analysis. The pure fluorohydrin was obtained by preparative glpc and exhibited infrared absorption at 3440, 1705, and 1120 cm^{-1} and nmr signals at τ 9.07 (doublet, J = 5 cps), 8.92, 8.56 (doublets, J = 15 cps), 8.00 (broad multiplet), and 6.38 (singlet).

Fluorohydrin Vb was converted into Ib, mp 53–55°, by treatment with refluxing methanolic base in the manner described for Va.

Thermal Decomposition of Va and Vb. A 50:50 mixture of Va and Vb (5.0 g) was heated at 150° in a small flask equipped with a reflux condenser. After 15–20 min the liquid turned pink and then brown, accompanied by vigorous foaming and evolution of a pungent, irritating gas. The dark tarry residue was dissolved in ether, washed with sodium bicarbonate solution and distilled water, separated from the aqueous phases, and dried. The dark oil remaining after evaporation of the solvent was chromatographed on silica gel, using methylene chloride as the eluting solvent. The light tan solid obtained by this procedure was sublimed to a volatile, white, crystalline substance (IV): mp 50–51°, yield *ca.* 50%.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.15; H, 9.58.

Compound IV exhibited infrared absorption at 1682, 1382, and 1262 cm^{-1} and nmr peaks at τ 8.96 (doublet, J = 6.0 cps, 3 H), 8.96 (singlet, 3 H), and 7.65 (multiplet, *ca.* 7 H). The mass spectrum of IV (ionizing voltage 70 V) confirms the basic differences in I, II, and IV (Table V). The *intensity of the P + 1 ion peak* was 10.70% P (calcd for $C_{10}H_{16}O_2$ 11.14% P).

The identity of IV obtained by rearrangement of fluorohydrins Va and Vb with the major product from the gas phase pyrolysis of Ia and Ib was established by direct comparison of melting points, glpc retention times, and infrared spectra and nmr spectra.

Reaction of Ia with *p*-Toluenesulfonic Acid. To a solution of Ia (2.0 g) in benzene (50 ml) was added 0.1 g of *p*-toluenesulfonic acid, and the resulting solution was held at room temperature for 1 hr. The acid catalyst was removed by washing with sodium bicarbonate solution and the benzene solution was then washed with water, dried, and distilled. The crude reaction product proved to be largely (*ca.* 90%) a single compound (VIa), which was obtained pure by glpc. The infrared spectrum of VIa (3470, 3080, 1820, 1710, 1645, and 905 cm^{-1}) indicated the presence of a methylene double bond, a saturated carbonyl group, and a hydroxyl group.

Table V

m/e	Base peak, %	*m/e*	Base peak, %
53	24.4	83	50.0
55	71.2	84	24.3
56	19.4	97	42.1
67	24.2	98	31.5
69	71.2	111	29.0
70	100.0	123	29.0
71	18.3	124	14.5
81	24.3	125	97.2
82	25.5	140	18.4
		168	24.2

The nmr spectrum of VIa displayed signals at τ 9.02 (a three-proton doublet, $J \sim 6$ cps), 8.28 (a three-proton doublet, $J \sim 1$ cps), 6.18 (a one-proton singlet), 4.82 (a broad two-proton doublet), and an envelope of poorly defined peaks in the region τ 7.5–8.4.

Reaction of Ib with *p*-Toluenesulfonic Acid. The rearrangement of isomer Ib was conducted in essentially the same manner described above for Ia. Analysis of the crude reaction mixture by glpc disclosed the presence of a major component (*ca.* 60%); however, other products having similar retention times frustrated our attempts to obtain pure samples of this compound (VIb). Fortunately, we discovered that a glpc column (4% QF-1 on Chromosorb G), previously used for analysis and purification of fluorohydrins Va and Vb, cleanly rearranged Ib to VIb. This compound (VIb) exhibited an infrared spectrum (ν_{max} 3470, 3085, 1820, 1712, 1645, and 905 cm^{-1}) and nmr spectrum (τ 8.95, 8.86, 8.30, 7.4–8.8, and 4.85) consistent with the assigned structure and essentially the same as the spectrum of impure VIb obtained from the arylsulfonic acid reaction.

Acknowledgment. This work was supported in part by Grants GP-2025 and GP-7807 from the National Science Foundation.

Purine Nucleosides. XXII. The Synthesis of Angustmycin A (Decoyinine) and Related Unsaturated Nucleosides[1]

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Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received March 6, 1968*

Abstract: The antibiotic angustmycin A (decoyinine) (**10**) has been prepared in several steps from psicofuranine (**1a**). The synthesis of 1′,3′,4′-*O*-orthoformylpsicofuranine (**5**) proved the β configuration of **1a** and provided the required blocked derivative for the synthesis of 6′-*O*-*p*-toluenesulfonyl-1,′3′,4′-*O*-orthoformylpsicofuranine (**6**). Compound **6** was treated with potassium *t*-butoxide to give 1′,3′,4′-*O*-orthoformyldecoyinine (**7**), which was deblocked to yield 6-amino-9-(6-deoxy-β-D-*erythro*-hex-5-enofuran-2-ulosyl)purine (**10**), identical with natural angustmycin A and decoyinine. The synthesis of 6-amino-9-(5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**8**) was accomplished from adenosine **16** by a similar base-catalyzed treatment of 5′-*O*-*p*-toluenesulfonyl-2′,3′-*O*-ethoxymethylideneadenosine (**3**). Reaction of 6-amino-9-(2,3-*O*-isopropylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**13**) with bromine provided the first reported $N^3 \rightarrow 4'$-furanose cyclonucleoside, **14**. Palladium-catalyzed hydrogenation of **13** proceeded stereospecifically to yield 6-amino-9-(5-deoxy-α-L-*lyxo*-pentofuranosyl)purine (**15**) after deblocking. A new synthesis of the 4′ epimer of **15**, 5′-deoxyadenosine (**20**), was accomplished from adenosine.

Angustmycin A (**10**) was isolated and purified by Yüntsen and coworkers[2] in 1956. Degradation studies disclosed the presence of adenine and a hexose sugar. On the basis of these studies structure **11** was proposed.[3] Hoeksema, Slomp, and van Tamelen[4]

