

C-NUCLEOSIDES. 24.<sup>1</sup> SYNTHESIS OF PYRAZOLO[1,5-*a*]PYRIMIDINE  
C-NUCLEOSIDE THROUGH CYCLOCONDENSATION OF ENAMINONE  
GLYCOSIDE WITH AMINOPYRAZOLES

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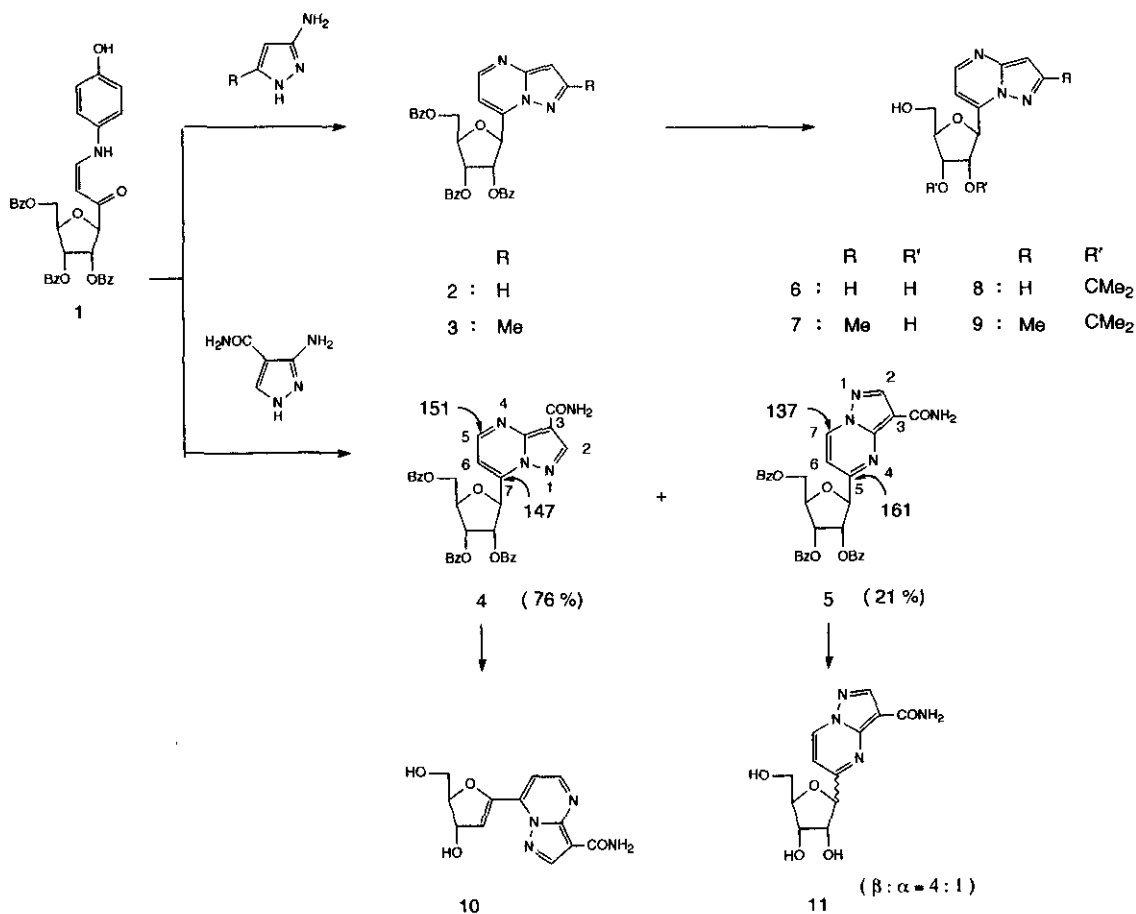
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**Abstract**- A versatile intermediate enaminone glycoside (1) for  
C-nucleoside synthesis was treated with aminopyrazoles to give  
pyrazolo[1,5-*a*]pyrimidine C-nucleosides.

