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SYNTHESIS OF A *C*-NUCLEOSIDE ANALOG OF THE ANTIBIOTIC CORDYCEPIN*,†

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ABSTRACT

A *C*-nucleoside analog of cordycepin, 6-amino-8-(3-deoxy-β-D-*erythro*-pentofuranosyl)purine (**6**), has been synthesized. 3-Deoxy-2,5-di-*O*-(*p*-nitrobenzoyl)-β-D-*erythro*-pentofuranosyl bromide reacted with mercuric cyanide in nitromethane to give 2,5-anhydro-4-deoxy-3,6-di-*O*-(*p*-nitrobenzoyl)-D-*ribo*-hexononitrile which, after acid hydrolysis and removal of the protecting groups, afforded 2,5-anhydro-4-deoxy-D-*ribo*-hexonic acid. Reaction of this acid with 4,5,6-triaminopyrimidine gave the corresponding amide, which was pyrolyzed to give compound **6**. The mass- and n.m.r.-spectral data for the synthesized analog are quite similar to those of the natural antibiotic.

INTRODUCTION

Since the discovery of such antibiotics as formycin A and B, pyrazomycin, showdomycin, and pseudouridine C, whose structures indicated that antibiotic activity is not restricted to *N*-nucleosides[1,2], the sythesis of *C*-nucleosides has attracted considerable attention. Attempts to modify, and possibly enhance, the antibiotic activity of established nucleoside antibiotics has led to the synthesis of their *C*-nucleoside analogs[3].

In connection with a program sponsored by the U. S. Army Research and Development Command on the synthesis of the *C*-nucleoside analogs of nucleoside antibiotics active against malaria, we now report the synthesis of such an analog of cordycepin, namely, 6-amino-8-(3-deoxy-β-D-*erythro*-pentofuranosyl)purine (**6**). The antibiotic cordycepin (3′-deoxyadenosine) inhibits the growth of plasmodia[4], trypanosoma[5], avian tubercle bacilli[6], and tumor cells[7–9], and acts as a negative-feedback inhibitor of purine nucleotide biosynthesis.

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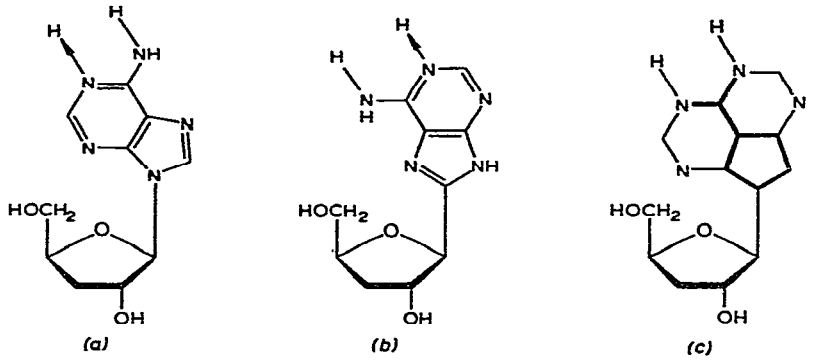
DISCUSSION

The positions of the active sites (*i.e.*, hydrogen bonds in the purine ring and the hydroxyl groups in the sugar moiety of the *C*-nucleoside **6**) are quite close to those of natural cordycepin. This is illustrated in the following diagram, which depicts possible hydrogen bonding in (*a*) natural cordycepin and (*b*) the synthetic *C*-nucleoside



analog **6**. A third formula (*c*) depicts the two structures superimposed, to illustrate their similarity (the nitrogen atoms of the imidazole ring have been omitted to avoid confusion).

Because the furanose ring of this synthetic analog of cordycepin is attached to adenine by a C–C bond, this nucleoside would be expected to be less susceptible to enzymic hydrolysis than cordycepin, which is deactivated by hydrolysis to adenine and 3-deoxy-D-*erythro*-pentose.

