

87. Imidazole-Analogues of 6-Epicastanospermine and of 3,7a-Diepialexine

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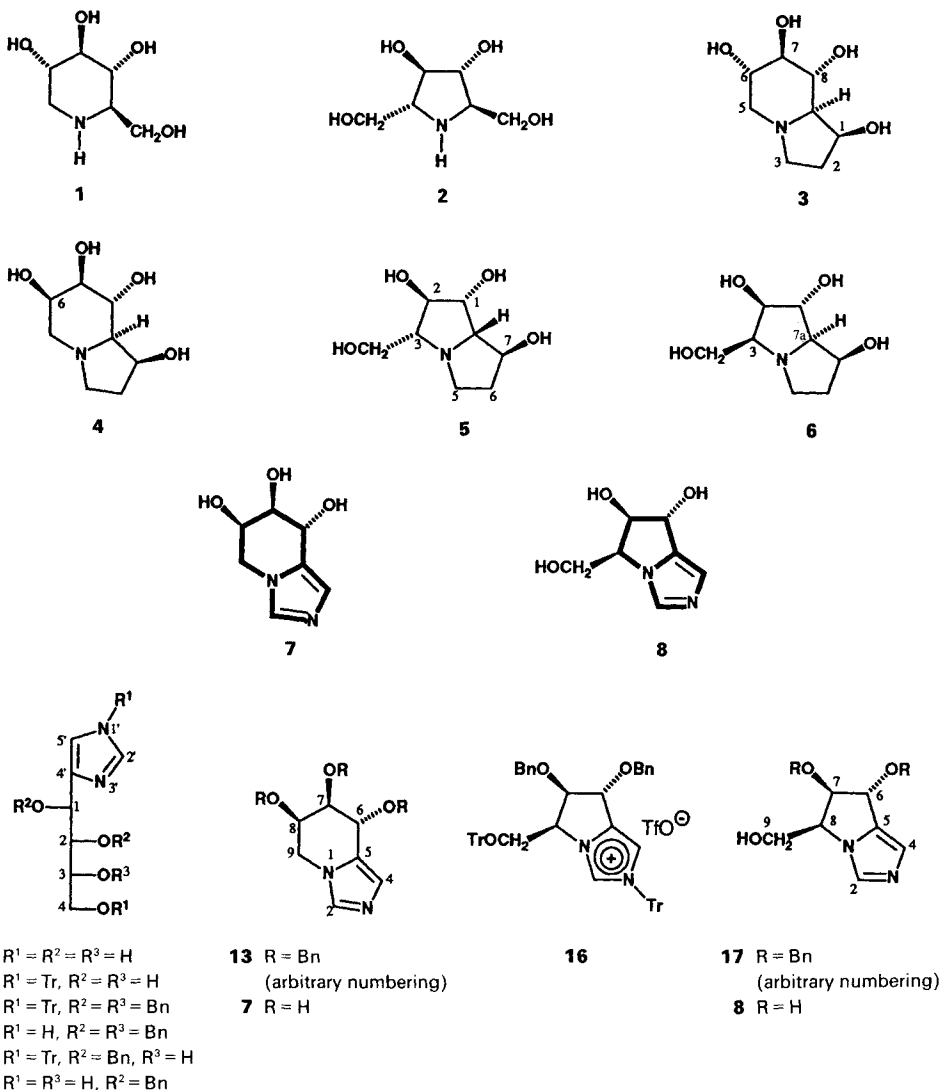
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The chiral bicyclic imidazol derivatives **7** and **8** were obtained from D-glucose derivative **9** by a sequence of selective protection/deprotection and intramolecular S_N2 reactions. Triols **7** and **8** are analogues of 6-epicastanospermine (**4**) and of 3,7a-diepialexine (**6**), respectively, and are potential glycosidase inhibitors. However, their anti-HIV activity proved to be only marginal.

