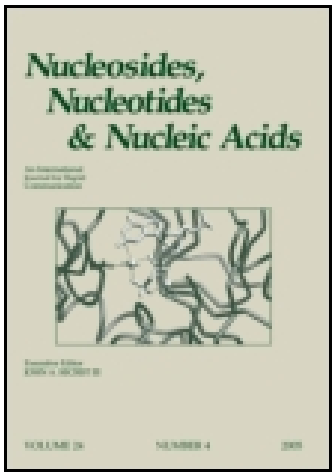

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Homo-C-Nucleoside Analogs II. Synthesis and Anomeric Configuration of 4-(2,5-Anhydro-D-Gluco-PEntitol-1-YL)-2-Phenyl2H-1,2,3-Triazole

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HOMO-*C*-NUCLEOSIDE ANALOGS† II. SYNTHESIS AND ANOMERIC CONFIGURATION OF 4-(2,5-ANHYDRO-D-*GLUCO*-PENTITOL-1-YL)-2-PHENYL-2*H*-1,2,3-TRIAZOLE††

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ABSTRACT Treatment of 4-(**D**-*gluco*-pentitol-1-yl)-2-phenyl-2*H*-1,2,3-triazole (**1**) with *p*-toluenesulfonyl chloride in pyridine solution, afforded the homo-C- nucleoside analog, 4-(2,5-anhydro-**D**-*gluco*-pentitol-l-yl)-2-phenyl-2*H*-1,2,3-triazole (**2**) as well as its partial *p*-toluenesulfonyl derivative (**3**). 4-(5-Chloro-5-deoxy-**D**-*gluco*- pentitol-l-yl)-2-phenyl-2*H*-1,2,3-triazole (**8**), was isolated as a byproduct from the reaction. The structure and anomeric configuration of **2** was determined by acylation, ^{1}H , ^{13}C NMR, and NOE, spectroscopy as well as mass spectrometry.

In recent years, the chemistry of homo-*C*-nucleosides[3] and their biological activity have been of interest. Several synthetic routes have been followed for these compounds, based on building the heterocyclic base moieties on a suitably functionalized glycosyl derivative. In a previous paper[1], we have reported the synthesis of homo-*C*-nucleoside 2-phenyl-2*H*-1,2,3-triazole analog by dehydrative cyclization of **D**-*galacto*-pentitol-1-yl-2-phenyl-2*H*-1,2,3-triazole with *p*-toluenesulfonyl chloride in pyridine solution. The dehydrative cyclization process takes place in basic medium through the formation of a

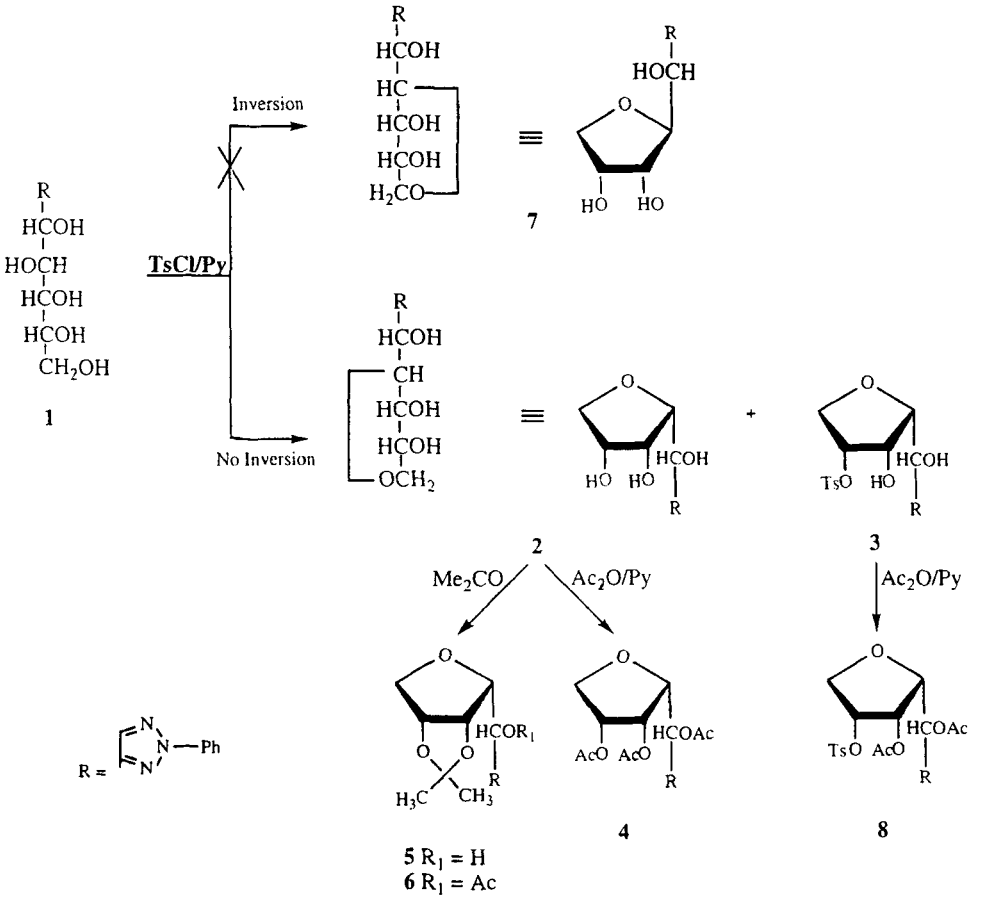
†For part I see ref. 1.

