92 (*s*); 138.09 (*s*); 148.64 (*s*).

(1S)- and (1R)-2,3,4,6-Tetra-O-benzyl-1-C-[1-(methylsulfonyl)-1H-imidazol-2-yl]-D-glucitol (12 and 13, resp.). At 5°, a soln. of **10/11** 12:88 (100 mg, 0.16 mmol) in pyridine (2 ml, freshly distilled) was treated with 4-(dimethylamino)pyridine (23 mg, 0.19 mmol) and methanesulfonyl chloride (MsCl, 20 μ l, 0.26 mmol), and kept for 2.5 h at 5°. After the addition of ice/sat. NH₄Cl soln., normal workup and prep. TLC (AcOEt) afforded 44 mg (39%) of **12/13** 1:5 (¹H-NMR), 6 mg (5%) of **14/15**, 3 mg (3%) of **10/11**. *R_f* (AcOEt) 0.54. IR (CHCl₃): 3350m, 3090w, 3067w, 3043w, 3008w, 2927m, 2866m, 1604w, 1536w, 1498m, 1454m, 1375s, 1330w, 1262m, 1178m, 1167m, 1151s, 1091s, 1028m, 970m. ¹H-NMR (CDCl₃, 200 MHz, **12/13** 1:5): signals of **13**: 3.08 (*s*, Me); 3.65 (dd, *J* = 5.0, 9.9, irradi. at 4.06 → *m*, H-C(6)); 3.71 (dd, *J* = 3.3, 9.9, irradi. at 4.06 → *d*, *J* ≈ 9.6, H'-C(6)); 3.89 (dd, *J* = 4.2, 7.5, irradi. at 4.06 → *s*, H-C(4)); 4.08 (*t*, *J* = 4.4, H-C(3)); 4.04–4.12 (*m*, irradi. at 3.68 → *d*, *J* ≈ 8.0, H-C(5)); 4.38 (*d*, *J* = 10.8, PhCH); 4.49–4.71 (*m*, 5 PhCH, H-C(2)); 4.82 (*d*, *J* = 10.8, PhCH); 4.94 (*d*, *J* = 10.8, PhCH); 5.40 (*d*, *J* = 4.3, H-C(1)); 6.99 (*d*, *J* = 1.7, NCH=C); 7.01–7.50 (*m*, 21 arom. H); signals of **12**: 3.03 (*s*, 0.6 H, Me); 5.50 (*d*, *J* = 8.7, 0.2 H, H-C(1)). ¹³C-NMR (CDCl₃, 50 MHz, **12/13** 1:5, only signals of **13** listed): 43.29 (*q*); 65.49 (*d*); 71.25 (*t*); 71.49 (*d*); 73.43 (*t*); 73.85 (*t*); 74.73 (*t*); 76.40 (*d*); 77.65 (*d*); 79.21 (*d*); 120.38 (*d*); 127.32 (*d*); 127.70–128.61 (several *d*); 137.49 (*s*); 137.88 (*s*, 2 C); 138.20 (*s*); 148.61 (*s*).

(1S)- and (1R)-2,3,4,6-Tetra-O-benzyl-5-O-(methylsulfonyl)-1-C-[1-(methylsulfonyl)-1H-imidazol-2-yl]-D-glucitol (14 and 15, resp.). At 5°, a soln. of **10/11** 12:88 (100 mg, 0.16 mmol) in pyridine (2 ml, freshly distilled) was treated with 4-(dimethylamino)pyridine (23 mg, 0.19 mmol) and MsCl (20 μ l, 0.26 mmol), and allowed to warm up to 25° within 1 h. After stirring for 2 h at 25°, a second fraction of MsCl (10 μ l, 0.13 mmol) was added and stirring continued for a further 3.5 h. After the addition of ice/sat. NH₄Cl soln., normal workup and prep. TLC