For the synthesis of the *C*-analog of cordycepin, we used a modification of the procedure of Bobek and Farkaš[10] and condensed 4,5,6-triaminopyrimidine with 2,5-anhydro-4-deoxy-D-*ribo*-hexonic acid (**4**). Acid **4** was synthesized from the known methyl 2,3-anhydro-β-D-ribofuranoside, which is accessible in seven steps from D-xylose[11], by reduction with Raney nickel to methyl 3-deoxy-β-D-*erythro*-pentofuranoside[12,13]. This was *p*-nitrobenzoylated, and the product treated with hydrogen bromide in acetic acid to give 3-deoxy-2,5-di-*O*-(*p*-nitrobenzoyl)-β-D-*erythro*-pentofuranosyl bromide (**1**). Reaction of this bromide with mercuric cyanide in nitromethane afforded the new, crystalline 2,5-anhydro-4-deoxy-3,6-di-*O*-(*p*-nitrobenzoyl)-D-*ribo*-hexononitrile (**2**) in 86% yield. The β-D configuration of the nitrile was evident from its n.m.r. spectrum, which showed a coupling constant of 2.8 Hz for the anomeric proton, quite close to that of natural cordycepin. The formation of the β-D anomer was expected from the *trans* rule[14], as well as by analogy with the configuration of the nitrile obtained by treating tri-*O*-benzoyl-D-ribofuranosyl bromide with mercuric cyanide[10] under similar conditions. The mass spectrum of the nitrile showed a small, molecular-ion peak at *m/e* 441, as well as fragments resulting from the loss of NO, $CH_2OCOC_6H_4NO_2$, and 2 ($NO_2C_6H_4COOH$) (*m/e* 411, 261, and 107).

Hydrolysis of 2,5-anhydro-4-deoxy-3,6-di-*O*-(*p*-nitrobenzoyl)-D-*ribo*-hexononitrile with hydrogen chloride in aqueous 1,4-dioxane afforded 2,5-anhydro-4-deoxy-3,6-di-*O*-(*p*-nitrobenzoyl)-D-*ribo*-hexonic acid (3) in crystalline form. The i.r. spectrum of this compound showed two carbonyl absorptions, at 1775 and 1720 cm^{-1}; its n.m.r. spectrum showed the anomeric proton at δ 6.19 p.p.m., with a coupling constant of 2.0 Hz; and its mass spectrum did not reveal a molecular ion at *m/e* 460, but, instead, showed a strong fragment at *m/e* 416 due to loss of CO_2.