††For a preliminary report see ref 2.

2,5-anhydro furanose ring structure rather than the 1,4-anhydro-furano- or 1,5-anhydro-pyrano- ring structure formed in acid medium. The dehydrative cyclization of pentahydroxypentyl-2-phenyl-2*H*-1,2,3-triazoles in basic medium is a simple synthon for the elaboration of the carbon-bridged group of homo-*C*-nucleoside triazoles which requires multistep reactions. In this work, the dehydrative cyclization of **D**-*gluco*-pentitol-l-yl-2-phenyl-2*H*-1,2,3-triazole **1** in basic medium was studied, and the structure and anomeric configuration of the products were determined by ^{1}H NMR, ^{13}C NMR, NOE spectroscopy and mass spectrometry.

RESULTS AND DISCUSSION

Treatment of compound **1** with slightly more than one molar equivalent of *p*-toluenesulfonyl chloride in pyridine afforded the homo-*C*-nucleoside analog namely, 4-(2,5-anhydro-**D**-*gluco*-pentitol-1-yl)-2-phenyl-2 *H*-1,2,3-triazole (**2**) in 23% yield, as well as its 4-*p*-toluenesulfonyl derivative **3** (Scheme 1). The ^{1}H NMR spectrum of **2** showed three doublets corresponding to three secondary hydroxyl groups (Table 1) which disappeared by deuteration. In addition, the absence of a triplet corresponding to a primary hydroxyl group is in accord with 2,5-anhydro- ring structure. Acetylation of **2** gave the tri-*O*-acetyl derivative **4**. Its ^{1}H NMR spectra showed three singlets corresponding to three *O*-acetyl groups. Comparison of the ^{1}H NMR spectrum of **2** and **4** revealed downfield shift of H-l′, H-3′, and H-4′ due to α-acetylation at these positions, in accord with C-2′, C-5′ cyclization. Additional evidence for C-2′, C-5′ cyclization was obtained from ^{13}C NMR spectra of compounds **2** and **4** (Table 3). The C-2′ signal of **4** (having two acetoxyl groups at the β-position) was shifted farthest upfield (δ 79.4) than that for **2** (δ 82.6). Similarly C-5′ signal (having one β-acetoxyl group) showed less upfield shift (from δ 71.0 for **2** to 69.3 for **4**). However, the signal for C-l′ (one acetoxyl group at the α-position) was shifted downfield (from δ 64.8 for **2** to 67.1 for **4**). On the other hand, the chemical shift of the anomeric carbon C-2′ for compounds **2** and **4** was shown at lower field than the rest of the other glycosyl carbons, in agreement with the proposed C-2′, C-5′ ring structure. In addition, the chemical shift of C-5′ for **2** is observed downfield (δ 71.0) than the expected range for the primary carbon carrying hydroxyl group (δ 60-64) in 1,4-furanosides[1], excluding 1,4-cyclization.



Scheme 1

The assignment of the anomeric configuration of **2** is not as easy as for *C*-nucleosides which usually show the anomeric proton as the most downfield proton in the spectrum. Compound **2** showed the anomeric proton (H-2′) overlapped with H-4′ as a multiplet at δ 4.12. Its acetyl derivative **4** showed the anomeric proton (H-2′) as a doublet of doublets at δ 4.68 having coupling constant $J_{2',3'}$ 4.5 Hz. This coupling constant value cannot define[4-7] the anomeric configuration.

Likewise, its tri-*O*-acetyl derivative **4** showed the anomeric proton (H-2′) as a doublet of doublets at δ 4.68 having coupling constant $J_{2',3'}$ 4.5 Hz. The isopropylidene derivative **5** showed the anomeric proton (H-2′) as a doublet of doublets at δ 3.82 having coupling

constant $J_{2',3'}$ 3.4 Hz. Its 1'-*O*-acetyl derivative **6** showed the anomeric proton as a doublet of doublets at δ 4.23 having a coupling constant $J_{2',3'}$ 3.7 Hz. These coupling constant values, although small, were not small enough (0-1 Hz) for unequivocal assignment of a trans arrangement of H-2′ and H-3′. The Δδ value (0.23) for the chemical shift difference of the two methyl signals of the 2,2-dimethyldioxolane ring is in the range expected[8-10] for the β-configuration. The latter can be obtained from **1** by a mechanism involving inversion in the configuration of C-2′. However, this type of dehydrative cyclization process in basic medium usually takes place through the formation of a 5′-primary *p*-toluenesulfonyl derivative which cyclizes by S_N2 displacement by the favorably disposed O-2′ of the 5′-*p*-toluenesulfonyl group with retention in the configuration of C-2′. The ^{13}C NMR spectrum of **5** showed the two methyl signals of the 2,2-dioxolane ring at δ 25.9 and 24.4 having Δδ 1.5 which are more close to the values[11,12] for the α-**D**-configuration (26.3±2 and 24.9±3; Δδ 1.4) than that for the β-configuration (25.5±2 and 27.5±2; Δδ 2.0). In addition, the acetonide carbon (δ 112.6) for **5** is in the range[12] of the values for α-anomers (112-113) rather than for β-anomers (113-114).