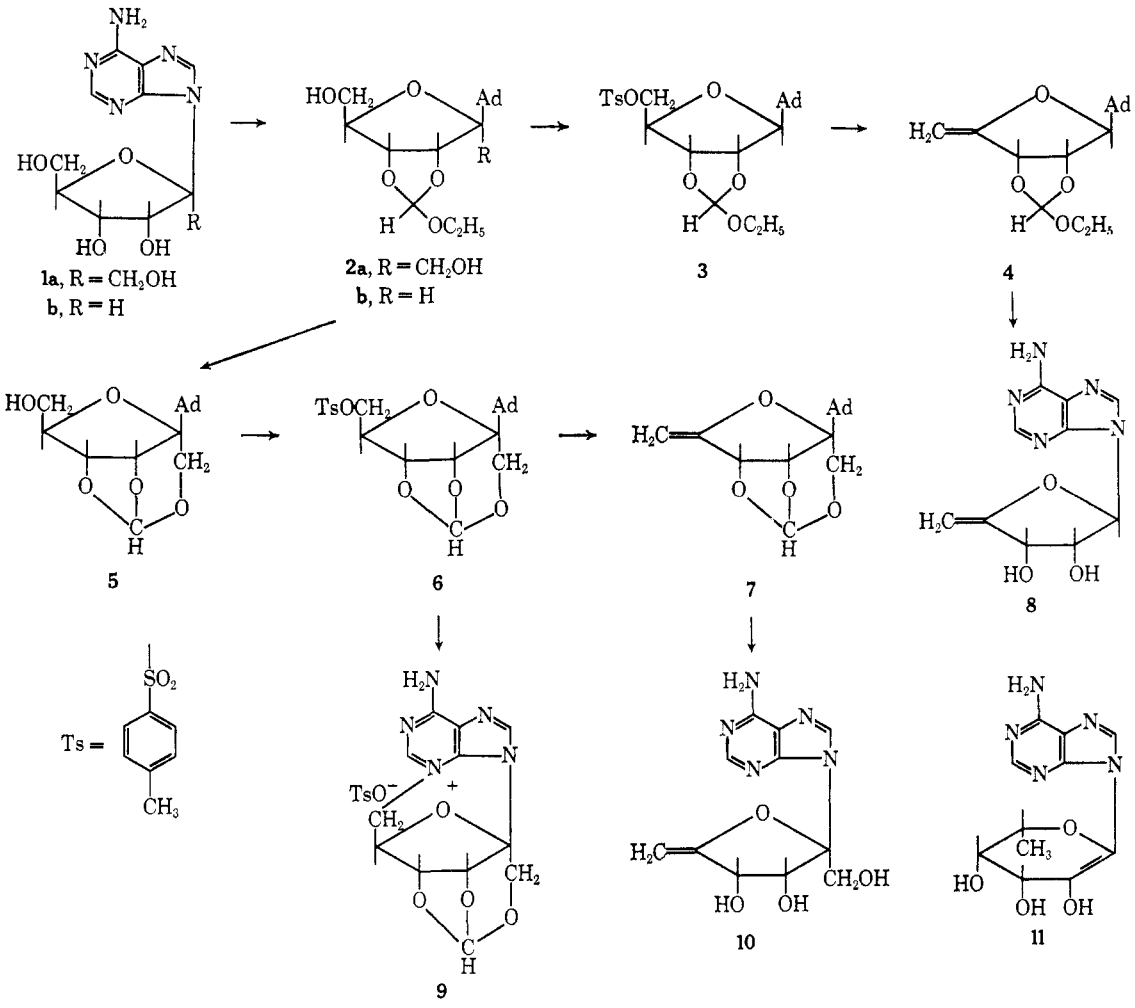
(1) This research was supported by Institutional Research Grant No. CA-08109 from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) H. Yüntsen, K. Ohkuma, Y. Ishii, and H. Yonehara, *J. Antibiot.* (Tokyo), *Ser. A*, **9**, 195 (1956).

(3) H. Yüntsen, *ibid.*, **11**, 79, 233 (1958).

(4) H. Hoeksema, G. Slomp, and E. E. van Tamelen, *Tetrahedron Lett.*, 1787 (1964).

Scheme I



reported that the nucleoside antibiotic decoyinine, isolated[5] along with psicofuranine,[6,7] appeared to be identical with angustmycin A. These workers[4] investigated the structure of the hexose nucleoside, decoyinine, using pmr spectroscopy as well as chemical methods and assigned the antibiotic structure **10**. The data of Yüntsen[2,3] were reinterpreted in accordance with structure **10**. It has been noted that psicofuranine (**1a**) and decoyinine (**10**) are in reversible equilibrium in a fermentation with *S. hygroscopicus*, var. *decoyicus*.[4]

The nucleoside antibiotic **10** has been found to possess significant antibacterial and antitumor activity.[8] The mechanism of action[9-11] and mode of biosynthesis[12] of angustmycin A (decoyinine) have been studied.

Since psicofuranine (**1a**) has been prepared chemically,[6,13,14] a successful conversion of psicofuranine to angustmycin A would constitute a total synthesis. A promising synthetic approach was the possibility of utilizing an E2 elimination of *p*-toluenesulfonate from the $C_{6'}$ carbon. This procedure has proved to be effective in our laboratory for introducing a 2′,3′ double bond in adenosine derivatives.[15] The use of psicofuranine as starting material involved the problem of its known instability[16] in acid and base and the problem of selectively blocking the primary hydroxyl at $C_{1'}$ in the presence of the primary hydroxyl group at $C_{6'}$.

Treatment of psicofuranine (**1a**) with triethyl orthoformate according to the general procedure of Eckstein and Cramer[17] gave a multicomponent mixture as judged by thin layer chromatography (tlc). When the reaction was allowed to proceed at 15° for 48–96 hr, a major product and several minor components including unchanged starting material were observed with tlc. Spectroscopic and chemical investigation of the major component (isolated in 65% yield) defined its structure

(5) See footnote 5 of ref 4.
(6) W. Schroeder and H. Hoeksema, *J. Amer. Chem. Soc.*, **81**, 1767 (1959).
(7) T. E. Eble, H. Hoeksema, G. A. Boyack, and G. M. Savage, *Antibiot. Chemotherapy*, **9**, 419 (1959).
(8) See, for example, C. Lewis, H. R. Reames, and L. E. Rhuland, *ibid.*, **9**, 421 (1959); J. J. Vavra, A. Dietz, B. W. Churchill, P. Siminoff, and H. J. Koepsell, *ibid.*, **9**, 427 (1959); N. Tanaka, N. Miyairi, and H. Umezawa, *J. Antibiot.* (Tokyo), *Ser. A*, **13**, 265 (1960); N. Tanaka, T. Nishimura, H. Yamaguchi, and H. Umezawa, *ibid.*, **14**, 98 (1961).
(9) N. Tanaka, *ibid.*, **16**, 163 (1963).
(10) A. Bloch and C. A. Nichol, *Biochem. Biophys. Res. Commun.*, **16**, 400 (1964).
(11) N. Miyairi, N. Tanaka, and H. Umezawa, *J. Antibiot.* (Tokyo), *Ser. A*, **14**, 119 (1961).
(12) B. M. Chassy, T. Sugimori, and R. J. Suhadolnik, *Biochim. Biophys. Acta*, **130**, 12 (1966).
(13) W. Schroeder, U. S. Patent 2,993,039 (1961); *Chem. Abstr.*, **55**, 23568 (1961), and U. S. Patent 3,014,900 (1961); *Chem. Abstr.*, **56**, 11694 (1962).
(14) J. Farkaš and F. Šorm, *Tetrahedron Lett.*, 813 (1962); *Collect. Czech. Chem. Commun.*, **28**, 882 (1963).
(15) J. R. McCarthy, Jr., M. J. Robins, L. B. Townsend, and R. K. Robins, *J. Amer. Chem. Soc.*, **88**, 1549 (1966).
(16) E. R. Garrett, *ibid.*, **82**, 827 (1960).
(17) F. Eckstein and F. Cramer, *Chem. Ber.*, **98**, 995 (1965).

as 3′,4′-*O*-ethoxymethylidinepsicofuranine (**2a**) (Scheme I). This is presumably the thermodynamic product of near equilibrium, and an examination of molecular models shows the absence of 1,3-nonbonded interactions in this product which can be present in the six-membered ring of the isomeric 1′,3′-*O*-ethoxymethylidinepsicofuranine structure. The stereochemistry of the asymmetric orthoformyl carbon was not investigated, but the orthoformate proton resonance (pmr) appeared as a sharp singlet at δ 6.07 in DMSO-d_6 indicating the selective formation of only one of the two possible diasterioisomers[18] in this equilibrium reaction. The 1′-hydroxymethylene protons appeared as a crude doublet at δ 4.03 and the 6′-hydroxymethylene group as a similar peak at δ 3.44. Addition of D_2O and a trace of deuterated acetic acid caused the 1′ peak to collapse to a sharp singlet at δ 4.12 while the 6′ peak at δ 3.52 remained a crude doublet.

