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TOTAL, ASYMMETRIC SYNTHESIS OF (1*R*)-1-C-(6'-AMINO-7'H-PURIN-8'-YL)-1,4-ANHYDRO-3-AZIDO-2,3-DIDEOXY-D-*erythro*-PENTITOL.[1]

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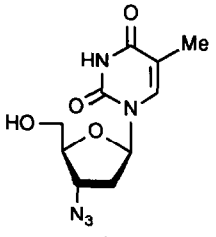
Summary: *The "naked sugar" (+)-(1*R,2R,*4*R*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-*yl acetate* ((+)-**3**) *was converted in ten synthetic steps into the new C-nucleoside (1*R*)-1-C-(6'-amino-7'H-purin-8'-yl)-1,4-anhydro-3-azido-2,3-dideoxy-D*-erythro-*pentitol* ((+)-**2**) in 19% overall yield.

As a result of the considerable anti-HIV activity shown by AZT[2,3] (3'-azido-3'-deoxythymidine: **1**) there has recently been a big surge of interest in the synthesis of deoxygenated nucleoside analogues bearing an azido group on their sugar moiety.[4-6] The C-nucleosides have also attracted a wide interest because of their biological activity.[7,8] Recently, Watanabe and co-workers[9] reported the synthesis of 1-methyl-5-(3-azido-2,3-dideoxy-β-D-*erythro*-pentafuranosyl)uracil, a C-nucleoside isostere of AZT. We present here a highly stereoselective synthesis of the new azido C-nucleoside (1*R*)-1-C-(6'-amino-7'H-purin-8'-yl)-1,4-anhydro-3-azido-2,3-dideoxy-D-*erythro*-pentitol ((+)-**2**) which was obtained by condensation of 4,5,6-triaminopyrimidine with the dimethyl acetal of 2,5-anhydro-3-azido-3,4-dideoxy-L-*ribo*-hexouronic acid. The latter compound was synthesized in six steps from the "naked sugar" ((+)-**3**[10] ((+)-(1*R*,2*R*,4*R*)-2-*endo*-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl acetate)[11] following a similar approach to that we had developed in this laboratory for the total syntheses of 2,5-anhydro-3-deoxy-D-*ribo*-hexonic acid and related 2'-deoxyadenosine ((+)-**4**).[12]



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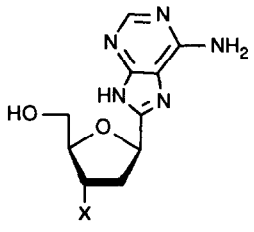
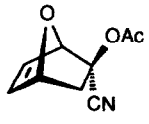


