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Synthesis of 1-(3-(1,2,4-Triazol-1-yl)-2,3,6-trideoxy-*L-arabino*-hexofuranosyl)uracils via an α,β-Unsaturated Aldehydohexose

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Summary. Mercuric catalyzed hydrolysis of acetylated *L*-rhamnal **1** gave the α,β-unsaturated aldehyde **2**. 1,2,4-Triazole was coupled, in a Michael type addition reaction, to **2** at C-3 in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (*DBU*) to give, after acetylation at the anomeric center, an anomeric mixture of 1,5-di-*O*-acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-*L-arabino*-hexofuranose (**3**). Reaction of **3** with silylated 2,4-dihydroxypyrimidines **4** in the presence of trimethylsilyl triflate as catalyst followed by deprotection with 33% methylamine in absolute ethanol afforded the corresponding nucleosides **7** and **8**.

Keywords. Michael type addition; *L*-Nucleosides; 2′,3′,6′-Trideoxy-*L*-hexofuranose nucleosides; 3′-(1,2,4-Triazol-1-yl) nucleosides.

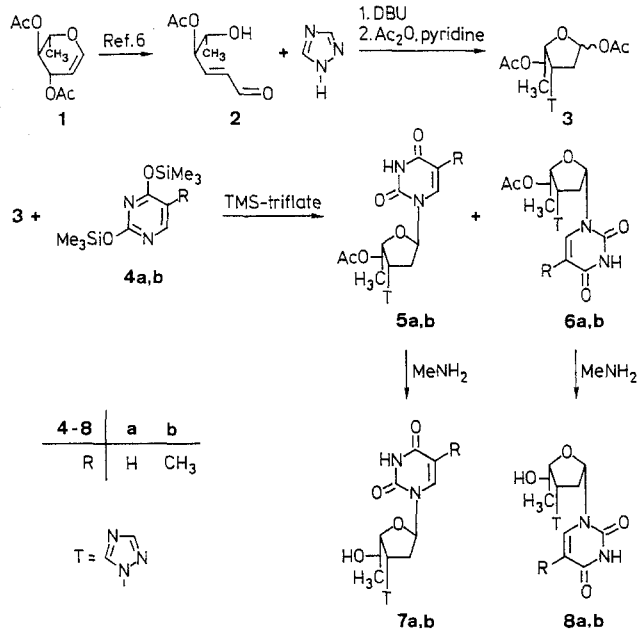
Synthese von 1-(3-(1,2,4-Triazol-1-yl)-2,3,6-trideoxy-*L-arabino*-hexofuranosyl)uracilen über eine α,β-ungesättigte Aldohexose

Zusammenfassung. Die quecksilberkatalysierte Hydrolyse von acetyliertem *L*-Rhamnal **1** ergab die α,β-ungesättigten Aldehyde **2**. 1,2,3-Triazol wurde in Gegenwart von 1,8-Diazabicyclo[5.4.0]-7-undecen mittels einer Addition vom Michael-Typ an C-3 von **2** gekoppelt und ergab dann nach Acetylierung am anomeren Zentrum eine anomere Mischung von 1,5-Di-O-acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-*L-arabino*-hexofuranose (**3**). Die Reaktion von **3** mit silyliertem 2,4-Di-hydroxypyrimidinen **4** in Gegenwart von Trimethylsilyltriflat in absolutem Ethanol ergab die entsprechenden Nucleoside **7** und **8**.

Introduction

3′-Deoxythymidine analogues with a five-membered ring in the 3′α-position were obtained by epoxide opening of the corresponding 1-(2,3-anhydro-β-*D-lyxo*-furanosyl)thymidines followed by 2′-deoxygenation [1]. Such compounds have also been prepared by ring closure reactions of 3′-azido-2′,3′-dideoxynucleosides [2, 3] or by ring closure with the amino group of the corresponding 3′-amino-2′,3′-dideoxynucleosides [4].

The main prerequisite of these routes is the availability of the nucleosides used as starting materials. In a previous report [5] from this laboratory the synthesis



of nucleoside analogues of 3-(1,2,4-triazol-1-yl)-2,3-dideoxy-*D-arabino*-hexopyranoses and 3-(1,2,4-triazol-1-yl)-2,3-dideoxy-*D-ribo*-hexofuranoses was described. The present paper deals with an extension of this research to the synthesis of 3′-triazolyl nucleosides of 2,3,6-trideoxy-*L-arabino*-hexofuranoses.