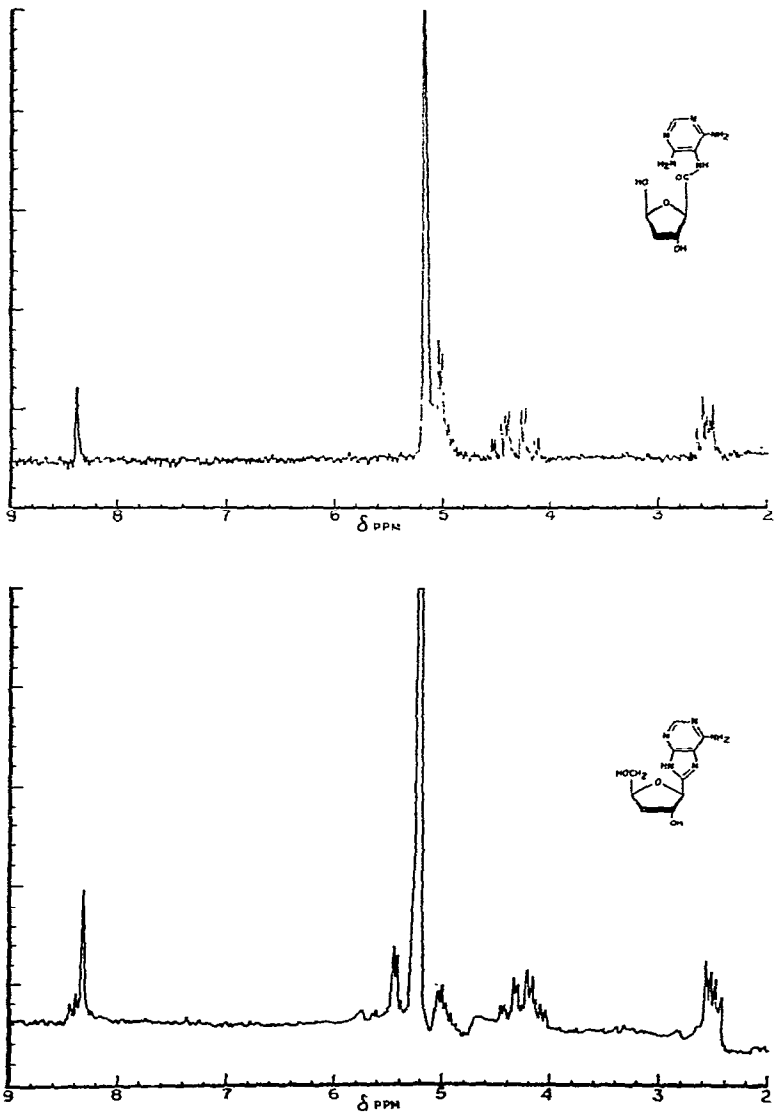


Fig. 1. N.m.r. spectra of 4,6-diamino-5-(2,5-anhydro-4-deoxy-D-*ribo*-hexonoyl)aminopyrimidine (5) (upper spectrum) and 6-amino-8-(3-deoxy-β-D-*erythro*-pentofuranosyl)purine (6).

Removal of the protecting *p*-nitrobenzoyl groups from **3** by potassium hydroxide in aqueous 1,4-dioxane, followed by chromatography on Dowex 1 X-8 (OAc^-) ion-exchange resin afforded 2,5-anhydro-4-deoxy-D-*ribo*-hexonic acid (**4**) as a syrup which was converted into the crystalline methyl ester. The i.r. spectra of the acid and ester showed carbonyl bands at 1730 and 1740 cm^{-1}, respectively. Condensation of acid **4** with 4,5,6-triaminopyridine in aqueous hydrochloric acid gave crystalline 4,6-diamino-5-(2,5-anhydro-4-deoxy-D-*ribo*-hexonoyl)aminopyrimidine (**5**), which showed an amide band at 1640 cm^{-1}. Its n.m.r. spectrum (see Fig. 1) showed a singlet at δ 8.36 p.p.m. due to H-2 of the heterocycle, followed by a doublet at δ 5.02 p.p.m. with a coupling constant of J 2.1 Hz due to H-2′. The multiplets due

