# Purine Nucleosides XXVIII. The Synthesis of 7-(2′-Deoxy-α- and β-D-Ribofuranosyl)purines from 2′-Deoxyribofuranosylimidazoles. Preparation of the 2′-Deoxy Derivative of the Nucleoside from Pseudovitamin $B_{12}$ Factor G (1)

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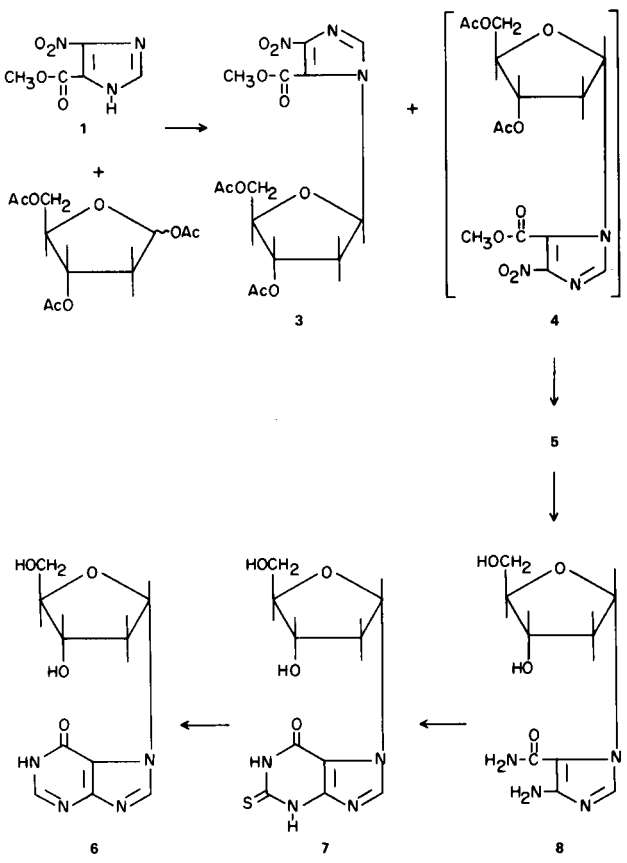
The synthesis of 1-(2′-deoxyribofuranosyl)imidazoles have been achieved for the first time *via* the fusion method of glycosidation. 4-Amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)-imidazole (**8**) and 4-amino-5-carboxamido-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**10**) have been obtained and their structures established by spectroscopic methods. The first examples of 7-(2′-deoxyglycosyl)purines [7-(2′-deoxy-α-D-ribofuranosyl)hypoxanthine (**6**) and 7-(2′-deoxy-β-D-ribofuranosyl)hypoxanthine (**11**)] have been obtained from the requisite 2′-deoxyribofuranosylimidazoles. The preparation of **6** has furnished the 2′-deoxy derivative (α-configuration) of the nucleoside from pseudovitamin $B_{12}$ Factor G, which constitutes the first 2′-deoxy derivative of *any* nucleoside isolated from the various naturally occurring pseudovitamin $B_{12}$ factors.

Characterization (2c) of the nucleoside from pseudovitamin $B_{12}$ as 7-α-D-ribofuranosyladenine and the subsequent assumptions (3) that nucleosides isolated from other vitamin $B_{12}$ analogs were 7-D-ribosylpurines has prompted the investigation of new synthetic routes for the preparation of 7-D-ribosylpurines. Some of the previous routes were proved inadequate by the finding (4) that a number of previously reported 7-glycosylpurines were actually 3-glycosylpurines. A number of methods and routes have been reported (4,5,6) which furnish 7-glycosylpurines, however, there have been no reports of the synthesis of 7-(2′-deoxyribofuranosyl)purines. The 2′-deoxy-α-derivatives of the nucleosides from pseudovitamin $B_{12}$ analogs were considered to be of special interest.

