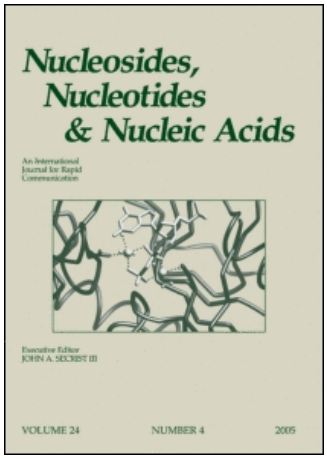

Nucleosides, Nucleotides and Nucleic Acids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597286

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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Online Publication Date: 01 September 1999
To cite this Article: Al-soud, Yaseen A., Al-masoudi, Wasfi A., El-halawa, Rajab Abu and Al-masoudi, Najim (1999) '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', Nucleosides, Nucleotides and Nucleic Acids, 18:9, 1985 - 1994
To link to this article: DOI: 10.1080/07328319908044859
URL: http://dx.doi.org/10.1080/07328319908044859

NUCLEOSIDES & NUCLEOTIDES, 18(9), 1985–1994 (1999)

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

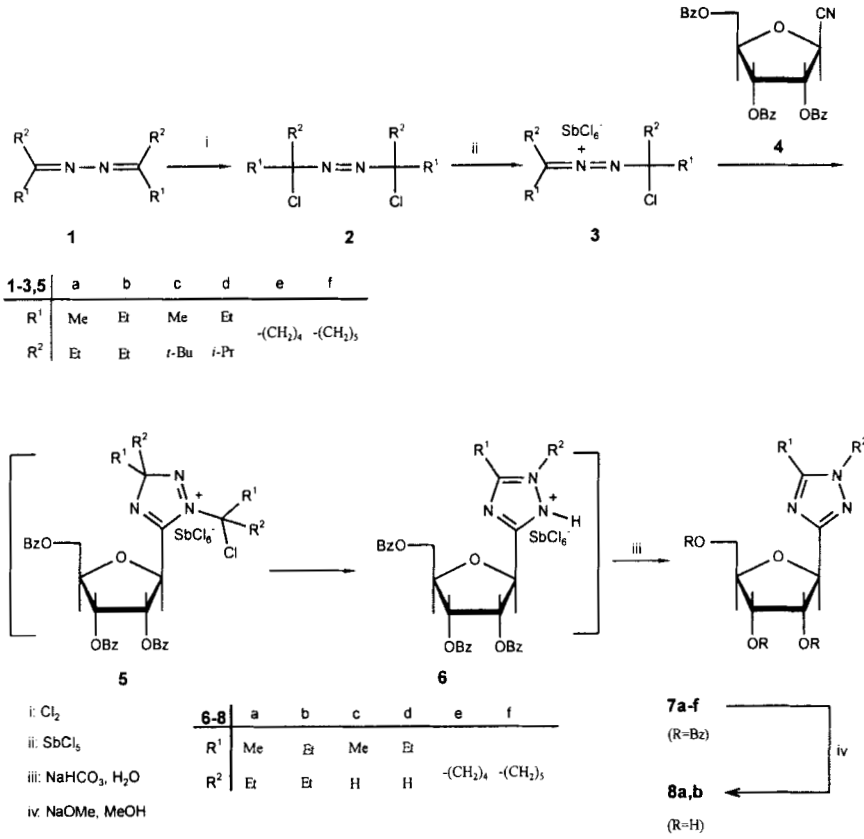
In our present study, the α, α'-dichloroazoalkanes **2** were used as starting material for the synthesis of the target molecules and prepared by chlorination of **1**. Compounds **2** were converted to the salts **3** in the presence of a Lewis acid such as $SbCl_5$ at - 60 °C. The cumulene intermediates **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).

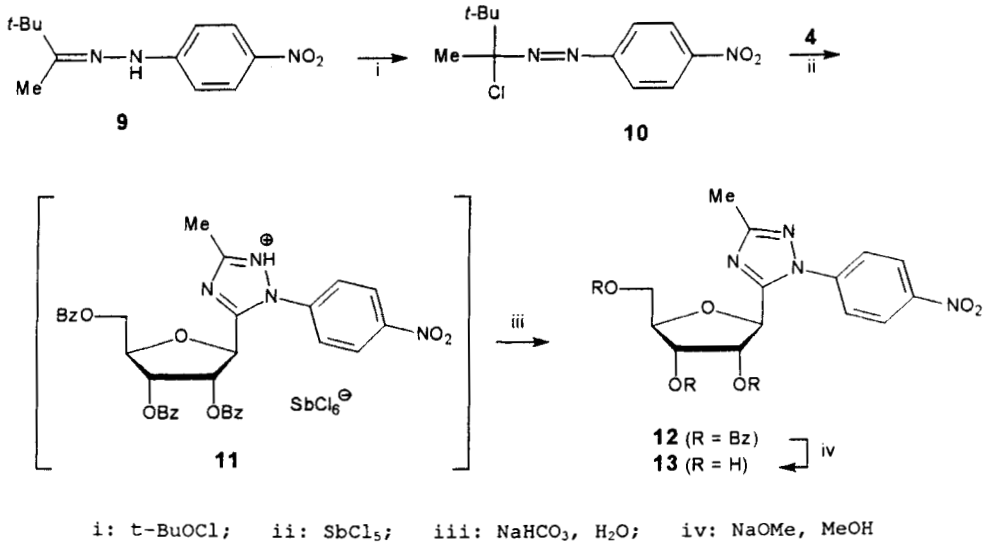
Analogously, (1-chloro-1,2,2-trimethylpropyl)azo-(4-nitrobenzene) (**10**) was prepared from chlorination of the hydrazone **9**. Reaction of **10** with the glycosyl cyanide **4** gave, after the 1,2-shift along with elimination of the *tert*-butyl group, the unisolated salt **11**. Hydrolysis of **11**, *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.



i: t-BuOCl; ii: $SbCl_5$; iii: $NaHCO_3$, H_2O; iv: NaOMe, MeOH

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^+).

ACKNOWLEGEMENT

We thank Professor E. De Clercq of Rega Medical Institute, Leuven, Belgium, for the anti-HIV and anti-HSV evaluations. Mass measurments were recorded by Mrs. M.J. Quelle and Mr. K. Hägele and elemental analysis were performed by Mrs. W.B. Böer of faculty of chemistry, University of Konstanz (Germany).

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Received 3/4/99
Accepted 4/27/99