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Synthesis of 3-β-D-ribofuranosylpyrazole-1-carboxamide

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Abstract

The synthesis of 3-β-D-ribofuranosylpyrazole-1-carboxamide (**12**) is described. Treatment of glycosyl enaminone **4** with semicarbazide hydrochloride in dioxane afforded three cyclocondensation products, 5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyrazole-1-carboxamide (**5**), 3-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyrazole-1-carboxamide (**6**), and 3(5)-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyrazole (**7**), in 51, 5, and 16% yields, respectively. Compound **5** was gradually converted to **7** at room temperature as a result of the elimination of the carbamoyl group. Treatment of the **4** with hydrochloric acid in methanol at room temperature afforded 3,3-dimethoxy-1-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)propane-1-one (**9**) in 90% yield. Treatment of **9** with semicarbazide afforded the corresponding semicarbazone **10**, which was cyclized in trifluoroacetic acid to afford **6**. Deblocking of **6** with 10% aq ammonia gave **12**.

Keywords: Synthesis; *C*-Nucleoside; Pyrazole-1-carboxamide; glycosyl enaminone

1. Introduction

The synthetic nucleoside analogue, 1-β-D-ribofuranosyl-1,2,4-triazole-3-carboxamide (ribavirin, **1**), possesses broad-spectrum activity against both RNA and DNA viruses in vitro and in vivo [1]. Tiazofurin (2-β-D-ribofuranosylthiazole-4-carboxamide, **2**) and selenazofurin (2-β-D-ribofuranosylselenazole-4-carboxamide, **3**) [2] are two widely studied *C*-nucleosides endowed with several biological effects.

The biological effects of theses *C*-nucleosides, which are structurally related to ribavirin, appear to be due to inhibition of inosine monophosphate dehydrogenase (IMPDH), which induces the shutdown of guanine nucleotide synthesis [3]. These findings prompted us to synthesize pyrazole *C*-nucleoside **12**, which is structurally related to **1**, **2**, and **3**. During the course of our research, we developed a preparative precursor, glycosyl enaminone **4**, and used it in the synthesis of isoxazole [4], pyrazolo[1,5-*a*]-pyrimidine [5], pyrido[2,3-*d*]pyrimidine [6] *C*-nucleosides and 3-β-D-ribofuranosyl-1*H*-pyrazole-4-carboxamide [7]. We report herein the synthesis of **12** from **4** (Scheme 1).

Treatment of **4** with semicarbazide hydrochloride in dioxane at room temperature for 4 days afforded three cyclocondensation products,