Nuclear overhauser effect[13] NOE can afford reliable assignment of the anomeric configuration without need for comparison with the other corresponding anomer, by irradiation of the anomeric proton and noting the appropriate NOE enhancement for the respective hydrogens on the same face of the ring. Irradiation of the anomeric proton (H-2′) for **4** showed enhancement of H-3′ (12.7%), H-4′ (4.3%) and H-5″ (cis to H-4′, 1.6%), while the enhancement for H-5′ (trans to H-4′) is zero. This indicates that H-2′, H-3′, H-4′ and H-5″ are on the same face of the ring, i.e., α-**D** configuration. Similarly, irradiation of the anomeric proton (H-2′) for **5** showed enhancement of H-3′ (5.4%), H-4′ (0.3%) and H-5″ (3.3%) supporting a *cis* arrangement of H-2′, H-3′, H-4′ and H-5″ on the same face of the ring, i.e. the α-**D**- configuration of **5.** Therefore, the Δδ criterion[8-10] is an exception for anomeric assignment, in this case.

The anomeric configuration of **2** was supported from its chiroptical properties. It showed a positive specific rotation ($[\alpha]_D^{22}$ + 12.02°), which increases with a decrease in wavelength (positive o.r.d).

The mass spectrum of **2** showed a weak molecular ion at *m/z* 277. The base peak was shown at *m/z* 173 corresponding to the fragment BCHO. The fragments BCHOH at *m/z* 174 and BCH_2OH at *m/z* 175, characteristic for *C*-nucleosides[4] as well as the fragments characteristic for homo-C-nucleosides[1] at *m/z* 103, 86, and 85 were abundant.

The homo-*C*-nucleoside **2** was isolated also as its 4′-*O*-*p*-toluenesulfonyl derivative **3** by column chromatography in a crystalline form. Its ^1H NMR spectrum (Table 1) showed a downfield shift of H-4′ (δ 4.57) compared to that of **2** (δ 4.12) due to *p*-toluenesulfonation at this position. The position of the *p*-toluenesulfonyl group was confirmed by acetylation of **3** giving the di-*O*-acetyl-mono-*O*-*p*-toluenesulfonyl derivative **7**. Its ^1H NMR spectrum (Table 1) showed a downfield shift of H-1′ and H-3′ signals compared to those for **3**, due to acetylation at these positions.

The 5′-chloro-5′-deoxy-**D**-*gluco*-pentitol-1-yl-2-phenyl-2 *H*-1,2,3-triazole **8** was isolated by chromatography from the reaction mixture as a byproduct (3%). The acyclic structure of **8** (Scheme 2) was indicated by the presence of four doublets exchangeable upon deuteration, corresponding to four secondary hydroxyl groups. Its mass spectrum showed molecular ion peaks MH at *m/z* 316 and 314 in the ratio of the chlorine isotopes. The base peak was shown at *m/z* 174 corresponding to the fragment BCHOH. The position of the chlorine atom was indicated by the downfield shift of the geminal protons H-5′ and H-5″ for **8** compared to that of compound **1**, due to the anisotropic effect of the chlorine atom. Acetylation of **8** gave the tetra-*O*-acetyl derivative **9**. Its ^1H NMR spectrum showed four singlets at δ 2.06, 2.10, 2.11 and 2.13 corresponding to four *O*-acetyl groups. The position of the chlorine atom was ascertained from the downfield shift of the protons H-1′, H-2′, H-3′ and H-4′ compared to that of **8**, due to acetylation at these positions. Acetonation of **8** gave a mixture of 1′,2′:3′,4′-di-*O*-isopropylidene derivative **10** and 3′,4′-mono-*O*-isopropylidene derivative **11**, which were separated by column chromatography. The mass spectrum of **10** showed molecular ion peaks at *m/z* 395 and 393 in the ratio of the chlorine isotopes. The base peak was shown at *m/z* 43 corresponding to CH_3CO group. The mass spectrum of compound **11** showed molecular ion peaks at *m/z* 355 and 353 in the ratio of the chlorine isotopes and the base peak was shown at *m/z* 59 corresponding to the fragment CH_3COO group.

EXPERIMENTAL

Evaporations were performed under diminished pressure below 60°C. TLC was conducted on silica gel Merck 0.2 mm thick (Kieselgel 60 F 254), with solvent **A** (10:1 v/v, chloroform-methanol), **B** (3:1 v/v, ethylacetate-hexane), **C** (2:3 v/v ethylacetate-hexane), **D** (5:1 v/v, toluene-ethanol), **E** (8:1 v/v, chloroform-methanol) and **F** (50:10:1 v/v, ethylacetate-hexane-methanol). Compounds were detected by UV light or by spraying with 5% methanolic sulfuric acid followed by charring at 140°C for a few minutes. Optical rotations were obtained at 20°±2°C with Perkin-Elmer 241 polarimeter (10 cm, 1 ml microcell). ^{1}H NMR spectrum (Tables 1 and 2) were recorded with General Electric 500 MHz, Bruker 360 MHz and Bruker WP 270 SY instruments. Assignments were verified by selective proton decoupling. ^{13}C NMR spectra (Table 3) were recorded with General Electric 500 instrument at 125 MHz. Assignment of peaks were verified by comparing coupled and decoupled spectra or by ^{1}H-^{13}C Cosy experiments. Chemical shifts in δ ppm, were referenced to $CDCl_3$ (77.7), DMSO-d_6 (39.50) or tetramethylsilane Me_4Si (TMS) as internal standards. Mass spectra were recorded with a Finnigan 4021 low resolution EI-CI spectrometer at 70 ev. High resolution mass spectra were recorded with a VG Analytical Model 70-250S spectrometer. Combustion analyses were performed at M-H-W laboratories, Phoenix, Az, USA.