Product **2a** was treated with boron trifluoride etherate in absolute dioxane which effected facile ring closure to the orthoformyl tridentate (**5**). This ring formation accomplished selective blocking of the $C_{1'}$ hydroxyl group. The procedure of Kochetkov[19] utilizing sodium methoxide to form a tridentate orthobenzoate from a 1,2-*O*-methoxybenzylidine orthoester failed to effect ring closure of **2a** to **5**.

The formation of **5** provides the first unequivocal proof of anomeric configuration of psicofuranine (**1a**). The syntheses[6,13,14] of psicofuranine from poly-*O*-acylpsicofuranosyl halide and a chloromercury adenine derivative proved all the general structural features of the molecule but could readily lead to either anomer as discussed by Baker and coworkers.[20] The problem of the anomeric configuration of psicofuranine has been discussed in a recent review.[21] Examination of structure **5** reveals that only the β anomer with the 1′-CH_2OH function below the plane of the sugar could form this tridentate orthoformate. The pmr spectrum of **5** in DMSO-d_6 exhibited a sharp singlet at δ 6.47 corresponding to the orthoformate proton and a well-defined AB system centered at δ 3.96 with peaks at δ 3.72, 3.89, 4.02, and 4.20 corresponding to the 1′ protons in the rigid ring system.[22] The triplet centered at δ 1.21 and the quartet at δ 3.68 corresponding to the ethoxyl group in the spectrum of **2a** were absent. The peak assigned to the 6′-hydroxymethylene group of **5** appeared as a poorly defined multiplet centered at δ 3.57 similar to the corresponding peak in the spectrum of **2a**.

Treatment of **5** with *p*-toluenesulfonyl chloride in pyridine gave 6′-*O*-*p*-toluenesulfonyl-1′,3′,4′-*O*-orthoformylpsicofuranine (**6**) in good yield. A small sample of compound **6** was heated in refluxing absolute dioxane to yield a white precipitate which exhibited an ultraviolet absorption spectrum similar to the spectrum of adenosine cyclonucleoside[23,24] with $\lambda_{max}^{H_2O}$ 272 mμ. The cyclonucleoside **9** had chromatographic properties similar to adenosine cyclonucleoside (saltlike behavior) and very different from the covalent tosylate **6** (λ_{max}^{EtOH} 259 mμ). Conversion of **6** to **9** further confirms the anomeric configuration of psicofuranine since cyclonucleoside formation is possible only with the β anomer. The previously unknown[21] anomeric configuration of angustmycin A (decoyinine) thus was also determined by the successful conversion of **6** to **10**.

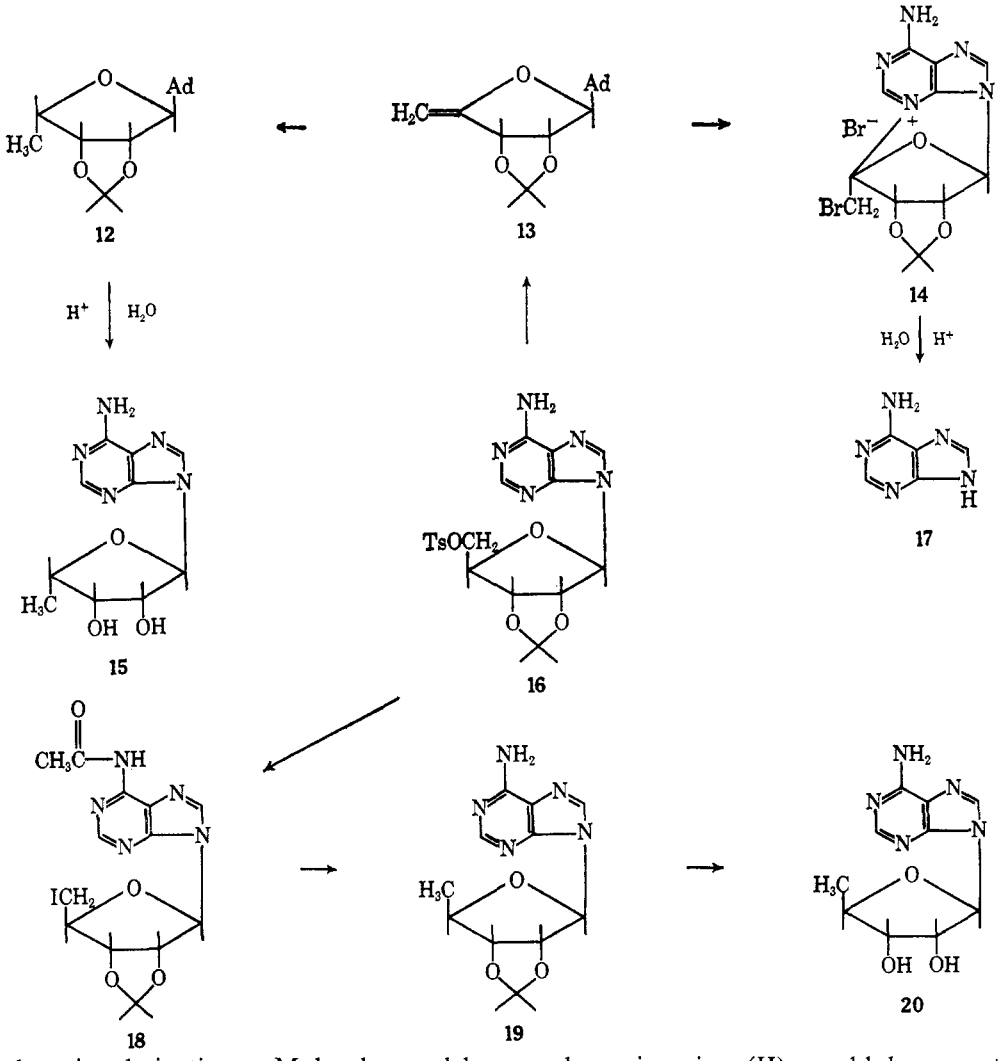
Treatment of 6′-*O*-*p*-toluenesulfonyl-1′,3′,4′-*O*-orthoformylpsicofuranine (**6**) with potassium *t*-butoxide in *t*-butyl alcohol–pyridine gave a 67% yield of 6-amino-9-(1,3,4-*O*-orthoformyl-6-deoxy-β-D-*erythro*-hex-5-enofuran-2-ulosyl)purine (**7**) (1′,3′,4′-*O*-orthoformylangustmycin A). It is noteworthy that E2 elimination is favored over cyclonucleoside formation under these conditions. Careful investigation of reaction conditions led to selective opening of the orthoformyl blocking function with aqueous acetic acid in dioxane at 50° for 30 hr. Subsequent treatment with alcoholic ammonia to remove formyl groups gave angustmycin A (decoyinine) (**10**) in 62% yield. Minor quantities of unreacted **7** and adenine formed by hydrolysis of the glycosidic linkage were readily separated from angustmycin A on a Dowex 1-X2 column.[25]