(+)-**2** X=N_3
(+)-**4** X=OH

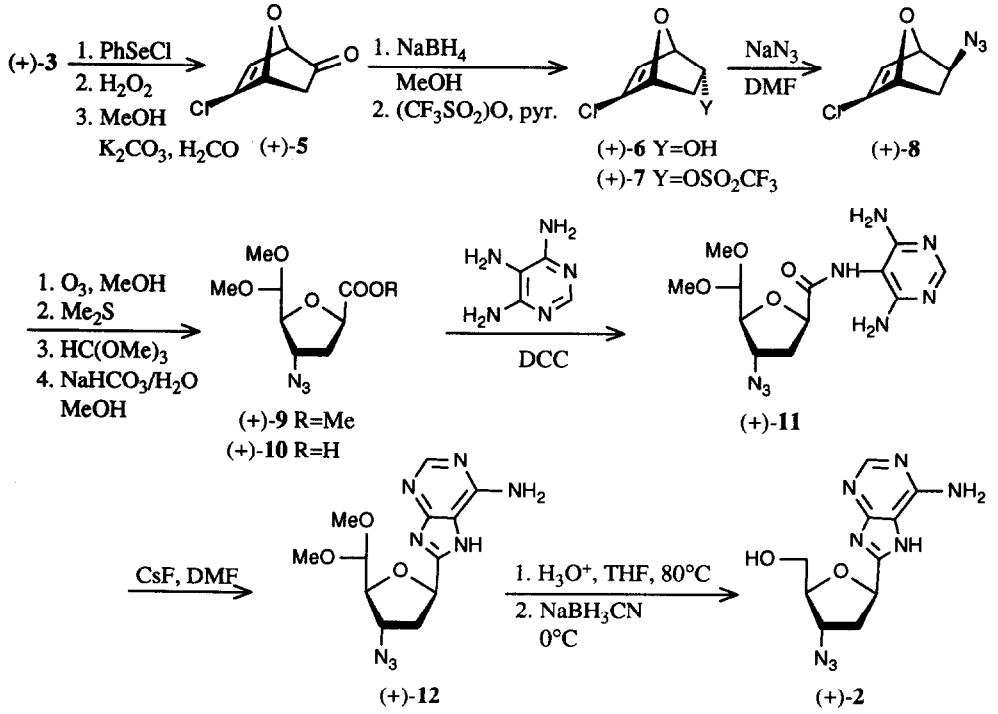


(+)-**3**

Results and Discussion

The one-pot transformation of the "naked sugar" (+)-**3** into the chloro-enone (+)-**5**[13] was achieved in 89% yield via addition of benzeneselenyl chloride, oxidative elimination of the PhSe moiety with H_2O_2, and saponification. Reduction of the ketone (+)-**5** with $NaBH_4$ in MeOH at -10°C afforded the *endo*-alcohol (+)-**6**, treatment of which with $(CF_3SO_2)_2O$ and pyridine gave the triflate (+)-**7**.[12] S_N2 displacement of the triflate group by NaN_3 in anhydrous DMF gave the corresponding *exo*-azido derivative (+)-**8** in 93% yield. Ozonolysis of (+)-**8** in anhydrous MeOH (-80°C) followed by work-up with Me_2S and $HC(OMe)_3$ afforded the dimethylacetal of the hexouronate (+)-**9** (93%). Saponification of (+)-**9** with $NaHCO_3$ in aqueous methanol (20°C, 11 days) gave (+)-**10** (71%; on heating or/and using Na_2CO_3 or NaOH instead of $NaHCO_3$ led to lower yield) whose condensation with 4,5,6-triaminopyrimidine in the presence of N,N'-dicyclohexylcarbodiimide in CH_3CN led to the amide (+)-**11** (86%). An alternative lower yielding (71%) method of preparation of (+)-**11** involved the treatment of (+)-**10** first with ClCOOEt and Et_3N, followed by the addition of 4,5,6-triaminopyrimidine in THF/DMF.

Scheme



All attempts to dehydrate (+)-**11** into the corresponding 6-amino-7H-purin-8-yl system under acidic conditions (H_2SO_4, heating) failed and led to polymeric material. Fortunately, heating (+)-**11** in anhydrous DMF in the presence of an excess of anhydrous CsF (130°C, 20 h) afforded (+)-**12** in 97% yield. Acidic

hydrolysis (H_2SO_4, THF, H_2O) of the dimethyl acetal (+)-**12** liberated the corresponding aldehyde which was reduced, without isolation, using $NaBH_3CN$ at 0°C to give the new C-nucleoside (+)-**2** in 74% yield after purification by flash chromatography.

The structure of all the new compounds ((+)-**2**, (+)-**8** - (+)-**12**) presented here was established by their elemental analysis, spectral data, mode of formation, and reactivity. The relative *exo* configuration of the azido group in (+)-**8** was confirmed by the absence of vicinal coupling constant between the proton H-C(5) and the bridgehead proton H-C(4).[14] Confirmation that no epimerization had taken place at the "anomeric centre" of (+)-**2** was established by its CD spectrum which showed a positive Cotton Effect, near 260 nm, analogous with the CD spectrum of 2'-deoxy-adenosine-C ((+)-**4**), Cordycepin-C[15] and other related C-nucleosides.[12] Furthermore, typical W type ^4J coupling constant of 1.5 to 2 Hz were measured between the protons at C(2) and C(5) in (+)-**10**, (+)-**11** and (+)-**12**, and between the protons H-C(1) and H-C(4) in (+)-**2**, respectively.