4-(2,5-Anhydro-D-*gluco*-pentitol)-2-phenyl-2 *H*-1,2,3- triazole (2). 4-(D-*gluco*-Pentitol-l-yl)-2-phenyl-2 *H*-1,2,3-triazole[14] **1** (500 mg, 1.8 mmol) was dissolved in anhydrous pyridine (7 ml) and treated portionwise with *p*-toluenesulfonyl chloride (356 mg; 1.1 mole eq.) and the mixture was kept at room temperature for 24 h then heated at 60°C for 10 min. A few drops of water were added to decompose the excess of *p*-toluenesulfonyl chloride and the solution was evaporated to a syrup and the remaining pyridine was removed by coevaporation with toluene (3 X 20 mL). The residual syrup was applied to a column of silica gel G 60 (2 X 46 cm), eluted with solvent F and fractions (3 mL) were collected with a flow rate of 3 mL/10 min and identical fractions were combined. Fractions 160-204 were combined and evaporated till dryness, giving a syrup which was recrystallized from chloroform-hexane as colorless needles of **2**, yield 110 mg, 23%; m.p. 139-140°C; R_f 0.42 (D), 0.23 (F); $[\alpha]_D^{22}$ + 12.02°C (0.86 in

Table 1. ^{1}H NMR Data, chemical shifts (δ) and first-order coupling constants (J Hz)[a] for compounds **1-7.**

Compound	Glycosyl part										2-Phenyl-2 *H*-1,2,3-triazole			
									Ts		H-5	phenyl		
	H-1′	H-2′	H-3′	H-4′	H-5′	H-5″	OH	OAc	CMe_2	ar(Me)		*o*	*m*	*p*
(1)[bi]	4.89d $J_{1',2'}$ 5.5	3.92d *J* 6.7	3.54dd $J_{2',3'}$ 3.2	3.49m	3.36m	3.24dd $J_{4',5'}$ 8.5 $J_{5',5''}$ 11.8	4.27t 4.35d 4.45d 4.57d 5.40d				7.94s	7.98d	7.55t	7.39t
(2)[bi]	4.96d $J_{1',2'}$ 6.2	4.12m	3,98t *J* 4.9 *J* 3.6	4.12m	3.78dd $J_{4',5'}$ 6.4	3.61dd $J_{4',5''}$ 6.1 $J_{5',5''}$ 8.5	4.85d 5.15d 5.55d				7.96s	7.98t	7.54t	7.38t
(3)[ci]	5.34d $J_{1',2'}$ 2.8	4.41m	4.51m	4.57m	4.41m	4.18dd $J_{4',5''}$ 5.5 $J_{5',5''}$ 10.0				7.82m (2.44s)	7.82s	8.00d	7.49t	7.33m
(4)[cii]	6.29d $J_{1',2'}$ 8.8	4.68dd $J_{1',2'}$ 8.8	5.46dd $J_{2',3'}$ 4.5	5.41m	4.14dd $J_{4',5'}$ 6.8	3.93dd $J_{4',5''}$ 7.0 $J_{5',5''}$ 9.4		1.97s 2.01s 2.13s			7.74s	7.98m	7.45m	7.35m
(5)[cii]	5.34d $J_{1',2'}$ 6.0	3.82dd $J_{2',3'}$ 3.4	4.73dd $J_{3',4'}$ 6.1	4.81dd	4.07d $J_{4',5'}$ 0	3.55dd $J_{4',5''}$ 3.5 $J_{5',5''}$ 10.8			1.529s 1.299s Δδ 0.23		7.89s	8.04m	7.44m	7.34m
(6)[cii]	6.21d $J_{1',2'}$ 9.6	4.23dd $J_{2',3'}$ 3.7	4.55dd $J_{2',3'}$ 3.6	4.76dd $J_{3',4'}$ 6.0 $J_{4',5'}$ 3.6	4.12d $J_{4',5'}$ 0	3.63dd $J_{4',5''}$ 3.8 $J_{5',5''}$ 10.8		2.09s	1.428s 1.204 Δδ 0.224		7.87s	8.03d	7.46m	7.33m
(7)[ci]	5.50s $J_{1',2'}$ 4.1	4.19dd $J_{1',2'}$ 6.1 $J_{2',3'}$ 2.1	5.51m	4.65dd $J_{4',5'}$ 5.8	4.24dd $J_{4',5'}$ 5.8	4.19dd $J_{4',5''}$ 5.8 $J_{5',5''}$ 10.4		1.90s 2.10s		7.29d 7.41d (2.41s)	7.70s	7.99d	7.78t	7.33m

[a]J values were measured after exchanging with CD_3CO_2D; [b] In $(CD_3)_2SO$, [c] In $CDCl_3$; [i]at 500 MHz and [ii]at 270 MHz.