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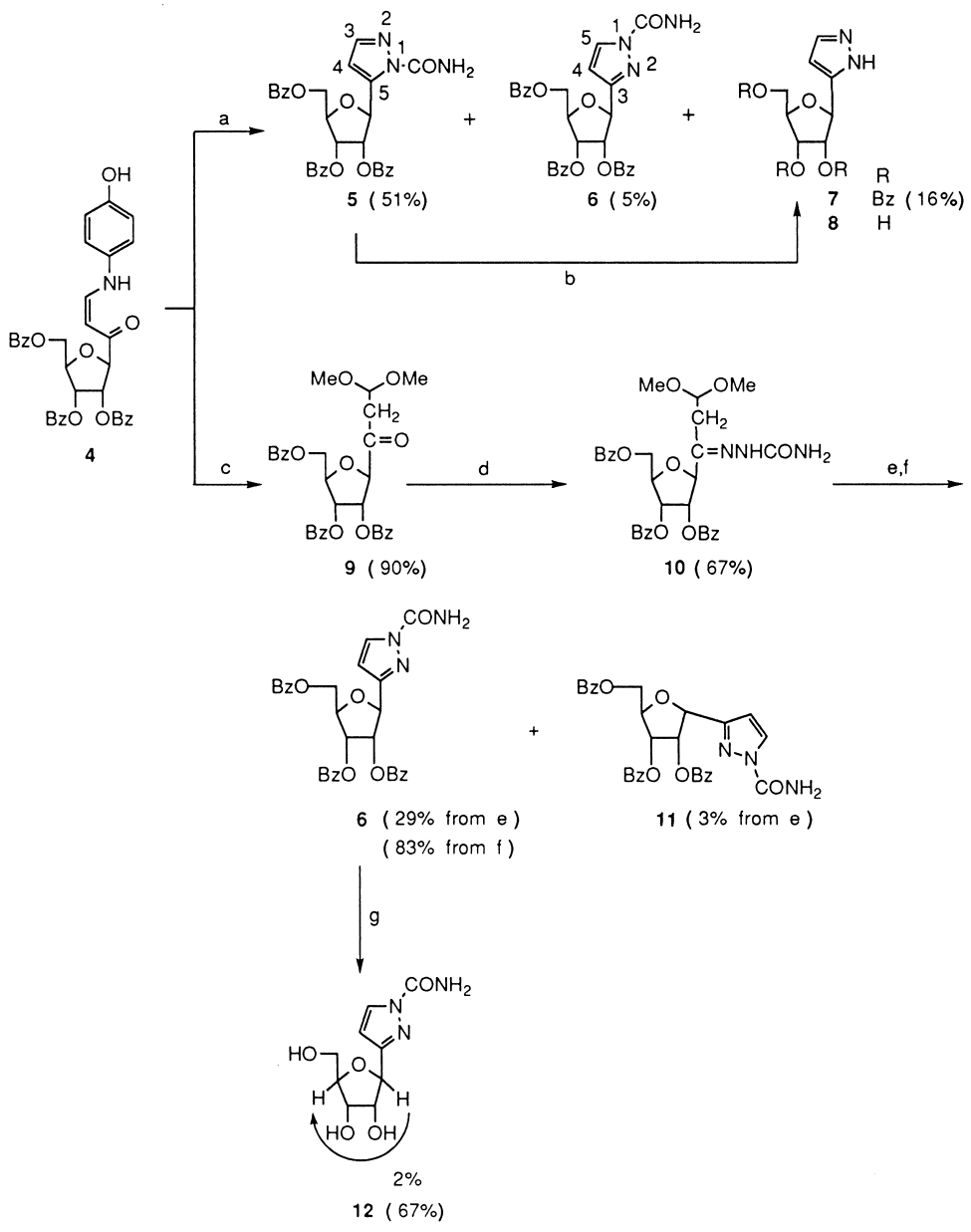
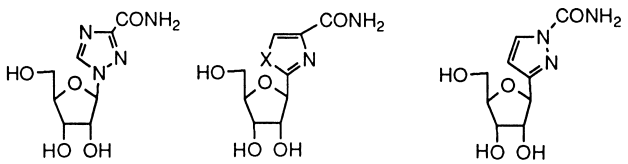


Scheme 1. Reagents and conditions: a. dioxane, $NH_2NHCONH_2$·HCl, r.t., 4 days; b. dioxane, $NH_2NHCONH_2$·HCl, r.t., 5 days; c. MeOH, HCl, r.t., 15 h; d. EtOH, $NH_2NHCONH_2$ HCl, r.t., 5 h; e. dioxane, HCl, r.t., 7 h; f. TFA, r.t., 30 min; g. aq NH_4OH, refrigerator, 3 days.

5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyrazole-1-carboxamide (**5**), 3-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyrazole-1-carboxamide (**6**), and 3(5)-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyrazole (**7**), in 51, 5, and 16% yields, respectively. To ascertain the structures, the position of the ribose group in these compounds (**5** and **6**) was determined by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of compound **6**, the chemical shift of C-3 was found to be 153 ppm, whilst the chemical shift of C-5 in compound **5** was observed at 144 ppm. These values are consistent with the observation that the carbon (C-3 in compound **6**) bonded to a nitrogen atom is deshielded relative to benzene, and occurs further downfield compared with the carbon (C-5 in compound **5**) bonded to an sp^2 nitrogen. In the enaminone system, –N–C=C–C=O, attack can occur at either the β or the carbonyl carbon atoms. The preponderant product **5** would result from preferential reaction at

the β-carbon in the glycosyl enaminone. Compound **5** was gradually converted to **7** [8] at room temperature as a result of the elimination of the carbamoyl group. Deprotection of **5** by base afforded the decarbamoylated pyrazole **8** [8], which was also obtained by reaction of **4** with hydrazine hydrate in good yield. Variation in the reaction temperature, time, and solvent did not improve the yield of compound **6**.