(AcOEt) afforded 33 mg (29.5%) of **14/15** 15:85. R_f (AcOEt) 0.64. IR (CHCl₃): 3600–3300w, 3090w, 3067w, 3043w, 3008w, 2928m, 2870m, 1604w, 1537w, 1497m, 1454m, 1408m, 1375s, 1262m, 1175s, 1152s, 1098s, 1043s, 1028s, 969s. ¹H-NMR (CDCl₃, 200 MHz, **14/15** 15:85): signals of **15**: 2.94 (s, Me); 3.25 (s, Me); 3.45 (d, $J = 6.7$, OH–C(1)); 3.80 (dd, $J = 5.0, 6.2$, irradi. at 4.28 → d, $J \approx 4.5$, H–C(3)); 3.85–3.90 (m, irradi. at 5.20 → s, 2 H–C(6)); 4.28 (dd, $J = 2.5, 6.2$, irradi. at 5.20 → d, $J \approx 6.2$, H–C(4)); 4.42–4.62 (m, 4 PhCH, H–C(2)); 4.70–4.85 (m, 4 PhCH); 5.16–5.23 (m, H–C(5)); 5.38 (dd, $J = 4.1, 7.0$, irradi. at 3.45 → d, $J \approx 4.1$, H–C(1)); 6.96 (d, $J = 1.7$, NCH=C); 7.15–7.45 (21 arom. H); signals of **14**: 2.90 (s, 0.6 H, Me); 3.09 (s, 0.6 H, Me). ¹³C-NMR (CDCl₃, 200 MHz, **14/15** 15:85, only signals of **15** listed): 38.50 (q); 43.50 (q); 67.40 (d); 69.05 (t); 73.38 (t); 74.49 (t); 74.59 (t); 74.95 (t); 78.08 (d); 78.41 (d); 80.03 (d); 83.19 (d); 120.35 (d); 127.50–128.80 (several d); 137.60 (s); 137.66 (s); 137.80 (s); 137.89 (s); 148.10 (s).

(1*S*)- and (1*R*)-2,3,4,6-Tetra-O-benzyl-5-O-(methylsulfonyl)-1-C-(1*H*-imidazol-2-yl)-D-glucitol (**16** and **17**, resp.). a) At 5°, a soln. of crude **10/11** 12:88 (50 mg, 0.08 mmol) in CH₂Cl₂/pyridine 1:10 (2.2 ml) was treated with MsCl (14 µl, 0.18 mmol), and kept for 17 h at 25°. After addition of ice/sat. NH₄Cl soln., normal workup and FC (AcOEt/hexane 2:1) afforded 28 mg (50%) of **16/17** 1:5 (¹H-NMR) and 23 mg (46%) of **10/11**. Selected ¹H-NMR (CDCl₃, 200 MHz) signal of **16**: 5.11 (d, $J = 4.5, 0.2$ H, H–C(1)).

b) Similarly, a pure sample of **11** (15 mg, 0.005 mmol) gave 8 mg (47%) of **17** and 5 mg (33%) of **11**.

Data of **17**: R_f (AcOEt) 0.41. IR (CHCl₃): 3550–3460w, 3455m, 3450–3200w, 3090w, 3067w, 3043w, 3007w, 2929m, 2872m, 1605w, 1545w, 1497m, 1454s, 1401w, 1355s, 1174s, 1094s, 1028s, 970w. ¹H-NMR (CDCl₃, 200 MHz): 2.94 (s, Me); 3.73–3.95 (m, H–C(3), 2 H–C(6)); 4.19 (dd, $J = 2.3, 5.7$, irradi. at 5.15 → d, $J \approx 5.5$, H–C(4)); 4.26 (d, $J = 11.5$, PhCH); 4.32 (dd, $J = 2.5, 5.6$, irradi. at 5.11 → d, $J \approx 5.6$, H–C(2)); 4.40–4.50 (m, 3 PhCH); 4.54 (d, $J = 11.0$, PhCH); 4.62 (d, $J = 11.0$, PhCH); 4.68 (d, $J = 11.1$, PhCH); 4.76 (d, $J = 11.0$, PhCH); 5.11 (d, $J = 2.5$, irradi. at 4.32 → s, H–C(1)); 5.15 (m, irradi. at 3.90 → d, $J \approx 2.0$, H–C(5)); 6.95 (s, 2 NCH=C); 7.20–7.40 (m, 20 arom. H).