Table 2. ^{1}H NMR Data, chemical shifts (δ) and first-order coupling constants (J Hz)[a] for compounds **8-11.**

Compound	Glycosyl part									2-Phenyl-2 *H*-1,2,3-triazole			
										H-5	phenyl		
	H-1′	H-2′	H-3′	H-4′	H-5′	H-5″	OH	OAc	CMe_2		*o*	*m*	*p*
(8)[bi]	4.88d $J_{1',2'}$ 7.1	3.93d *J* 7.0	3.72m	3.23bd $J_{3',4'}$ 8.4	3.77dd $J_{4',5'}$ 1.8	3.56dd $J_{4',5'}$ 6.1 $J_{5',5''}$ 11.0	4.57d 4.89d 5.05d 5.49d			7.97s	7.98m	7.58m	7.39t
(9)[cii]	6.13d $J_{1',2'}$ 8.5	5.84dd $J_{2',3'}$ 2.6	→ 5.21 ←		3.63dd $J_{4',5'}$ 3.7	4.49dd $J_{4',5'}$ 5.8 $J_{5',5''}$ 12.4		2.06s 2.10s 2.11s 2.13s		7.77s	8.02d	7.44t	7.35t
(10)[cii]	5.25d $J_{1',2'}$ 8.5	4.23dd $J_{2',3'}$ 1.1	4.34dd $J_{3',4'}$ 6.8	3.80dd	4.49dd $J_{4',5'}$ 6.7	4.10dd $J_{4',5'}$ 7.1 $J_{5',5''}$ 14.0			1.560s 1.527s Δδ 0.033 1.514s 1.403s Δδ 0.111	7.82s	8.02d	7.46t	7.32m
(11)[cii]	6.26d $J_{1',2'}$ 9.2	5.83dd *J* 2.4	5.41*dd	3.74m*	3.68 - 3.45 m				1.532s 1.407s Δδ 0.125	7.82s	8.04d	7.46m	7.34m

[a]J Values were measured after exchanging with CD_3CO_2D. [b] In $(CD_3)_2SO$, [c] In $CDCl_3$; [i]at 500 MHz and [ii]at 270 MHz. *Interchangeable.

Table 3. ^{13}C NMR Data, chemical shifts (δ) for compounds **2-5** at 125 MHz.

Compound	Glycosyl part								2-Phenyl-2 *H*-1,2,3-triazole					
	C-1′	C-2′	C-3′	C-4′	C-5′	Ac		CMe_2	C-4	C-5	C-*a*	C-*o*	C-*m*	C-*p*
						CO	CH_3							
(2)[a]	64.8	82.6	→71.1←		71.0				139.2	134.9	151.4	118.2	129.6	127.4
(3)[a]	67.8	80.1	72.1	71.9	69.9				140.2	135.4	145.8	119.7	130.0	128.6
(4)[b]	67.1	79.4	71.3	71.4	69.3	170.1 169.8 169.2	21.0 20.5 20.3		139.6	134.7	145.3	119.1	129.3	127.9
(5)[b]	66.0	*84.0	*81.0	*72.9				25.9 24.4 Δδ 1.5 O O C 112.6	139.8	134.6	148.9	118.9	129.2	127.4

[a]In $(CD_3)_2SO$, [b]In $CDCl_3$. *Interchangeable.

methanol), $[\phi]_{589}$ + 33.3°, $[\phi]_{578}$ + 34.6°, $[\phi]_{546}$ + 40.1°, $[\phi]_{436}$ + 69.5°, and $[\phi]_{365}$ + 121.9°; for ^{1}H NMR and ^{13}C NMR spectral data see Tables 1 and 3; mass spectral data (selected ions): *m/z* 277 (0.3, M), 260 (1, M - OH), 259 (2, M - H_2O), 200 (3, M - Ph), 188 (6, $BHCH_2CHO$), where B = 2-phenyl-2 *H*-1,2,3-triazole moiety), 187 (4), 176 (10, $BHCH_2OH$), 175 (94, BCH_2OH), 174 (64, BCHOH), 173 (100, BCHO), 172 (6, BCO), 159 (1, $BHCH_2$), 158 (6, BCH_2), 146 (2, BH_2), 145 (1, BH), 144 (1, B), 117 (4, B - HCN), 107 (4), 103 (5, M - CHOH), 93 (5, $PhNH_2$), 92 (16, PhNH), 91 (30, PhN), 86 (54, M - BCHOH - OH), 85 (7, M - BCHOH - H_2O), 77 (30, Ph), 69 (13), 65 (14, B - Ph - H), 58 (20) and 43 (29).

Anal. Calcd for $C_{13}H_{15}N_3O_4$: C, 56.30; H, 5.45; N, 15.15. Found: C, 56.20; H, 5.55; N, 15.14.