Next, acetalization of the glycosyl enaminone **4** with hydrochloric acid in methanol at room temperature for 12 h afforded 3,3-dimethoxy-1-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)propane-1-one (**9**) in 90% yield after purification by silica gel column chromatography. While acetal **9** gave satisfactory ^{1}H and ^{13}C NMR spectra, it appeared to be unstable. Treatment of acetal **9** with semicarbazide hydrochloride in ethanol at room temperature afforded the corresponding semicarbazone **10** in 67% yield. The semicarbazone **10** was treated with hydrochloric acid in dioxane at room temperature to afford two products These were readily separated by preparative thin-layer chromatography (PTLC) and identified as **6** and its α isomer **11** in a combined yield 32% and in a 10:1 ratio, based on the intensities of the signal for the anomeric and the pyrazole ring protons. The assignments of the anomeric configuration at C-1′ to products **6** and **11** were based on comparison of their ^{1}H NMR spectra. In the β isomers the H-1′ signal is consistently found at higher field than in the corresponding α isomers [9]. The chemical shift of the anomeric proton in compound **11** (δ 5.64) appeared downfield from that of compound **6** (δ 5.38) since the β-face location of this anomeric proton placed it out of the shielding influence of the 2′-oxygen. The anomerization was circumvented by treatment of **10** in trifluoroacetic acid at room temperature. The isolated yield of **6** was routinely 80–90% after purification by silica gel column chromatography, with no trace of the α isomer being observed. The removal of the sugar protecting groups in compound **6** was accomplished with 10% aqueous ammonia to produce 3-β-D-ribofuranosylpyrazole-1-carboxamide (**12**) in 67% yield. The stereochemistry of compound **12** was determined by a nuclear Overhauser effect experiment. Irradiation of the 1′-H signal (δ 4.64) in pyrazole **12** gave a 2% enhancement of the signal at δ 3.77 assignable to the 4′-H. This data indicate that the β-ribofuranoside configuration had been preserved during the reaction sequence.



Ribavirin **12**

2. Experimental

Mass spectra were taken on a Hitachi M-80 instrument by direct insertion at 70 eV; fast-atom-bombardment mass spectra (FABMS) were run on a JMS-HX 110 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured with a JNM-GX-270 or an A-600 (Jeol) spectrometer, with tetramethylsilane as an internal standard. The IR spectrum was measured with a FT/IR-230 (Jasco) spectrometer. UV spectra were recorded with a Shimazu UV-31 00PC spectrophotometer. Optical rotations were measured with a Jasco DIP-370 polarimeter (10 cm cell) at 25 °C. Elemental analyses were carried out by the microanalysis service of the University of Meijo. Analytical TLC was performed on glass plates coated with a 0.5 mm layer of Silica Gel GF_{254} (E. Merck). The compounds were detected by UV light (254 nm).

5- and 3-(2,3,5-Tri-O-*benzoyl*-β-D-*ribofuranosyl)pyrazole-1-carboxamide* (**5**) *and* (**6**)*, 3-(2,3,5-Tri*-O-*benzoyl*-β-D-*ribofuranosyl)pyrazole* (**7**).—To a solution of **4** (103.6 mg, 0.171 mmol) in dioxane (5 mL) was added a solution of semicarbazide hydrochloride (19.1 mg, 0.171 mmol) in 95:5 dioxane–water (5 mL). The mixture was stirred at room temperature for 4 days, and then the reaction mixture was evaporated. TLC (99:1 $CHCl_3$–MeOH) showed that the light yellow syrup contained three major components (R_f 0.31, 0.25, and 0.20). The residue was purified by PTLC with 99:1 $CHCl_3$–MeOH as eluent after three elutions.