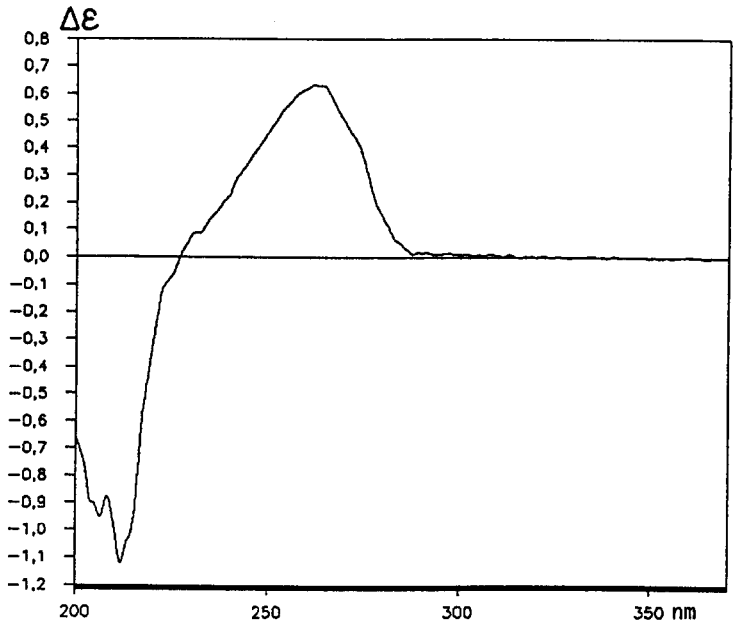


Figure. CD spectrum of (+)-**2** measured in 95% EtOH

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Experimental Part

General remarks, see ref. 16. CD spectra were measured with Auto-dichrography Mark V (Jobin-Yvon) instrument. Optical rotations, were measured with Perkin-Elmer 241 and JASCO DIP-370 polarimeters. All our ^{1}H-NMR spectral attributions were confirmed by double irradiation experiments. FC (flash column chromatography) were run on silica gel (Merck 0.040-0.063 mm).

(1*R*,4*R*)-5-Chloro-7-oxabicyclo[2.2.1]hept-5-en-2-one ((+)-**5**). Prepared form (+)-(1*R*,2*R*,4*R*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl acetate ((+)-**3**, 11.2 g, 62.5 mmol) by the procedure of Warm et al.[13] Yield: 7.76 g (89%). $[\alpha]^{25}_{589}$ = +862 (c = 2.03, CH_2Cl_2); lit.[13]: $[\alpha]^{25}_{589}$ = +817.5 (c = 2.38, CH_2Cl_2).