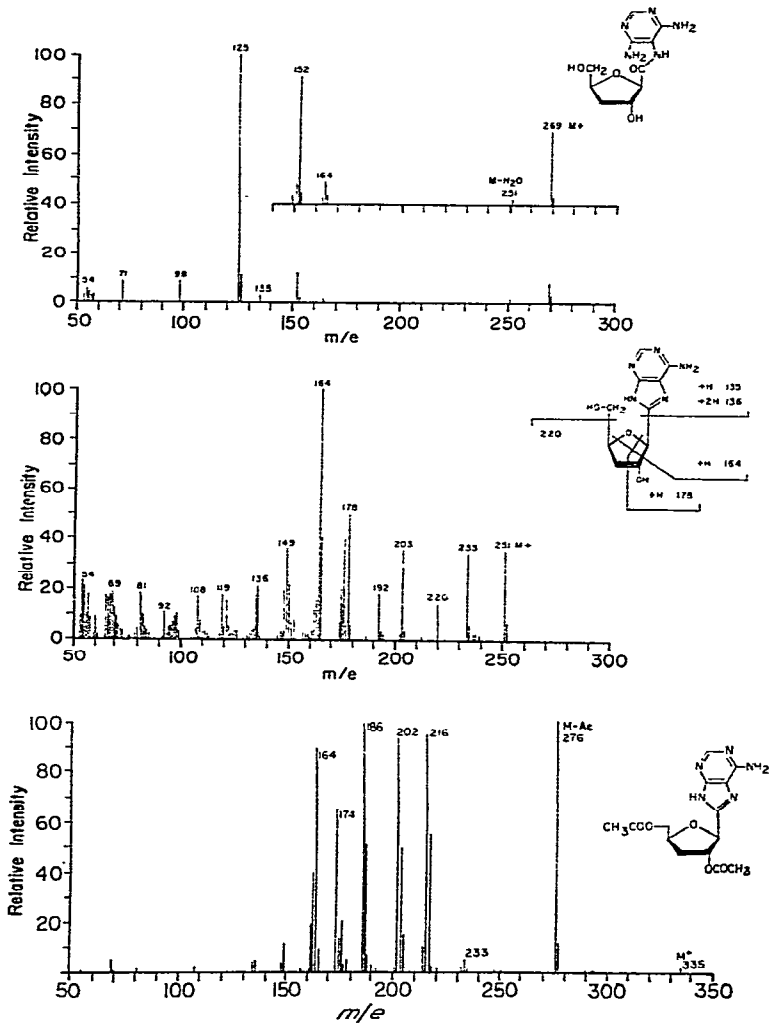
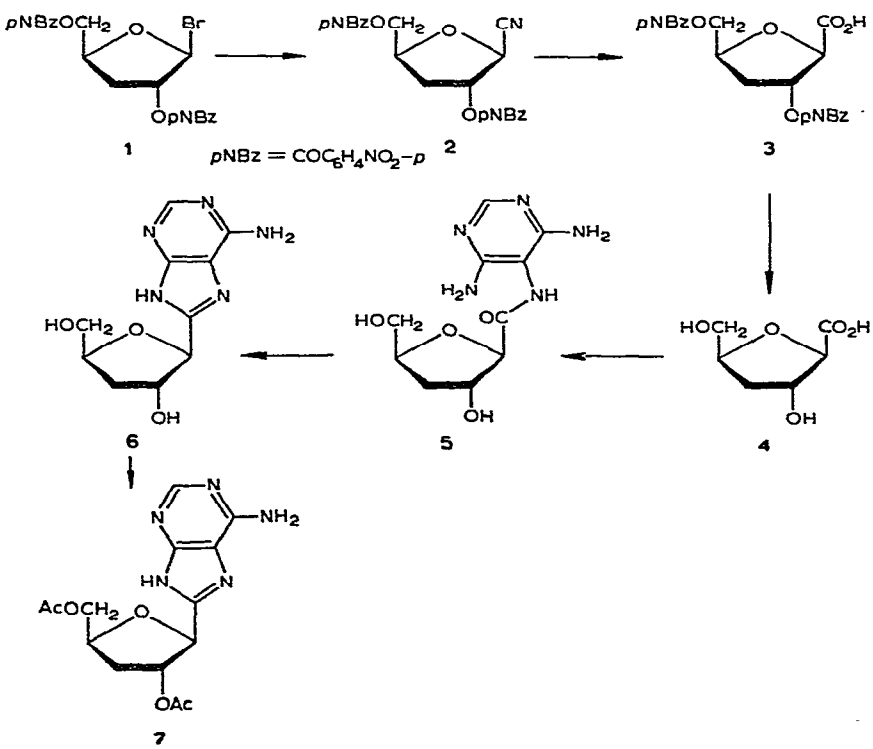


Fig. 2. Mass spectra of compounds **5**, **6**, and **7**.

to H-3′ and H-5′ were hidden under the HOD peak, but an ABX system appeared as two quadruplets centered at δ 4.18 and 4.46 p.p.m. and was assigned to the methylene group of C-6′ of the sugar moiety. The quadruplet had a large geminal coupling of J 12.4 Hz, and small couplings of 3.6 and 2.6 Hz. The C-4′ methylene protons of the 2,5-anhydro-4-deoxy-D-*ribo*-hexonoyl group appeared as a multiplet at δ 2.57 p.p.m. The mass spectrum (see Fig. 2) of amide **5** showed a molecular peak at *m/e* 269, in addition to a peak at *m/e* 251, due to the loss of H_2O, probably arising from its cyclization to a purine. A peak characteristic of the amides of 4,5,6-triaminopyrimidine appeared at *m/e* 125 due to the liberation of 4,5,6-triaminopyrimidine.

Cyclization of the amide **5** to the desired *C*-nucleoside **6** was achieved by fusion. The mass spectrum of compound **6** (see Fig. 2) was almost identical to that of natural cordycepin; it showed a molecular peak at 251 and a peak corresponding to the loss of water (233), as well as peaks due to the adenine ring (134), the base plus H (135), and the base plus 2 H (136); a peak at *m/e* 164, corresponding to the base peak plus 30 mass units, resulted from the splitting of the furanose ring in such a way that the base retained C-1′, the ring-oxygen atom, and a rearranged hydrogen atom. All of these peaks are also found in the mass spectrum of cordycepin[15,16].