4-(1,3,4-Tri-*O*-acetyl-2,5-anhydro-D-*gluco*-pentitol- 1-yl)-2 *H*-1,2,3-triazole (4). Compound **2** (20 mg) was dissolved in pyridine (2 mL) and the mixture kept at room temperature for 26 h. The mixture was evaporated to dryness and traces of pyridine were removed by spin coevaporation with toluene (3 X 5 mL). The residual syrup was purified by chromatography on silica gel and eluted with solvent (C) to give a colorless syrup, R_f 0.64 (B); for ^{1}H NMR and ^{13}C NMR spectral data, see Tables 1 and 3. Mass spectral data (selected ions); *m/z* 403 (1, M), 242 (1, M - 2 OAc -Ac), 241 (1, M - OAc - ACOH - Ac), 216 (1, BCHOAc), 188 (2, $BHCH_2CHO$), 187 (26, BCH_2CHO), 174 (10, BCHOH), 173 (3, BCHO), 127 (7, M - BCHOAc - AcOH), 91 (4, PhN), 85 (22, M - BCHOAc - AcOH- CH_2CO), 77 (4, Ph), 69 (8), 68 (8, furan) and 43 (100, CH_3CO); accurate measurement of the molecular ion peak: Found 403.1371 (Calcd. for $C_{19}H_{21}N_3O_7$, 403.1379).

4-(2,5-Anhydro-3,4-*O*-isopropylidene-D-*gluco*-pentitol-1-yl)-2 *H*-2-phenyl-1,2,3-triazole (5). Compound **2** (20 mg) in a mixture of dry acetone (15 mL) and 2,2-dimethoxypropane (15 mL) was treated with *p*-toluenesulfonic acid (20 mg) and the mixture kept at room temperature for 5 h with stirring. TLC indicated the disappearance of the starting material and formation of a more mobile spot. The mixture was poured onto an ice-cold, saturated solution of sodium hydrogen-carbonate, extracted with chloroform and the organic layer washed with water, dried over anhydrous magnesium sulfate and evaporated till dryness. It gave a colorless syrup which was purified by

chromatography on silica gel, giving chromatographically pure syrup, which was recrystallized from petroleum ether (60-80°) as colorless needles; yield 20 mg; (73%), m.p. 150-152°; for ^{1}H NMR and ^{13}C NMR spectral data see Tables 1 and 3; mass spectral data (selected ions); *m/z* 318 (1, MH), 317 (3, M), 302 (1, M - CH_3), 259 (0.2, M - CH_3COCH_3), 242 (6, M - CH_3 - AcOH), 187 (4, BCHCHOH), 175 (20, BCHOH), 174 (9, BCHOH), 173 (22, BCHO), 172 (4, BCO), 158 (4, BCH_2), 145 (1, BH), 144 (2, B), 92 (6, PhNH), 91 (22, PhN), 87 (5, M - BCO - CH_3COCH_3), 86 (100, MH - BCHOH - CH_3COCH_3), 77 (22, Ph), 69 (25, protonated furan), 68 (3, furan), 65 (7, B - Ph - 2 H), 64 (9), 59 (23, CH_3COO), 58 (42, CH_3COCH_3), 44 (21, CH_3CHO) and 43 (70, CH_3CO); accurate measurement of the molecular ion peak: Found 317.1388 (Calcd. for $C_{16}H_{19}N_3O_4$, 317.1376).

(1-*O*-Acetyl-2,5-anhydro-3,4-*O*-isopropylidene-D-*gluco*-pentitol-1-yl)-2-phenyl-2 *H*-1,2,3-triazole (6). Compound **5** (10 mg) was dissolved in pyridine (1 mL), treated with acetic anhydride (1 mL), kept at room temperature for 12 h and the mixture processed as described for **4**. It gave a syrup which was purified on a short column (1 X 10 cm) of silica gel using solvent (C) as an eluant giving 6 as colorless syrup, yield 15 mg; for ^{1}H NMR spectral data see Table 1; mass spectral data (selected ions): *m/z* 360 (2, MH), 359 (11, M), 345 (4, MH - CH_3), 344 (20, M - CH_3), 300 (3, M - OAc), 299 (15, M - AcOH), 284 (3, M - CH_3 - AcOH), 256 (6, M - AcOH - Ac), 242 (14, M - CH_3COCH_3 - AcO), 240 (5, M - AcOH - AcO), 224 (10, M - CH_3COCH_3 - OAc - H_2O), 216 (6), 187 (5, BCHCHOH), 175 (8, BCH_2OH), 174 (64, BCHOH), 173 (9, BCHO), 172 (8, BCO), 158 (6, BCH_2), 145 (1, BH), 144 (3, B), 143 (35, B - H), 128 (6), 115 (4, PhN_2), 92 (5, PhNH), 91 (15, PhN), 86 (2, M - BCO - CH_3COCH_3 - Ac), 85 (8), 77 (16, Ph), 69 (17, protonated furan), 68 (10, furan), 59 (15, OAc), 58 (5, CH_3COCH_3), 57 (CH_3COCH_3 - H), and 43 (100, CH_3CO); accurate measurement of the molecular ion peak: Found 359.1473 (Calcd. for $C_{18}H_{21}N_3O_5$; 359.1481).