The fusion method has been applied with considerable success to the synthesis of certain 9-(2′-deoxy-α- and β-D-ribofuranosyl)purines (7) and 9-(2′-deoxy-α- and β-D-ribopyranosyl)purines (8). However, this approach, fusion of a preformed purine, did not appear to be suitable for the preparation of 7-(2′-deoxy-α- and β-D-ribofuranosyl)-purines. The chemical synthesis of imidazole 2′-deoxynucleosides has not yet been accomplished (9) although these compounds might serve as valuable precursors (5,10) in the synthesis of 7-(2′-deoxy-D-ribofuranosyl)-purines. This prompted us to investigate the possibility of utilizing the fusion method of glycosidation to obtain imidazole 2′-deoxynucleosides from which we now wish to report the first synthetic preparation of 7-(2′-deoxy-α and β-D-ribofuranosyl)purines.

A mixture of methyl 4(5)-nitroimidazole-5(4)-carboxylate (**1**) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose (**2**) was heated at 145° with chloroacetic acid to afford a 34% yield of crystalline methyl 4-nitro-1-(3′,5′-di-*O*-acetyl-2′-

REACTION SCHEME I



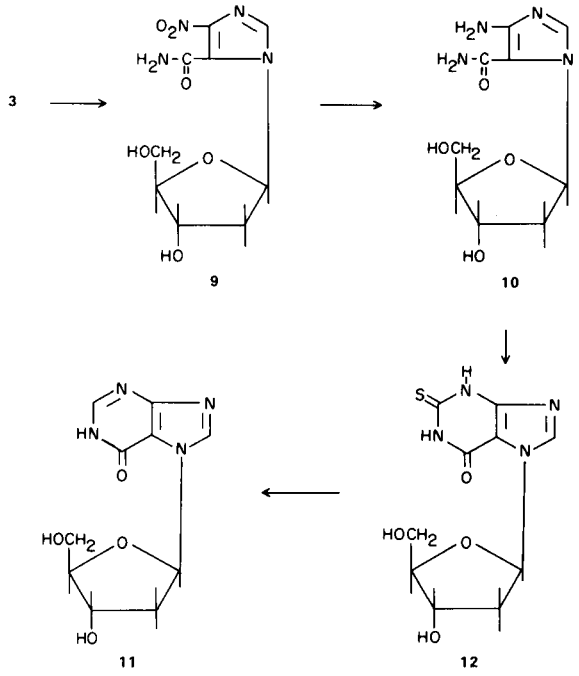
deoxy-β-D-ribofuranosyl)imidazole-5-carboxylate (**3**). The structure of **3** was established on the basis of pmr and ultraviolet absorption spectra. The anomeric configuration of **3** was established from the proton magnetic resonance (pmr) spectrum in deuterated chloroform. The signal for the anomeric proton exhibited a "pseudo-triplet" centered at δ 6.4 (1 proton), a peak width of 13.0 Hz and an apparent splitting constant of 6.5 Hz. This is in excellent agreement with the values reported for several 2′-deoxy-β-D-ribofuranosylheterocycles (peak width of 13.0 ± 1 Hz and apparent splitting constant of 6.5 ± 0.5 Hz), (11) but not in agreement with the values observed for 2′-deoxy-α-D-ribofuranosylheterocycles [a multiplet of four (quartet) with $J_{H1'}$ of 3.1 ± 0.4 Hz and 7.2 ± 0.3 Hz with a peak width of 10.4± 0.4 Hz] (7).

The ultraviolet absorption maxima for **3** (Table I) were very similar to those reported (10) for methyl 4-nitro-1-(2′,3′,5′-tri-*O*-acetyl-β-D-ribofuranosyl)imidazole-5-carboxylate, the structure of which has been unambiguously assigned (10). The above uv and pmr data conclusively established the site of glycosidation and the anomeric configuration of **3** and therefore all the nucleosides shown in reaction Scheme II.