The n.m.r. spectrum of our cordycepin analog (see Fig. 1) was quite similar to that of cordycepin, except that cordycepin shows two low-field protons at δ 8.68 and 8.58 p.p.m. assigned to H-2 and H-8 of adenine, and our product showed only H-2,



which appeared at δ 8.32 p.p.m. Furthermore, cordycepin shows the anomeric proton at δ 6.42, and the *C*-nucleoside analog shows it at higher field (δ 5.42; J 2.2 Hz), because the furanosyl group is attached to a nitrogen atom in the first compound, and to a carbon atom in **6**. However, the coupling constants of the remaining protons in both compounds, and their chemical shifts, are close. The C-5′ methylene protons of the sugar residue of **6** gave rise to two quadruplets, at δ 4.13 and 4.38, split by a large, geminal coupling of 12.1 Hz, and small coupling constants of 3.1 Hz and 4.4 Hz. The C-2′ and C-4′ protons appeared as a multiplet downfield from the C-5′ protons at δ 5.05 p.p.m. A multiplet of two-proton intensity appeared between δ 2.44 and 2.56 p.p.m., and was assigned to the C-3′ methylene group, which is not attached to oxygen atoms. In cordycepin, this methylene group is centered at δ 2.66 p.p.m.

Acetylation of 6-amino-8-(3-deoxy-β-D-*erythro*-pentofuranosyl)purine with acetic anhydride–pyridine by the method used by Haskell and Hanessian[17] for the *O*-acetylation of 9-β-D-arabinofuranosyladenine afforded the 6-amino-8-(2,5-di-*O*-acetyl-3-deoxy-β-D-*erythro*-pentofuranosyl)purine (**7**). This compound showed an ester band at 1740 cm^{-1}, in addition to the C=N band at 1640 cm^{-1}. Its mass spectrum (see Fig. 2) showed a molecular peak at *m/e* 335, followed by a peak at 275 corresponding to the loss of AcO.

EXPERIMENTAL

General. — Melting points were determined on a Kofler block and are uncorrected. Evaporations were performed under diminished pressure in a rotary evaporator, with a water bath at 40–50°, unless otherwise stated. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan, U. S. A. Specific rotations were measured with a 0.2-dm tube in a Bendix-NPL automatic polarimeter. I.r. absorption spectra were recorded, for potassium bromide discs, with a Perkin–Elmer Model 621 grating infrared spectrophotometer. N.m.r. spectra were recorded at 100 MHz with a Varian HA-100 spectrometer, and chemical shifts are reported in p.p.m. downfield from an internal or external standard of tetramethylsilane (δ 0.00). N.m.r. spectra were analyzed on a first-order basis, and the coupling constants recorded are the measured line-spacings. Mass spectra were obtained by Mr. M. P. Gilles with a Varian M66 mass spectrometer, with a source of 85 eV; intensities are given in parentheses as percentages of the base peak. X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities. Thin-layer chromatograms were obtained on silica gel (with a fluorescent indicator) on plastic plates, obtained from the Eastman Kodak Company (catalog No. 6060). Column chromatography was conducted with Merck silica gel (60–200 mm particle size).

Methyl 3-deoxy-2,5-di-O-(p-*nitrobenzoyl*)-β-D-erythro-*pentofuranoside*[12,13]. — A solution of methyl 2,3-anhydro-β-D-ribofuranoside (17 g), prepared from D-xylose

in seven steps by the method of Anderson *et al.*[11], in absolute ethanol (250 ml) was shaken with 10 spatulasful of Raney nickel catalyst in an atmosphere of hydrogen at 40 lb.in.$^{-2}$ for 8 h at 75°, and then overnight at room temperature. The suspension was filtered, and the catalyst was washed with absolute ethanol. The filtrate and washings were combined, evaporated to dryness, and co-evaporated with toluene, to give a colorless oil. A solution of this oil in pyridine (400 ml) was cooled, and *p*-nitrobenzoyl chloride (65 g) was added portionwise. The resulting solution was stirred overnight at room temperature, cooled, treated with water (10 ml), and the resulting mixture concentrated and then diluted with chloroform. The chloroform solution was successively washed with a saturated solution of aqueous sodium hydrogen carbonate, and water, dried (magnesium sulfate), and evaporated to a solid which crystallized from benzene–petroleum ether yielding 37 g of product: m.p. 106–109° (lit.[12,13] m.p. 108–110°), $[\alpha]_D$ −30° (*c* 0.5 chloroform); mass-spectral data: 446 (0.1; M^+), 415 (7; M−OMe), 266 (39), 167 (11; *p*-$O_2NC_6H_4CO_2H$), 150 (100; *p*-$O_2NC_6H_4CO$), 120 (20), 112 (12), 104 (21), 99 (67), 92 (4), 76 (4), 69 (13), and 65 (11).