4-(2,5-Anhydro-4-*O*-*p*-toluenesulfonyl-D-*gluco*-pentitol-1-yl)-2 *H*-2-phenyl-1,2,3-triazole (3). The early fractions (14-48) of the main *p*-toluenesulfonation mixture showed four mobile spots on TLC (solvent B), R_f 0.71, 0.63, 0.51 and 0.44 as partially *p*-toluenesulfonyl derivatives. The fractions were combined, evaporated to a syrup and rechromatographed on a column (2 X 46 cm) of silica gel, eluted with (solvent F).

Compound 3 was separated as a syrup which was recrystallized from chloroform-hexane as colorless needles (20 mg), m.p. 149°C; R_f 0.44 (B), 0.65 (E); for ^1H NMR spectral data see Table 1; mass spectral data (selected ions): *m/z* 432 (1, MH), 431 (1, M), 413 (4, M - H_2O), 241 (9, MH - 2 H_2O - Ts), 200 (9, MH - Ph - Ts - H_2O), 188 (24), 187 (18, BCH_2CHO), 186 (6, BCH_2CO), 175 (11, BCH_2OH), 174 (89, BCHOH), 173 (25, BCHO), 172 (17, BCO), 171 (4, OTs), 158 (17, BCH_2), 155 (10, Ts), 146 (1, BH_2), 145 (1, BH), 118 (2, B - CN), 117 (2, B - HCN), 107 (6), 103 (6, PhCN), 92 (24, $C_6H_5CH_3$ or PhNH), 91 (100, $C_6H_4CH_3$ or PhN), 90 (6), 89 (6), 86 (10), 77 (37, Ph), 73 (16), 68 (4, furan), 65 (29, B - Ph - 2 H), 64 (14) and 57 (20).

Anal. Calcd for $C_{20}H_{21}N_3SO_6$; C, 55.67; H, 4.90; N, 9.74. Found: C, 55.71; H, 4.98; N, 9.62.

4-(2,5-Anhydro-1,3-di-*O*-acetyl-4-*O*-*p*-toluenesulfonyl-D-*gluco*-pentitol-l-yl)-2-phenyl-2 *H*-1,2,3-triazole (7). Compound **3** (10 mg) in pyridine (1 mL) was treated with acetic anhydride (1 mL) at room temperature for 24 h. The mixture was processed as described for **4**. It gave colorless syrup (15 mg); for ^1H NMR spectral data see Table 1; mass spectral data (selected ions): *m/z* 516 (0.2, MH), 515 (0.1, M), 456 (7, M - OAc), 455 (26, M - AcOH), 283 (5, M - BCHO - OAc), 258 (5), 242 (7), 241 (39, MH - BCHOAc - OAc), 240 (M - BCHOAc - OAc), 228 (9), 225 (10, M - BCHOAc - OAc - CH_3), 224 (64, M - BCHOAc -AcOH - CH_3), 216 (3, BCHOAc), 200 (7), 188 (5, BCH_2CHOH), 187 (6, BCH_2CHO), 174 (13, BCHOH), 173 (9, BCHO), 172 (9, BCO or TsOH), 171 (3, BCO or OTs), 158 (5), 155 (17, Ts), 149 (6), 145 (1, BH), 144 (1, B), 92 (6, PhNH or $C_6H_5CH_3$), 91 (36, PhN), 77 (10, Ph), 69 (5, BH_2 - Ph), 65 (6), 57 (7) and 43 (100, CH_3CO); accurate measurement of the molecular-ion peak (MH): Found 516.1437 (Calcd. for $C_{24}H_{26}O_8N_3S$, 516.1441).

4-(5-Chloro-5-deoxy-D-*gluco*-pentitol-1-yl)-2 *H*-2-phenyl- 1,2,3-triazole (8). This compound was separated at fractions (38-65) of the main *p*-toluenesulfonation chromatography, before fractions containing **2**, using solvent (F) having close and lower mobility than **2**, R_f 0.49 (F), 0.34 (E). It was isolated as a colorless syrup which was recrystallized from chloroform-hexane as colorless needles, yield 16 mg (3%); m.p. 147°C, $[\alpha]_D^{22}$ + 43.8° (c 0.634 in methanol); for ^1H NMR spectral data see Table 2; mass spectral data (selected ions), CI-ammonia: *m/z* 333 (3.5 $^{37}MHNH_3$). 331(10,

$^{35}MHNH_3$), 316 (17, ^{37}MH), 314 (50, ^{35}MH), 296 (20, MH - H_2O), 295 (5, M - H_2O), 277 (1, M - 2 H_2O), 259 (2, M - 3 H_2O), 241 (10, M - 4 H_2O), 216 (6, $BCHOHCH_2CO$), 200 (4), 188 (25, $BCHOHCH_2$), 176 (8), 175 (83, BCH_2OH), 174 (100, BCHOH), 173 (37, BCHO), 172 (8, BCO), 171(6), 170 (10), 159 (12, BCH_3), 158 (23, BCH_2), 118 (4, B - CN), 117 (4, B - HCN), 103 (10, M - BCHOH - 2 H_2O), 93 (15, $PhNH_2$), 92 (27, PhNH), 91 (60, PhN), 86 (20, M - BCHOH - 2 H_20 - OH), 77 (58, Ph), 69 (8, protonated furan), 68 (3, furan), 65 (22, B - Ph - 2 H), 51 (23) and 43 (26).