(1*R*,4*R*,5*S*)-5-*Exo*-Azido-2-chloro-7-oxabicyclo[2.2.1]hept-2-ene ((+)-**8**). A mixture of triflate (+)-**7** (derived from (+)-**5** according to ref. 12; 2.06 g, 12.01 mmol), anhydrous DMF (18 mL) and NaN_3 (2.6 g, 40 mmol) was stirred at 20°C for 6 h. The mixture was poured into Et_2O (250 mL) and the solution was washed with H_2O (80 mL, twice). After drying ($MgSO_4$), the solvent was distilled off under reflux and reduced pressure, yielding 1.21 g (95.5%) of a yellowish oil which was decomposed quickly on standing at 20°C. IR ($CHCl_3$) ν: 3000, 2096, 1592, 1448, 1328, 1245, 1176, 1031, 1002, 934, 889, 852, 639, 618 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 6.08 (d, J = 2.0 Hz, H-C(3)); 4.95 (dd, ^3J = 2.0, ^4J = 1.0 Hz, H-C(4)); 4.79 (dd, ^3J = 4.5, ^4J = 1.0 Hz, H-C(1)); 3.49 (dd, ^3J = 7.0, 2.5 Hz, H-C(5)); 2.0 (dd, ^2J = 12.5, ^3J = 7.0, H_{endo}-C(6)); 1.8 (ddd, ^2J = 12.5, ^3J = 4.5, 2.5 Hz, H_{exo}-C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 142.3 (s, C(2)); 126.7 (d, ^1J(C,H) = 180 Hz, C(3)); 84.6 (d, ^1J(C,H) = 170 Hz, C(4)); 80.9 (d, ^1J(C,H) = 179 Hz, C(1)); 59.7 (d, ^1J(C,H) = 155 Hz, C(5)); 31.8 (t, ^1J(C,H) = 135 Hz, C(6)). MS (CI, NH_3) m/z: 245 (2), 243 (3), 315 (2), 266 (1), 241 (4), 212 (4), 117 (19), 116 (55), 115 (54), 108 (21), 104 (34), 102 (100), 81 (58), 75 (9), 73 (12).

Dimethyl acetal of methyl 2,5-anhydro-3-azido-3,4-dideoxy-L-*ribo*-hexouronate ((+)-**9**). Ozone (3% in O_2) was bubbled through a solution of (+)-**8** (2 g, 11.6 mmol) in anhydrous MeOH (77 mL) cooled to -78°C. After the appearance of a persistent blue colour (ca. 75 min), the solution was stirred for 30 min at -78°C. Me_2S (17.5 mL, 240 mmol) and then methyl orthoformate (23 mL, 209 mmol) were added dropwise under stirring. The temperature was allowed to reach 20°C in ca. 60 min, and the mixture was stirred at 20°C for 18 h. The yellow solution was diluted with Et_2O (480 mL) and washed with H_2O (190 mL, once, 100 mL, 4 times). After drying ($MgSO_4$) the solvent was distilled off in vacuo. The residue was taken with CH_2Cl_2 (20 mL) and the solvent distilled off to dryness in vacuo yielding 2.65 g (93%), yellowish oil. $[\alpha]^{25}_{365}$ = +48, $[\alpha]^{25}_{436}$ = +25, $[\alpha]^{25}_{546}$= +13, $[\alpha]^{25}_{578}$ = +11, $[\alpha]^{25}_{589}$ = +10.5 (c = 0.54, CH_2Cl_2). IR ($CHCl_3$) ν: 2950, 2830, 2100, 1750, 1440, 1355, 1105 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.56 (t, ^3J = 7.5 Hz, H-C(5)); 4.36 (d, ^3J = 5.0 Hz, H-C(1)); 4.20 (dt, ^3J = 7.0, 4.0 Hz, H-C(3)); 3.95 (dd, ^3J = 5.0, 3.5 Hz, H-C(2)); 3.73 (s, COOMe), 3.45 (s, 2 MeO); 2.20 (m, H_2C(4)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 111.7 (s, C(6)); 104.5 (d, ^1J(C,H) = 167 Hz, C(1)); 84.6 (d, ^1J(C,H) = 151 Hz, C(2)); 76.5 (d, ^1J(C,H) = 153 Hz, C(5)); 61.4 (d, ^1J(C,H) = 151 Hz, C(3)); 56.3, 54.9, 51.9 (3q, ^1J(C,H) ≈ 147 Hz, 3 MeO); 36.0 (t, ^1J(C,H) = 136 Hz, C(4)). MS (CI, NH_3) m/z: 264 ([M + 19]$^+$, 12), 263 ([M + 18]$^+$, 100), 246 ([M + 1]$^+$, 2), 231 (5), 220 (2), 215 (10), 214 (42), 200 (2), 199 (16), 75 (48). Anal. calc. for $C_9H_{15}N_3O_5$ (245.237): C 44.08, H 6.17, N 17.13; found: C 44.05, H 6.26, N 17.02.