3-Deoxy-2,5-di-O-(p-*nitrobenzoyl*)-*β*-D-erythro-*pentofuranosyl bromide*[12] (**1**). — A suspension of dry, finely powdered methyl 3-deoxy-2,5-di-*O*-(*p*-nitrobenzoyl)-*β*-D-*erythro*-pentofuranoside (4 g) in acetic acid (30 ml) was cooled, and immediately treated with acetyl bromide (18 ml) and a cold solution of 33% (w/w) hydrogen bromide in acetic acid (16 ml). The mixture was stirred for 30 min at 10°; the starting material dissolved, and the product was precipitated. The mixture was evaporated under diminished pressure, and the residue co-evaporated with toluene to dryness and then crystallized by dissolving it in dichloromethane and adding ether, to give compound **1** (3 g): m.p. 120–128° (lit.[12] m.p. 118–124°); mass spectral data: 414 (M−Br), 329 (1.7) and 327 (1.7; M−*p*-$O_2NC_6H_4CO_2H$), 247 (M−Br−*p*-$O_2NC_6H_4CO_2H$), 167 (100; *p*-$O_2NC_6H_4CO_2H$), 162 (44) and 160 (61; M−2 *p*-$O_2NC_6H_4CO_2H$), 150 (95; *p*-$O_2NC_6H_4CO$), 132 (12), 121 (86), 109 (19), 104 (23), 102 (6), 82 (60), 81 (59), 76 (53), 75 (44), and 65 (72).

2,5-Anhydro-4-deoxy-3,6-di-O-(p-*nitrobenzoyl*)-D-ribo-*hexononitrile* (**2**). — A suspension of powdered mercuric cyanide (predried for several hours at 60° under vacuum) (2.8 g) in a mixture of dry nitromethane (80 ml) and dry benzene (10 ml) was evaporated until ~30 ml of the solvent had distilled, and then cooled to room temperature. Compound **1** (5 g) was added, and the mixture was stirred for 40 h at room temperature; after about 0.5 h, most of the mercuric cyanide had dissolved and, during the succeeding period, a colorless powder was precipitated. The suspension was filtered, and the filtrate added to a mixture of cold 0.5M potassium bromide (500 ml) and methyl alcohol (75 ml). A pale-yellow syrup separated; this solidified to a white powder on being stirred. The mixture was extracted with dichloromethane (5 × 100 ml), and the combined extracts were successively washed with 1M potassium bromide (2 × 150 ml) and water (200 ml), dried (magnesium sulfate), and evaporated, yielding colorless needles. T.l.c. in 20:1 (v/v) benzene–ether indicated the presence of a slow- and a fast-moving impurity; both were completely removed by two recrystallizations from dichloromethane–methanol. The product separated in colorless needles

(3.8 g; 86%), m.p. 176–183°. Two recrystallizations from benzene gave an analytically pure sample, m.p. 181–182° (unchanged by further recrystallization), $[\alpha]_D$ −67.8° (*c* 1.03, pyridine), R_F 0.48 (20:1 benzene–ether); ν_{max}^{KBr} 3100, 1950, 1720 (COO), 1605, 1530, 1350, 1285, and 725 cm^{-1} (substituted phenyl); mass-spectral data: 441, 425 (2), 411 (5; M−NO), 261 (23; M−$CH_2OCOC_6H_4NO_2$), 232 (14), 230 (17), 214 (11), 213 (10), 201 (22), 168 (16), 150 (100; $O_2NC_6H_4CO$) 141 (14; M−2 $O_2NC_6H_4CO$), 140 (9), 125 (15), 121 (11), 112 (16), 107 (60), 104 (45), 93 (56), 92 (49), 77 (15), and 65 (40); n.m.r. data (100 MHz, pyridine-d_5): δ 2.50 (2-proton multiplet, H-4,4′), 4.5–5.00 (multiplet; H-6,6′,5, and HOD), 5.58 (1-proton singlet, H-3); 6.13 (1-proton doublet, $J_{2,3}$ 2.8 Hz, H-2), and 8.1–8.4 (8-proton multiplet, 2 substituted-phenyl groups).