The preparation of 7-(2′-deoxy-α-D-ribofuranosyl)purines from a 2′-deoxyribofuranosylimidazole required the preparation of the α-anomer of **3**. Therefore, the filtrate from which methyl 4-nitro-1-(3′,5′-di-*O*-acetyl-2′-deoxy-β-D-ribofuranosyl)imidazole-5-carboxylate (**3**) had crystallized was carefully examined, since previous studies (7,8) have indicated that the fusion reaction should have produced both the α- and β-anomers. The ultraviolet spectra of this filtrate were identical to the ultraviolet spectra of the crystalline product **3**, however, a pmr spectrum indicated that only a small amount of **3** was still present in the filtrate. The pmr spectrum also revealed a considerable amount (12) of a second product which exhibited a signal at δ 7.8 (1 proton) and a multiplet centered at δ 6.5 (1 proton) with a peak width of approximately 10 Hz. Attempts to separate the nucleoside material (**4**) from the decomposition products by column chromatography with alumina and silica gel absorbents were not successful. Therefore, the fractions from the alumina column which contained material that absorbed in the ultraviolet region were combined and treated with methanol saturated with ammonia. This provided 5-carboxamido-4-nitro-1-(2′-deoxy-α-D-ribofuranosyl)imidazole (**5**) as a glass by deacetylation of the carbohydrate moiety and a conversion of the 5-methyl ester group to a carboxamide group. This nucleoside had an ultraviolet absorption spectra maxima (Table I) identical to 5-carboxamido-4-nitro-1-(β-D-ribofuranosyl)imidazole (10).

Attempts to obtain this nucleoside (**5**) as a crystalline compound by cellulose chromatography as well as by

REACTION SCHEME II




treatment with various solvents proved to be unsuccessful. Hydrogenation of **5** with a catalytic amount of 5% palladium on carbon furnished a crystalline compound which was assigned the structure 4-amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)imidazole (**8**). Although the ultraviolet spectra of **8** was identical to 4-amino-5-carboxamido-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**10**, *vide infra*), the mixture melting point of these two compounds was depressed from that of either **10** or **8**.

The pmr spectrum of **8** in dimethylsulfoxide-$d_6$ conclusively established the structural assignment as 4-amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)imidazole. A signal centered at δ 6.4 (1 proton) was assigned to the anomeric (H1′) proton (a multiplet of four with $J_{1',2}$ of 3.5 Hz and 7.0 Hz with a peak width of 10.5 Hz).

This pmr data along with the ultraviolet absorption spectra have established the site of glycosidation and anomeric configuration of all nucleosides shown in Reaction Scheme I.

Treatment of 4-amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)imidazole (**8**) with methylisothiocyanate in pyridine at reflux temperature afforded a near quantitative yield of 7-(2′-deoxy-α-D-ribofuranosyl)purin-6-one-2-thione (**7**). The action of Raney nickel on **7** afforded a smooth removal of the mercapto group to yield 7-(2′-deoxy-α-D-ribofuranosyl)purin-6-one (**6**), the 2′-deoxy derivative of the nucleoside isolated from pseudovitamin $B_{12}$ Factor G. This has provided a route for the preparation of 7-(2′-deoxyribofuranosyl)purines possessing the same anomeric

TABLE I

Ultraviolet Absorption Data of Certain Imidazole and Purine 2′-Deoxynucleosides (a)