(1*R*)-1,5-Anhydro-2,3,4,6-tetra-O-benzyl-1-C-(1*H*-imidazol-2-yl)-L-iditol (**18**). At 25°, a soln. of **17** (4 mg, 0.006 mmol) in DMF (1 ml) was treated with NaH (5 mg, 0.21 mmol) and stirred for 3 h at 100°. Normal workup and FC (AcOEt/hexane 1:1) gave 2.1 mg (59%) of **18**. R_f (AcOEt) 0.49. UV (MeOH): 258 (3.1), 211 (4.4). CD (MeOH): 223 (–12000). IR (CHCl₃): 3448m, 3222w, 3088w, 3066w, 3008w, 2960m, 2927m, 2860w, 1558m, 1540m, 1456m, 1362w, 1262s, 1015s, 918m. ¹H-NMR (CDCl₃): 3.37–3.40 (m, irradi. at 3.62 → br. s, irradi. at 4.12 → dd, $J \approx 0.9, 2.1$, H–C(4)); 3.57 (dd, $J = 5.7, 9.8$, irradi. at 4.12 → d, $J \approx 10.2$, H–C(6)); 3.62 (dd, $J = 2.1, 2.6$, irradi. at 3.39 → d, $J \approx 2.6$, H–C(3)); 3.77 (dd, $J = 6.6, 10.1$, irradi. at 4.12 → d, $J = 9.8$, H'–C(6)); 3.79–3.82 (br. s, irradi. at 3.39 → change, irradi. at 3.62 → d, $J \approx 1.7$, irradi. at 5.10 → change, H–C(2)); 4.12 (ddd, $J = 1.8, 5.8, 6.6$, H–C(5)); 4.15 (d, $J = 11.8$, PhCH); 4.24 (d, $J = 12.1$, PhCH); 4.25 (d, $J = 12.1$, PhCH); 4.34 (d, $J = 12.1$, PhCH); 4.39 (d, $J = 12.4$, PhCH); 4.48 (d, $J = 12.3$, PhCH); 4.53 (d, $J = 12.2$, PhCH); 4.56 (d, $J = 12.1$, PhCH); 5.1 (d, $J = 1.6$, H–C(2)); 6.96–7.40 (m, 22 arom. H); 9.76 (br. s, exchange with D₂O, NH). ¹³C-NMR (CDCl₃, 75 MHz): 69.64 (t); 70.37 (d); 71.93 (t); 72.22 (t); 72.39 (d); 73.33 (t); 73.41 (t); 73.53 (d); 74.61 (d); 75.60 (d); 115.20 (d); 127.70–128.76 (several d); 137.53 (s); 137.68 (s); 137.78 (s); 138.06 (s); 145.88 (s). FAB-MS: 592 (35, [M + 2]⁺), 591 (100, [M + 1]⁺).

(1*S*)- and (1*R*)-2,3,4,6-Tetra-O-benzyl-1-O-(3,5-dinitrobenzoyl)-1-C-(1*H*-imidazol-2-yl)-D-glucitol (**19** and **20**, resp.). a) From Crude **10/11**: At 25°, a soln. of **10/11** 12:88 (500 mg, 0.82 mmol) in pyridine (20 ml, freshly distilled) was treated with 3,5-dinitrobenzoyl chloride (228 mg, 0.99 mmol) and kept for 2 h at 0° and for 18 h at 25°. After the addition of ice/H₂O (20 ml), normal workup afforded a yellow foam. FC (AcOEt/hexane 10:15) gave 478.5 mg (72.5%) of **19/20** 15:85 (¹H-NMR). Foam.

b) Similarly, a pure sample of **10** (2.8 mg, 0.005 mmol) gave 2.4 mg of **19** (65%).

c) Similarly, a pure sample of **11** (80 mg, 0.13 mmol) gave 72 mg of **20** (68%).