In the last 20 years, a number of papers and patents dealing with the chemistry or biological activity of pyrazolo[1,5-*a*]pyrimidines have been reported.<sup>2</sup> Robins<sup>3</sup> and his collaborators have synthesized *N*-nucleoside analogue of pyrazolo[1,5-*a*]pyrimidine. Despite this, no *C*-nucleoside related to the ring system has previously been synthesized. Recent report from our laboratory have described the preparation of a functionalized *C*-glycoside, 1-(2,3,5-tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)-3-(4-hydroxy)anilino-2-propen-1-one (1), and its utilization in the synthesis of isoxazole<sup>4</sup> and quinoline<sup>1</sup> *C*-nucleosides. Since our interest in enaminone glycoside (1) continues, we now describe the cyclocondensation of aminopyrazoles with 1 to pyrazolo[1,5-*a*]pyrimidine *C*-nucleosides.

Cyclocondensation of enaminone glycoside (1) with 3-aminopyrazole in acetic acid gave 7-(2,3,5-tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)pyrazolo[1,5-*a*]pyrimidine (2) in 98% yield. When the same reaction of 1 with 3-amino-5-methylpyrazole was performed, 7-(2,3,5-tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)-2-methylpyrazolo[1,5-*a*]pyrimidine (3) was obtained in 81% yield. However, the reaction of 1 with 3-amino-4-pyrazolecarboxamide, two cyclocondensation products, 7-(2,3,5-tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxamide (4) and isomeric

5-ribofuranosyl compound (5) were isolated in yields of 76% and 21%, respectively. The position of the ribose group in these compounds was determined by  $^{13}\text{C}$  nmr spectra.<sup>5</sup> In the  $^{13}\text{C}$  nmr spectrum of compound (4), the chemical shift of C-5 was found to be 150.9 ppm, whilst the chemical shift of C-7 in compound (5) was observed at 136.8 ppm. These values are consistent with the observation that the carbon (C-5 in compound 4) bonded to nitrogen atom is deshielded relative to benzene, and occurs further downfield compared with the carbon (C-7 in compound 5) bonded to bridgehead nitrogen. Debenzoylation of compounds (2 and 3) with methanolic sodium carbonate afforded the deprotected compounds (6 and 7). The assignments of anomeric configuration of compounds (6 and 7) were made on the basis of the difference in the chemical shifts of the two methyl signals of the corresponding 2',3'-*O*-isopropylidene derivatives (8 and 9). The  $^1\text{H}$  nmr chemical shift differential value ( $\Delta\delta$ ) of the methyl groups in the isopropylidene derivatives is indicative of  $\beta$  stereochemistry in accordance with the Imbach's rule<sup>6</sup> ( $<0.15$  and  $>0.15$  ppm for the  $\alpha$  and  $\beta$  anomers, respectively).



From the  $^{13}\text{C}$  nmr spectra, it was observed that the shifts for the three carbons of the 2',3'-*O*-isopropylidene group of 8 and 9 show approximately in the  $\beta$  range<sup>7</sup> ( $25.5 \pm 0.2$ ,  $27.5 \pm 0.2$ , and  $114.5 \pm 0.6$ ) (see Experimental). This indicates that the  $\beta$ -ribofuranoside configuration had been preserved during the reaction sequence. However, the removal of the sugar protecting groups in 4 with alkaline afforded 7-dihydrofuran compound (10) in 97% yield. Structure assignment of 10 was obtained by the  $^1\text{H}$  nmr spectrum, which exhibited the signal of an olefinic proton at  $\delta$  7.10 ( $J_{2',3'}=4.0$  Hz). Several instances of *C*-glycosyl compounds containing a dihydrofuran moiety have been reported where side reactions gave furan derivatives.<sup>8</sup> The deprotection of 5 with alkaline afforded 5-( $\beta$ -D-ribofuranosyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxamide (11) and  $\alpha$  isomer in a combined yield of 51% and a 4:1 ratio, based on the intensities of the signals for the anomeric and the pyrazolopyrimidine ring protons. The assignment of the anomeric configuration at C-1' to 11 was based on the  $^1\text{H}$  nmr spectrum. In the  $\beta$  isomer the H-1' signal is consistently found at higher field than in the corresponding  $\alpha$  isomer.<sup>9</sup> These isomers could not be separated by preparative tlc.