Compound **5**. Yield 48.3 mg (51%); R_f 0 31; ^{1}H NMR ($CDCl_3$): δ 7.27–8.07 (m, 16 H, H-3, Ph), 7.11 (br s, 1 H, $CONH_2$, exchanged with D_2O), 6.60 (d, 1 H, $J_{3,4}$ 1.2 Hz, H-4), 6.08 (d, 1 H, $J_{1',2'}$ 2.6 Hz, H-1′), 5.94 (dd, 1 H, $J_{1',2'}$, 2.6, $J_{2',3'}$, 5.1 Hz, H-2′), 5.73 (dd, 1 H, $J_{2',3'}$ 5.1, $J_{3',4'}$ 8.1 Hz, H-3′), 5.44 (br s, 1 H, $CONH_2$, exchanged with D_2O), 4.81 (dd, 1 H, $J_{4',5'a}$ 3.7, $J_{5'a,5'b}$ 12.0 Hz, H-5′b), 4.70 (m, 1 H, H-4′), 4.60 (dd, 1 H, $J_{4',5'a}$ 3.7, $J_{5'a,5'b}$ 12.0 Hz, H-5′a); ^{13}C NMR ($CDCl_3$): δ 78.0, 76.8,

75.7, 71.2 (C-1′, 2′, 3′, 4′), 166.2, 165.3, 165.1 (C=O), 151.4 ($CONH_2$), 144.10 (C-5), 141.3 (C-3), 128.3–133.3 (Ph), 109.1 (C-4), 63.6 (C-5′). Although this compound was homogeneous by TLC, we were unable to obtain proper microanalytical data for it.

Compound **6**. Yield 4.7 mg (5%); R_f 0.25; ^{1}H NMR ($CDCl_3$): δ 8.12 (d, 1 H, $J_{4,5}$ 2.7 Hz, H-5), 7.34–8.06 (m, 15 H, Ph), 6.95 (br s, 1 H, $CONH_2$, exchanged with D_2O), 6.48 (d, 1 H, $J_{4,5}$ 2.7 Hz, H-4), 6.03 (dd, 1 H, $J_{1',2'}=J_{3',4'}$ 5.3 Hz, H-2′), 5.88 (dd, 1 H, $J_{2',3'}=J_{3',4'}$ 5.3 Hz, H-3′), 5.38 (d, 1 H, $J_{1',2'}$ 5.3 Hz, H-1′), 5.34 (br s, 1 H, $CONH_2$, exchanged with D_2O), 4.82 (dd, 1 H, $J_{4',5'a}$ 3.7, $J_{5'a,5'b}$ 12.0 Hz, H-5′b), 4.75 (m, 1 H, H-4′), 4.58 (dd, 1 H, $J_{4',5'a}$ 3.7, $J_{5'a,5'b}$ 12.0 Hz, H-5′a); ^{13}C NMR ($CDCl_3$): δ 166.1, 165.4, 165.3 (C=O), 153.1 (C-3), 150.1 ($CONH_2$), 133.5 (C-5), 128.4–133.3 (Ph), 107.6 (C-4), 80.1, 77.7, 75.3, 72.6 (C-1′, 2′, 3′, 4′), 63.8 (C-5′). Anal. Calcd for $C_{30}H_{25}N_3O_8 \cdot 0.1\ H_2O$: C, 64.65; H, 4.56; N, 7.54. Found: C, 64.38, H, 4.53; N, 7.46.

Compound **7**. Yield 14.0 mg (16%); R_f 0.20; Identity was confirmed by comparing the IR and ^{1}H NMR spectra with the spectra of the product prepared by reaction of **4** with hydrazine hydrate.

3,3-Dimethoxy-1-(2,3,5-tri-O-*benzoyl*-β-D-*ribofuranosyl)propane-1-one* (**9**).—To a solution of **4** (402.2 mg, 0.663 mmol) in MeOH (34 mL) was added concentrated hydrochloric acid (1 mL). The mixture was stirred at room temperature for 15 h, and then the reaction mixture was evaporated to dryness. The residue was chromatographed on a column of silica gel with $CHCl_3$ as eluent. This afforded 335.8 mg (90%) of **9** as a colorless foam; ^{1}H NMR ($CDCl_3$): δ 7.26–8.09 (m, 15 H, Ph), 5.91 (dd, 1 H, $J_{1',2'}=J_{2',3'}$ 5.4 Hz, H-2′), 5.65 (dd, 1 H, $J_{2',3'}=J_{3',4'}$ 5.4 Hz, H-3′), 4.84 (t, 1 H, $J_{2,3}$ 5.5 Hz, H-3), 4.75–4.79 (m, 2 H, H-1′, 5′b), 4.72 (m, 1 H, H-4′), 4.62 (dd, 1 H, $J_{4',5'a}$ 4.4, $J_{5'a,5'b}$ 11.7 Hz, H-5′a), 3.31, 3.29 (each s, each 3 H, CH_3), 3.00 (d, 2 H, $J_{2,3}$ 5.5 Hz, H-2); ^{13}C NMR ($CDCl_3$): δ 203.8 (C-1), 166.2, 164.2 (C=O), 128.2–133.5 (Ph, C-5), 101.3 (C-3), 85.9, 78.0, 72.7, 72.1 (C-1′, 2′, 3′, 4′), 64.0 (C-5′), 53.69, 53.65 (CH_3), 42.4 (C-2). Due to the unstable nature of this compound, a good elemental analysis could not be obtained.