Data of **19/20** 12:88: R_f (AcOEt) 0.75. UV (MeOH): 209 (4.7). IR (CHCl₃): 3570w, 3407w, 3102w, 3067w, 3043w, 3007w, 2962w, 2870w, 1954w, 1736m, 1629w, 1599w, 1599w, 1548s, 1497w, 1455w, 1345s, 1263s, 1166m, 1092s, 1028w, 922w, 823w. FAB-MS: 804 (52, [M + 2]⁺), 803 (100, [M + 1]⁺), 591 (28, [M + 1 – C₇H₄N₂O₆]⁺).

Data of **19**: UV (MeOH): 214 (4.8). CD (MeOH): 222 (–340000). IR (CH₂Cl₂): 3562w, 3438m, 3102m, 3033m, 2962w, 2927w, 1737s, 1630m, 1548s, 1497w, 1454m, 1345s, 1288m, 1209w, 1163w, 1096s, 1027s. ¹H-NMR (CDCl₃): 2.91 (br. s, OH); 3.64 (dd, $J = 4.5, 9.8$, irradi. at 4.09 → d, $J \approx 9.5$, H–C(6)); 3.70 (dd, $J = 3.3, 9.7$, irradi. at 4.09 → d, $J \approx 9.8$, H'–C(6)); 3.71 (dd, $J = 3.5, 7.1$, irradi. at 3.81 → d, $J \approx 7.0$, irradi. at 4.60 → d, $J \approx 3.6$, H–C(3)); 3.81 (dd, $J = 3.5, 7.8$, irradi. at 4.09 → d, $J \approx 3.5$, H–C(4)); 4.04–4.13 (m, H–C(5)); 4.51 (d, $J = 11.8$, PhCH); 4.54 (d, $J = 12.0$, PhCH); 4.55 (d, $J = 10.6$, PhCH); 4.56 (d, $J = 10.9, 2$ PhCH); 4.58 (d, $J = 11.7$, PhCH); 4.60 (dd, $J = 3.4, 7.1$, irradi. at 6.38 → d, $J \approx 7.3$, H–C(2)); 4.67 (d, $J = 11.5$, PhCH); 4.78 (d, $J = 11.1$, PhCH); 6.38 (d, $J = 3.8$, irradi. at 4.60 → s, H–C(1)); 7.05–7.38 (m, 22 arom. H); 8.93 (d, $J = 2.1, 2$ arom. H); 9.18 (t, $J = 2.1, 1$

arom. H); 9.98 (br. s, NH). ¹H-NMR (CDCl₃ + 5% CD₃OD): 3.65 (dd, *J* = 4.4, 9.7, H-C(6)); 3.70 (dd, *J* = 2.9, 9.8, H'-C(6)); 3.75 (dd, *J* = 4.2, 6.4, irradi. at 4.48 → *d*, *J* ≈ 4.0, H-C(3)); 3.82 (dd, *J* = 4.1, 7.8, irradi. at 3.75 → *d*, *J* ≈ 7.6, H-C(4)); 4.01 (ddd, *J* = 2.9, 4.4, 7.6, H-C(5)); 4.34 (*d*, *J* = 11.2, PhCH); 4.48 (dd, *J* = 5.0, 6.4, irradi. at 3.75 → *d*, *J* ≈ 5.1, H-C(2)); 4.50 (*d*, *J* = 11.2, PhCH); 4.51 (*d*, *J* = 11.8, PhCH); 4.56 (*d*, *J* = 11.5, PhCH); 4.58 (dd, *J* = 11.8, PhCH); 4.59 (*d*, *J* = 11.5, PhCH); 4.67 (*d*, *J* = 11.2, 2 PhCH); 6.24 (*d*, *J* = 4.9, irradi. at 4.48 → *s*, H-C(1)); 7.05–7.41 (*m*, 22 arom. H); 8.95 (*d*, *J* = 2.1, 2 arom. H); 9.16 (*t*, *J* = 2.1, 1 arom. H). ¹³C-NMR (CDCl₃): 70.79 (*t*); 70.94 (*d*); 71.63 (*d*); 73.50 (*t*); 73.61 (*t*); 74.67 (*t*); 75.65 (*t*); 77.23 (*d*); 78.69 (*d*); 79.20 (*d*); 122.40 (*d*); 127.83–129.50 (several *d*); 133.17 (*s*); 137.41 (*s*, 2 C); 137.88 (*s*, 2 C); 142.28 (*s*); 148.42 (2*s*); 161.27 (*s*).