## EXPERIMENTAL

Mass spectra were taken on a Hitachi M-80 instrument by direct insertion at 70 eV; fast-atom bombardment (FAB) mass spectra were run on a JMS-HX 110 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were measured with a JNM-GX-270 or an A-600 (JEOL) spectrometer, with tetramethylsilane as an internal standard. *J* Values are given in Hz. Analytical tlc was performed on glass plates coated with a 0.5-mm layer of silica gel GF<sub>254</sub> (Merck). The compounds were detected by uv light (254 nm).

7-(2,3,5-Tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)pyrazolo[1,5-*a*]pyrimidine (2). A solution of compound (1) (81.3 mg, 0.14 mmol) and 3-aminopyrazole (22.3 mg, 0.27 mmol) in acetic acid (3 ml) was heated at 50 °C for 2 h. Acetic acid was removed under reduced pressure and the residue was chromatographed over a column of silica gel with chloroform-hexane (5:1) as eluent. This afforded 73.9 mg (98%) of compound (2) as colorless crystals; mp 110-111 °C (from methanol);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  4.67 (1 H, dd,  $J=12.2, 3.9$ , 5'-Ha), 4.86 (1 H, m, 4'-H), 4.95 (1 H, dd,  $J=12.2, 3.0$ , 5'-Hb), 5.85

(1 H, dd,  $J=7.4$ , 5.3, 3'-H), 6.04 (1 H, d,  $J=3.5$ , 1'-H), 6.11 (1 H, dd,  $J=5.3$ , 3.5, 2'-H), 6.75 (1 H, d,  $J=2.4$ , 3-H), 7.13 (1 H, d,  $J=4.0$ , 6-H), 7.29-8.10 (16 H, m, ArH, 2-H), 8.38 (1 H, d,  $J=4.0$ , 5-H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ )  $\delta$  63.1 (C-5'), 71.6, 74.1, 78.2, 79.2 (C-1', -2', -3', -4'), 97.3 (C-3), 104.8 (C-6), 128.4-133.5 (Ar-C), 144.8 (C-2), 148.8 (C-5), 149.0 (C-3a, -7), 165.0, 165.2, 166.2 (C=O); FABms (nitrobenzyl alcohol as matrix) Found:  $[\text{M}+\text{H}]^+$   $m/z$  564.1804. Calcd for  $\text{C}_{32}\text{H}_{26}\text{N}_3\text{O}_7$ ;  $[\text{M}+\text{H}]$ , 564.1771. Anal. Calcd for  $\text{C}_{32}\text{H}_{25}\text{N}_3\text{O}_7$ ; C, 68.20; H, 4.47; N, 7.46. Found: C, 68.21; H, 4.44; N, 7.48.

7-(2,3,5-Tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)-2-methylpyrazolo[1,5-*a*]pyrimidine (3). A solution of compound (1) (101.6 mg, 0.17 mmol) and 3-amino-5-methylpyrazole (19.5 mg, 0.2 mmol) in acetic acid (10 ml) was stirred at room temperature for 12 h. Acetic acid was removed under reduced pressure and the residue was chromatographed over a column of silica gel with chloroform as eluent. This afforded 78.4 mg (81%) of compound (3) as a foam;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  2.31 (3 H, s, Me), 4.68 (1 H, dd,  $J=12.5$ , 4.4, 5'-Ha), 4.86 (1 H, m, 4'-H), 4.93 (1 H, dd,  $J=12.5$ , 3.7, 5'-Hb), 5.85 (1 H, t,  $J=5.4$ , 3'-H), 6.01 (1 H, d,  $J=4.4$ , 1'-H), 6.07 (1 H, t,  $J=4.4$ , 2'-H), 6.49 (1 H, s, 3-H), 7.02 (1 H, d,  $J=4.4$ , 6-H), 7.32-8.09 (15 H, m, ArH), 8.31 (1 H, d,  $J=4.4$ , 5-H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ )  $\delta$  14.4 (Me), 63.4 (C-5'), 71.9, 74.2, 78.0, 79.5 (C-1', -2', -3', -4'), 96.4 (C-3), 103.7 (C-6), 128.4-133.5 (Ar-C), 144.4 (C-7), 148.5 (C-5), 149.7 (C-3a), 155.1 (C-2), 164.9, 165.3, 166.2 (C=O). FABms (nitrobenzyl alcohol as matrix) Found:  $[\text{M}+\text{H}]^+$   $m/z$  578.1903. Calcd for  $\text{C}_{33}\text{H}_{28}\text{N}_3\text{O}_7$ ;  $[\text{M}+\text{H}]$ , 578.1928.

