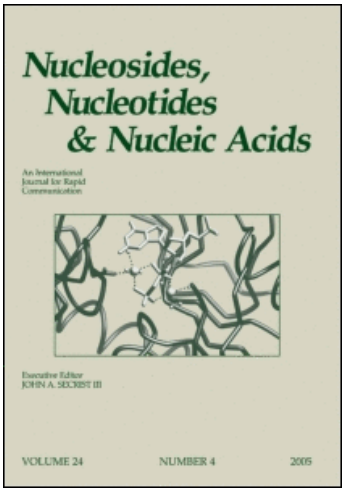

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Synthesis and Antiviral Activity of 1,5-and 1,3-Dialkyl-1,2,4-triazole *C*-Nucleosides Derived from 1-(Chloroalkyl)-1-aza-2-azoniaallene Salts

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SYNTHESIS AND ANTIVIRAL ACTIVITY OF 1,5- AND 1,3-DIALKYL-1,2,4-TRIAZOLE *C*-NUCLEOSIDES DERIVED FROM 1-(CHLOROALKYL)-1-AZA-2-AZONIAALLENE SALTS

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ABSTRACT. Reactions of α, α'-dichloroazo compounds **2** with $SbCl_5$ gave 1-(chloroalkyl)-1-aza-2-azoniaallene salts **3** as reactive intermediates. Cycloadditions of **3** with the ribofuranosyl cyanide **4** afforded the β-D-ribofuranosyl-1,2,4-triazolium salts **5**, which rearranged spontaneously to salts **6.** Hydrolysis of **6** gave the 1,2,4-triazole C-nucleosides **7**, which yielded the free nucleosides **8** after deblocking. Analogously, **12** was prepared from the cycloaddition of **4** with the α-chloroazo compound **10** in the presence of $SbCl_5$. Deblocking of **12** with sodium methoxide afforded **13**. Compounds **8a,b,e,f** and **13** were tested against HIV-1, HIV-2, HSV-1 and HSV-2 and were found to be inactive.

In the last twenty years a considerable number of *C*-glycosyl nucleosides have been isolated from the natural products[1,2], but only few 1,2,4-triazole *C*-ribofuranosyl nucleosides were reported[3-8]. The discovery of 'ribavirin' as a potential antiviral agent[9-13] and its broad spectrum of activity against both DNA and RNA viruses prompted some laboratories to synthesize *C*-nucleoside analogues[14]. The biological properties of these compounds led to studies of their chemistry and biochemistry[15-20]. Recently, we reported the synthesis of some acyclic *C*-1,2,4-triazole nucleosides and their homo-*C*-analogues as potential herbicides, fungicides and insecticides[21]. In 1997, Shaban and Nasr[17] reported more thane one thousand of references on *C*-nucleosides. Recently, a successful method for the synthesis of 1,2,4-triazole *C*-nucleosides has been described[22] from the cycloaddition of the 1-aza-2-azoniaallene cations, which were prepared from the alkyl-1-chlorodialkyl-azocarbazate with sugar nitriles *via* spontaneous transformations. We report here the synthesis of some new 1,2,4-triazole *C*-nucleosides *via* an alternative route including the cycloaddition of 1-(chloroalkyl)-1-aza-2-

azoniaallene salts **3** with the ribofuranosyl cyanide **4**[23]. Jochims and co-workers[24] have recently used the reactive intermediates **3**, which were prepared from α,α'-dichloroazoalkanes, for the synthesis of pyrazoles and formazanium salts.