Introduction. – Naturally occurring N-containing 1-deoxysugars have been discovered in several plants during the last decade [1]. They can be considered as polyhydroxylated piperidines (e.g. DNJ (**1**)), pyrrolidines (e.g. DMDP (**2**)), octahydroindolizines (e.g. castanospermine (**3**) and 6-epicastanospermine (**4**)), and hexahydro-1*H*-pyrrolizines (e.g. alexine (**5**) and 3,7a-diepialexine (**6**)). All these polyhydroxylated ‘alkaloids’ are sugar mimics which act as glycosidase inhibitors [2]. *E.g.*, castanospermine (**3**) behaves as a potent inhibitor of several glycosidases, including lysosomal α -glucosidase, α - and β -glucosidase in fibroblast extracts [3]. Very interesting is the observation that **3** is able to inhibit experimental metastasis of some cancers. Last, but not least, **3** inhibits replication of human immunodeficiency virus (HIV) syncytium formation and other virus replication [3]. The chemotherapeutic potential of these N-containing 1-deoxysugar derivatives, which block the hydrolytic action of various glycosidases, seems to be outstanding and is only now beginning to be exploited. Syntheses of mono- and bicyclic glycosidase inhibitors with modified structure – and *configuration* – are, therefore, of particular relevance [4]. We describe herein the synthesis of the chiral bicyclic compounds **7** and **8**, which are the imidazole analogues of 6-epicastanospermine (**4**) and of 3,7a-diepialexine (**6**), respectively, the starting compound for both being D-glucose.

Synthesis of 7 and 8. – The imidazole derivative **9** had been obtained in 1931 by *Parrod* from D-glucose [5]. The less hindered imidazole N-atom and the primary OH-group in **9** were selectively tritylated using trityl chloride in THF in the presence of Et_3N to give **10** in good yield. Benzylation of the three secondary OH groups was achieved in excellent yield by reaction of the sodium trialkoxide salt of **10** with BnBr and Bu_4NI in THF [6]. Removal of the two trityl moieties of **11** was performed easily with 6*N* HCl and gave **12** as colourless crystals. This latter product is ideally set up for cyclisation, and reaction of **12**, with triflic anhydride ($(\text{CF}_3\text{SO}_2)_2\text{O}$) in pyridine and CH_2Cl_2 led to **13** in good yield by the

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expected, spontaneous intramolecular S_N2 displacement of the selectively formed primary triflate. Catalytic hydrogenolysis of **13** gave triol **7** as a colourless foam whose absolute configuration is as indicated in *Formula 7*. This bicyclic compound is most stable in the form of its hydrochloride salt.

When benzylation of **10** was carried out as described above but at a lower temperature (-5°), the dibenzyl ether **14** was obtained instead of the tribenzyl ether **11**. Removal of the trityl groups with HCl led to **15** as colourless crystals. Treatment of **14** with $(CF_3SO_2)_2O$ and anhydrous pyridine at low temperature (-30°) in CH_2Cl_2 under Ar gave a yellow solution. We surmised that this colour was due to the formation of the annulated imidazolium triflate **16** via an intramolecular S_N2 reaction. This seemed to be a reason-

able assumption, since acidification of the coloured solution with HCl gave compound **17** (69% yield) as colourless crystals. Catalytic hydrogenolysis of **17** led to the expected target molecule **8** (94% yield) as colourless and stable crystals.

Structure Analyses. – The structures of the monocyclic products **10–12**, **14**, **15** were fully supported by ¹H- and ¹³C-NMR data (see *Tables 1* and *2*). The absolute configura-

Table 1. ¹H-NMR Data^{a)} (CDCl₃) of the Imidazolyl Derivatives **10–12**, **14**, and **15**.
At 400 MHz, 300 K; δ in ppm and *J* in Hz, internal standard TMS.

	H–C(2')	H–C(5')	H–C(1)	H–C(2)	H–C(3)	H _a –C(4)	H _b –C(4)
10	7.46	6.82	4.82	3.86	3.94	3.45	3.34
11	7.48	6.79	4.72	4.23	3.82	3.46	3.26
12 ^{b)}	7.63	7.04	4.80	3.90	3.74	3.87	3.77
14 ^{b)} ^{c)}	–	6.80	4.72	3.99	3.94	3.39	3.22
15 ^{b)}	7.62	7.00	4.76	3.82	3.75	3.62	
	<i>J</i> (2',5')	<i>J</i> (1,2)	<i>J</i> (2,3)	<i>J</i> (3,4a)	<i>J</i> (3,4b)	<i>J</i> (4a,4b)	
10	1.0	2.5	7.5	4.0	6.0	9.0	
11	1.2	5.0	6.0	2.5	6.0	10.0	
12 ^{b)}		4.0	6.0				
14 ^{b)} ^{c)}	1.2	4.2	6.4	3.4	5.4	9.6	
15 ^{b)}		4.5	6.0				

a) Substituents at O- and N-atoms are omitted for the sake of clarity.

b) For convenience, **12**, **14**, and **15** are numbered like the parent **9**.

c) At 250 MHz.