The α,β-unsaturated aldehyde **2** was prepared by a known procedure [6] and used in a Michael type addition reaction with 1,2,4-triazole in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (*DBU*) in methylene chloride to produce an anomeric mixture of 1,5-di-*O*-acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-*L-arabino*-hexofuranoses **3** in 50% yield after acetylation of the crude mixture with acetic anhydride in dry pyridine.

Application of the reported [7, 8] procedure for nucleoside synthesis using trimethylsilyl trifluoromethanesulfonate (*TMS*-triflate) as Lewis acid resulted in the protected 3′-(1,2,4-triazol-1-yl) nucleosides **5** and **6** in 50% and 45% total yield for **5a**, **6a** and **5b**, **6b**, respectively. Deprotection of **5** and **6** with 33% methylamine in absolute ethanol gave the corresponding nucleosides **7** and **8**.

The structural assignment of the nucleosides **7** and **8** was based mainly on NMR studies. Thus, 2D-COSY and ^{1}H-n.O.e. experiments on compound **5b** and **6b** gave an unambiguously configurational assignment of these two nucleosides. For compound **5b** the α-configuration was confirmed by a 8% n.O.e. in 2′β-H, when 1′-H was irradiated. The *arabino* configuration of **5b** was proved by irradiation of 3′-H generating a 11% n.O.e. in 4′-H and a 7% n.O.e. in 2′α-H. For compound **6b** the β-configuration was confirmed by a 8% n.O.e. in 6-H when 2′β-H was irradiated. Besides, irradiation of 2′α-H gave a 30% n.O.e. in 1′-H and irradiation of 5′-H a 3% n.O.e. in 6-H. The *arabino* configuration of **6b** was proved by irradiation of 2′α-H generating a 20% n.O.e. in 3′-H and irradiation of 5′-H generating a 3% n.O.e. in 3″-H of the 1,2,4-triazole ring.

Experimental Part

NMR spectra were recorded on a Bruker AC 250 FT NMR spectrometer at 250 MHz for ^{1}H-NMR and 62.9 MHz for ^{13}C-NMR with tetramethylsilane (*TMS*) as internal standard. EI mass spectra were obtained on a Varian MAT 311 A spectrometer and FAB mass spectra on a Kratos MS-50 spectrometer. Microanalyses for **5b**, **6a**, **b**, **7a**, **b**, and **8a**, **b** were carried out at NOVO-NORDISK Microanalytical Laboratory A/S, Novo Allé, DK-2880 Bagsvaerd, Denmarkt, giving good agreement between calculated and found CHN values. Column chromatography was done on silica gel (0.040 – 0.063 mm).

1,5-Di-O-acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-L-arabino-hexofuranose (**3**)

A solution of **2** [6] (6.8 g, 37.5 mmol) in dry CH_2Cl_2 (75 ml) was added dropwise over a period of 2 h to a suspension of 1,2,4-triazole (3.9 g, 56.4 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (*DBU*, 0.6 ml, 4.2 mmol) in methylene chloride (180 ml) with stirring at O°C. The temperature was allowed to rise to room temperature and stirring was continued overnight. The solvent was evaporated under reduced pressure and the residue mixed with acetic anhydride (30 ml, 300 mmol) and pyridine (7.3 ml, 90 mmol) and stirred at room temperature for 3 h. The solvents were evaporated under reduced pressure followed by coevaporation twice with xylene (20 ml). The residue was chromatographed on silica (1 000 g) with benzene/diethyl ether/methanol (20/75/5, *v/v/v*), to give 0.85 g (8%) of the most polar anomer of **3** and 4.5 g (42%) of the less polar anomer of **3**. Besides, a small fraction (0.53 g, 5%) of other isomers was obtained. All compounds were isolated as oils.

Most polar anomer of **3**: Yield 0.85 g (8%). ^{1}H-NMR ($CDCl_3$) δ 1.18 (d, J = 6.2 Hz, 3 H, 6-H), 1.86 (s, 3 H, CH_3CO), 2.17 (s, 3 H, CH_3CO), 2.61 (dd, J = 14.8 Hz, 1.0 Hz, 2α-H), 2.92 – 3.05 (m, 1 H, 2β-H), 4.22 (dd, J = 8.5 Hz, 5.7 Hz, 1 H, 4-H), 4.56 – 4.65 (m, 1 H, 5-H), 5.21 – 5.28 (m, 1 H, 3-H), 6.43 (dd, J = 5.9 Hz, 1.5 Hz, 1 H, 1-H), 7.89 (s, 1-H, 5′-H), 8.46 (s, 1 H, 3′-H). ^{13}C-NMR ($CDCl_3$) δ 16.76 (C-6), 20.34 (CH_3CO), 20.73 (CH_3CO), 37.22 (C-2), 58.71 (C-3), 67.65 (C-5), 82.84 (C-4), 96.12 (C-1),142.91 (C-5′), 150.81 (C-3′), 168.68 (CO), 169.06 (CO).