Data of 20: UV (MeOH): 210 (5.7). CD (MeOH): 211 (–210000). IR (CH₂Cl₂): 3566w, 3426m, 3101m, 3033m, 2921m, 2872m, 1734s, 1630m, 1599w, 1549s, 1497w, 1454m, 1345s, 1497w, 1454m, 1345s, 1288m, 1209w, 1166m, 1076s, 1028m, 984w. ¹H-NMR (CDCl₃): 3.63 (*d*, *J* = 4.6, 2 H-C(6)); 3.84 (*t*, *J* = 4.2, irradi. at 4.71 → *d*, *J* ≈ 4.2, H-C(3)); 3.96 (dd, *J* = 4.7, 6.5, H-C(4)); 4.07–4.11 (*m*, irradi. at 3.63 → *d*, *J* ≈ 7.0, H-C(5)); 4.29 (*d*, *J* = 11.5, PhCH); 4.53 (*d*, *J* = 11.7, 2 PhCH); 4.58 (*d*, *J* = 11.8, PhCH); 4.61 (*d*, *J* = 10.9, PhCH); 4.67 (*d*, *J* = 10.7, PhCH); 4.71 (dd, *J* = 3.7, 8.5, H-C(2)); 4.74 (*d*, *J* = 12.2, PhCH); 4.90 (*d*, *J* = 11.8, PhCH); 6.45 (*d*, *J* = 8.4, irradi. at 4.70 → *s*, H-C(1)); 6.69 (br. s, NCH=CHN); 6.98 (br. s, NCH=CHN); 7.20–7.50 (*m*, 20 arom. H); 8.97 (*d*, *J* = 2.1, 2 arom. H); 9.10 (*t*, *J* = 2.1, 1 arom. H); 9.16 (br. s, NH). ¹H-NMR (CDCl₃ + 5% CD₃OD): 3.62 (*d*, *J* = 4.4, 2 H-C(6)); 3.84 (*t*, *J* = 4.4, H-C(3)); 3.91 (dd, *J* = 4.2, 6.7, H-C(4)); 4.04–4.09 (*m*, H-C(5)); 4.28 (*d*, *J* = 11.3, PhCH); 4.47–4.60 (*m*, 6 PhCH); 4.65 (*d*, *J* = 4.6, 7.5, H-C(2)); 4.84 (*d*, *J* = 11.8, PhCH); 6.50 (*d*, *J* = 7.5, H-C(1)); 6.86 (br. s, NCH=CHN); 7.06–7.30 (*m*, 20 arom. H); 8.90 (*d*, *J* = 2.1, 2 arom. H); 9.08 (*t*, *J* = 2.1, 1 arom. H). ¹³C-NMR (CDCl₃): 71.14 (*t*); 71.25 (*d*); 72.14 (*d*); 73.53 (*t*, 3 C); 75.21 (*t*); 76.96 (*d*); 77.72 (*d*); 78.51 (*d*); 122.32 (*d*); 128.05–129.77 (several *d*); 133.23 (*s*); 137.46 (*s*); 137.53 (*s*); 137.82 (*s*); 137.93 (*s*); 142.43 (*s*); 148.38 (2*s*); 162.30 (*s*).