Table 2. ¹³C-NMR Data (CDCl₃) of Imidazolyl Derivatives **10–12**, **14**, and **15**.
At 100.6 MHz, 300 K; δ in ppm, internal standard TMS; *J* values omitted.

	C(2')	C(4')	C(5')	C(1)	C(2)	C(3)	C(4)
10	137.97	140.93	119.33	66.97	74.35	71.17	65.31
11	138.88	139.47	120.60	76.68	80.83	78.52	63.51
12 ^{a)}	135.29			73.43	81.64	78.45	60.38
14 ^{a)} ^{b)}	138.68	138.81	121.04	76.47	81.07	70.91	64.87
15 ^{a)}	135.54			74.50	81.37	71.37	63.54

a) For convenience, **12**, **14**, and **15** are numbered like the parent **9**.

b) At 62.9 MHz.

Table 3. ¹H-NMR Data^{a)} of Bicyclic Compounds **13**, **7**, **17**, and **8**.
At 400 MHz, 300 K; δ in ppm and *J* in Hz; internal standard TMS.

	Solvent	H–C(2)	H–C(4)	H–C(6)	H–C(7)	H–C(8)	H _a –C(9)	H _b –C(9)	<i>J</i> (6,7)	<i>J</i> (7,8)	<i>J</i> (8,9a)	<i>J</i> (8,9b)	<i>J</i> (9a,9b)
13	CDCl ₃	7.46	7.05	4.70	4.15	4.35	4.16	4.12	4.0	1.5	5.5	10	11
7	CD ₃ OD	7.54	6.96	4.82	3.91	4.36	4.16	4.04	5.5	2.0	4.5	7.0	12.5
7	D ₂ O	7.58	7.02	4.87	3.96	4.40	4.22	4.10	7.0	2.0	4.0	5.5	13
17	CDCl ₃	7.57	6.94	4.92	4.72	4.57	3.98	3.94	3.0	6.0	4.5	5.5	12
8 ^{b)}	CD ₃ OD	7.66	6.87	4.85	4.60	4.53	3.97	3.81	3.5	5.9	3.7	7.3	11.7

a) Substituents at O-atoms are omitted, and the numbering is arbitrary for the sake of clarity; for systematic names, see *Exper. Part*.

b) At 250 MHz.

tion of bicyclic compound **13** was ascertained by correlation with the absolute configuration of D-glucose and by the 3J coupling constants (Table 3). Triol **7** has the same absolute configuration as **13** (Table 3). This is obviously the case, since the asymmetric centres C(6), C(7), and C(8) have not been altered during the synthetic transformations of imidazole-glucose **9** into the target molecule **7**, neither by the protection/deprotection steps nor by the intramolecular S_N2 reaction which affected only the achiral C(9) atom (^{13}C -NMR data in Table 4).

Table 4. ^{13}C -NMR Data^{a)} of Bicyclic Compounds **13**, **7**, **17**, and **8** Using Selective ^1H -Decoupling Techniques. At 100.6 MHz, 300 K; δ in ppm; internal standard TMS.

	Solvent	C(2)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
13	CDCl_3	136.28	128.48	125.39	43.04	74.89	72.29	68.81
7	CD_3OD	136.83	127.02	131.36	66.22	74.32	67.43	46.92
7	D_2O	139.50	128.41	131.86	67.36	75.23	69.40	48.91
17	CDCl_3	131.18	122.78		76.44	89.06	59.45	61.38
8^{b)}	CD_3OD	132.37	121.31	137.99	73.16	84.14	62.77	61.59

^{a)} Substituents at O-atoms are omitted, and the numbering is arbitrary, for the sake of clarity; for systematic names, see *Exper. Part*.

^{b)} At 62.9 MHz.