Dimethyl acetal of 2,5-anhydro-3-azido-3,4-dideoxy-L-*ribo*-hexouronic acid ((+)-**10**). A solution of (+)-**9** (234 mg, 0.95 mmol), in 10% aqueous $NaHCO_3$ (2 mL) and MeOH (2 mL) was stirred at 20°C for 11 days. H_2O (10 mL) was added and the solution washed with CH_2Cl_2 (17 mL, 4 times). After the addition of H_2O (30 mL), the aqueous solution was cooled to 0°C and acidified with 1.5 N HCl until pH 3. The mixture was extracted with CH_2Cl_2 (17 mL, 4 times). The combined org. extracts were dried ($MgSO_4$) and the solvent distilled off in vacuo, yielding 155 mg (71%), colourless solid, after recrystallization form Et_2O/hexane. M.p. 47-48°C. $[\alpha]^{25}_{405}$ = +189, $[\alpha]^{25}_{435}$ = +167, $[\alpha]^{25}_{546}$= +70, $[\alpha]^{25}_{577}$ = +41, $[\alpha]^{25}_{589}$ = +44 (c = 0.19, CH_2Cl_2). IR (KBr) ν: 2940 (br.), 2100, 1740, 1448, 1350, 1260, 1200, 1100 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 10.37 (br.s, COOH); 4.62 (br.t, ^3J = 7.5, ^4J = 1.5 Hz, H-C(5)); 4.44 (d, ^3J = 4 Hz, H-C(1)); 4.23 (dt, ^3J = 5.0, ^3J = 6.0 Hz, H-C(3)); 4.03 (br.dd, ^3J = 6.0, 4.0, ^4J = 1.5 Hz, H-C(2)); 3.48 (2s, 2 MeO); 2.34 (m, H_2C(4)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 174.8 (s, C(6)); 103.7 (d, ^1J(C,H) = 159 Hz, C(1)); 84.5 (d,

^1J(C,H) = 154 Hz, C(2)); 76.7 (d, ^1J(C,H) = 157 Hz, C(5)); 61.0 (d, ^1J(C,H) = 156 Hz, C(3)); 56.2, 55.7 (2q, 2 MeO); 36.0 (t, ^1J(C,H) = 136 Hz, C(4)). MS (CI, NH_3) m/z: 250 ([M + 18]$^+$, 19), 249 ([M + 17]$^+$, 100), 217 (14), 75 (19). Anal. calc. for $C_8H_{13}N_3O_5$ (231.210): C 41.56, H 5.67, N 18.17; found: C 41.60, H 5.63, N 18.17.

Dimethyl acetal of 2,5-anhydro-3-azido-3,4-dideoxy-D,L-*ribo*-hexouronic acid ((±)-**10**). Prepared by the above procedures from (±)-**7**,[12] (±)-**10** had m.p. 53-55°C.