RESULTS AND DISCUSSION

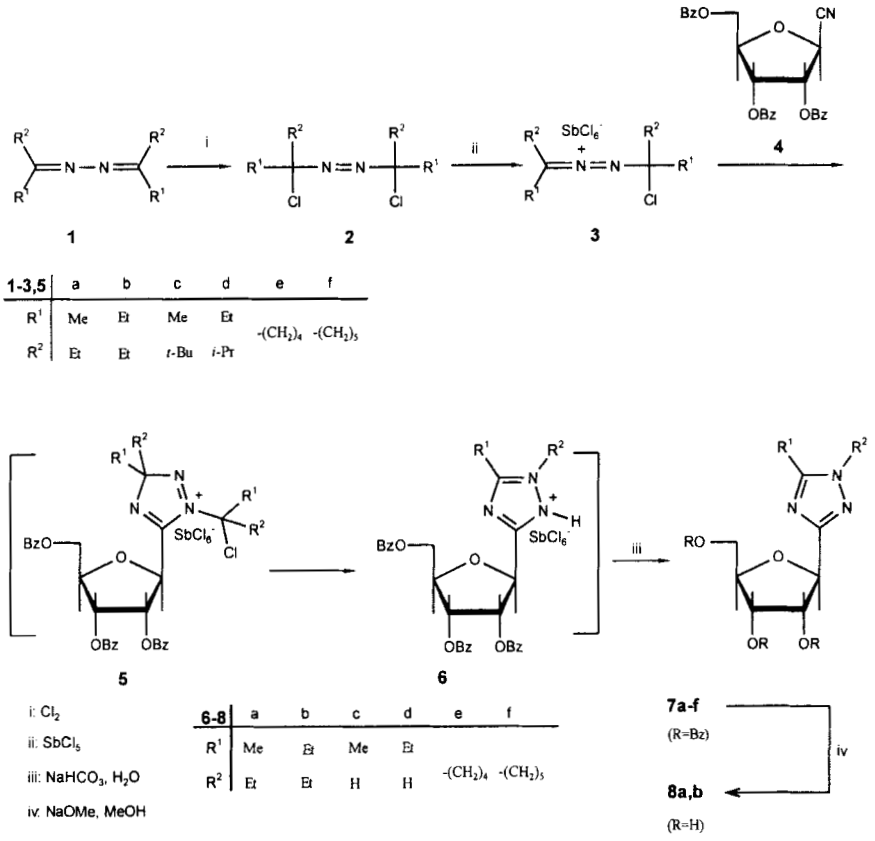
In our present study, the α, α'-dichloroazoalkanes **2** were used as starting material for the synthesis of the target molecules and prepared by chlorination of **1**. Compounds **2** were converted to the salts **3** in the presence of a Lewis acid such as $SbCl_5$ at - 60 °C. The cumulene intermediates **3** underwent a cycloaddition reaction with the glycosyl cyanide **4** to give the β-D-ribofuranosyl-1,2,4-triazolium hexachloroantimonates **5**. The reaction proceeded through time periods of 1 h at - 60 °C, 1 h at 0 °C and 10 min at room temperature. During these periods the intermediates **5a,b** underwent [1,2-shift] migration[25,26] of alkyl group (R^2) from C-5 to N-1 and elimination of the ($CClR^1R^2$) group from N-2 to give the protonated triazoles **6a,b**. Hydrolysis of triazolium salts **6a,b**, *in situ*, with 7.5 mol. equiv. of aqueous $NaHCO_3$[25,27] resulted in the formation of nucleosides **7a,b** in yields of 49 and 63%, respectively. Reaction of **3c** with the ribofuranosyl cyanide **4** gave, after hydrolysis with aqueous $NaHCO_3$ solution, the nucleoside **6c** (78% yield). The elimination of the *tert*-butyl group, as isobutene, might have occurred during and not after the 1,2-rearrangement[28] **5** → **6**. Analogously, reaction of **3d** with **4** gave, unexpectedly after hydrolysis with aqueous $NaHCO_3$ solution, the nucleoside **6d** (74% yield) by elimination of the isopropyl group during the migration.

The nucleosides **7e** and **7f** have been synthesized previously from the cycloaddition of, respectively, cyclopentyl- and cyclohexylazocarbazates with glycosyl cyanide **4** in the presence of $SbCl_5$. We examined here the synthesis of **7e** and **7f** from the cycloaddition of the reactive intermediates α, α'-dichloroazoalkanes **1e** and **1f**, respectively with **4** in the presence of $SbCl_5$. The yields were 75 and 70% yield, respectively (Scheme 1).