7-(2,3,5-Tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxamide (4) and 5-(2,3,5-Tri-*O*-benzoyl- $\beta$ -D-ribofuranosyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxamide (5). A solution of compound (1) (25.5 mg, 0.04 mmol) and 3-amino-4-pyrazolocarboxamide hemisulfate (8.8 mg, 0.05 mmol) in acetic acid (2 ml) was heated at 50 °C for 7 h. Acetic acid was removed under reduced pressure and the residue was chromatographed over a column of silica gel with chloroform-hexane (3:1) as eluent. The first compound eluted, 4 (19.3 mg, 76%), was obtained as colorless crystals; mp 118-120 °C (from isopropanol);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  4.69 (1 H, dd,  $J=12.3$ , 3.9, 5'-Ha), 4.87 (1 H, m, 4'-H), 4.97 (1 H, dd,  $J=12.3$ , 3.0, 5'-Hb), 5.65 (1 H, br s, NH exchanges with  $\text{D}_2\text{O}$ ), 5.86 (1 H, t,  $J=5.1$ , 3'-H), 6.00 (1 H, t,  $J=5.1$ , 2'-H), 6.09 (1 H, d,  $J=5.1$ , 1'-H), 7.29 (1 H, d,  $J=4.4$ , 6-H), 7.34-8.11 (15 H, m, ArH), 7.83 (1 H, br s, NH exchanges with  $\text{D}_2\text{O}$ ), 8.52 (1 H, d,  $J=4.4$ , 5-H), 8.54 (1 H, s, 2-H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ )  $\delta$  63.2 (C-5'), 72.0, 74.5, 77.4, 78.0 (C-1', -2', -3', -4'), 105.7 (C-3), 106.0 (C-6), 128.4-133.6 (Ar-C), 146.5, 147.0 (C-3a, -7), 146.7, (C-2), 150.9 (C-5), 163.6, 165.0, 165.3, 166.1 (C=O); FABms (nitrobenzyl alcohol as matrix) Found:  $[\text{M}+\text{H}]^+$   $m/z$  607.1871. Calcd for  $\text{C}_{33}\text{H}_{27}\text{N}_4\text{O}_8$ ;  $[\text{M}+\text{H}]$ , 607.1829. Anal. Calcd for  $\text{C}_{33}\text{H}_{26}\text{N}_4\text{O}_8 \cdot 1/2\text{H}_2\text{O}$ ; C, 64.39; H, 4.42; N, 9.10. Found: C,

64.33; H, 4.33; N, 9.08.