Less polar anomer of **3**: Yield 4.5 g (42%). ^{1}H-NMR ($CDCl_3$) δ 1.22 (d, J = 5.8 Hz, 3 H, 6-H), 1.92 (s, 3 H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 2.61 (ddd, J = 15.0 Hz, 8.0 Hz, 3.0 Hz, 1 H, 2α-H), 2.88 (ddd, J = 15.0 Hz, 5.9 Hz, 3.4 Hz, 1 H, 2β-H), 4.28 – 4.38 (m, 2 H, 4-H, 5-H), 5.19 – 5.26 (m, 1 H, 3-H), 6.65 (dd, J = 5.9 Hz, 3.0 Hz, 1 H, 1-H), 7.91 (s, 1 H, 5′-H), 8.05 (s, 1 H, 3′-H). ^{13}C-NMR ($CDCl_3$) δ 17.11 (C-6), 20.60 (CH_3CO), 20.91 (CH_3CO), 38.88 (C-2), 59.35 (C-3), 67.88 (C-5), 82.19 (C-4), 97.01 (C-1), 142.92 (C-5′), 151.81 (C-3′),168.77 (CO), 169.55 (CO). FAB MS (*m/z*, %) [glycerol] 284 (M + 1, 100).

1-(5-O-Acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-α-L-arabino-hexofuranosyl)uracil (**5a**) *and 1-(5-O-Acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-β-L-arabino-hexofuranosyl)uracil*
[**6a**, $C_{14}H_{17}N_5O_5 \cdot 1.5\,H_2O$]

Trimethylsilyl trifluoromethanesulfonate (1.1 ml, 6.0 mmol) was added to the mixture of **3** (1.6 g, 5.6 mmol) and silylated uracil **4a** [9] (2.3 g, 9.0 mmol) in anhydrous acetonitrile (50 ml) cooled to 0° C with stirring. After 2 h the reaction mixture was diluted with methylene chloride (100 ml) and quenched with a cold saturated aqueous solution of $NaHCO_3$ (50 ml). The organic layer was washed with cold water (2 × 20 ml) and dried with $MgSO_4$. Evaporation of the solvent gave a white foam which was purified on silica (130 g) with CH_2Cl_2/*Me*OH (97/3, *v/v*) to give the pure anomers **5a** and **6a**.

5a: Yield 0.35 g (18%); m. p. 114 – 116°C (hygroscopic). ^{1}H-NMR ($CDCl_3$) δ 1.24 (d, J = 6.2 Hz, 3 H, 6′-H), 1.97 (s, 3 H, CH_3CO), 2.89 (dd, J = 14.0 Hz, 7.0 Hz, 2′β-H), 3.11 (dt, J = 14.0 Hz, 7.0 Hz, 1 H, 2′α-H), 4.27 (dq, J = 8.4 Hz, 6.2 Hz, 1 H, 5′-H), 4.69 (dd, J = 8.4 Hz, 4.5 Hz, 1 H, 4′-H), 5.31 – 5.36 (m, 1 H, 3′-H), 5.80 (d, J = 8.1 Hz, 1 H, 5-H), 6.27 (t, J = 7.0 Hz, 1 H, 1′-H), 7.36 (d, J = 8.1 Hz, 1 H, 6-H), 8.01 (s, 1 H, 5″-H), 8.18 (s, 1 H, 3″-H), 10.33 (br, 1 H, NH). ^{13}C-NMR ($CDCl_3$) δ 17.38 (C-

6'), 20.76 (CH_3CO), 37.62 (C-2'), 60.44 (C-3'), 68.20 (C-5'), 84.49 (C-4'), 91.25 (C-1'), 102.35 (C-5), 141.99 (C-6), 143.56 (C-5''), 150.26 (C-3''), 152.36 (C-2), 163.77 (C-4), 168.94 (CO). FAB MS (*m/z*, %) [3-nitrobenzyl alcohol] 336 ($M+1$, 97).