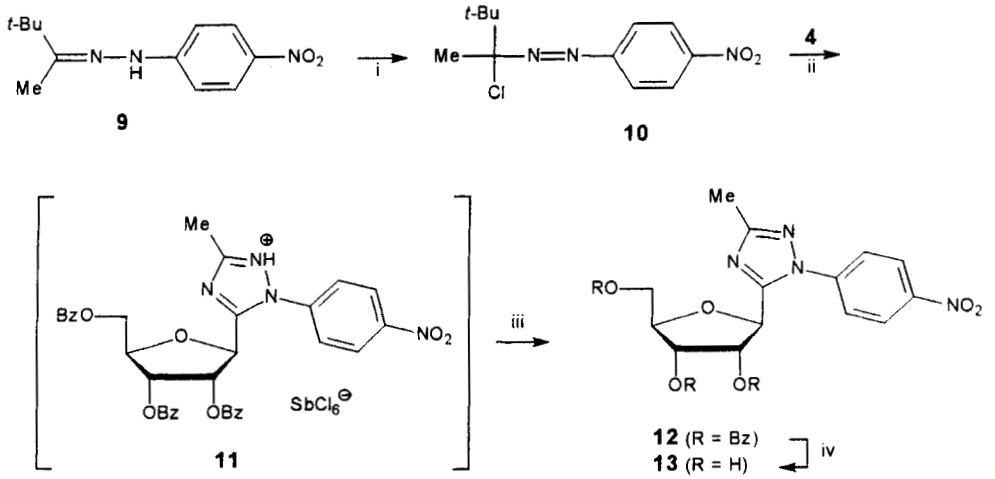
Analogously, (1-chloro-1,2,2-trimethylpropyl)azo-(4-nitrobenzene) (**10**) was prepared from chlorination of the hydrazone **9**. Reaction of **10** with the glycosyl cyanide **4** gave, after the 1,2-shift along with elimination of the *tert*-butyl group, the unisolated salt **11**. Hydrolysis of **11**, *in situ*, with 7.5 mol. equiv. of $NaHCO_3$ solution gave the nucleoside **12** in 59% yield (Scheme 2).

Deblocking of **7a,b** and **12** with 0.3 M NaOMe solution proceeded smoothly to give the free nucleosides **8a,b** and **13** in 74, 80 and 67%, respectively. Similar treatment of of **7c,d** with

Scheme 1.



Scheme 2.



0.3 M NaOMe solution resulted in decomposion of the triazole ring, due to the instability of non *N*-alkylated triazoles, in the presence of base. Debenzoylation of **7e,f** with 0.3 M NaOMe afforded the free nucleosides **8e,f** which were identical to those prepared previously[22].

The structures of the new synthesized C-nucleosides were determined on the basis of their ^{1}H-, ^{13}C-NMR and mass spectra or in comparison with those reprted previously[22], and were found to be consistent with the assigned structures.

In summary, we achieved the synthesis of some C-triazole nucleosides by cycloadditions of the reactive intermediates 1-(chloroalkyl)-1-aza-2-azoniaallene salts with a ribofuranosyl cyanide and studied the anti-HIV and anti-HSV activities of the deprotected analogues.

BIOLOGICAL EVALUATION

The free nucleosides **8a, b,e,f** and **13** were evaluated for their inhibitory activity of HIV-1 (III B) and HIV-2 (ROD) induced cytopathicity in human MT-4 lymphocyte cells. The same compounds were tested against HSV-1 (KOS) and HSV-2 (G) in E_6SM cell cultures. All compounds were found to be inactive against HIV-1, HIV-2, HSV-1 and HSV-2 in the above mentioned strains.

EXPERIMENTAL

General. The melting points are uncorrected. Unless otherwise stated, the ^{1}H- and ^{13}C-NMR spectra were acquired on a Brucker AC 250 spectrometer at 250 and 62.9 MHz, respectively, in $CDCl_3$ with tetramethylsilane as an internal standard and on a δ scale in ppm. The cycloadditions were carried out with exclusion of moisture. Silica gel 60 (Merck) was used for column chromatography. EI and FAB mass spectra were recorded on a MAT 312 spectrometer using 4-nitrobenzylalcohol or glycerol as matrix. Some molecular ions were detected by doping the samples with Na^+ ion.

1,5-Dialkyl-3-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-1*H*-1,2,4-triazole (7).

General procedure. A solution of $SbCl_5$ (3.0 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise, with stirring, to a cold (- 60 °C) solution of **2** (10 mmol) and the ribofuranosyl cyanide **4** (3.77 g, 8.0 mmol) in CH_2Cl_2 (20 ml). After stirring at - 60 °C for 1 h, then at 0 °C for 1 h, and finally at 23 °C for 10 min, the product was extracted with $CHCl_3$ (3 x 60 ml). The combined organic extracts were dried (Na_2SO_4), filtered and evaporated to dryness after treatment with decolorizing charcoal to give a foam, which was purified by crystallization or by column chromatography.