The synthetic product **10** was rigorously compared with natural decoyinine[26] and angustmycin A[27] by means of ultraviolet, infrared, and pmr spectroscopy, optical rotation, chromatography in four different solvent systems on tlc, and melting and mixture melting point behavior. In all cases the products proved to be identical. Thus decoyinine and angustmycin A are identical and possess the structure 6-amino-9-(β-D-*erythro*-hex-5-enofuran-2-ulosyl)purine (**10**). The potency of synthetic **10** against *S. faecalis* was found to be the same as natural decoyinine.[28]

In order to explore the possible generality of this synthetic route for the synthesis of other 4′-exocyclic methylene nucleosides, adenosine was chosen for further investigation. A preliminary account of this study has been published.[29] Treatment of 5′-*O*-*p*-toluenesulfonyl-2′,3′-*O*-isopropylidineadenosine[30] (**16**) with potassium *t*-butoxide in *t*-butyl alcohol–pyridine at room temperature gave a 35% yield of 6-amino-9-(2,3-*O*-isopropylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**13**) (Scheme II). However, attempts to remove the isopropylidine blocking group by mild acid hydrolysis gave only adenine plus unreacted **13**. Treatment of 2′,3′-*O*-ethoxymethylidineadenosine (**2b**)[17] with *p*-toluenesulfonyl chloride in pyridine at −20° provided 5′-*O*-*p*-toluenesulfonyl-2′,3′-*O*-ethoxymethylidineadenosine (**3**) in good yield. Potassium *t*-butoxide catalyzed elimination of *p*-toluenesulfonate from **3** gave 6-amino-9-(2,3-*O*-ethoxymethylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**4**) in 31% yield. Cyclonucleoside formation (observed by tlc) competes successfully with E2 elimination in the

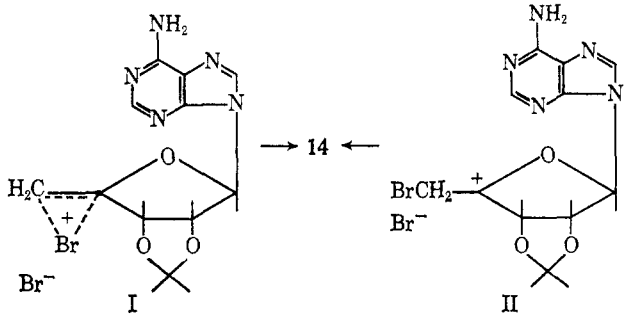
(18) B. E. Griffin, M. Jarman, C. B. Reese, and J. E. Stulston, *Tetrahedron*, **23**, 2301 (1967).
(19) N. K. Kochetkov, A. J. Khorlin, A. F. Bochkov, and I. G. Yazlovetsky, *Carbohyd. Res.*, **2**, 84 (1966).
(20) E. J. Reist, P. A. Hart, and B. R. Baker, *J. Org. Chem.*, **24**, 1640 (1959).
(21) J. J. Fox, K. A. Watanabe, and A. Bloch, *Progr. Nucleic Acid Res. Mol. Biol.*, **5**, 251 (1966).
(22) These peaks correspond to an AB system with J_{AB} = 10.5 Hz and $\Delta\nu$ = 15.2 Hz at 60 MHz ($\Delta\nu$ = 0.25 δ unit). See K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 3.
(23) V. M. Clark, A. R. Todd, and J. Zussman, *J. Chem. Soc.*, 2952 (1951).
(24) A. Hampton and A. W. Nichol, *J. Org. Chem.*, **32**, 1688 (1967).
(25) C. A. Dekker, *J. Amer. Chem. Soc.*, **87**, 4027 (1965).
(26) The authors wish to thank Dr. G. B. Whitfield of the Upjohn Co. for a generous sample of decoyinine.
(27) The authors wish to thank Dr. Noboru Otake of the University of Tokyo for an authentic sample of angustmycin A.
(28) Dr. A. Bloch, Roswell Park Memorial Institute, Buffalo, N. Y., private communication.
(29) J. R. McCarthy, Jr., M. J. Robins, and R. K. Robins, *Chem. Commun.*, 536 (1967).
(30) R. Kuhn and W. Jahn, *Chem. Ber.*, **98**, 1699 (1965).

Scheme II



case of these adenosine derivatives. Molecular models illustrate the greater ease of formation of the cyclonucleoside ring with **3** and **16** than in the case of the more rigid tricyclic orthoformylpsicofuranine molecule **6**. Successive treatment of **4** with aqueous acetic acid in dioxane and then with methanolic ammonia gave a 78% yield of 6-amino-9-(5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**8**), the 4′,5′-unsaturated derivative of adenosine. Attempted preparation of **8** by direct elimination of *p*-toluenesulfonate from 5′-*O*-*p*-toluenesulfonyladenosine[30] gave dark reaction mixtures containing several components but very little of the desired product **8**. Similar results were observed using acyl protecting groups on other nucleosides, and it therefore would appear that base stable blocking groups are necessary for successful elimination.

For a preliminary study of the chemistry of the 4′,5′-exocyclic methylene function of these nucleosides, 6-amino-9-(2,3-*O*-isopropylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**13**) was selected because of its ease of synthesis. Treatment of **13** with bromine in chloroform gave an immediate precipitate with simultaneous decolorization of the solution. The ultraviolet absorption maximum of the product **14** (276 mμ in methanol) indicated cyclonucleoside formation. Examination of molecular models indicated the proximity of the 3-nitrogen atom of the adenine ring to the 4′-carbon of the double bond. Thus, attack of the 3-nitrogen on *endo*-bromium ion (I) or on the planar carboxonium ion (II) would be expected to lead to $N^3 \rightarrow 4'$-cyclonucleoside **14**. Support for structure **14**



was obtained from acid hydrolysis studies. Holmes and Robins[31] treated 2′,3′-*O*-isopropylidine-$N^3 \rightarrow 5'$-adenosine cyclonucleoside (the other possible cyclonucleoside type isomeric with **14**) with 1 *N* HCl on the steam bath for 40 min and obtained 5-deoxy-5-(6-aminopurin-3-yl)ribose. Identical treatment of **14** gave only adenine (**17**) which is the expected hydrolysis product of the 1′-aldosyl-4′-ketosyldiglycoside **14**.

Further proof of structure **14** was obtained by low-pressure hydrogenation over 5% palladium–carbon catalyst. The pmr spectrum of the resulting product exhibited a singlet at δ 1.50 (3 protons) corresponding to a methyl group (5′ protons) attached to an electron-

(31) R. E. Holmes and R. K. Robins, *J. Org. Chem.*, 28, 3483 (1963).

deficient carbon (4′-carbon). The peak δ 5.26 (s, 2 protons) corresponding to the bromomethylene group (5′ protons) in the spectrum of **14** was absent. The uv spectra of **14** and the hydrogenation product were very similar indicating that no reduction of the adenine ring or other changes had occurred. This represents the first observation of a 4′-cyclonucleoside derivative of a furanose nucleoside.

Hydrogenation of 6-amino-9-(2,3-*O*-isopropylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**13**) occurred stereospecifically to give **12** as observed in related systems.[32,33] In contrast similar hydrogenation of 6-amino-9-(5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**8**) gave both epimers **15** and **20** as observed with tlc. Reaction of **12** in dilute formic acid at room temperature for 11 days gave 6-amino-9-(5-deoxy-α-L-*lyxo*-pentofuranosyl)purine (**15**) with concomitant glycosidic cleavage to adenine, which was removed by passage through Dowex 1-X2. The 4′ epimer, 5′-deoxyadenosine (**20**), was synthesized for direct comparison with **15**. A more convenient method of preparation of 5′-deoxyadenosine (**20**) than previously reported[34] was achieved in our laboratory by hydrogenation of 6-acetamido-9-(2,3-*O*-isopropylidine-5-iodo-5-deoxy-β-D-*ribo*-pentofuranosyl)purine,[35] followed by deblocking. Comparison of physical constants, pmr spectra, and chromatographic mobilities of **15** and **20** showed the compounds to be different. It is interesting to note that in aqueous acetic acid compound **12** remains completely unchanged under identical conditions that give at least 90% deblocking of its 4′ epimer **19**.