6a: Yield 0.63 g (32%); m. p. 219–221°C. ^{1}H-NMR ($CDCl_3$) δ 1.25 (d, $J=6.2$ Hz, 3 H, 6'-H), 1.97 (s, 3 H, CH_3CO), 2.47 (ddd, $J=15.2$ Hz, 6.5 Hz, 3.0 Hz, 1 H, 2' β H), 3.14 (ddd $J=15.2$ Hz, 8.0 Hz, 7.8 Hz, 1 H, 2' α H), 4.05 (dd, $J=8.5$ Hz, 5.3 Hz, 1 H, 4'-H), 4.41 (dq, $J=8.5$ Hz, 6.2 Hz, 1 H, 5'-H), 5.15 (ddd, $J=8.0$ Hz, 5.3 Hz, 3.0 Hz, 1 H, 3'-H), 5.89 (d, $J=8.2$ Hz, 1 H, 5-H), 6.33 (dd, $J=7.8$ Hz, 6.5 Hz, 1 H, 1'-H), 8.01 (s, 1 H, 5''-H), 8.08 (s, 1 H, 3''-H), 8.42 (d, $J=8.2$ Hz, 1 H, 6-H), 9.75 (br, 1 H, NH). ^{13}C-NMR ($CDCl_3$) δ 17.57 (C-6'), 20.68 (CH_3CO), 37.77 (C-2'), 53.30 (C-3'), 68.10 (C-5'), 81.98 (C-4'), 82.70 (C-1'), 102.87 (C-5), 141.07 (C-6), 143.93 (C-5''), 150.60 (C-3''), 152.66 (C-2), 163.23 (C-4), 168.76 (CO). FAB MS (*m/z*, %) [3-nitrobenzyl alcohol] 336 ($M+1$, 75).

1-[5-O-Acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-α-L-arabino-hexofuranosyl]thymine [**5b**; $C_{15}H_{19}N_5O_5 \cdot H_2O$] *and 1-[5-O-Acetyl-3-(1,2,4-triazol-1-yl)-2,3,6-trideoxy-β-L-arabino-hexofuranosyl]thymine* [**6b**; $C_{15}H_{19}N_5O_5 \cdot H_2O$]

Trimethylsilyl trifluoromethanesulfonate (0.83 ml, 4.6 mmol) was added to the mixture of **3** (1.2 g, 4.1 mmol) and silylated thymine **4b** [9] (1.62 g, 6.0 mmol) in anhydrous acetonitrile (25 ml) cooled to 0°C with stirring. After 2 h the reaction mixture was diluted with dichloromethane (100 ml) and quenched with a cold saturated solution of $NaHCO_3$ (50 ml). The organic layer was washed with cold water (25 ml) and dried with $MgSO_4$. After evaporation the residue was purified on silica (100 g) with CH_2Cl_2/*Me*OH (97/3, *v/v*) to give the pure anomers **5b** and **6b**.

5b: Yield 0.18 g (13%); m. p. 110–112°C (hygroscopic). ^{1}H-NMR ($CDCl_3$) δ 1.23 (d, $J=6.1$ Hz, 3 H, 6'-H), 1.96 (s, 6 H, CH_3, CH_3CO), 2.84 (dd, $J=14.2$ Hz, 7.0 Hz, 1 H, 2' β-H), 3.14 (dt, $J=14.2$ Hz, 7.0 Hz, 1 H, 2' α-H), 4.29 (dq, $J=8.3$ Hz, 6.1 Hz, 1 H, 5'-H), 4.70 (dd, $J=8.3$ Hz, 5.0 Hz, 4'-H), 5.31–5.35 (m, 1 H, 3'-H), 6.24 (t, $J=7.0$ Hz, 1 H, 1'-H), 7.17 (s, 1 H, 6-H), 7.99 (s, 1 H, 5''-H), 8.15 (s, 1 H, 3''-H), 10.1 (br, 1 H, NH). ^{13}C-NMR ($CDCl_3$) δ 12.29 (CH_3), 17.36 (C-6'), 20.77 (CH_3CO), 37.35 (C-2'), 60.59 (C-3'), 68.34 (C-5'), 84.45 (C-4'), 91.18 (C-1'), 110.85 (C-5), 138.09 (C-6), 143.44 (C-5''), 150.35 (C-3''), 152.30 (C-2), 164.12 (C-4), 168.94 (CO). FAB MS (*m/z*, %) [glycerol] 350 ($M+1$, 100).