3,3-Dimethoxy-1-(2,3,5-tri-O-*benzoyl*-β-D-*ribofuranosyl)propane-1-one semicarbazone* (**10**).—To a solution of **9** (141.6 mg, 0.252 mmol) in EtOH (11 mL) was added semicarbazide hydrochloride (33.7 mg, 0.302 mmol) at room temperature for 5 h, and then the reaction mixture was evaporated. The residue was chromatographed on a column of silica gel with $CHCl_3$ as eluent. This afforded 105.1 mg (67%) of **10** as a colorless foam; ^{1}H NMR ($CDCl_3$): δ 8.90 (br s, 1 H, NH, exchanged with D_2O), 7.34–8.07 (m, 15 H, Ph), 6.19 (dd, 1 H, $J_{1',2'}=J_{2',3'}$ 5.4 Hz, H-2), 5.83 (dd, 1 H, $J_{2',3'}=J_{3',4'}$ 5.4 Hz, H-3′), 4.82 (d, 1 H, $J_{1',2'}$ 5.4 Hz, H-1′), 4.77 (dd, 1 H, $J_{4',5'a}$ 3.2, $J_{5'a,5'b}$ 12.2 Hz, H-5′b), 4.68 (m, 1 H, H-4′), 4.53 (t, 1 H, $J_{2,3}$ 4.8 Hz, H-3), 4.49 (dd, 1 H, $J_{4',5'a}$ 3.2, $J_{5'a,5'b}$ 12.2 Hz, H-5′a), 3.35, 3.24 (each s, each 3 H, OCH_3), 2.74, 2.59 (each dd, each 1 H, $J_{2a,2b}$ 14.0, $J_{2,3}$ 4.8 Hz, H-2); ^{13}C NMR ($CDCl_3$): δ 166.1, 165.5, 165.3 (C=O), 157.5 ($CONH_2$), 143.9 (C-1), 128.4–133.5 (Ph), 103.1 (C-3), 83.6, 80.0, 72.9, 72.1 (C-1′, 2′, 3′, 4′), 63.7 (C-5′), 54.4, 54.3 (CH_3), 32.7 (C-2). Anal. Calcd for $C_{32}H_{33}N_3O_{10} \cdot H_2O$; C, 60.28; H, 5.53; N, 6.59. Found: C, 60.36, H, 5.33; N, 6.45.

3-(2,3,5-Tri-O-*benzoyl*-β- *and* α-D-*ribofuranosyl)pyrazole-1-carboxamide* (**6** and **11**).—Method A: solution of **10** (70.8 mg, 0.114 mmol) in dioxane (6 mL) containing one drop of concentrated hydrochloric acid was stirred at room temperature for 7 h. After this time, two compounds were detected (TLC) in the reaction mixture that had R_f values of 0.26 and 0.24 (99:1 $CHCl_3$–MeOH), respectively. Water was added, and the mixture was neutralized with satd aq $NaHCO_3$ and then extracted with $CHCl_3$ (3×10 mL). The extracts were combined, washed with water and dried over $MgSO_4$. The extracts, on evaporation, afforded a yellow oil which was separated by PTLC with 99:1 $CHCl_3$–MeOH as eluent after two elutions.

Compound **6**.—R_f 0.26; colorless foam 18.4 mg (29%); Identification was confirmed by comparing IR and ^{1}H NMR spectra.