Table 5. Crystallographic Data of **8**

Formula	$\text{C}_7\text{H}_{10}\text{N}_2\text{O}_3$	Radiation [$\text{\AA}$]	$\text{MoK}\alpha$ ($\lambda = 0.71069$)
Space group	Orthorhombic, $P2_12_12_1$	Scan mode	$\omega/2\theta$
a [$\text{\AA}$]	6.540 (6)	Collected intensities	$+h, +k, +l$
b [$\text{\AA}$]	8.258 (2)	Absorption [cm^{-1}]	0.77
c [$\text{\AA}$]	13.754 (2)	No. of ind. reflections	931
α [$^\circ$]	90.0	No. of refl. used in ref.	895 ($ F > 2\sigma(F)$)
β [$^\circ$]	90.0	No. of variables	109
γ [$^\circ$]	90.0	Observations/parameter	8.2
V [$\text{\AA}^3$]	743 (1)	Max. and min. $\Delta\rho$ [$\text{e} \cdot \text{\AA}^{-3}$]	0.56, -0.22
Z	4	R	0.049
$F(000)$	360	R_w	0.055
Temperature [K]	293	Weighting scheme	$0.8480(\sigma^2(F) + 3.281 \cdot 10^{-3}(F)^2)^{-1}$
θ_{max} [$^\circ$]	27		

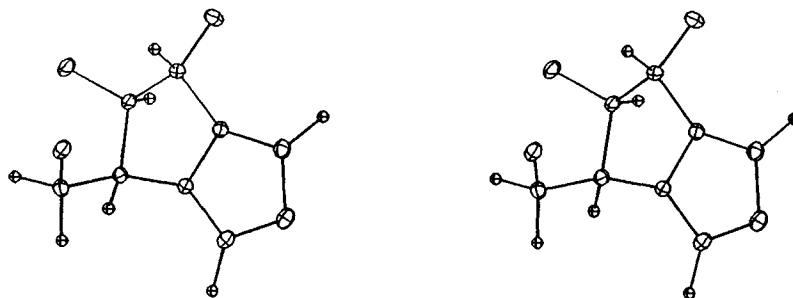


Figure. Stereopair view of **8**. Hydroxy H-atoms are not represented.

Similar comments can be made for the structure analyses of the monocyclic compounds **14** and **15** (Tables 1 and 2). As to the corresponding bicyclic compounds, their absolute configuration is as indicated by *Formulae 17* and **8** (cf. Tables 3 and 4). Nevertheless, it was desirable to confirm the (*S*)-configuration at C(8) which resulted from an intramolecular S_N2 reaction. This was ascertained by an X-ray analysis (see the Figure and Table 5).

X-Ray Structure Determination for 8. Reflection intensities were collected at room temperature on a four-circle diffractometer *Enraf-Nonius CAD4* equipped with a graphite monochromator and using $\text{MoK}\alpha$ radiation. Unit-cell parameters were determined from 25 accurately centered, independent, and strong reflexions by least-squares method. Four standard reflexions monitored every 3600 s during data collection showed no intensity loss. The usual corrections except for absorption were applied. The structure was solved by direct methods with *SHELXS-86* [7] and refined with *SHELXS-76* [8]. Non-H-atoms were refined anisotropically. The positions for H-atoms were calculated. Details of crystal data and parameters of data collection are given in Table 5. Crystallographic data are deposited with the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB1 1EW, England.

In vitro anti-HIV Tests. – Compounds **7** and **8** were evaluated for their antiviral activity in CEM-T4 cells infected with HIV1 (strain GB8). Their activity was assessed by light microscopic measurement of inhibition of syncytium formation. In this assay, both products showed an antiviral activity less than castanospermin which was used as the reference substance.

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Experimental Part

General. Flash chromatography (FC) was performed on silica gel (60 *Merck*; 230–400 mesh). TLC: aluminium sheets silica gel (60 *F 254 Merck*). M.p.: *Kofler* hot bench or *Büchi SMP 20* apparatus; corrected. $[\alpha]_D^{20}$: *Perkin-Elmer-PE-241* polarimeter. UV spectra (λ_{max} in nm (ϵ)): *Varian Techtron 635*. IR spectra (cm^{-1}): *Perkin-Elmer 157-G*. ^1H - and ^{13}C -NMR spectra: *Bruker WM-400*, *AC-250* apparatus using double-irradiation techniques; tetramethylsilane (= TMS; ^1H -NMR) and CDCl_3 ($\delta(\text{CDCl}_3) = 77.00$ with respect to TMS; ^{13}C -NMR) as internal references; δ in ppm and J in Hz. High-resolution (HR)MS were measured on a *MAT-311* spectrometer at the University of Rennes. Microanalyses were carried out by the Laboratory of Microanalyses of the Technical University of Lodz.