1-Ethyl-5-methyl-3-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-1*H*-1,2,4-triazole (7a). From **2a** (2.11 g, 10 mmol). Yield: 2.17 g, 49%; m.p. 94 - 98°C, decomp. at 165 °C. ^{1}H-NMR (600 MHz): δ 8.05 (d, 2H, J 7.9 Hz, ArH); 7.92, 7.90 (2d, 4H, J 5.0 Hz, ArH); 7.50 (t, 2H, J 7.6 Hz, ArH); 7.38 – 7.26 (2d, 4H, J 5.0 Hz, ArH); 6.04 (t, 1H, $J_{2',3'}$ 5.3 Hz, H-2'); 5.97 (t, 1H, $J_{3',4'}$ 5.6 Hz, H-3'); 5.44 (d, 1H, $J_{1',2'}$ 5.0 Hz, H-1'); 4.73 (m, 1H, $J_{4',5''}$ 4.7 Hz, H-4'); 4.66 (dd, 1H, $J_{4',5'}$ 3.8 Hz, H-5'); 4.63 (dd, 1H, $J_{5',5''}$ 11.0 Hz, H-5''); 4.06 (q, 2H, J 7.3 Hz, N-$\underline{CH_2}CH_3$); 2.55 (s, 3H, CH_3); 1.41 (t, 3H, N-$CH_2\underline{CH_3}$). ^{13}C-NMR: δ 166.2, 165.3, 165.2 (C=O); 156.4; 151.9 (C=N); 133.4, 133.1, 129.8, 129.7, 129.6, 128.9, 128.8, 128.6, 128.4, 128.3 (Ar); 80.5 (C-1'); 76.4 (C-4'); 74.8 (C-2'); 72.6 (C-3'); 64.2 (C- 5'); 44.4 (N-$\underline{CH_2}CH_3$); 14.4, 11.3 ($2CH_3$). Anal. calc. for $C_{31}H_{29}N_3O_7$: C, 67.02; H, 5.26; N, 7.56. Found: C, 67.13; H, 5.31; N, 7.42; m/z (FAB>0): 556 (MH^+).

1,5-Diethyl-3-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-1*H*-1,2,4-triazole (7b). From **2b** (2.39 g, 10 mmol). Yield: 2.87 g, 63%; m.p. 100 - 104 °C, decomp. at 170 °C. ^{1}H-NMR: δ 7.98 (d, 2H, J 7.3 Hz, ArH); 7.86 (d, 2H, J 7.4 Hz, ArH); 7.77 (d, 2H, J 7.5 Hz, ArH); 7.39 - 7.14 (m, 9H, ArH); 5.92 (m, 2H, H-2', H-3'); 5.30 (d, 1H, $J_{1',2'}$ 3.6 Hz, H-1'); 4.67 - 4.52 (m, 3H, H-4', H-5', H-5''); 3.88 (q, 2H, J 7.2 Hz, N-$\underline{CH_2}CH_3$); 2.46 (q, 2H, J 7.5 Hz, $\underline{CH_2}CH_3$); 1.26 (t, 3H, J 7.2 Hz, N-$CH_2\underline{CH_3}$); 1.18 (t, 3H, J 7.5 Hz, $CH_2\underline{CH_3}$). ^{13}C-NMR: δ 166.0, 165.3, 165.2 (C=O); 159.2; 157.1 (C=N); 133.3, 132.9, 129.9, 129.8, 129.7, 129.4, 129.2, 128.4, 128.3, 128.2 (Ar); 79.8 (C-1'); 77.9 (C-4'); 75.3 (C-2'); 73.0 (C-3'); 64.6 (C-5'); 43.1 (N-$\underline{CH_2}CH_3$); 19.3 ($\underline{CH_2}CH_3$); 15.6 ($CH_2\underline{CH_3}$); 11.8 (N-$CH_2\underline{CH_3}$). Anal. calc. for $C_{32}H_{31}N_3O_7$: C 67.48; H, 5.48, N, 7.38. Found: C, 67.62; H, 5.32; H, 5.32; N, 7.21; m/z (FAB>0) 570 (MH^+).