6b: Yield 0.42 g (32%); m. p. 270–272°C. ^{1}H-NMR ($CDCl_3$) δ 1.25 (d, $J=6.2$ Hz, 3 H, 6'-H), 1.96 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3CO), 2.47 (ddd, $J=15.1$ Hz, 7.4 Hz, 3.0 Hz, 1 H, 2' β-H), 3.09 (ddd, $J=15.1$ Hz, 9.1 Hz, 7.4 Hz, 1 H, 2' α-H), 4.02 (dd, $J=8.5$ Hz, 5.5 Hz, 1 H, 4'-H), 4.44 (dq, $J=8.5$ Hz, 6.2 Hz, 1 H, 5'-H), 5.12 (ddd, $J=9.1$ Hz, 5.5 Hz, 3.0 Hz, 1 H, 3'-H), 6.33 (t, $J=7.4$ Hz, 1 H, 1'-H), 8.01 (s, 1 H, 5''-H), 8.05 (s, 1 H, 3''-H), 8.28 (s, 1 H, 6-H). ^{13}C-NMR ($CDCl_3$) δ 12.55 (CH_3), 17.69 (C-6'), 20.68 (CH_3CO), 37.51 (C-2'), 58.55 (C-3'), 68.23 (C-5'), 81.74 (C-4'), 82.36 (C-1'), 111.54 (C-5), 136.48 (C-6), 143.94 (C-5''), 150.60 (C-3''), 152.60 (C-2), 163.50 (C-4), 168.73 (CO). FAB MS (*m/z*, %) [glycerol] 350 ($M+1$, 100).

General Procedure for the Peparation of **7** *and* **8**

Compound **5** or **6** (0.10 g, 0.3 mmol) was added to a 33% solution of methylamine in absolute ethanol (10 ml) and stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure and the residue chromatographed on silica (10 g) with CH_2Cl_2/*Me*OH (90/10, *v/v*).

1-(3-(1,2,4-Triazol-1-yl)-2,3,6-trideoxy-α-L-arabino-hexofuranosyl)uracil [**7a**; $C_{12}H_{15}N_5O_4 \cdot 0.25\,H_2O$]

Yield 0.075 g (86%); m. p. 258–260°C (decomp.). ^{1}H-NMR (Me_2SO-d_6) δ 1.05 (d, $J=6.1$ Hz, 3 H, 6'-H), 2.61–2.80 (m, 2 H, 2' α-H, 2' β-H), 3.30–3.35 (m, 1 H, 5'-H), 4.27 (dd, $J=9.0$ Hz, 4.0 Hz, 1 H, 4'-H), 4.79 (d, $J=3.0$ Hz, 1 H, 5'-OH), 5.37–5.41 (m, 1 H, 3'-H), 5.68 (d, $J=8.0$ Hz, 1 H, 5-H), 6.55 (t, $J=7.0$ Hz, 1 H, 1'-H), 7.79 (d, $J=8.0$ Hz, 1 H, 6-H), 8.03 (s, 1 H, 5''-H), 8.49 (s, 1 H, 3''-H), 11.20

(br, 1 H, NH). ^{13}C-NMR (Me_2SO-d_6) δ 21.23 (C-6′), 37.13 (C-2′), 60.07 (C-3′), 64.09 (C-5′), 86.42 (C-4′), 86.89 (C-1′), 101.85 (C-5), 141.21 (C-6), 145.34 (C-5″), 150.39 (C-3″), 151.30 (C-2), 163.05 (C-4). FAB MS (*m/z*, %) [glycerol] 294 ($M+1$, 80).

1-(3-(1,2,4-Triazol-1-yl)-2,3,6-trideoxy-β-L-arabino-hexofuranosyl)uracil [**8 a**; $C_{12}H_{15}N_5O_4 \cdot H_2O$]