(1*R*,2*S*,3*R*)-4-(*Triphenylmethoxy*)-1-[1'-(*triphenylmethyl*)-1'-*H*-imidazol-4'-yl]butane-1,2,3-triol (**10**). To a stirred suspension of **9**; HCl [1] (4.52 g, 20 mmol) in anh. THF (20 ml) were added Et_3N (8.4 ml, 60 mmol) and trityl chloride (TrCl ; 11.16 g, 40 mmol) in anh. THF (70 ml). After 20 h at r.t., CHCl_3 (50 ml) was added and the soln. stirred at r.t. for 24 h, until all TrCl was consumed (TLC). The resulting suspension was filtered, and the salts were successively washed with CHCl_3 , toluene, and CH_2Cl_2 . After evaporation of the solvents, the residue was purified by FC ($\text{CHCl}_3/\text{EtOH}$ 9:1): **10** as a colourless foam (10.87 g, 81%). $[\alpha]_D^{20} = +11$ ($c = 1.2$, CHCl_3). UV (MeOH): 207 (60900), 254 (1250), 260 (1250). IR (KBr): 3410, 3060, 3025, 2912, 1590, 1480, 1442, 1215, 1125, 1030, 745, 700. ^1H -NMR: Table 1. ^{13}C -NMR: Table 2. Anal. calc. for $\text{C}_{45}\text{H}_{40}\text{N}_2\text{O}_4$ (672.83): C 80.33, H 5.99, N 4.16; found: C 79.8, H 6.1, N 4.0.

(1*R*,2*S*,3*R*)-1,2,3-*Tris*(benzyloxy)-4-(*triphenylmethoxy*)-1-[1'-(*triphenylmethyl*)-1'-*H*-imidazol-4'-yl]butane (**11**). To a stirred soln. of **10** (2.0 g, 3.0 mmol) in anh. THF (15 ml) was added 50% NaH in oil (480 mg, ca. 10 mmol) at 0°. The mixture was kept at 0° until the evolution of H_2 ceased. To this stirred soln. was added at r.t. Bu_4NI (12 mg), then BnBr (1.1 ml, 9.25 mmol). After 1 d, the starting material had disappeared (TLC) and the mixture was

treated with MeOH (1 ml). *Florisil* (1.2 g) was added and the mixture stirred at r.t. for another 30 min. The resulting suspension was evaporated and the residue successively washed with petroleum ether and extracted with CH_2Cl_2 . After evaporation of the CH_2Cl_2 extracts, the residue was purified by FC(CH_2Cl_2 /acetone 95:5): **11** as colourless foam (2.70 g, 95%). $[\alpha]_{\text{D}}^{20} = -19$ ($c = 1.6$, CHCl_3). UV (MeOH): 209 (81000), 259 (2700). IR (KBr): 3440, 2930, 2870, 1600, 1495, 1450, 1230, 1030, 745, 700. $^1\text{H-NMR}$: Table 1. $^{13}\text{C-NMR}$: Table 2. Anal. calc. for $\text{C}_{66}\text{H}_{58}\text{N}_2\text{O}_4$ (943.20): C 84.05, H 6.20, N 2.97; found: C 83.8, H 6.1, N 2.8.

(2*R*,3*S*,4*R*)-2,3,4-*Tris*(benzyloxy)-4-[1'-*H*-imidazol-4'-(5')-yl]butan-1-ol (**12**). A soln. of **11** (2.36 g, 2.5 mmol) in THF (3 ml) and 6*N* HCl (0.8 ml) was heated under reflux for 2 h. After evaporation, the residue was taken up in H_2O and the resulting soln. washed with Et_2O . The aq. soln. was then neutralised with NaHCO_3 and extracted with CH_2Cl_2 . The CH_2Cl_2 solns. were dried (MgSO_4) and evaporated. The residue was purified by FC (AcOEt/EtOH 85:15): **12** (1.07 g, 93%) as colourless crystals. M.p. 116–117° (AcOEt/ CH_2Cl_2). $[\alpha]_{\text{D}}^{20} = -44.5$ ($c = 1.12$, CHCl_3). UV (MeOH): 210 (24000), 253 (450), 258 (560), 265 (440). IR (KBr): 3220, 3090, 3060, 3030, 2910, 2860, 1500, 1455, 1215, 1065, 1030, 740, 700. $^1\text{H-NMR}$: Table 1. $^{13}\text{C-NMR}$: Table 2. HR-MS: 458.2191 ($\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4$, calc. 458.2205).