Compound (5) was eluted as the second fraction (5.2 mg, 21%) as foam;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  4.55 (1 H, dd,  $J=12.3, 3.2$ , 5'-Ha), 4.87 (1 H, m, 4'-H), 4.98 (1 H, dd,  $J=12.3, 3.0$ , 5'-Hb), 5.43 (1 H, d,  $J=5.9$ , 1'-H), 5.65 (1 H, br s, NH exchanges with  $\text{D}_2\text{O}$ ), 5.87 (1 H, t,  $J=5.9$ , 3'-H), 6.19 (1 H, t,  $J=5.9$ , 2'-H), 7.25 (1 H, d,  $J=6.9$ , 6-H), 7.31-8.04 (16 H, m, ArH, NH exchanges with  $\text{D}_2\text{O}$ ), 8.62 (1 H, d,  $J=6.9$ , 7-H), 8.62 (1 H, s, 2-H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ )  $\delta$  63.4 (C-5'), 72.7, 74.9, 81.2, 82.3 (C-1', -2', -3', -4'), 105.1 (C-3), 106.9 (C-6), 128.3-133.7 (Ar-C), 136.8 (C-7), 145.2 (C-3a), 147.6 (C-2), 160.8 (C-5), 164.4, 165.2, 165.5, 166.0 (C=O). FABms (nitrobenzyl alcohol as matrix) Found:  $[\text{M}+\text{H}]^+$   $m/z$  607.1893. Calcd for  $\text{C}_{33}\text{H}_{27}\text{N}_4\text{O}_8$ ;  $[\text{M}+\text{H}]$ , 607.1829.

**General Procedure for the Deprotection.** Sufficient methanolic sodium carbonate (0.5 ml, 0.4 mmol) was added to the protected C-nucleoside (0.04 mmol) in methanol (2 ml). The mixture was kept at room temperature for 5 h, and evaporated under reduced pressure. The residue was purified by plc to afford the free C-nucleoside.

7-( $\beta$ -D-Ribofuranosyl)pyrazolo[1,5-a]pyrimidine (6). colorless needles, mp 161-164 ° C (from isopropanol), 64%;  $^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ )  $\delta$  3.79 (1 H, dd,  $J=12.3, 3.7$ , 5'-Ha), 3.94 (1 H, dd,  $J=12.3, 2.5$ , 5'-Hb), 4.07-4.17 (2 H, m, 3', 4'-H), 4.34 (1 H, dd,  $J=3.7, 4.7$ , 2'-H), 5.51 (1 H, d,  $J=3.7$ , 1'-H), 6.75 (1 H, d,  $J=2.4, 3$ -H), 7.34 (1 H, d,  $J=4.0, 6$ -H), 8.21 (1 H, d,  $J=2.4, 2$ -H), 8.53 (1 H, d,  $J=4.0, 5$ -H);  $^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ )  $\delta$  60.5 (C-5'), 70.3, 74.3, 79.5, 83.0 (C-1', -2', -3', -4'), 96.3 (C-3), 105.3 (C-6), 144.4 (C-2), 147.9, 148.4 (C-3a, -7), 149.6 (C-5). FABms (nitrobenzyl alcohol as matrix) Found:  $[\text{M}+\text{H}]^+$   $m/z$  252.0994. Calcd for  $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_4$ ;  $[\text{M}+\text{H}]$ , 252.0984. Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{N}_4\text{O}_4$ ; C, 52.58; H, 5.22; N, 16.72. Found: C, 52.26; H, 5.30; N, 16.80.

7-( $\beta$ -D-Ribofuranosyl)-2-methylpyrazolo[1,5-a]pyrimidine (7). foam, 92%;  $^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ )  $\delta$  2.51 (3 H, s, Me), 3.78 (1 H, dd,  $J=12.3, 3.7$ , 5'-Ha), 3.93 (1 H, dd,  $J=12.3, 2.7$ , 5'-Hb), 4.10-4.18 (2 H, m, 3', 4'-H), 4.38 (1 H, t,  $J=4.4, 2$ '-H), 5.40 (1 H, d,  $J=4.4, 1$ '-H), 6.53 (1 H, s, 3-H), 7.21 (1 H, d,  $J=4.4, 6$ -H), 8.45 (1H, d,  $J=4.4, 5$ -H);  $^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ )  $\delta$  14.4 (Me), 62.9 (C-5'), 72.7, 75.4, 82.1, 86.0 (C-1', -2', -3', -4'), 96.7 (C-3), 106.5 (C-6), 148.6 (C-7), 150.6 (C-5), 150.8, (C-3a), 156.3 (C-2). FABms (nitrobenzyl alcohol as matrix) Found:  $[\text{M}+\text{H}]^+$   $m/z$  266.1129. Calcd for  $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_4$ ;  $[\text{M}+\text{H}]$ , 266.1141.