Dimethyl acetal of 2,5-anhydro-3-azido-3,4-dideoxy-N-(4',6'-diaminopyrimidin-5'-yl)-L-*ribo*-hexouronamide ((+)-**11**). A mixture of (+)-**10** (190 mg, 0.82 mmol), 4,5,6-triaminopyrimidine (liberated from its sulfate salt (*Aldrich*) by ion exchange chromatography[17] on Dowex 50W8, dried in a desiccator over P_4O_{10}, 1 atm., 20°C; 108 mg, 0.86 mmol), anhydrous CH_3CN (6 mL) and N,N'-dicyclohexylcarbodiimide (213 mg, 1.03 mmol) was stirred at 20°C for 2½ days (TLC control on silica gel, CH_2Cl_2/MeOH 10:1). MeOH (38 mL) was added and the solvent was distilled off under reduced pressure (180 Torr, bath temperature: 30°C) yielding a white solid that was dissolved in a minimum amount of MeOH. Silica gel (5.6 g) and CH_2Cl_2 (20 mL, 3 times) were added and the solvent distilled off under reduced pressure (rotavap), first under 350 Torr, then at 15 Torr. The solid was placed on top of a column of silica gel (20 g, silica gel-60) and eluted with CH_2Cl_2/MeOH 50:1 first, then with CH_2Cl_2/MeOH 20:1 and finally with CH_2Cl_2/MeOH 10:1. The main fraction was recrystallized from methanol, yielding 239 mg (86%), colourless solid, m.p. 162-163°C. $[\alpha]^{25}_{405}$ = +413, $[\alpha]^{25}_{433}$ = +349, $[\alpha]^{25}_{546}$= +137, $[\alpha]^{25}_{577}$ = +81, $[\alpha]^{25}_{589}$ = +99 (c = 0.105, MeOH). IR (KBr) ν: 3470, 3290, 3100, 2090, 1678, 1635, 1579, 1475, 1100, 1010, 718 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.21 (s, CONH); 8.01 (s, H-C(2')); 5.12 (s, 4H, 2 NH_2); 4.79 (br.t, ^3J = 4.0, ^4J = 2.0 Hz, H-C(5)); 4.46 (m, ^3J = 4.0, 2.0, ^4J = 2.0 Hz, H-C(2)); 4.18 (dt, ^3J = 6.0, 2.0 Hz, H-C(3)); 4.16 (d, ^3J = 4 Hz, H-C(1)); 3.77, 3.78 (2s, 2 MeO); 2.48 (m, H_2C(4)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 171.3 (s, C(6)); 158.5 (d, ^1J(C,H) = 11 Hz, C(4')), C(6')); 156.3 (d, ^1J(C,H) = 198 Hz, C(2')); 103.1 (d, ^1J(C,H) = 161 Hz, C(1)); 96.6 (s, C(5')); 83.7 (d, ^1J(C,H) = 152 Hz, C(2)); 78.6 (d, ^1J(C,H) = 194 Hz, C(5)); 61.7 (d, ^1J(C,H) = 149 Hz, C(3)); 56.1, 54.8 (2q, 2 MeO); 35.8 (t, ^1J(C,H) = 136 Hz, C(4)). MS (70 eV) m/z: 338 (M$^{+\cdot}$, 30), 152 (12), 136 (12), 125 (16), 124 (10), 86 (13), 75 (100), 55 (24). Anal. calc. for $C_{12}H_{18}N_8O_4$ (338.328): C 42.60, H 5.36, N 33.12; found: C 42.76, H 5.47, N 32.99.

Dimethyl acetal of 2,5-anhydro-3-azido-3,4-dideoxy-N-(4',6'-diaminopyrimidin-5'-yl)-D,L-*ribo*-hexouronamide ((±)-**11**). Prepared by the above procedure from (±)-**10**, (±)-**11** had m.p. 203-204°C. Anal. calc. for $C_{12}H_{18}N_8O_4$ (338.328): C 42.60, H 5.36, N 33.12; found: C 42.53, H 5.44, N 33.00.