(6*R*,7*R*,8*R*)-6,7,8-*Tris*(benzyloxy)-5,6,7,8-tetrahydroimidazo[1,5-*a*]pyridine (**13**). To a stirred soln. of **12** (2.66 g, 5.8 mmol) in anh. CH_2Cl_2 (130 ml) under dry Ar at -30° were added anh. pyridine (1.5 ml, 18 mmol) and $(\text{CF}_3\text{SO}_2)_2\text{O}$ (2.2 ml, 13.2 mmol). The colourless soln. was stirred for 24 h at -20° , treated with aq. NaHCO_3 soln. (excess) at 0° , and extracted with CH_2Cl_2 . The org. layer was dried (MgSO_4), filtered, and evaporated. The residue was purified by FC(CHCl_3 /EtOH 95:5): **13** (1.90 g, 74%) as a foam. $[\alpha]_{\text{D}}^{20} = -37.0$ ($c = 1.2$, CHCl_3). UV (MeOH): 211 (16500), 240 (2100). IR (nujol): 3060, 3040, 2915, 2875, 1610, 1495, 1455, 1350, 1265, 1205, 1100, 1060, 1030, 740, 700. $^1\text{H-NMR}$: Table 3. $^{13}\text{C-NMR}$: Table 4. MS: 440 (8, M^+), 411 (4), 349 (100, $[M - \text{C}_7\text{H}_7]^+$).

(6*R*,7*R*,8*R*)-5,6,7,8-Tetrahydroimidazo[1,5-*a*]pyridine-6,7,8-triol (**7**). To a stirred suspension of 10% Pd(OH) $_2$ /C (140 mg) in AcOH (4 ml) under H_2 at r.t. was added a soln. of **13** (88 mg, 0.2 mmol) in AcOH (4 ml). The suspension was stirred under H_2 (1 atm) at r.t. for 20 h until complete disappearance of **13** (TLC, CHCl_3 /EtOH 9:1). The catalyst was filtered off over *Celite* and washed with AcOH. The combined filtrates were evaporated at r.t., and the resulting residue was dissolved in H_2O . This aq. soln. was successively passed over *Amberlite CG 400* (OH^-) and *Amberlite CG 120* (H^+) columns. Elution of **7** was performed with 2*N* aq. NH_3 and isolated as a colourless foam (25 mg, 74%) after lyophilisation. $[\alpha]_{\text{D}}^{20} = -11.0$ ($c = 1.12$, MeOH). UV (MeOH; 7·HCl): 216 (4400). IR (KBr): 3300, 3040, 2900, 1600, 1540, 1450, 1325, 1120, 1090, 1070, 780, 640. $^1\text{H-NMR}$: Table 3. $^{13}\text{C-NMR}$: Table 4. HR-MS: 170.06880 ($\text{C}_7\text{H}_{10}\text{N}_2\text{O}_3$, calc. 170.06914).

(2*R*,3*S*,4*R*)-3,4-*Bis*(benzyloxy)-4-[1'-(triphenylmethyl)-1'-*H*-imidazol-4'-yl]-1-(triphenylmethoxy)butan-2-ol (**14**). To a stirred soln. of **10** (3.36 g, 5.0 mmol) in anh. THF (40 ml) was added 50% NaH in oil (820 mg, ca. 17 mmol) at -5° . The reaction was kept at -5° until the evolution of H_2 ceased. To this soln. were added at -5° Bu $_4$ Ni (20 mg) and BnBr (1.8 ml, 15.2 mmol). Stirring was continued at -5° for 24 h until disappearance of the starting material (TLC). Workup as described for **11** (see above) led to **14** as a colourless foam (3.15 g, 74%). $[\alpha]_{\text{D}}^{20} = -7.0$ ($c = 1.0$, CHCl_3). UV (MeOH): 210 (53000), 253 (sh, 1540), 259 (1540). IR (KBr): 3440, 3060, 3020, 2920, 2860, 1595, 1490, 1445, 1215, 1125, 1085, 1065. $^1\text{H-NMR}$: Table 1. $^{13}\text{C-NMR}$: Table 2. Anal. calc. for $\text{C}_{59}\text{H}_{52}\text{N}_2\text{O}_4$ (853.08): C 83.07, H 6.14, N 3.28; found: C 82.5, H 6.0, N 3.3.