7-(2,3-O-Isopropylidene- $\beta$ -D-ribofuranosyl)pyrazolo[1,5-a]pyrimidine (8). To a solution of deprotected C-nucleoside (6) (8.1 mg, 0.03 mmol) in acetone (1 ml) was added PTSA (5 mg) and the mixture was stirred at room temperature for 4 h. The reaction mixture was neutralized with saturated sodium hydrogen carbonate solution, and the solvent was evaporated. The residue was purified by plc with  $\text{CHCl}_3$ -MeOH (9:1) as eluent. This afforded 6.1 mg of

compound (8): foam, 65% ;  $^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ )  $\delta$  1.35, 1.63 (each 3 H, each s, isopropylidene Me), 3.75 (1 H, dd,  $J=12.1$ , 5.1, 5'-Ha), 3.83 (1 H, dd,  $J=12.1$ , 3.7, 5'-Hb), 4.31 (1 H, q,  $J=3.4$ , 4'-H), 4.77 (1 H, dd,  $J=3.4$ , 6.4, 3'-H), 4.94 (1 H, dd,  $J=3.4$ , 6.4, 2'-H), 5.60 (1 H, d,  $J=3.4$ , 1'-H), 6.76 (1 H, d,  $J=2.4$ , 3-H), 7.26 (1 H, d,  $J=4.4$ , 6-H), 8.20 (1 H, d,  $J=2.4$ , 2-H), 8.52 (1 H, d,  $J=4.4$ , 5-H);  $^{13}\text{C}$  nmr( $\text{CD}_3\text{OD}$ )  $\delta$  25.7, 27.8 (isopropylidene Me), 63.3 (C-5'), 82.9, 83.1, 85.6, 87.7 (C-1', -2', -3', -4'), 97.6 (C-3), 106.7 (C-6), 115.5 (isopropylidene  $\text{C}_{\text{quat}}$ ), 145.9 (C-2), 148.5, 150.2 (C-3a, -7), 150.7 (C-5).

7-(2,3-*O*-Isopropylidene- $\beta$ -D-ribofuranosyl)-2-methylpyrazolo[1,5-*a*]pyrimidine (9). Compound (9) was prepared from compound (7) as described above for compound (8); foam, 43%;  $^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ )  $\delta$  1.36, 1.63 (each 3 H, each s, isopropylidene Me), 2.51 (3 H, s, Me), 3.76 (1 H, dd,  $J=11.7$ , 4.4, 5'-Ha), 3.84 (1 H, dd,  $J=11.7$ , 3.7, 5'-Hb), 4.31 (1 H, m, 4'-H), 4.82 (1 H, dd,  $J=3.7$ , 6.6, 3'-H), 4.98 (1 H, dd,  $J=3.7$ , 6.6, 2'-H), 5.50 (1 H, d,  $J=3.7$ , 1'-H), 6.54 (1 H, s, 3-H), 7.14 (1 H, d,  $J=4.4$ , 6-H), 8.44 (1 H, d,  $J=4.4$ , 5-H);  $^{13}\text{C}$  nmr( $\text{CD}_3\text{OD}$ )  $\delta$  14.4 (Me), 25.7, 27.8 (isopropylidene Me), 63.3 (C-5'), 83.0, 83.5, 85.1, 87.5 (C-1', -2', -3', -4'), 96.8 (C-3), 106.4 (C-6), 115.4 (isopropylidene  $\text{C}_{\text{quat}}$ ), 147.5 (C-7), 150.4 (C-5), 150.9 (C-3a), 156.5 (C-2).