Compound **11**. R_f 0.24; colorless foam 1.9 mg (3%); ^{1}H NMR ($CDCl_3$): δ 8.14 (d, 1 H, $J_{4,5}$ 2.7 Hz, H-5), 7.29–8.08 (m, 15 H, Ph), 6.99 (br s, 1 H, $CONH_2$, exchanged with D_2O), 6.58 (d, 1 H, $J_{4',5'}$ 2.7 Hz, H-4), 6.10 (dd, 1 H, $J_{1',2'}=J_{2',3'}$ 4.8 Hz, H-2′), 5.93 (dd, 1 H, $J_{2',3'}$ 4.8, $J_{3',4'}$ 6.4 Hz, H-3′), 5.64 (d, 1 H, $J_{1',2'}$ 4.8 Hz, H-1′), 5.07 (br s, 1 H, $CONH_2$, exchanged with D_2O), 4.87 (m, 1 H, H-4′), 4.76 (dd, 1 H, $J_{4',5'a}$ 4.1, $J_{5'a,5'b}$ 11.8 Hz, H-5′b), 4.63 (dd, 1 H, $J_{4',5'a}$ 4.1, $J_{5'a,5'b}$ 11.8 Hz, H-5′a); ^{13}C NMR ($CDCl_3$): δ 166.4, 165.6, 165.3 (C=O), 152.4 (C-3), 150.3 ($CONH_2$), 128.6–133.7 (Ph, C-5), 108.6 (C-4), 79.0, 77.2, 76.5, 73.1 (C-1′, 2′, 3′, 4′), 64.5 (C-5′).

Method B: A solution of **10** (21.6 mg, 0.035 mmol) in trifluoroacetic acid (0.5 mL) was stirred at room temperature for 30 min. Water was added, and the mixture was neutralized with satd aq $NaHCO_3$ and then extracted with $CHCl_3$ (3×10 mL). The extracts were combined, washed with water, and dried over $MgSO_4$. The extracts upon evaporation afforded an oil that was chromatographed on a column of silica gel with $CHCl_3$ as eluent. This afforded 16.1 mg (83%) of **6** as a colorless foam. Identification was confirmed by comparing IR and ^1H NMR spectra.

3-β-D-Ribofuranosylpyrazole-1-carboxamide (**12**).—To a solution of **6** (55.2 mg, 0.099 mmol) in MeOH (4 mL) was added 10% aq NH_4OH (1 mL) at 10 °C for 3 days, and then the reaction mixture was evaporated to dryness. The solid was recrystallized from 2-propanol to give colorless needles of **12**, 16.1 mg (67%); mp 123–124 °C. $[\alpha]_D$ −4.5° (*c* 0.8, MeOH); ^1H NMR [$(CD_3)_2SO$]: δ 8.18 (d, 1 H, $J_{4,5}$ 2.6 Hz, H-5), 7.75 (s, 2 H, $CONH_2$, exchanged with D_2O), 6.53 (d, 1 H, $J_{4,5}$ 2.6 Hz, H-4), 4.73–5.01 (br, 3 H, OH, exchanged with D_2O), 4.64 (d, 1 H, $J_{1',2'}$ 5.7 Hz, H-1′), 4.01 (dd, 1 H, $J_{1',2'}$ 5.7, $J_{2',3'}$ 10.6 Hz, H-2′), 3.91 (dd, 1 H, $J_{2',3'}$ 10.6, $J_{3',4'}$ 5.7 Hz, H-3′), 3.77 (m, 1 H, H-4′), 3.54 (dd, 1 H, $J_{4',5'a}$ 5.3, $J_{5'a,5'b}$ 11.2 Hz, H-5′b), 3.46 (dd, 1 H, $J_{4',5'a}$ 5.3, $J_{5'a,5'b}$ 11.2 Hz, H-5′a); ^{13}C NMR (CD_3OD): δ 156.9 (C-3), 153.0 ($CONH_2$), 130.5 (C-5), 108.0 (C-4), 86.4, 80.5, 77.3, 72.9 (C-1′, 2′, 3′, 4′), 63.5 (C-5′). FABMS (nitrobenzyl alcohol as matrix). Found: $[M+H]^+$ *m/z* 244.0933. Calcd for $C_9H_{14}N_3O_5$ [M + H] 244.0948. Anal. Calcd for $C_9H_{13}N_3O_5 \cdot 0.75\ H_2O$: C, 42.11; H, 5.69; N, 16.37. Found: C, 42.49, H, 5.39; N, 15.80.

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