| Number | Compound | pH | λ max nm | ε max x $10^{-3}$ | λ min nm | ε min x $10^{-3}$ |
|---|---|---|---|---|---|---|
| 3 | Methyl 4-nitro-1-(3′,5′-di-*O*-acetyl-2′-deoxy-β-D-ribofuranosyl)imidazole-5-carboxylate | 1 | 287 | 5.94 | 255 | 3.71 |
| | | MeOH | 281 | 4.82 | 255 | 3.34 |
| | | 11 | 287 | 5.57 | 255 | 3.34 |
| 9 | 5-Carboxamido-4-nitro-1-(2′-deoxy-β-D-ribofuranosyl)-imidazole | 1 | 293 | 5.20 | 255 | 2.72 |
| | | MeOH | 293 | 5.20 | 255 | 2.86 |
| | | 11 | 293 | 5.20 | 255 | 3.00 |
| 10 | 4-Amino-5-carboxamido-1-(2′-deoxy-β-D-ribofuranosyl)-imidazole | 1 | 240 | 7.10 | 248 | 6.80 |
| | | | 266 | 8.80 | | |
| | | MeOH | 276 | 9.95 | 240 | 3.12 |
| | | 11 | 272 | 10.50 | 240 | 3.12 |
| 8 | 4-Amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)-imidazole | 1 | 240 | 6.30 | 248 | 6.05 |
| | | | 266 | 8.00 | | |
| | | MeOH | 275 | 9.20 | 240 | 2.90 |
| | | 11 | 272 | 9.20 | 240 | 2.90 |
| 12 | 7-(2′-Deoxy-β-D-ribofuranosyl)purin-6-one-2-thione | 1 | 234 | 16.70 | 251 | 5.97 |
| | | | 282 | 19.90 | | |
| | | MeOH | 235 | 15.30 | 252 | 6.25 |
| | | | 283 | 18.80 | | |
| | | 11 | 233 | 17.60 | 250 | 9.10 |
| | | | 273 | 15.60 | | |
| 7 | 7-(2′-Deoxy-α-D-ribofuranosyl)purin-6-one-2-thione | 1 | 234 | 16.00 | 251 | 4.84 |
| | | | 282 | 19.00 | | |
| | | MeOH | 235 | 13.90 | 252 | 3.92 |
| | | | 284 | 19.60 | | |
| | | 11 | 232 | 16.90 | 250 | 8.15 |
| | | | 273 | 14.80 | | |
| 11 | 7-(2′-Deoxy-β-D-ribofuranosyl)hypoxanthine | 1 | 248 | 11.50 | 223 | 4.30 |
| | | MeOH | 255 | 9.65 | 228 | 3.20 |
| | | 11 | 262 | 10.70 | 225 | 3.20 |
| 6 | 7-(2′-Deoxy-α-D-ribofuranosyl)hypoxanthine | 1 | 249 | 11.30 | 222 | 4.00 |
| | | MeOH | 255 | 9.65 | 228 | 3.50 |
| | | 11 | 262 | 11.00 | 225 | 3.20 |

(a) Beckman DK-2 Spectrophotometer.

configuration (α) as the naturally occurring nucleosides isolated from pseudovitamin $B_{12}$ and pseudovitamin $B_{12}$ factors.

The synthesis of the β-anomer of **6** was then investigated to test the generality of this route. When **3** was treated with methanolic ammonia at room temperature, deacetylation of the riboside moiety as well as a conversion of the methyl ester to an amide was achieved in 82% yield. This nucleoside, 5-carboxamido-4-nitro-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**9**), furnished ultraviolet spectral data (Table I) very similar to 5-carboxamido-4-nitro-1-(β-D-ribofuranosyl)imidazole (10) but different from the ultraviolet absorption data reported for 4-carboxamido-5-nitro-1-(β-D-ribofuranosyl)imidazole (13). Catalytic reduction of the nitro group of **9** with 5% palladium on carbon in methanol in a hydrogen atmosphere proceeded smoothly to afford 4-amino-5-carboxamido-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**10**) in better than 90% yield. The absence of starting material (**9**) was established by TLC chromatography (Table II).

Treatment of **10** with methylisothiocyanate in pyridine at reflux temperature furnished 7-(2′-deoxy-β-D-ribofuranosyl)purin-6-one-2-thione (**12**) in near quantitative yield. The thione rather than the thiol form was indicated when