7-(1,4-Anhydro-2-deoxy-D-erythro-pent-1-enofuranosyl)pyrazolo[1,5-*a*]-pyrimidine-3-carboxamide (10). Compound (10) was prepared from compound (4) as described above for compound (6): pale yellow foam, 97%;  $^1\text{H}$  nmr [ $(\text{CD}_3)_2\text{SO}$ ]  $\delta$  3.59 (2 H, d,  $J=4.0$ , 5'-H), 4.42 (1 H, q,  $J=4.0$ , 4'-H), 4.96 (1 H, t,  $J=4.0$ , 3'-H), 5.06 (1 H, br s, OH exchanges with  $\text{D}_2\text{O}$ ), 5.62 (1 H, br s, OH exchanges with  $\text{D}_2\text{O}$ ), 7.10 (1 H, d,  $J=4.0$ , 2'-H), 7.51 (1 H, d,  $J=4.4$ , 6-H), 7.59 (2 H, br, NH exchanges with  $\text{D}_2\text{O}$ ), 8.70 (1 H, s, 2-H), 8.87 (1 H, d,  $J=4.4$ , 5-H);  $^{13}\text{C}$  nmr [ $(\text{CD}_3)_2\text{SO}$ ]  $\delta$  61.3 (C-5'), 74.7, 88.7 (C-3', -4'), 105.1 (C-3), 107.1 (C-6), 116.1 (C-2'), 136.8 (C-1'), 145.8 (C-2), 146.3, 146.5 (C-3a, -7), 151.4 (C-5), 162.5 (C=O). FABms (nitrobenzyl alcohol as matrix) Found:  $[\text{M}+\text{H}]^+$   $m/z$  277.0945. Calcd for  $\text{C}_{12}\text{H}_{13}\text{N}_4\text{O}_4$ ;  $[\text{M}+\text{H}]$ , 277.0937.

5-( $\alpha$ - and  $\beta$ -D-Ribofuranosyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxamide (11).

Compound (11) was prepared from compound (5) as described above for compound (6): foam, 51%;  $^1\text{H}$  nmr [ $(\text{CD}_3)_2\text{SO}$ ]  $\delta$  3.49-3.72 (2 H, m, 5'-H), 3.94-3.98 (8/5 H, m, 3' $\beta$ -H, 4' $\beta$ -H), 4.04 (4/5 H, t,  $J=5.4$ , 2' $\beta$ -H), 4.04 (1/5 H, 4' $\alpha$ -H), 4.12 (1/5 H, dd,  $J=4.2$ , 8.1, 3' $\alpha$ -H), 4.31 (1/5 H, t,  $J=4.2$ , 2' $\alpha$ -H), 4.79 (4/5 H, d,  $J=5.4$ , 1' $\beta$ -H), 5.12 (1/5 H, d,  $J=4.2$ , 1' $\alpha$ -H), 5.41 (br s, OH exchanges with  $\text{D}_2\text{O}$ ), 7.23 (1/5 H, d,  $J=7.3$ , 6 $\alpha$ -H), 7.44 (4/5 H, d,  $J=7.3$ , 6 $\beta$ -H), 7.48, 7.51 (br s, NH exchanges with  $\text{D}_2\text{O}$ ), 8.50 (1/5 H, s, 2 $\alpha$ -H), 8.52 (4/5 H, s, 2 $\beta$ -H), 9.19 (1/5 H, d,  $J=7.3$ , 5 $\alpha$ -H), 9.26 (4/5 H,  $J=7.3$ , 5 $\beta$ -H);  $^{13}\text{C}$  nmr [ $(\text{CD}_3)_2\text{SO}$ ]  $\delta$  61.4 (C-5'),

71.3, 76.9, 84.3, 85.4 (C-1', -2', -3', -4'), 104.7 (C-3), 107.1 (C-6), 137.5 (C-7), 144.7 (C-3a), 146.1 (C-2), 162.6 (C-5), 164.4 (C=O). FABms (glycerol as matrix) Found:  $[M+H]^+$   $m/z$  295.1042. Calcd for  $C_{12}H_{15}N_4O_5$ ;  $[M+H]$ , 295.1042.

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