Anal. Calc. for $C_{20}H_{15}N_3O_9$: C, 54.43; H, 3.43; N, 9.52. Found: C, 54.39; H, 3.50; N, 9.59.

2,5-Anhydro-4-deoxy-3,6-di-O-(p-*nitrobenzoyl*)-D-ribo-*hexonic acid* (**3**). — A solution of compound **2** (2.2 g) in 1,4-dioxane (10 ml) was treated with 5M hydrogen chloride in 1,4-dioxane (2 ml), and water (0.3 ml). The mixture was heated for 8 h at 50°, kept overnight at room temperature, and then diluted with a small volume of ether to precipitate the ammonium chloride, which was filtered off. The filtrate was evaporated to a syrup, and this was dissolved in a small volume of ethyl acetate, whereupon it crystallized (yield 2 g, 87%). After two recrystallizations from methanol, the pure product had m.p. 183–186°, $[\alpha]_D$ +60.6° (*c* 0.69, pyridine) (R_F 0.55; 2:1 benzene–methanol); ν_{max}^{KBr} 3300, 3100, 1775 (COOH), 1720 (COO), 1605, 1525, 1550, 1275, and 725 cm^{-1} (substituted phenyl); mass-spectral data: 416 (1; M−CO_2), 368 (1), 293 (5; M−*p*-$O_2NC_6H_4CO_2$), 266 (1), 249 (0.5), 167 (83; $O_2NC_6H_4CO_2H$), 150 (100; $O_2NC_6H_4CO$), 120 (37), 104 (34), 81 (33), 76 (33), 65 (14), and 51 (17); n.m.r. data (100 MHz, pyridine-d_5): 2.45 (2-proton multiplet, H-4,4′), 4.82 (2-proton multiplet, H-6,6′), 5.16 (1-proton singlet, H-3), 6.19 (1-proton singlet, $J_{2,3}$ 2.0, H-2), 8.1–8.3 (8-proton multiplet, 2 substituted-phenyl groups), and 9.65 (1-proton singlet, OH).

2,5-Anhydro-4-deoxy-D-ribo-*hexonic acid* (**4**). — A solution of compound **3** (1.5 g) in 1,4-dioxane (6 ml) was stirred with 30% aqueous potassium hydroxide (4 ml) for 2 h at room temperature. The mixture was then heated for 4 h at 40°, made neutral by portionwise addition of Dowex 50W X-8 cation-exchange resin, and the whole mixture applied to a column (2.5 × 25 cm) packed with the same resin. The acidic fractions obtained by elution of the column with water were combined, and evaporated under diminished pressure to a syrup that contained some crystals of *p*-nitrobenzoic acid; it was suspended in water (30 ml), the suspension was filtered, and the filtrate was applied to a column (2.5 × 25 ml) of Dowex 1 X-8 (OAc^-) ion-exchange resin. The column was successively eluted with water (100 ml), 5% aqueous acetic acid (50 ml), and 7% aqueous formic acid (200 ml). The formic acid eluate contained the product; it was evaporated under diminished pressure, and the residue co-evaporated with three 50-ml portions of water (to remove the last traces of formic acid); yield 0.5 g (95%) of a chromatographically homogeneous syrup; $[\alpha]_D$ +24.9°

(*c* 1.16, ethanol); ν_{max}^{KBr} 3350 (OH), 2925, 1730 (COO), 1635, 1215, 1100, 975, and 835 cm^{-1}.

Methyl 2,5-anhydro-4-deoxy-D-ribo-*hexonate.* — A solution of compound **4** (0.1 g) in ethanol (20 ml) was treated with a solution of diazomethane in ether, and the resulting mixture was kept for 1 h at room temperature. The mixture was then evaporated to a syrup, which was distilled at 150°/0.2 torr, to give an analytically pure sample that crystallized in the distilling tube; m.p. 123°; ν_{max}^{KBr} 3350 (OH), 2925, 1740 (COO), 1225, and 1100 cm^{-1}.