(1*R*)- and (1*S*)-1,5-Anhydro-2,3,4,6-tetra-O-benzyl-1-C-(1*H*-imidazol-2-yl)-D-glucitol (**21** and **22**, resp.).

a) **From 19/20:** At –10°, a soln. of **19/20** 15:85 (478 mg, 0.60 mmol) in DMF (25 ml) was treated with NaH (37 mg, 1.54 mmol) and stirred for 45 min, while turning slowly violet. After addition of a cold sat. NH₄Cl soln., normal workup gave 353 mg of a violet oil (¹H-NMR: **21/22** 25:75). FC (AcOEt/hexane) gave 208 mg (59%) of **22** and 81 mg (23%) of **21**. Both compounds were contaminated by traces (< 3%) of the other isomer. Pure **22** was obtained by recrystallization in THF/hexane 1:1. Isomer **21** did not crystallize and was used as such for the next step.

b) **From Pure 19:** Similarly, a pure sample of **19** (2.4 mg, 0.002 mmol) gave 1.4 mg (79%) of **21/22** 20:88 (¹H-NMR).

c) **From Pure 20:** Similarly, a pure sample of **20** (59 mg, 0.073 mmol) gave 40 mg (92%) of **21/22** 17:83 (¹H-NMR).

Data of 21: R_f (AcOEt) 0.53. UV (MeOH): 230 (3.4). CD (MeOH): 226 (+3360). IR (CHCl₃): 3454w, 3212w, 3090w, 3067w, 3043w, 3008w, 2961m, 2927m, 2857m, 1672w, 1603w, 1497w, 1454m, 1400w, 1361w, 1262s, 1095s, 1028s, 909m, 804w, 823m, 658w, 598w. ¹H-NMR (C₆D₆): 3.73 (*d*, *J* = 3.1, irradi. at 4.4 → *s*, 2 H-C(6)); 3.92 (dd, *J* = 8.2, 9.5, irradi. at 4.0 → *d*, *J* ≈ 8.5, H-C(3)); 3.99 (dd, *J* = 5.6, 8.7, irradi. at 5.32 → *d*, *J* ≈ 8.7, H-C(2)); 4.27 (*d*, *J* = 12.1, PhCH); 4.30–4.55 (*m*, 3 PhCH, H-C(5), H-C(4)); 4.63 (*d*, *J* = 11.3, PhCH); 4.76 (*d*, *J* = 11.5, PhCH); 4.87 (*d*, *J* = 11.5, PhCH); 4.88 (*d*, *J* = 11.5, PhCH); 5.32 (*d*, *J* = 5.6, H-C(1)); 6.8–7.4 (*m*, 22 arom. H). ¹³C-NMR (CDCl₃, 50 MHz): 68.51 (*t*); 69.97 (*d*); 73.59 (*t*); 73.72 (*d*); 74.30 (*t*); 74.59 (*t*); 75.00 (*t*); 77.52 (*d*); 79.41 (*d*); 81.70 (*d*); 127.77–128.69 (several *d*); 137.37 (*s*); 137.97 (*s*); 138.02 (*s*); 138.35 (*s*); 144.67 (*s*). FAB-MS: 592 (42, [M + 2]⁺), 591 (100, [M + 1]⁺).