It is interesting to note that the adenosine derivative **8** has been found[28] to exhibit approximately equal antibacterial potency against *Streptococcus faecalis* as angustmycin A (**10**). The biological activity of **8** and related nucleosides containing the 4′,5′-exocyclic methylene function will be reported in a separate communication.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Pmr spectra were determined with a Varian A-60 instrument. Optical rotations were determined on a Perkin-Elmer Model 141 automatic digital readout polarimeter. Thin layer chromatography (tlc) was run on glass plates coated with S (SilicAR TLC-7GF, product of Mallinckrodt Chemical Works) or A (Aluminum Oxide HF 254, distributed by Brinkmann Instruments, Inc.) using the following solvent systems: (1) ethyl acetate–methanol 9:1, (2) upper phase of ethyl acetate–*n*-propyl alcohol–water 4:1:2, (3) acetone–water 2:1, (4) methanol–water 7:3. Tlc support (S or A) and the solvent system number are given in parentheses. Migrated spots were observed under uv light. All evaporations were accomplished under reduced pressure using a Büchler rotating evaporator unless otherwise specified.

3′,4′-*O*-Ethoxymethylidinepsicofuranine (2a). Psicofuranine[36] (**1a**) (0.5 g, 0.0017 mol) and AR grade trichloroacetic acid (1.15 g, 0.007 mol) were added to 15 ml of absolute[37] *p*-dioxane and the mixture was stirred at room temperature until a clear solution was obtained. Triethyl orthoformate (2.65 g, 0.0178 mol) was added and the colorless solution was stirred at 15° (bath temperature) while protected from moisture. The reaction was monitored by tlc and after 2–4 days one major spot (S, 2) ($R_f \cong 0.6$) plus minor faster spots and psicofuranine were observed. The solution was diluted with 100 ml of ethanol and treated immediately with excess Amberlite IR-45 (OH^- form) resin.[38] The mixture was stirred until neutral, the resin removed by filtration, and the filtrate evaporated to dryness. The resulting white solid was dissolved in 100 ml of boiling ethanol; the solution was concentrated to 40 ml and cooled at 0° overnight. The white crystals (0.39 g, 66%) which separated were collected by filtration. Recrystallization of a small amount of this product, **2a**, from acetone gave an analytically pure sample: mp 248–250°; uv λ_{max}^{EtOH} 259 mμ (ε 15,600); $\lambda_{max}^{pH\ 11}$ 260 mμ (ε 16,200); pmr (DMSO-d_6–D_2O–DOAc-d_4) δ 1.25 (t, 3, J = 7 Hz, $-OCH_2CH_3$), 3.78 (q, 2, J = 7 Hz, $-OCH_2CH_3$), 6.17 (s, 1, methylidine-H), 4.12 (s, 2, 1′ CH_2OD), 5.99 (d, 1, $J_{3',4'}$ = 7 Hz, 3′ H), 4.95 (doublet of doublets, 1, $J_{4',3'}$ = 7 Hz, $J_{4',5'}$ = 2.5 Hz, 4′ H), 4.58 [m, 1, $J_{5',4'}$ = 2.5 Hz (plus multiple splitting with 6′), 5′ H], 3.52 (crude doublet with multiple splitting, 2, 6′ H), 8.35 (split peak, 2, 2, and 8 protons of adenine ring); pmr (DMSO-d_6) δ 4.03 (d, 2, J = 5.5 Hz, 1′ CH_2OH).

Anal. Calcd for $C_{14}H_{19}N_5O_6$: C, 47.55; H, 5.38; N, 19.8. Found: C, 47.47; H, 5.59; N, 19.8.

1′,3′,4′-*O*-Orthoformylpsicofuranine (5). 3′,4′-*O*-Ethoxymethylidinepsicofuranine (**2a**) (0.353 g, 0.001 mol) was dissolved in 40 ml of boiling absolute[37] dioxane and cooled to room temperature. Boron trifluoride etherate (8 ml) was added and the reaction was allowed to stand 15 min while protected from moisture. A small amount of fine white solid separated from solution during this time. The mixture was poured into 250 ml of freshly prepared saturated aqueous sodium carbonate solution (still warm) and then was extracted with 100 ml of ether. The aqueous layer was further extracted with three 40-ml portions of ether–dioxane (3:1) and the combined organic phase was dried over sodium sulfate, filtered, and evaporated to dryness. The resulting white solid (0.33 g) was dissolved in 4 ml of dioxane, and 4 ml of chloroform was added. This solution was applied to a column of neutral alumina (20 g) packed in dioxane–chloroform (1:1), the column was washed with 100 ml of dioxane–chloroform (1:1) followed by 100 ml of dioxane–methanol (98:2), and these washes were discarded. Elution with dioxane–methanol (95:5) was begun and all fractions with appreciable absorption at 259 mμ were combined and evaporated to dryness. The resulting white solid was crystallized from 7 ml of ethanol giving two crops of white crystals of **5** (0.18 g, 59%); tlc (A, 1) $R_f \cong 0.2$, (A, 2) $R_{2a}/R_5 = 0.7$; mp 256–258° (when placed on a rapidly heating block preheated to 240°); uv λ_{max}^{EtOH} 259 mμ (ε 18,400), $\lambda_{max}^{pH\ 1}$ 257 mμ (ε 17,500), $\lambda_{max}^{pH\ 11}$ 259 mμ (ε 18,700); pmr (DMSO-d_6) δ 6.47 (s, 1, orthoformyl proton), 3.96 (AB pattern [q], 2, $J_{1a',1b'}$ = 10.5 Hz, $\Delta\nu$ = 15.2 Hz at 60 MHz,[22] 1′ CH_2O–), 5.89 (d, 1, $J_{3',4'}$ = 4.5 Hz, 3′H), 4.63 (m, 2, 4′, and 5′ H's), 3.57 (m, 2, 6′ CH_2OH), 5.01 (t, 1, J = 4.8 Hz, 6′ CH_2OH), 7.33 (s, 2, 6 NH_2), 8.21 (s, 1, 2 or 8 proton), 8.26 (s, 1, 2, or 8 proton).

Anal. Calcd for $C_{12}H_{13}N_5O_5$: C, 46.9; H, 4.23; N, 22.8. Found: C, 46.9; H, 4.44; N, 22.65.

1′,3′,4′-*O*-Orthoformyl-6′-*O*-*p*-toluenesulfonylpsicofuranine (6). 1′,3′,4′-*O*-Orthoformylpsicofuranine (**5**, 0.34 g, 0.0011 mol) was dissolved in 5 ml of AR pyridine (dry) and cooled to 0°. Purified *p*-toluenesulfonyl chloride (0.6 g, 0.0031 mol) was added and the reaction was allowed to stand 2 days at 0° while protected from light and moisture. The yellow solution was poured into 20 ml of ice-cold saturated aqueous sodium bicarbonate solution. This solution was extracted with three 25-ml portions of chloroform and the combined organic phase was washed with three 15-ml portions of ice water, dried over sodium sulfate, filtered, and evaporated to dryness *in vacuo* (oil pump) at 20° (bath temperature). Ethanol was added to the light yellow glass causing it to solidify. Compound **6** (0.4 g, 78%) was collected by filtration and washed thoroughly with cold ethanol: uv λ_{max}^{MeOH} 259 and 225 mμ, ir band 1170 cm^{-1} (covalent –OTs). Tlc (A, 1) showed the product to be homogeneous with $R_f \cong 0.8$. This intermediate was used directly without further purification.