TABLE II

$R_f$ Values of Imidazole and Purine 2′-Deoxynucleosides (a,b)

| Number | Compound | Chromatographic Solvent Systems (c) A | B | C |
|---|---|---|---|---|
| 9 | 5-Carboxamido-4-nitro-1-(2′-deoxy-β-D-ribofuranosyl)imidazole | 0.74 | 0.35 | 0.75 |
| 10 | 4-Amino-5-carboxamido-1-(2′-deoxy-β-D-ribofuranosyl)imidazole | 0.73 | 0.19 | 0.58 |
| 12 | 7-(2′-Deoxy-β-D-ribofuranosyl)-purin-6-one-2-thione | 0.58 | 0.57 | 0.61 |
| 11 | 7-(2′-Deoxy-β-D-ribofuranosyl)-hypoxanthine | 0.73 | 0.24 | 0.52 |
| 8 | 4-Amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)imidazole | 0.72 | 0.18 | 0.55 |
| 7 | 7-(2′-Deoxy-α-D-ribofuranosyl)-purin-6-one-2-thione | 0.51 | 0.53 | 0.64 |
| 6 | 7-(2′-Deoxy-α-D-ribofuranosyl)-hypoxanthine | 0.70 | 0.25 | 0.50 |

(a) All compounds were developed on Whatman No. 1 chromatographic paper using the descending technique. (b) Short-wave ultraviolet light (254 nm) was used to detect compounds. (c) Chromatographic solvent systems: A, 5% aqueous ammonium bicarbonate (w/w); B, *n*-butanol saturated with water; C, *n*-propanol-ammonium hydroxide (spec. grav. 0.90)-water, 6:3:1 (v/v/v).

there was observed a strong absorption band in the infrared spectrum at 1550 $cm^{-1}$ which was assigned (14) as C=S stretching and part of a -NC(=S)- system. The thiol form was also eliminated by the absence of a band at 2550-2600 $cm^{-1}$ usually attributable (14,15) to -SH stretching. The pmr spectrum of **12** provided additional proof for this assignment when there was observed a broad absorption peak at δ 12.2 (2 protons) in dimethylsulfoxide-$d_6$ which was assigned to the protons residing at N1 and N3. Raney nickel effected a facile removal of the sulfur group from **12** and afforded 7-(2′-deoxy-β-D-ribofuranosyl)purin-6-one [**11**, 7-(2′-deoxy-β-D-ribofuranosyl)hypoxanthine], the 2′-deoxy β-anomer of the nucleoside from pseudovitamin $B_{12}$ Factor G. The complete removal of the mercapto group to afford **11** was ascertained by TLC (Table II) and the ultraviolet absorption spectra (Table I) of the reaction mixture.

This investigation has provided the first synthesis of 2′-deoxyribofuranosylimidazoles and a general route for the preparation of 7-(2′-deoxy-D-ribofuranosyl)purines.

## EXPERIMENTAL (16)

Methyl 4-nitro-1-(3′,5′-di-*O*-acetyl-2′-deoxy-β-D-ribofuranosyl)-imidazole-5-carboxylate (**3**).

Methyl 5(4)-nitroimidazole-4(5)-carboxylate (17) (**1**, 7.0 g.) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose (7) (**2**, 14 g.) were heated in a 100 ml. pear shaped flask by an oil bath preheated to 145°. When the temperature of the reaction mixture reached 130°, 0.5 g. of chloroacetic acid was added and a vacuum (0.01 mm.) was applied with continued heating for 1 hour. An additional 0.5 g. of chloroacetic acid was then added and a vacuum again applied for 1 additional hour. The light tan semisolid was cooled to room temperature and triturated with 300 ml. of benzene, the solid (2.8 g.) was collected by filtration and identified as unreacted starting material. The benzene solution was extracted with cold aqueous sodium carbonate solution (4 x 100 ml.), water (3 x 100 ml.) and then dried over anhydrous magnesium sulfate. After the drying agent was removed by filtration, the benzene was removed by evaporation *in vacuo* (18) to afford a syrup. This syrup was dissolved in 50 ml. of anhydrous ethanol and allowed to stand at room temperature for 24 hours. The colorless crystals which had separated (3.1 g., 34%) from solution were collected by filtration. The solid was recrystallized from ethanol to afford heavy colorless crystals, m.p. 118-120°, $[\alpha]_D^{27}$ -43.9 (C = 1.0, chloroform).