Yield 0.08 g (93%); m. p. 128–130°C (hygroscopic). ^{1}H-NMR (Me_2SO-d_6) δ 1.05 (d, $J=6.1$ Hz, 3 H, 6′-H), 2.31 (ddd, $J=14.8$ Hz, 6.2 Hz, 2.3 Hz, 1 H, 2′ β-H), 3.00–3.13 (m, 1 H, 2′ α-H), 3.30–3.32 (m, 1 H, 5′-H), 3.76 (dd, $J=9.0$ Hz, 5.0 Hz, 1 H, 4′-H), 5.27–5.33 (m, 1 H, 3′-H), 5.74 (d, $J=8.0$ Hz, 1 H, 5-H), 6.16 (dd, $J=7.9$ Hz, 6.3 Hz, 1 H, 1′-H), 8.03 (s, 1 H, 5″-H), 8.42 (d, $J=8.0$ Hz, 1 H, 6-H), 8.50 (s, 1 H, 3″-H), 11.34 (br, 1 H, NH). ^{13}C-NMR (Me_2SO-d_6) δ 21.37 (C-6′), 36.71 (C-2′), 58.16 (C-3′), 63.73 (C-5′), 82.21 (C-4′), 84.12 (C-1′), 101.84 (C-5), 141.20 (C-6), 145.88 (C-5″), 150.40 (C-3″), 151.22 (C-2),162.94 (C-4). FAB MS (*m/z*, %) [glycerol] 294 ($M+1$, 50).

1-(3-(1,2,4-Triazol-1-yl)-2,3,6-trideoxy-α-L-arabino-hexofuranosyl)thymine [**7 b**; $C_{13}H_{17}N_5O_4 \cdot 1.5\,H_2O$]

Yield 0.05 g (58%); m. p. 242–243°C. ^{1}H-NMR (Me_2SO-d_6) δ 1.03 (d, J = 6.1 Hz, 3 H, 6′-H), 1.83 (s, 3 H, CH_3), 2.55–2.64 (m, 1 H, 2′ α-H), 2.76 (dt, $J=14.6$ Hz, 7.3 Hz, 1 H, 2′ β-H), 3.28–3.30 (m, 1 H, 5′-H), 4.30 (dd, $J=8.9$ Hz, 4.0 Hz, 1 H, 4′-H), 4.76 (d, $J=5.0$ Hz, 1 H, 5′-OH), 5.39 (dd, $J=8.9$ Hz, 4.4 Hz, 1 H, 3′-H), 6.61 (t, $J=7.3$ Hz, 1 H, 1′-H), 7.67 (s, 1 H, 6-H), 8.02 (s, 1 H, 5″-H), 8.49 (s, 1 H, 3″-H), 11.28 (br, 1 H, NH). ^{13}C-NMR (Me_2SO-d_6) δ 11.97 (CH_3), 21.24 (C-6′), 36.76 (C-2′), 60.09 (C-3′), 64.12 (C-5′), 86.21 (C-4′, C-1′), 109.70 (C-5), 136.63 (C-6), 145.34 (C-5″), 150.39 (C-3″), 151.28 (C-2), 163.60 (C-4). FAB MS (*m/z*, %) [glycerol] 308 ($M+1$, 100).

1-(3-(1,2,4-Triazol-1-yl)-2,3,6-trideoxy-β-L-arabino-hexofuranosyl)thymine [**8 b**; $C_{13}H_{17}N_5O_4 \cdot H_2O$]

Yield 0.08 g (85%); m. p. 264–266°C. ^{1}H-NMR (Me_2SO-d_6) δ 1.05 (d, $J=6.1$ Hz, 3 H, 6′-H), 1.86 (s, 3 H, CH_3), 2.31 (ddd, $J=14.8$ Hz, 6.5 Hz, 2.3 Hz, 1 H, 2′ β-H), 3.04 (dt, $J=14.8$ Hz, 8.0 Hz, 1 H, 2′ α-H), 3.28–3.32 (m, 1 H, 5′-H), 3.73 (dd, $J=8.9$ Hz, 5.1 Hz, 1 H, 4′-H), 4.76 (d, $J=4.1$ Hz, 1 H, 5′-OH), 5.27–5.33 (m, 1 H, 3′-H), 6.18 (dd, $J=8.0$ Hz, 6.5 Hz, 1 H, 1′-H), 8.09 (s, 1 H, 5″-H), 8.47 (s, 1 H, 6-H), 8.51 (s, 1 H, 3″-H), 11.30 (br, 1 H, NH). ^{13}C-NMR (Me_2SO-d_6) δ 12.36 (CH_3), 21.42 (C-6′), 36.42 (C-2′), 58.23 (C-3′), 63.72 (C-5′), 81.76 (C-4′), 83.90 (C-1′), 109.48 (C-5), 137.03 (C-6), 145.89 (C-5″), 150.45 (C-3″) 151.16 (C-2), 163.53 (C-4). FAB MS (*m/z*, %) [glycerol] 308 ($M+1$, 100).

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