6-Amino-9-(1,3,4-*O*-orthoformyl-6-deoxy-β-D-*erythro*-hex-5-enofuran-2-ulosyl)purine (1′,3′,4′-*O*-Orthoformylangustmycin A) (7). 1′,3′,4′-*O*-Orthoformyl-6′-*O*-*p*-toluenesulfonylpsicofuranine (**6**, 0.38 g, 0.00082 mol) was dissolved in 30 ml of dry AR pyridine at 20° and 30 ml of *t*-butyl alcohol was added. Potassium *t*-butoxide

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(38) Mallinckrodt Chemical Works.

(0.46 g, 0.0041 mol) was added and the resulting dark solution was stirred at room temperature for 5 min. The solution was then poured into a stirring mixture of 150 ml of ethanol and 5 ml of Amberlite IRC-50 (H^+ form) resin.[38] The mixture was stirred until neutral and the resin was filtered and washed with 50 ml of ethanol. The combined filtrate was evaporated to dryness *in vacuo* (oil pump) and extracted with three 50-ml portions of boiling chloroform. The combined extracts were evaporated to dryness and the resulting white solid was crystallized from 10 ml of ethanol to yield two crops of 1′,3′,4′-*O*-orthoformylangustmycin A (**7**) as needles (0.16 g, 67%): mp 254–257° dec (when placed on a rapidly heating block preheated to 245°); uv λ_{max}^{EtOH} 258 mμ (ε 13,300); $\lambda_{max}^{pH\ 11}$ 258 mμ (ε 14,200); pmr (DMSO-d_6) δ 6.58 (s, 1, orthoformyl H), 4.31 and 4.58 (two complex multiplets corresponding to four protons of the overlapping 1′ CH_2O– and 6′ $=CH_2$ AB patterns), 6.36 (d, 1, $J_{3',4'}$ = 5 Hz, 3′ H), 5.14 (d, 1, $J_{4',3'}$ = 5 Hz, 4′ H), 7.46 (s, 2, 6 NH_2), 8.22 and 8.34 (singlets, 2 and 8 protons).

Anal. Calcd for $C_{12}H_{11}N_5O_4$: C, 49.8; H, 3.80; N, 24.15. Found: C, 49.8; H, 3.90; N, 23.94.

Angustmycin A (Decoyinine) [6-Amino-9-(6-deoxy-β-D-*erythro*-hex-5-enofuran-2-ulosyl)purine] (10). 1′,3′,4′-*O*-Orthoformylangustmycin A (**7**, 0.23 g, 0.0008 mol) was dissolved in 60 ml of absolute[37] dioxane and 60 ml of 20% aqueous acetic acid was added. The solution was heated at 50° (bath temperature) for 30 hr. Tlc (**S**, 1) showed **10**, a small amount of unreacted **7**, a small quantity of adenine, and a spot presumably corresponding to the formyl esters of **10**. The solution was evaporated *in vacuo* (oil pump) at less than 40° (bath temperature) and ethanol was added several times during the evaporation. The resulting white solid was treated with 150 ml of methanol presaturated with ammonia at −5° and this solution was stirred at room temperature overnight. The solution was evaporated to dryness and the resulting light yellow solid was dissolved in 5 ml of methanol–water (7:3) and applied to a column (1 × 10 cm) of Dowex 1-X2 (OH^- form, 200–400 mesh) packed in the same solvent. Elution was effected with methanol–water (7:3) under pressure and 10-ml fractions were collected. Tlc showed that fractions 1–3 contained unreacted **7** and fractions 15–26 contained angustmycin A (**10**). Fractions 15–26 were combined and evaporated to dryness under reduced pressure. Crystallization of the resulting white solid from 1.5 ml of water gave 0.1 g (42%) of colorless needles of angustmycin A monohydrate, mp 129.5–133°, softens 125°, resolidifies and decomposes 156–170°. A second crop of 0.029 g of crystalline **10** was obtained from the filtrate and 0.020 g of crystalline starting material **7** was obtained from fractions 1–3 to give a total yield of 0.129 g (63% allowing for recovered **7**) of **10**. The analytically pure sample of **10** had mp 130–133° (softens 125°, completely resolidified by 150°, decomposes 156–159°). A sample of natural angustmycin A was subjected to the same column and crystallization procedure for direct comparison. Its melting point behavior and a mixture melting point were identical with that for the synthetic sample: uv synthetic **10**, $\lambda_{max}^{H_2O}$ 259 mμ (ε 15,500); $\lambda_{max}^{pH\ 11}$ 259 mμ (ε 15,500); natural **10** $\lambda_{max}^{H_2O}$ 259 mμ (ε 15,500); $\lambda_{max}^{pH\ 11}$ 259 mμ (ε 15,500); synthetic **10**; $[\alpha]^{26}D$ +43.5° (*c* 1, H_2O); natural **10**, $[\alpha]^{26}D$ +43.8 (*c* 1, H_2O). The ir spectra of synthetic and natural **10** were superimposable in every detail and the samples had the same pmr spectra with complex overlap as reported in ref 4. Tlc in four different solvent systems showed identical mobilities for the synthetic and natural compounds.

Anal. Calcd for $C_{11}H_{13}N_5O_4 \cdot H_2O$: C, 44.40; H, 5.05; N, 23.55. Found (synthetic): C, 44.40; H, 5.05; N, 23.79. Found (natural): C, 44.15; H, 5.08; N, 23.51.

1′,3′,4′-*O*-Orthoformyl-N^3→6′-cyclopsicofuranine-*p*-toluenesulfonate (9). 1′,3′,4′-*O*-Orthoformyl-6′-*O*-*p*-toluenesulfonylpsicofuranine (**6**, 3.3 mg) was dissolved in 2 ml of absolute[37] dioxane and the solution was heated at reflux for 12 hr. The mixture containing white crystals was cooled and filtered to yield 1.7 mg of **9**, uv $\lambda_{max}^{H_2O}$ 271 mμ, $\lambda_{max}^{pH\ 1}$ 270 mμ. Tlc (A, 1) showed similar migration of **9** and 2′,3′-*O*-isopropylidine-N^3→5′-cycloadenosine-*p*-toluenesulfonate[31] which was *much* slower in organic phase systems than **6**.

5′-*O*-*p*-Toluenesulfonyl-2′,3′-*O*-ethoxymethylidineadenosine (3). A solution of 5 g (0.0155 mol) of 2′,3′-*O*-ethoxymethylidineadenosine (**2b**)[17] in 100 ml of warm, dry AR pyridine was cooled to −20° and 5 g (0.026 mol) of *p*-toluenesulfonyl chloride was added. The yellow solution was allowed to stand at −20° for 2 days while protected from moisture. A solution of 2.5 g of sodium bicarbonate in 75 ml of ice water was added and the resulting mixture was extracted with three 75-ml portions of chloroform. The combined organic phase was washed with water, dried over sodium sulfate, filtered, and evaporated to a light yellow foam *in vacuo* (oil pump) at 20° (bath temperature). This product was dissolved in a small volume of methanol (*without* heating) and stored at −20°. Clear tan crystals formed which were collected by rapid filtration (hygroscopic) and immediately placed in a desiccator *in vacuo* over phosphorus pentoxide for 24 hr (5.25 g, 71%): uv λ_{max}^{MeOH} 259 mμ, ir band at 1170 cm^{-1} (covalent –OTs).