*Anal.* Calcd. for $C_{14}H_{17}N_3O_9$: C, 45.29; H, 4.61; N, 11.32. Found: C, 45.40; H, 4.62; N, 11.52.

5-Carboxamido-4-nitro-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**9**).

Methyl 4-nitro-1-(3′,5′-di-*O*-acetyl-2′-deoxy-β-D-ribofuranosyl)-imidazole-5-carboxylate (**3**, 5.0 g.) was allowed to stand at room temperature for 14 hours in methanol saturated previously at -10° with ammonia. The solution was evaporated *in vacuo* to a syrup; the syrup was dissolved in a minimum amount of methanol and allowed to crystallize at room temperature, yield 3.0 g. (82%); becomes amorphous at 180° and decomposes at 254°. After two recrystallizations from methanol the melting point was unchanged, $[\alpha]_D^{27}$ -33.0 (C = 1.035 water).

*Anal.* Calcd. for $C_9H_{12}N_4O_6$: C, 39.71; H, 4.44; N, 20.58. Found: C, 39.87; H, 4.67; N, 20.46.

4-Amino-5-carboxamido-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**10**).

5-Carboxamido-4-nitro-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**5**, 3.0 g.) was dissolved in 100 ml. of methanol (previously purged with nitrogen before addition of catalyst) and then shaken for 2 hours at 45 psi using 1.5 g. of 5% palladium on carbon. The catalyst was collected by filtration, washed with hot methanol and the combined filtrates evaporated *in vacuo* to dryness. A colorless crystalline product (**10**) was obtained (2.4 g., 90.5%), which after recrystallization from methanol melted at 194-196°, $[\alpha]_D^{27}$ -44.0 (C = 1.06, water).

*Anal.* Calcd. for $C_9H_{14}N_4O_4$: C, 44.63; H, 5.83; N, 23.13. Found: C, 44.51; H, 6.02; N, 23.05.

7-(2′-Deoxy-β-D-ribofuranosyl)purin-6-one-2-thione (**12**).

4-Amino-5-carboxamido-1-(2′-deoxy-β-D-ribofuranosyl)imidazole (**10**, 1.0 g.) was dissolved in 100 ml. of pyridine containing 2.0 g. of methylisothiocyanate and the solution heated at reflux temperature for 14 hours. The light yellow solution was evaporated *in vacuo* to an amber syrup which was triturated with boiling benzene (2 x 50 ml.) until a light tan precipitate (1.4 g., m.p. 156-160° bubbles) was obtained. This solid was dissolved in 50 ml. of water by the addition of concentrated ammonium hydroxide and then reprecipitated with the addition of 50% aqueous acetic acid to pH 5. The colorless powder which had separated from solution was collected by filtration and recrystallized from methanol to yield a colorless powder, m.p. 185°, decomposition with bubbling; $[\alpha]_D^{27}$ -15.4 (C = 0.455, 0.1 *N* sodium hydroxide).

*Anal.* Calcd. for $C_{10}H_{12}N_4O_4S$: C, 42.26; H, 4.26; N, 19.71. Found: C, 42.15; H, 4.60; N, 19.34.

7-(2′-Deoxy-β-D-ribofuranosyl)purin-6-one [7-(2′-Deoxy-β-D-ribofuranosyl)hypoxanthine (**11**)].

7-(2′-Deoxy-β-D-ribofuranosyl)purin-6-one-2-thione (**12**, 200 mg.) was added to 10 ml. of water and dilute ammonium hydroxide was added until all the solid had dissolved. Raney nickel (500 mg.) was added and the mixture heated at reflux temperature for one hour. An additional portion of Raney nickel was then added (500 mg.) and the mixture heated at reflux temperature for one additional hour. The catalyst was collected by filtration and the filtrate evaporated *in vacuo* to a colorless solid (90 mg., 50%). This solid was recrystallized from methanol to give fine colorless needles, m.p. 210-212°, $[\alpha]_D^{27}$ 7.92 (C = 0.530, 0.1 *N* sodium hydroxide).