(2*R*,3*S*,4*R*)-3,4-*Bis*(benzyloxy)-4-[1'-*H*-imidazol-4'-(5')-yl]butane-1,2-diol (**15**). A soln. of **14** (1.70 g, 2.0 mmol) in THF (3 ml) and 6*N* HCl (0.8 ml) was heated to reflux for 2 h. After evaporation of the THF the residue was diluted with H_2O and this soln. washed with Et_2O . The aq. layer was neutralised with NaHCO_3 and extracted with CH_2Cl_2 . The CH_2Cl_2 solns. were dried (MgSO_4) and evaporated. The residue was purified by FC (AcOEt/EtOH 85:15): **15** as colourless crystals (644 mg, 86%). M.p. 110–112° (AcOEt/ CH_2Cl_2). $[\alpha]_{\text{D}}^{20} = -44.0$ ($c = 0.8$, CHCl_3 /EtOH 10:1). UV (MeOH): 211 (15500), 253 (300), 258 (370), 264 (290). IR (KBr): 3510, 3100, 2900, 2850, 1495, 1450, 1210, 1120, 1070, 1030, 740, 695. $^1\text{H-NMR}$: Table 1. $^{13}\text{C-NMR}$: Table 2. Anal. calc. for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4$ (368.44): C 68.46, H 6.57, N 7.60; found: C 68.6, H 6.4, N 7.5.

(5*S*,6*R*,7*R*)-6,7-*Bis*(benzyloxy)-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazol-5-methanol (**17**). To a stirred soln. of **14** (1.00 g, 1.17 mmol) in anh. CH_2Cl_2 (30 ml) at -30° under dry Ar were added anh. pyridine (0.5 ml) and $(\text{CF}_3\text{SO}_2)_2\text{O}$ (0.35 ml, 2.1 mmol). The resulting yellow soln. was stirred at -20° for 24 h and then evaporated. The residue was taken up in THF (8 ml) to which were added 10 drops of 6*N* HCl. The resulting mixture was heated to reflux for 2.5 h and then evaporated. The solid residue was washed with Et_2O and neutralised with aq. NaHCO_3 soln. and the aq. soln. extracted with CH_2Cl_2 . The CH_2Cl_2 soln. was dried (MgSO_4) and evaporated and the residue purified by FC (CHCl_3 /EtOH 9:1): **17** was isolated (282 mg, 69%) as colourless crystals. M.p. 130° (i-Pr $_2$ O/ CH_2Cl_2). $[\alpha]_{\text{D}}^{18} = -46.0$ ($c = 1.08$, CHCl_3). UV (MeOH): 210 (16500), 252 (250), 258 (320), 263 (250). IR (KBr): 3150, 3040, 2940, 2860, 1475, 1455, 1240, 1100, 1080, 1015, 750, 700. $^1\text{H-NMR}$: Table 3. $^{13}\text{C-NMR}$: Table 4. HR-MS: 350.1627 ($\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_3$, calc. 350.1630).

(5*S*,6*R*,7*R*)-6,7-Dihydro-5-(hydroxymethyl)-5H-pyrrolo[1,2-*c*]imidazole-6,7-diol (**8**). To a soln. of **17** (147 mg, 0.42 mmol) in 98% EtOH (15 ml), 5% Pd/C (200 mg) was added and the resulting suspension stirred at r.t. under H₂ (1 atm) for 120 h until complete consumption of **17** (TLC). The catalyst was filtered off over *Celite* and washed with EtOH. The combined filtrates were evaporated at r.t.: **8** as colourless crystals (71 mg, 94%). M.p. 227–228° (MeOH). $[\alpha]_D^{18} = -41.0$ ($c = 0.5$, EtOH). UV (MeOH): 211 (4900). IR (KBr): 3350, 3160, 3100, 2940, 2490, 1670, 1505, 1485, 860, 790. ¹H-NMR: *Table 3*. ¹³C-NMR: *Table 4*. HR-MS: 170.0703 (C₇H₁₀N₂O₃, calc. 170.06914).

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