Anal. Calcd for $C_{26}H_{23}N_5O_7S$: C, 50.3; H, 4.82; N, 14.67. Found: C, 50.1; H, 4.95; N, 14.52.

6-Amino-9-(2,3-*O*-ethoxymethylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (4). To a solution of 4 g (0.0084 mol) of 5′-*O*-*p*-toluenesulfonyl-2′,3′-*O*-ethoxymethylidineadenosine (**3**) in 20 ml of dry AR pyridine were added 100 ml of *t*-butyl alcohol and then 6 g (0.0536 mol) of potassium *t*-butoxide. The resulting dark orange solution was allowed to stir at room temperature for 30 min while protected from moisture. The solution was diluted with 300 ml of methanol followed by addition of 20 ml of Amberlite IRC-50 (H^+ form)[38] and the mixture was stirred until neutral. The resin was removed by filtration and solvents were removed under reduced pressure. The residue was extracted with three 75-ml portions of boiling chloroform. The combined extract was evaporated to a light yellow solid foam. This foam was dissolved in 20 ml of warm chloroform and applied to a column of neutral alumina (90 g) packed in chloroform. The column was washed with 150 ml of chloroform followed by 150 ml of ethyl acetate and these washes were discarded. Elution of the product was effected with ethyl acetate–ethanol (1:1). Fractions with appreciable absorption at 260 mμ were combined and evaporated to dryness under reduced pressure. Crystallization of the residue from 10 ml of ethanol provided **4** as white crystals (0.8 g, 31%): mp 155–156°; uv λ_{max}^{MeOH} 258 mμ (ε 14,600), $\lambda_{max}^{pH\ 11}$ 258 mμ (ε 15,200); pmr ($CDCl_3$) δ 1.24 (t, 3, *J* = 7 Hz, $-OCH_2CH_3$), 3.66 (q, 2, *J* = 7 Hz, $-OCH_2CH_3$), 6.07 (s, 1, methylidine H), 6.37 (d, 1, *J* = 1.2 Hz, 1′ H), 5.61 (d, 1, $J_{2',3'}$ = 7 Hz, 2′ H), 5.42 [d (with secondary splitting $J_{3',5'} \cong 1$ Hz), 1, $J_{3'2'}$ = 7 Hz, 3′ H], 4.51 [AB pattern (with secondary splitting $J_{5',3'} \cong 1$ Hz), 2, $J_{5a',5b'}$ = 2.3 Hz, Δν = 7.1 Hz at 60 MHz, 5′ $=CH_2$], 6.66 (s, 2, 6 NH_2), 7.88 (s, 1, 2, or 8 H), 8.28 (s, 1, 2, or 8 H).

Anal. Calcd for $C_{13}H_{15}N_5O_4$: C, 51.1; H, 4.92; N, 23.0. Found: C, 51.0; H, 5.19; N, 23.1.

6-Amino-9-(5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (4′,5′-Didehydro-5′-deoxyadenosine) (8). To a solution of 2.2 g (0.0072 mol) of 6-amino-9-(2,3-*O*-ethoxymethylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**4**) in 90 ml of dioxane was added 90 ml of 20% aqueous acetic acid and the solution was heated at 50° (bath temperature) for 3.5 hr. The solvents were removed *in vacuo* (oil pump) and ethanol was added and then removed *in vacuo*. This process was repeated several times and the resulting solid was treated with 50 ml of methanol presaturated with ammonia at −5°. This solution was allowed to stand at room temperature overnight and then evaporated to dryness. The residue was dissolved in 10 ml of methanol–water (7:3) and applied to a column (1 × 15 cm) of Dowex 1-X2 (OH^- form, 200–400 mesh) packed in the same solvent. The column was eluted with methanol–water (7:3) under pressure and 60-ml fractions were collected. Tlc showed that fractions 1–4 contained unreacted **4** and fractions 12–25 contained the product (**8**). Fractions 12–25 were combined and evaporated to dryness. The white solid was crystallized from methanol giving two crops, 0.9 and 0.08 g of white crystals. Recovered starting material **4** (0.56 g) from fractions 1–4 raised the total yield of product **8** to 78%. A small sample of **8** was crystallized from acetone to give needles: mp 195–196° dec (when placed on a rapidly heating block preheated to 185°); uv λ_{max}^{MeOH} 258 mμ (ε 14,700); $[\alpha]^{26}D$ −46.4° (*c* 1, absolute *p*-dioxane); pmr (DMSO-d_6–D_2O), δ 6.33 (d, 1, $J_{1',2'}$ = 4.7 Hz, 1′ H), 4.97 (m, 2, 2′, and 3′ H's), 4.48 (AB pattern, 2, $J_{5a',5b'}$ = 2.3 Hz, Δν = 5.2 Hz at 60 MHz, 5′ $=CH_2$), 8.34 (s, 1, 2, or 8 H), 8.46 (s, 1, 2 or 8 H).

Anal. Calcd for $C_{10}H_{11}N_5O_3$: C, 48.2; H, 4.42; N, 28.1. Found: C, 48.1; H, 4.55; N, 27.95.

6-Amino-9-(2,3-*O*-isopropylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (13). To a solution of 13.1 g (0.03 mol) of 5′-*O*-*p*-toluenesulfonyl-2′,3′-*O*-isopropylidineadenosine[30] in 100 ml of dry AR pyridine were added 100 ml of *t*-butyl alcohol and then 16.8 g (0.15 mol) of potassium *t*-butoxide. The dark solution was stirred at room temperature for 30 min while protected from moisture. The reaction was then poured into a stirred mixture of 200 ml of ethanol and 65 ml of Amberlite IRC-50 (H^+ form) resin.[38] The mixture was stirred until neutral and filtered; the filtrate was evaporated to dryness *in vacuo* (oil pump). The residue was extracted with three 75-ml portions of boiling chloroform and the combined extract evaporated to dryness. The resulting solid was

dissolved in 150 ml of boiling ethanol; the solution was filtered through a carbon–Celite bed and concentrated to 50 ml. The crystals of **13** which separated upon cooling (3 g, 35%) were recrystallized from ethanol to give analytically pure material: mp 182–183°; uv λ_{max}^{MeOH} 258 mμ (ε 15,600); pmr spectrum similar to that of **4**.

Anal. Calcd for $C_{13}H_{15}N_5O_3$: C, 54.0; H, 5.19; N, 24.2. Found: C, 53.9; H, 5.18; N, 24.2.