Data of 22: R_f (AcOEt) 0.49. M.p. 152.5°. [α]_D²⁵ = 21.9 (*c* = 0.48, CHCl₃). UV (MeOH): 209 (4.5). CD (MeOH): 220 (–44000). IR (CHCl₃): 3454w, 3207w, 3090w, 3067w, 3043w, 3008w, 2924m, 2871m, 1606w, 1572w, 1497m, 1454m, 1398w, 1361m, 1282w, 1262m, 1069s, 1028m, 1004m, 915w, 856w, 822w, 635w. ¹H-NMR (CDCl₃, 200 MHz): 3.51 (*m*, *J* = 2.6, 6.1, 9.4, H-C(5)); 3.60–3.75 (*m*, H-C(4), 2 H-C(6)); 3.82 (*t*, *J* = 8.5, H-C(3)); 3.92 (*t*, *J* = 8.8, irradi. at 4.50 → *d*, *J* ≈ 8.5, H-C(2)); 4.13 (*d*, *J* = 10.4, PhCH); 4.39–4.58 (*m*, 2 PhCH₂, H-C(1)); 4.85 (*d*, *J* = 10.9, PhCH); 4.86 (*d*, *J* = 11.2, PhCH); 4.97 (*d*, *J* = 11.2, PhCH); 7.00 (*m*, 4 arom. H); 7.10–7.36 (*m*, 18 arom. H). ¹H-NMR (C₆D₆, 200 MHz): 3.29–3.37 (*m*, irradi. at 3.92 → br. s, H-C(5)); 3.50 (dd, *J* = 1.0, 11.0, H-C(6)); 3.60 (dd, *J* = 3.7, 11.0, H'-C(6)); 3.86–3.96 (*m*, H-C(3), H-C(4)); 4.08–4.10 (*m*, irradi. at 3.92 → change, H-C(2)); 4.20–4.40 (*m*, 3 PhCH); 4.53 (*d*, *J* = 10.5, PhCH); 4.59 (*d*, *J* = 11.1, PhCH); 4.79 (*d*, *J* = 9.5, H-C(1)); 4.88 (*d*, *J* = 11.1, PhCH); 4.90 (*d*, *J* = 11.1, PhCH); 5.07 (*d*, *J* = 11.2, PhCH); 6.90–7.40 (*m*, 22 arom. H). ¹³C-NMR (CDCl₃): 69.25 (*t*); 73.64 (*t*); 75.06 (*t*); 75.26 (*t*); 75.49 (*d*); 75.88 (*t*); 78.16 (*d*); 79.26 (*d*); 82.44 (*d*); 86.73 (*d*); 127.90–129.7 (several *d*); 138.12 (*s*); 138.31 (*s*); 138.54 (*s*); 139.00 (*s*); 145.36 (*s*). FAB-MS: 591 (100, [M + 1]⁺). Anal. calc. for C₃₇H₃₈N₂O₅ (590.72): C 75.23, H 6.48, N 4.79; found: C 74.94, H 6.39, N 4.79.

(1R)-1,5-Anhydro-1-C-(1H-imidazol-2-yl)-D-glucitol Hydrochloride (**23**·HCl). A suspension of Pd/C (10%, 80 mg) in 1N HCl (6 ml) was activated for 3 h under H₂ (7 bar) at 25°. After addition of a soln. of **21** (62 mg, 0.11 mmol) in MeOH (2 ml), the suspension was hydrogenated for 10 h at 9.5 bar and 25°, diluted with MeOH, and filtered through *Celite*. Evaporation of the filtrate and crystallization from MeOH/acetone gave 14 mg (50%) of **23**. White crystals. Crystallization of the filtrate afforded a second crop of 6 mg (21%) of **23**. M.p. 239°. *R_f* (AcOEt/MeOH/AcOH 7:5:1) 0.25. $[\alpha]_D^{20} = +131.6$ (*c* = 0.53, H₂O). UV (H₂O): 217 (3.8). CD (H₂O): 215.5 (+10000). IR (KBr): 3600–3138s, 2968m, 1600w, 1384w, 1341w, 1131m, 1111m, 1068m, 1052m, 1020m, 916w, 876w, 814w, 769w, 661w, 522w. ¹H-NMR (D₂O): 3.29–3.34 (*m*, H–C(5)); 3.48–3.57 (*m*, irradi. at 3.33 → change, H–C(3), H–C(4)); 3.77 (*dd*, *J* = 4.7, 12.5, irradi. at 3.33 → *d*, *J* ≈ 12.0, H–C(6)); 3.87 (*dd*, *J* = 2.4, 12.6, irradi. at 3.33 → *d*, *J* ≈ 12.0, H'–C(6)); 4.07 (*dd*, *J* = 6.3, 9.7, irradi. at 5.47 → *d*, *J* ≈ 9.5, irradi. at 3.50 → *m*, H–C(2)); 5.47 (*d*, *J* = 6.2, irradi. at 4.07 → *d*, *J* ≈ 2.5, H–C(1)); 7.43 (*s*, NCH=CHN). ¹³C-NMR (CD₃OD): 62.35 (*t*); 70.85 (*d*); 71.47 (*d*); 72.09 (*d*); 75.05 (*d*); 79.69 (*d*); 120.98 (*d*, 2 C); 146.93 (*s*). FAB-MS: 231 (100, [*M* + 1 – Cl]⁺), 230 (9, [*M* – Cl]⁺). Anal. calc. for C₉H₁₅ClN₂O₅ (266.68): C 40.53, H 5.67, Cl 13.29, N 10.50; found: C 40.52, H 5.51, Cl 13.35, N 10.21.