5-Methyl-3-(2,3,4-tri-O-benzoyl-β-D-ribofuranosyl)-1*H*-1,2,4-triazole (7c). From **2c** (2.39 g, 10 mmol). Yield: 3.29 g, 78%; m.p. 140 - 145 °C. ^{1}H-NMR: δ 11.4 (s, 1H, NH); 7.94 (d, 2H, J 7.7 Hz, ArH), 7.86 (d, 2H, J 7.7 Hz, ArH); 7.52 (d, 2H, J 7.4 Hz, ArH); 7.47 - 7.26 (m, 9H, ArH); 6.10 (pt, 1H, $J_{2',3'}$ 4.4 Hz, H-2'), 5.78 (pt, 1H, $J_{3',4'}$ 5.2 Hz, H-3'); 5.65 (d, 1H, $J_{1',2'}$ 3.6 Hz, H-1'); 4.87 - 4.69 (m, 3H, H-4', H-5', H-5''); 2.86 (s, 3H, CH_3). ^{13}C-NMR: δ 167.5, 165.8, 165.7 (C=O); 157.3; 153.4 (C=N); 134.0, 129.9, 129.8, 128.7, 128.6, 128.1, 128.0 (Ar); 80.7 (C-1'); 76.2 (C-4'); 75.6 (C-2'), 72.2 (C-3'); 64.6 (C-5'). Anal. calc. for $C_{29}H_{25}N_3O_7$: C, 66.03; H, 4.78; N, 7.97. Found: C, 65.84; H, 4.87; N, 7.72; m/z (FAB>0) 528 (MH^+).

5-Ethyl-3-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-1*H*-1,2,4-triazole (7d). From **2d** (2.67 g, 10 mmol). Yield: 3.20 g, 74%; m.p. 75 - 78 °C. ^{1}H-NMR: δ 8.09 - 7.89 (m, 6H, ArH); 7.57 - 7.30 (m, 9H, ArH); 6.05 (pt, 1H, $J_{2',3'}$ 5.0 Hz, H-2'); 5.69 (pt, 1H, $J_{3',4'}$ 5.5 Hz, H-3'); 5.47 (d, 1H, $J_{1',2'}$ 4.3 Hz, H-1'); 4.73 (m, 3H, H-4', H-5', H-5''); 2.79 (q, 2H, J 8.6 Hz, CH_2); 1.32 (t, 3H, CH_3). ^{13}C-NMR: δ 165.6, 165,4, 165.3 (C=O); 156.0, 151.8 (C=N); 133.4, 129.8, 129.7, 129.6, 129.1, 129.0, 128.4, 125.3 (Ar); 79.9 (C-1'); 77.5 (C-4'); 75.3 (C-2'); 72.7 (C-3'); 64.4 (C-5'); 20.4 (CH_2); 11.8 (CH_3). Anal. calc. for $C_{30}H_{27}N_3O_7$: C, 66.53; H, 5.02; N, 7.76. Found: C, 66.32; H, 4.93; N, 7.86; m/z (FAB): 542 (M^+).

5,6,7,8-Tetrahydro-2-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-1,2,4-triazolo[1,5-a] pyridine (7e). From **2e** (2.35 g, 10 mmol). Yield: 2.72 g, 75%; m.p. 123 - 126 °C. (Lit.[22] 126 - 127 °C). All the physical data were identical to those of the authentic sample prepared previously[22]

6,7,8,9-Tetrahydro-2-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-5*H*-1,2,4-triazolo-[1,5-a] azepine (7f). From **2f** (2.63 g, 10 mmol). Yield: 1.86 g, 70%, m.p. 125 - 127 °C (Lit.[22] 127 - 128 °C). All the physical data were identical to those of the authentic sample prepared previously.[22]

3,3-Dimethylbutan-2-one-(4-nitrophenyl)-hydrazone (9). A mixture of 4-nitro-phenyl-hydrazine (2.44 g, 15.93 mmol), 3,3-dimethylbutan-2-one (1.5 g, 15.0 mmol) and NaOAc (1.23 g, 15 mmol) in EtOH (40 ml) was heated under reflux for 8 h. The solvent was evaporated to dryness and the residue was extracted with $CHCl_3$ (3 x 30 ml). The combined organic extracts were diluted with $CHCl_3$ (50 ml) and treated with decolorizing charcoal, filtered and evaporated to dryness to give the hydrazone **9** (3.48 g, 93%) as an orange oil. ^{1}H-NMR: δ 8.15, 8.11, 7.07, 7.03 (AA'BB', 4H, ArH); 7.51 (bs, 1H, NH); 1.88 (s, 3H, CH_3); 1.19 (s, 9H, *tert*-but.). m/z (FAB>0) 236 (MH^+).