*Anal.* Calcd. for $C_{10}H_{12}N_4O_4$: C, 47.62; H, 4.80; N, 22.21. Found: C, 47.97; H, 4.87; N, 22.60.

4-Amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)imidazole (**8**).

The ethanol filtrate from which methyl 5-nitro-1-(3′,5′-di-*O*-acetyl-2′-deoxy-β-D-ribofuranosyl)imidazole-4-carboxylate (**3**) had crystallized was evaporated *in vacuo* to a syrup and this syrup then dissolved in 75 ml. of benzene. The benzene solution was applied to a column of Woelm neutral alumina, activity 1 (300 g., column diameter 4.5 cm.) packed in benzene. The column was eluted with 500 ml. of benzene, 500 ml. of 1% ethyl acetate-99% benzene (v/v), 500 ml. of 5% ethyl acetate-95% benzene (v/v) and finally with 1500 ml. of ethyl acetate with 200 ml. aliquots being collected. The last 200 ml. aliquot of the 5% ethyl acetate mixture and the first 600 ml. of 100% ethyl acetate were combined and evaporated *in vacuo* to a syrup. This syrup was treated with 1 liter of methanol (which had been previously saturated with ammonia at -10°) for 14 hours at room temperature and evaporated to a colorless glass *in vacuo*. The residue was dissolved in 100 ml. of methanol, purged with nitrogen and hydrogenated in a Paar hydrogenator for 1.5 hours at 45 psi with 1.0 g. of 5% palladium on carbon as a catalyst. The catalyst was removed by filtration, washed with hot methanol and the combined filtrates evaporated *in vacuo* at room temperature to a volume of about 50 ml. at which time a colorless precipitate separated, 1.3 g. (19.5% from unreacted **1**). Two recrystallizations from methanol gave pure **8**, m.p. 178-180°, $[\alpha]_D^{27}$ -52.5 (C = 1.09, water).

*Anal.* Calcd. for $C_9H_{14}N_4O_4$: C, 44.63; H, 5.83. Found: C, 44.80; H, 5.83.

7-(2′-Deoxy-α-D-ribofuranosyl)purin-6-one-2-thione (**7**).

4-Amino-5-carboxamido-1-(2′-deoxy-α-D-ribofuranosyl)imidazole (**8**, 500 mg.) was treated with 1.0 g. of methylisothiocyanate in pyridine by a procedure essentially the same as that used for the preparation of **12**. The crude product (650 mg., m.p. 175°, decomposition with bubbling) was recrystallized two times from methanol to give pure **7**; m.p. 195° decomposition with bubbling; $[\alpha]_D^{27}$ -63.8 (C = 0.885, 0.1 *N* sodium hydroxide).

*Anal.* Calcd. for $C_{10}H_{12}N_4O_4S$: C, 42.26; H, 4.26; N, 19.71. Found: C, 42.41; H, 4.32; N, 19.57.

7-(2′-Deoxy-α-D-ribofuranosyl)purin-6-one [7-(2′-Deoxy-α-D-ribofuranosyl)hypoxanthine (**6**)].

7-(2′-Deoxy-α-D-ribofuranosyl)purin-6-one-2-thione (**7**, 400 mg.) was added to 10 ml. of water and dilute ammonium hydroxide was added until a clear solution had been effected. Raney nickel (500 mg.) was added and the mixture heated at reflux temperature for one hour. At the end of this time an additional portion of Raney nickel (500 mg.) was added and the mixture heated at reflux temperature for one additional hour. The catalyst was collected by filtration and washed with 50 ml. of boiling water and the combined filtrate and washings evaporated *in vacuo* to a colorless solid. This solid was recrystallized from methanol to afford **6**; (160 mg., 37.7%), m.p. 200-202°, $[\alpha]_D^{27}$ -63.5 (C = 0.54, 0.1 *N* sodium hydroxide).

*Anal.* Calcd. for $C_{10}H_{12}N_4O_4$: C, 47.62; H, 4.80: N, 22.21. Found: C, 47.50; H, 5.03; N, 22.65.

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