Anal. Calcd for $C_{13}H_{16}N_3O_4C1$: C, 49.76; H, 5.14; N, 13.39. Found: C, 49.69; H, 5.17; N, 13.19.

4-(1,2,3,4-Tetra-*O*-acetyl-5-chloro-5-deoxy-D-*gluco*- pentitol-l-yl)-2-phenyl-2 *H*-1,2,3-triazole (9). Compound **8** (10 mg) was dissolved in pyridine (1 mL), treated with acetic anhydride (1 mL) and kept at room temperature for 12 h. The mixture was processed as described for 6. It gave colorless syrup, R_f 0.72 (B); for ^1H NMR spectral data see Table 2; mass spectral data (selected ions); (CI-ammonia): *m/z* 501 (7.8, $^{37}MHNH_3$), 499 (21.6, $^{35}MHNH_3$), 484 (7.7, ^{37}MH), 482 (21.4, ^{35}MH), 426 (63), 424 (100, MH - AcOH), and 94 (47, $PhNH_3^+$); (EI): *m/z* 482 (0.1, MH), 481 (0.03, M), 422 (0.5, M - OAc) , 319 (3, M - AcO - AcOH - Ac), 277 (3, M - AcO - AcOH - 2 Ac), 217 (4, $BCHOHCH_2CHO$), 216 (9, $BCHOHCH_2CO$), 187 (2, BCH_2CHO), 175 (3, BCH_2OH), 174 (17, BCHOH), 173 (3, BCHO), 145 (0.6, BH), 144 (0.1, B), 103 (3, B - HCN), 91 (4, PhN), 77 (4, Ph) and 43 (100, CH_3CO); accurate measurement of the protonated molecular-ion peak (MH^+) (CI-ammonia): Found 482.1336 (Calcd. for $C_{21}H_{25}N_3O_8C1$ 482.1330).

4-(5-Chloro-5-deoxy-1,2:3,4-di-*O*-isopropylidene-D-*gluco*- pentitol-l-yl)-2 *H*-2-phenyl-1,2,3-triazole (10). Compound **9** (10 mg) in dry acetone (10 mL) was treated with *p*-toluenesulfonic acid (10 mg) and the mixture stirred at room temperature for 12 h. TLC (solvent C) indicated the disappearance of the starting material and formation of two more mobile spots R_f 0.72 and 0.37. The mixture was processed as described for **6**, giving colorless syrup which was separated by chromatography on silica gel and eluted with solvent C. Compound **10** was eluted first from the column (fractions 1-5) as colorless syrup (5 mg), R_f 0.72 (C); for ^1H NMR spectral data see Table 2; mass spectral

data (selected ions): *m/z* 395 (1.7, ^{37}M); 393 (5, ^{35}M), 380 (4, ^{37}M - CH_3), 378 (11, ^{35}M - CH_3), 335 (1, M - CH_3COCH_3), 320 (8, M - CH_3 - CH_3CO - CH_2CO), 278 (15, M - CH_3COCH_3 - CH_3 - CH_2CO), 272 (13, M - 2 AcOH - H), 244 (M - 2 AcO - CN), 234 (20, M - 2 OAc - HCN), 215 (12, M - CH_3 - CH_3COCH - AcOH - HCl), 187 (18, $BCOCH_3$), 186 (69, $BCOCH_2$), 175 (1, BCH_2OH), 174 (8, BCHOH), 173 (4, BCHO), 172 (7, BCO), 158 (30, BCH_2), 149 (52), 92 (7, PhNH), 91 (22, PhN), 85 (9), 77 (35, Ph), 59 (63, OAc), 58 (5, CH_3COCH_3), 57 (13) and 43 (100); accurate measurement of the molecular-ion peak: Found 393.1458 (Calcd. for $C_{19}H_{24}N_3O_4C1$, 393.1455).

4-(5-Chloro-5-deoxy-3,4-*O*-isopropylidene-D-*gluco*- pentitol-l-yl)-2-phenyl-2 *H*-1,2,3-triazole (11). It was eluted from the silica gel column (fractions 8-13) after elution of compound **10**, using solvent C, as a colorless syrup, R_f 0.37 (C); for ^{1}H NMR spectral data see Table 2; mass spectral data (selected ions): *m/z* 355 (1.6, ^{37}M), 353 (4.4, ^{35}M), 340 (3, ^{37}M - CH_3), 338 (^{35}M - CH_3), 295 (0.2, M - CH_3COCH_3), 280 (1, M - CH_3 - CH_3COCH_3), 278 (3, CH_3CO - Cl), 216 (33, M - CH_3COCH_3 - CH_3CO - HCl), 188 (25, $BCHOCH_3$), 187 (21, $BCOCH_3$), 181(11), 176 (33, $BHCH_2OH$), 175 (18, BCH_2OH), 174 (19, BCHOH), 173 (5, BCHO), 172 (9, BCO), 158 (13, BCH_2), 149 (11), 92 (8, PhNH), 91 (16, PhN), 85 (12), 77 (21, Ph), 73 (11), 71 (10), 59 (100, OAc or CH_3CHOCH_3) and 43 (43, CH_3CO); accurate measurement of the molecular-ion peak: Found 353.1150 (Calcd. for $C_{16}H_{20}N_3O_4C1$, 353.1142).

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