(1-Chloro-1,2,2-trimethylpropyl)azo-(4-nitrobenzene) (10). A solution of *tert*-butyl hypochlorite (1.60 g, 14.54 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise, with exclusion of light, to a solution of 3,3-dimethylbutan-2-one-(4-nitrophenyl) hydrazone (**9**) (3.30 g, 14.04 mmol) in dry CH_2Cl_2 (20 ml) at -20 °C. After stirring at 0 °C for 3 h, the solvent was evaporated to dryness to afford the title azo compound **10** (3.37 g, 89%) as a red oil. ^{1}H-

NMR: δ 8.38, 8.34, 7.89, 7.85 (AA'BB', 4H, ArH), 1.87 (s, 3H, CH_3); 1.22 (s, 9H, *tert*-but.). m/z (FAB>0) 270/272 (MH^+).

3-Methyl-1-(4-nitrophenyl)-5-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-1*H*-1,2,4-triazole (12). From $SbCl_5$ (3.0 g, 10 mmol) in CH_2Cl_2 (15 ml) and a mixture of nitrile **4** (3.85 g, 8.0 mmol) and chloride **10** (2.69 g, 10 mmol) in CH_2Cl_2 (35 ml). Purification by column chromatography afforded **12** as pale orange crystals (3.6 g, 59%); m.p. 81 - 86 °C. $[\alpha]_D$ - 90° (c 1.0, $CHCl_3$). ^{1}H-NMR: δ 8.36, 8.02 (AA'BB', 4H, 4-NO_2-phH); 7.96 - 7.25 (m, 15H, ArH); 6.37 (dd, 1H, $J_{2',3'}$ 5.2 Hz, H-2'); 6.22 (dd, 1H, $J_{3',4'}$ 6.4 Hz, H-3'); 5.23 (d, 1H, $J_{1',2'}$ 3.2 Hz, H-1'); 4.81 - 4.76 (m, 2H, $J_{4',5'}$ 5.2 Hz, H-4', H-5'); 4.55 (dd, 1H, $J_{5',5''}$ 13.0 Hz, H-5''); 2.37 (s, 3H, CH_3). ^{13}C-NMR: δ 166.1, 165.3, 165.2 .(C=O); 161.7, 152.0 (C=N), 141.6; 133.7, 133.5, 133.2, 129.8, 129.7, 129.5, 128.5, 128.4, 125.0, 124.6 (Ar); 80.5 (C-1'); 75.3 (C-4'); 74.8 (C-2'); 72.7 (C-3'); 63.4 (C-5'); 13.8 (CH_3). Anal. calc. for $C_{35}H_{28}N_3O_9$: C, 64.81; H, 4.35; N, 8.64. Found: C, 64.54; H, 4.19; N, 8.71; m/z (FAB>0) 649 (MH^+); 705 (MNa^+).

Free nucleosides of the 1,2,4-triazole derivatives: *General procedur.* A solution of the nucleosides **7a**, **7b** and **12** (1.60 mmol) in 0.3 M NaOMe (15 ml) was stirred at r.t. for 5 h. The solution was neutralized with 0.5 M HCl, filtered and evaporated to dryness. The residue was partitioned between H_2O (20 ml) and Et_2O (3 x 20 ml). The aqueous layer was evaporated to dryness and the residue was co-evaporated with EtOH (2 x 20 ml) to give an oil, which was purified on an SiO_2 column (40 g). Elution, first, with $CHCl_3$ and finally with $CHCl_3$/MeOH (95 : 5) and evaporation of the appropriate fractions afforded the desired nucleosides as a foam or an oil, which slowly solidified to give powder.

1-Ethyl-5-methyl-3-(β-D-ribofuranosyl)-1*H*-1,2,4-triazole (8a). From **7a**. Yield: 0.29 g, 74%; m.p. 64 - 67 °C. ^{1}H-NMR (DMSO-d_6): δ 4.45 (d, 1H, $J_{1',2'}$ 5.3 Hz, H-1'); 4.10 (pt, 1H, $J_{2',3'}$ 4.9 Hz, H-2'); 4.06 (m, 3H, H-3', $C_{2'}$-OH, $C_{3'}$-OH); 4.03 (q, 2H, J 7.3 Hz, CH_2); 3.94 (t, 1H, $J_{5',OH}$ 7.3 Hz, $C_{5'}$-OH); 3.86 (m, 1H, J4',5'' 4.5 Hz, H-4'); 3.75 (q, 1H, $J_{4',5'}$ 5.0 Hz, H-5'); 3.41 (dd, 1H, $J_{5',5''}$ 11.5 Hz, H-5''); 2.34 (s, 3H, C_5-CH_3); 1.27 (t, 3H, J 7.3 Hz, $CH_2\underline{CH_3}$). ^{13}C-NMR (DMSO-d_6): δ 160.9, 152.8 (C=N); 85.2 (C-1'); 78.4 (C-4'), 75.2 (C-2'); 71.2 (C-3'); 62.5 (C-5'); 43.2 (CH_2); 15.2, 11.6 ($2CH_3$). Anal. calc. for $C_{10}H_{17}N_3O_4$: C, 49.37; H, 7.04; N, 17.27. Found: C, 49.16; H, 6.95; N, 17.38; m/z (FAB>0) 244 (MH^+).