Dimethyl acetal of (+)-(5*R*)-5-C-(6'-amino-7'H-purin-8'-yl)-2,5-anhydro-3-azido-3,4-dideoxy-L-*erythro*-pentose ((+)-**12**). A mixture of (+)-**11** (108.6 mg, 0.32 mmol; dried overnight under vacuum over P_4O_{10}), anhydrous CsF (336 mg, 2.22 mmol) and anhydrous DMF (3.6 mL) was placed in a 10 mL flask dried under Ar in a flame. The mixture was stirred at 130°C for 20 h. After cooling to 20°C, CH_2Cl_2/MeOH 1:1 (10 mL) was added. The mixture was filtered through silica gel -60 (3 g, rinsing with 38 mL MeOH). The solvent was distilled off in vacuo (10^{-2} Torr). The yellowish residue was mixed with silica gel (5.5 g) and a minimal amount of CH_2Cl_2/MeOH 1:1. After solvent evaporation, the solid mixture was placed on top of a silica gel (28 g) column and eluted with CH_2Cl_2, then with CH_2Cl_2/MeOH 100:1, then CH_2Cl_2/MeOH 100:2 and finally with CH_2Cl_2/MeOH 100:3, giving 59.4 mg (97%), white solid that was recrystallized form MeOH. M.p. 167-169°C. $[\alpha]^{25}_{405}$ = +266, $[\alpha]^{25}_{435}$ = +221, $[\alpha]^{25}_{546}$= +80, $[\alpha]^{25}_{577}$ = +41, $[\alpha]^{25}_{589}$ = +45 (c = 0.140, EtOH 95%). IR (KBr) ν: 2090, 1712, 1390, 1420, 1300, 1090 cm^{-1}. ^{1}H-NMR (250 MHz, CD_3OD) δ_H: 8.18 (s, H-C(2')); 5.28 (br.dd, ^3J = 8.0, 6.5, ^4J(H-C(2),(5)) = 1.5 Hz, H-C(5)); 4.44 (dd, ^3J = 7.1, 3.5 Hz, H-C(3)); 4.09 (br.dd, ^3J = 5.0, 3.2, ^4J = 1.5 Hz, H-C(2)); 3.47, 3.43 (2s, 2 MeO); 2.61 (ddd, ^2J = 13.0, ^3J = 8.0, 7.1 Hz, H-C(4) *anti* to azido); 2.45 (ddd, ^2J = 13.0, ^3J = 6.5, 3.2 Hz, H-C(4) *syn* with respect to azido). ^{13}C-NMR (62.9 MHz, CD_3SOCD_3) δ_C: 152.3 (d, ^1J(C,H) = 198 Hz, C(2')); 103.9 (d, ^1J(C,H) = 163 Hz, C(5)); 84.1 (d, ^1J(C,H) = 150 Hz, C(4)); 74.0 (d, ^1J(C,H) = 150 Hz, C(1)); 62.0 (d, ^1J(C,H) = 152 Hz, C(3)); 55.5, 54.1 (2q, 2 MeO); 36.2 (t, ^1J(C,H) = 135 Hz, C(2)). MS (70 eV) m/z: 321 ([M + 1]$^+$, 5), 320 (M$^{+\cdot}$, 1.3), 289 (1), 278 (3), 161 (2), 134 (2), 111 (2), 85 (2), 76 (7), 75 (100), 71 (2). Anal. calc. for $C_{12}H_{18}N_8O_3$ (338.328): C 45.00, H 5.03, N 34.98; found: C 44.99, H 5.07, N 34.97.

Dimethyl acetal of (±)-(5*RS*)-5-C-(6'-amino-7'H-purin-8'-yl)-2,5-anhydro-3-azido-3,4-dideoxy-D,L-*erythro*-pentose ((±)-**12**). Prepared by the above procedure from (±)-**11**, (+)-**12** had m.p. 211°C. Anal. calc. for $C_{12}H_{18}N_8O_3$ (338.328): C 45.00, H 5.03, N 34.98; found: C 44.96, H 4.92, N 34.82.