(1S)-1,5-Anhydro-1-C-(1H-imidazol-2-yl)-D-glucitol Hydrochloride (**24**·HCl). A suspension of Pd/C (10%, 125 mg) in 1N HCl (5 ml) was activated for 2.5 h under H₂ (7 bar) at 25°. After addition of a soln. of **22** (120 mg, 0.20 mmol) in MeOH (4 ml), the suspension was hydrogenated for 24 h at 7.5 bar and 25°, diluted with MeOH, and filtered through *Celite*. Evaporation of the filtrate and crystallization from H₂O/acetone 1:10 (22 ml) gave 38 mg (70%) of **24**. White crystals. M.p. 227°. *R_f* (AcOEt/MeOH/AcOH 7:5:1) 0.25. $[\alpha]_D^{25} = 30.0$ (*c* = 0.37, H₂O). UV (H₂O): 214 (3.9). CD (H₂O): 216 (–14 100). IR (KBr): 3600–3100s, 3170s, 3152s, 3062m, 2976m, 2898m, 2835m, 2807m, 2706w, 1611m, 1466m, 1421m, 1376m, 1350m, 1336m, 1318m, 1303m, 1256m, 1184m, 1136m, 1128m, 1115m, 1110m, 1081m, 1056s, 1006m, 994m, 920m, 896w, 760m, 725w, 668m. ¹H-NMR (D₂O): 3.48 (*t*, *J* = 9.5), 3.51 (*t*, *J* = 9.3, H–C(3), H–C(4)); 3.55–3.70 (*m*, irradi. at 4.70 → change at 3.65, H–C(2), H–C(5)); 3.76 (*dd*, *J* = 5.2, 12.4, irradi. at 3.6 → *d*, *J* ≈ 12.4, H–C(6)); 3.90 (*dd*, *J* = 1.5, 12.4, irradi. at 3.6 → *d*, *J* ≈ 12.4, H'–C(6)); 4.68–4.74 (covered by H₂O signal, H–C(1)); 7.41 (*s*, NCH=CHN). ¹H-NMR (CD₃OD): 3.20–3.59 (*m*, H–C(2), H–C(3), H–C(4), H–C(5)); 3.78 (*dd*, *J* = 4.8, 11.0, H–C(6)); 3.93 (*dd*, *J* = 2.2, 10.5, H'–C(6)); 4.63 (*d*, *J* = 8.8, H–C(1)); 7.53 (*s*, NCH=CHN). ¹³C-NMR (D₂O): 63.34 (*t*); 71.75 (*d*); 74.84 (*d*); 75.34 (*d*); 79.10 (*d*); 82.75 (*d*); 121.85 (*d*); 121.95 (*d*); 146.15 (*s*). FAB-MS: 231 (100, [*M* + 1 – Cl]⁺), 230 (12, [*M* – Cl]⁺). Anal. calc. for C₉H₁₅ClN₂O₅ (266.68): C 40.53, H 5.67, Cl 13.29, N 10.50; found: C 40.28, H 5.76, Cl 13.23, N 10.39.

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