1,5-Diethyl-3-(β-D-ribofuranosyl)-1*H*-1,2,4-triazole (8b). From **7b**. Yield: 0.33 g, 80%; m.p. 70 - 73 °C. ^{1}H-NMR (DMSO-d_6): δ 4.56 (d, 1H, $J_{1',2'}$ 4.9 Hz, H-1'); 4.10 (pt, 1H, $J_{2',3'}$ 5.2 Hz, H-2'); 4.06 (m, 3H, H-3', $C_{2'}$-OH, $C_{3'}$-OH); 4.04 (q, 2H, J 7.2 Hz, CH_2); 3.94 (t, 1H, $J_{5',OH}$ 5.5 Hz, $C_{5'}$-OH); 3.77 (q, 1H, $J_{4',5''}$ 4.5 Hz, H-4'); 3.55 (dd, 1H, $J_{4',5'}$ 4.8 Hz, H-5'); 3.41 (dd, 1H, $J_{5',5''}$ 11.5 Hz, H-5''); 2.70 (q, 2H, J 7.2 Hz, CH_2); 1.32 (t, 3H, J 7.2 Hz, CH_3); 1.22 (t, 3H, J 7.5 Hz, CH_3). ^{13}C-NMR (DMSO-d_6): δ 161.8, 156.8 (C=N); 84.9 (C-1'); 78.6 (C-4'); 75.0 (C-2'); 71.2 (C-3'); 42.7 (N-CH_2); 18.6 (CH_2); 15.2, 11.9 ($2CH_3$). Anal. calc. for $C_{11}H_{19}N_3O_4$: C, 51.35; H, 7.44; N, 16.33. Found: C, 51.14; H, 7.35; N, 16.41; m/z (FAB>0) 295 (MK^+).

3-Methyl-1-(4-nitrophenyl)-5-(β-D-ribofuranosyl)-1*H*-1,2,4-triazole (13). From **12** (1.04 g, 1.23 mmol). Yield: 0.28 g, 67%; m.p. 64 - 69 °C (amorphous). ^{1}H-NMR (DMSO-d_6): δ 8.42, 7.90 (AA'BB', 4H, ArH); 5.20 (d, 1H, $J_{2',OH}$ 6.0 Hz, $C_{2'}$-OH); 5.07 (d, 1H, $J_{3',OH}$ 5.0 Hz, $C_{3'}$-OH); 4.80 (t, 1H, $J_{5',OH}$ 5.6 Hz, $C_{5'}$-OH); 4.66 (d, 1H, $J_{1',2'}$ 6.0 Hz, H-1'); 4.51 (q, 1H, $J_{2',3'}$ 6.0 Hz, H-2'); 4.05 (q, 1H, $J_{3',4'}$ 5.0 Hz, H-3'); 3.88 (q, 1H, $J_{4',5''}$ 4.5 Hz, H-4'); 3.49 (dd, 1H, $J_{4',5'}$ 5.0 Hz, H-5'); 3.41 (dd, 1H, $J_{5',5''}$ 11.5 Hz, H-5''); 2.36 (s, 3H, CH_3). ^{13}C-NMR (DMSO-d_6): δ 160.7, 154.5 (C=N); 147.1, 141.5, 125.4 125.1 (Ar); 86.2 (C-1'); 74.5 (C-4'); 74.2 (C-2'), 71.4 (C-3'); 62.0 (C-5'), 13.4 (CH_3). Anal. calc. for $C_{14}H_{16}N_3O_6$: C, 50.00; H, 4.80; N, 16.66. Found: C, 49.87; H, 4.75; N, 16.56; m/z (FAB>0) 337 (MH^+).

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