(1*R*)-1-C-(6'-Amino-7'H-purin-8'-yl)-1,4-anhydro-3-azido-2,3-dideoxy-D-*erythro*-pentitol ((+)-**2**). A mixture of (+)-**12** (218 mg, 0.68 mmol), 15% aqueous H_2SO_4 (1.1 mL), THF (9 mL) and H_2O (4 mL) was stirred at 90°C for 3 days under Ar atmosphere. After cooling to 0°C, $NaBH_3CN$ (48 mg, 0.7 mmol) was added and the mixture stirred at 20°C for 40 min (TLC control, CH_2Cl_2/MeOH 10:1). 15% Aqueous ammonia was added until pH 8-9 and the solvent was distilled off in vacuo (20 Torr, bath temperature: 40°C). The residue was dried in a desiccator over P_4O_{10} (1 atm.). The white powder was extracted with CH_2Cl_2/MeOH 1:1 (15 mL, 6 times). The combined extracts were dried ($MgSO_4$) and the solvent was distilled off in vacuo. The residue was purified by FC (8 g silica gel; CH_2Cl_2/MeOH 50:1 to CH_2Cl_2/MeOH 25:3) yielding a first fraction containing 40 mg of (+)-**12**, and a second fraction affording 111.6 mg (74%) of (+)-**2**, colourless solid, recrystallized form 95% EtOH, m.p. 210-211°C. $[\alpha]^{25}_{405}$ = +338, $[\alpha]^{25}_{435}$ = +284, $[\alpha]^{25}_{546}$= +112, $[\alpha]^{25}_{577}$ = +68, $[\alpha]^{25}_{589}$ = +70 (c = 0.125, 95% EtOH). Circular dichroism: $\Delta\epsilon$ (262 nm) = +0.632 (c = $2.26 \cdot 10^{-4}$ M, 95% EtOH, see Figure). UV (95% EtOH) λ_{max} = 212 nm (ϵ = 22500), 264 (14500). IR (KBr) ν: 3320, 3120, 2920, 2100, 1660, 1610, 1305 cm^{-1}. ^{1}H-NMR (250 MHz, CD_3SOCD_3) δ_H: 8.12 (s, H-C(2')); 6.76 (s, NH_2); 5.14 (br.dd, J = 7, 6.5, ^4J = 2 Hz, H-C(1)); 4.30 (ddd, J = 9, 7, 3.1 Hz, H-C(3)); 3.74 (br.dt, J = 9, 5, ^4J = 2 Hz, H-C(4)); 3.56 (d, J = 5 Hz, H_2C(5)); 3.10 (s, OH); 2.58 (ddd, ^2J = 13, J = 7, 7 Hz, H_{exo}-C(2)); 2.36 (ddd, ^2J = 13, J = 6.5, 3.1 Hz, H_{endo}-C(2)). ^{13}C-NMR (62.9 MHz, CD_3SOCD_3) δ_C: 154.7 (s, C_{quat}); 152.2 (d, ^1J(C,H) = 196 Hz, C(2')); 151.1 (s, C_{quat}); 85.0 (d, ^1J(C,H) = 148 Hz, C(4)); 73.9 (d, ^1J(C,H) = 149 Hz, C(1)); 62.1 (d, ^1J(C,H) = 153 Hz, C(5)); 61.6 (t, ^1J(C,H) = 141 Hz, C(5)); 36.5 (t, ^1J(C,H) = 135 Hz, C(2)). (The two other quat. carbon centres were not visible). MS (70 eV) m/z: 277 ([M + 1]$^+$, 22), 276 ($M^{+\cdot}$, 18), 236 (2), 204 (22), 168 (27), 134 (24), 123 (38), 106 (68), 82 (100), 75 (59). Anal. calc. for $C_{10}H_{12}N_8O_2$ (276.260): C 43.48, H 4.38, N 40.56; found: C 43.41, H 4.46, N 40.54.

(1*RS*)-1-C-(6'-Amino-7'H-purin-8'-yl)-1,4-anhydro-3-azido-2,3-dideoxy-D,L-*erythro*-pentitol ((±)-**2**). Prepared by the above procedure form (±)-**12**; (±)-**2** had m.p. 212°C. Anal. calc. for $C_{10}H_{12}N_8O_2$ (276.260): C 43.48, H 4.38, N 40.56; found: C 43.42, H 4.45, N 40.45.

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