Anal. Calc. for $C_7H_{12}O_5$: C, 47.73; H, 6.87. Found: C, 47.56; H, 6.85.

4,6-Diamino-5-(2,5-anhydro-4-deoxy-D-ribo-*hexonoyl)aminopyrimidine* (**5**). — A solution of compound **4** (1.8 g) and 4,5,6-triaminopyrimidine (1.38 g) in 1M hydrochloric acid (14.8 ml) was boiled for 16 h under reflux and then evaporated under diminished pressure to a syrup which was mixed with water (20 ml). The suspension was filtered through active charcoal, and the filtrate concentrated to 10 ml, and applied to a column (2 × 30 ml) of Dowex 50 W X-8 cation-exchange resin. The column was washed with water, the effluent being discarded, and then with 3% aqueous ammonia (500 ml). The eluate was concentrated to 3 ml, and left overnight to crystallize. The product was collected by filtration; yield 1.5 g (46%). One recrystallization from water afforded pure, hydrated product, m.p. 214°, $[\alpha]_D$ +94.1° (*c* 0.23, methanol), which gave an anhydrous product on drying at 100°; R_F 0.33 (2:1 benzene–methanol); ν_{max}^{KBr} 3450 (OH), 3325, 1640 (CONH), 1595, 1520, 1480, 1340, 1120, 1095, and 1010 cm^{-1}; X-Ray powder diffraction data: 12.02 m, 8.84 s, 7.96 va (3), 6.04 s, 5.59 s, 5.24 s, 4.70 m, 4.54 s, 4.20 vs (1), 3.91 m, 3.77 s, 3.67 s, 3.37 vw, 3.22 vs (2), 3.11 w, 2.79 w, 2.77 w, 2.62 vw, and 2.53 w.

Anal. Calc. for $C_{10}H_{15}N_5O_4 \cdot 1.5H_2O$: C, 40.54; H, 6.12; N, 23.64. Found: C, 40.87; H, 6.07; N, 23.77.

After being dried at 100°, the compound had the following composition.

Anal. Calc. for $C_{10}H_{15}N_5O_4$: C, 44.61; H, 5.62; N, 26.01. Found: C, 44.75; H, 5.55; N, 26.03.

*6-Amino-8-(3-deoxy-β-*D-erythro-*pentofuranosyl)purine* (**6**). — When compound **5** (1.3 mg) was heated for 2 h at 215–220°, it yielded a dark-brown glass; this was suspended in water (20 ml), and the suspension filtered through active charcoal. The filtrate was concentrated to small volume, and chromatographed on silica gel; elution with 2:1 benzene–methanol and concentration to small volume afforded 0.55 g (84%) of **6**, m.p. 165°, $[\alpha]_D$ −11.1° (*c* 0.32, water); R_F 0.52 (2:1 benzene–methanol); ν_{max}^{KBr} 3300 (OH), 3110, 1660, 1600, 1420, 1310, 1060, and 800 cm^{-1}; X-Ray powder diffraction data: 12.8 s, 6.28 m, 4.98 s, 4.22 s, 3.83 vw, 3.50 m, and 3.37 vs.

Anal. Calc. for $C_{10}H_{13}N_5O_3 \cdot 0.5H_2O$: C, 46.15; H, 5.42; N, 26.91. Found: C, 46.09; H, 5.18; N, 26.94.

*6-Amino-8-(2,5-di-*O*-acetyl-3-deoxy-β-*D-erythro-*pentofuranosyl)purine* (**7**). — To a suspension of compound **6** (50 mg) in pyridine (2 ml), cooled to 5–10°, was added acetic anhydride (1 ml) with stirring. The mixture was stirred for 6 h at room temperature and then kept overnight in the refrigerator .The resulting solution was treated

with methanol (10 ml), and concentrated under diminished pressure. Three additions and evaporations of methanol followed by two additions and evaporations of toluene yielded a syrup which crystallized from ethanol; m.p. 226–228°.

Anal. Calc. for $C_{14}H_{17}N_5O_5$: C, 50.15; H, 5.11; N, 20.89. Found: C, 50.08; H, 5.08; N, 20.98.

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