5′-Bromo-5′-deoxy-2′,3′-*O*-isopropylidine-N³→4′-cycloadenosine Bromide (14). A solution of 0.29 g (0.001 mol) of 6-amino-9-(2,3-*O*-isopropylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)-purine (**13**) in 40 ml of dry AR chloroform was cooled to 10° and a solution of 0.17 g (0.00105 mol) of bromine in 20 ml of chloroform was added dropwise with stirring at 10°. Decolorization of the bromine solution was accompanied by the immediate precipitation of a solid. The mixture was stored at 0° for 12 hr after the addition was complete and then 10 ml of ligroin (bp 60–90°) was added. The product was collected by filtration and washed well with chloroform–ligroin (bp 60–90°) (1:1) to give 0.4 g (89%) of white solid. The solid was recrystallized from ethanol to give analytically pure needles of **14**: mp 156° dec: uv λ_{max}^{MeOH} 276 mμ (ε 12,700), $\lambda_{max}^{pH\ 1}$ 274 mμ (ε 13,900); pmr (DMSO-d_6), δ 5.26 (s, 2, 5′ CH_2Br); the pmr spectrum also confirmed the presence of 0.5 mol of ethanol by integration of the corresponding peaks.

Anal. Calcd for $C_{13}H_{15}Br_2N_5O_3 \cdot 0.5C_2H_5OH$: C, 35.4; H, 3.78; N, 15.0; Br, 34.2. Found: C, 35.6; H, 3.81; N, 14.8; Br, 33.9.

Acid Hydrolysis of Compound 14. A solution of 0.02 g of **14** in 1.5 ml of 1 *N* HCl was heated on the steam bath for 40 min. The solution was neutralized with aqueous ammonia and chromatographed (tlc) *vs.* adenine and 8-bromoadenine[39] in three different solvent systems. Only one uv absorbing spot was detected which had identical mobility with that of adenine and separated distinctly from 8-bromoadenine in each system. The uv spectra of the reaction solution showed $\lambda_{max}^{pH\ 1}$ 263 mμ and $\lambda_{max}^{pH\ 11}$ 269 mμ identical with those of adenine.

Hydrogenation of Compound 14. To a solution of the 5′-bromocyclonucleoside **14** (0.068 g, 0.00015 mol) in 5 ml of water containing 1.5 ml of 0.1 *N* aqueous sodium bicarbonate was added 0.038 g of 5% Pd–C catalyst and the mixture was hydrogenated at 3.5 psi on a Parr shaker for 8 min. The mixture was filtered through a Celite pad and the filtrate was evaporated to dryness. The uv absorption spectrum of this solid was unchanged from that of starting **14** indicating no reduction or other reaction of the purine ring. Pmr (D_2O–DMSO-d_6), δ 1.50 (s, 3, 5′ CH_3), occurred between the peaks at δ 1.42 (s, 3, $-CH_3$) and 1.67 (s, 3, $-CH_3$) corresponding to the isopropylidine group and there was no absorption at δ 5.26 where the 5′ CH_2Br singlet of starting material **14** had occurred.

6-Amino-9-(5-deoxy-β-D-*erythro*-pentofuranosyl)purine (5′-Deoxyadenosine) (20).[34] To a solution of 6-acetamido-9-(2,3-*O*-isopropylidine-5-iodo-5-deoxy-β-D-*erythro*-pentofuranosyl)purine[35] (**18**, 1.37 g, 0.003 mol) in 150 ml of ethanol containing 6.0 ml of 1 *N* aqueous sodium hydroxide was added 0.8 g of 5% Pd–C catalyst and the mixture was hydrogenated for 4 hr at 5 psi on a Parr shaker. Catalyst was removed by filtration through a Celite pad and the filtrate was evaporated to dryness. The residue was partitioned between 100 ml of chloroform and 50 ml of water. The organic layer was washed with a saturated aqueous solution of sodium dithionite (50 ml), a saturated aqueous solution of sodium bicarbonate (25 ml), and water (25 ml), dried over sodium sulfate, filtered, and evaporated to dryness. The resulting white solid foam **19** was dissolved in 20% aqueous acetic acid (75 ml) and heated at 50° (bath temperature) for 3 days. The light yellow solution was evaporated to dryness and residual acid was coevaporated with ethanol several times. The residue was dissolved in 10 ml of methanol–water (7:3) and applied to a column (1.5 × 6 cm) of Dowex 1-X2 (OH^- form, 200–400 mesh) packed in the same solvent. The product **20** was eluted in the first 100 ml of methanol–water (7:3) which was evaporated to dryness. Crystallization of this solid from 5 ml of ethanol gave white crystals of **20** (0.32 g, 43%). Recrystallization of the product from ethanol gave the analytically pure sample: mp 212–213° (softens 135–140°, some sublimation with increasing temperature); $[\alpha]^{27}D$ −53.2° (*c* 1.0, ethanol); uv λ_{max}^{EtOH} 259 mμ (ε 16,100); λ_{max}^{pH} 257 mμ (ε 16,600), $\lambda_{max}^{pH\ 11}$ 259 mμ (ε 16,600) [lit.[34] mp 210–212° (liquefied at 180° and resolidified); $[\alpha]^{25}D$ −52.7° (*c* 1.0, ethanol); uv λ_{max}^{EtOH} 259 mμ (ε 13,760); $\lambda_{max}^{EtOH,acid}$ 257 mμ (ε 14,280), $\lambda_{max}^{EtOH,base}$ 259 mμ (ε 14,280)].

Anal. Calcd for $C_{10}H_{13}N_5O_3$: C, 47.80; H, 5.21; N, 27.87. Found: C, 47.72; H, 5.22; N, 27.66.

6-Amino-9-(2,3-*O*-isopropylidine-5-deoxy-α-L-*lyxo*-pentofuranosyl)purine (12). A solution of 6-amino-9-(2,3-*O*-isopropylidine-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)purine (**13**, 0.5 g, 0.0017 mol) in 90 ml of ethanol was hydrogenated at 5 psi for 12 hr in the presence of 0.3 g of 5% Pd–C catalyst on a Parr shaker. The catalyst was removed by filtration through Celite and the filtrate was evaporated to dryness. The residue was crystallized from 5 ml of ethanol giving white crystals (0.34 g, 67%). An additional 0.15 g of white crystals was obtained from the concentrated filtrate (total yield 0.49 g, 97%). Recrystallization of the product from ethanol gave the pure sample of **12**, mp 168.5–169°, uv λ_{max}^{MeOH} 259 mμ (ε 14,900).

Anal. Calcd for $C_{13}H_{17}N_5O_3$: C, 53.60; H, 5.88; N, 24.05. Found: C, 53.44; H, 5.60; N, 24.20.

6-Amino-9-(5-deoxy-α-L-*lyxo*-pentofuranosyl)purine (15). A solution of 6-amino-9-(2,3-*O*-isopropylidine-5-deoxy-α-L-*lyxo*-pentofuranosyl)purine (**12**, 0.13 g, 0.00045 mol) in 25 ml of 5% aqueous formic acid was allowed to stand at room temperature for 11 days. The solution was then evaporated to dryness, dissolved in 3 ml of methanol–water (7:3) and applied to a column (1.5 × 13 cm) of Dowex 1-X2 (OH^- form, 200–400 mesh) packed in the same solvent. The column was eluted with methanol–water (7:3) under pressure and 10-ml fractions were collected. Fractions 1 and 2 contained unreacted starting material **12** and fractions 4–9 contained product **15**. Fractions 4–9 were combined and evaporated to dryness. The solid material was crystallized from ethanol to give white needles of **15** (0.05 g, 58% based on recovered starting material). Recrystallization of the product from ethanol gave the analytically pure sample: mp 252–254° dec; $[\alpha]^{26}D$ −85.0 (*c* 0.5, DMF–EtOH 1:1); uv λ_{max}^{EtOH} 259 mμ (ε 15,700), $\lambda_{max}^{pH\ 1}$ 257 mμ (ε 16,100), $\lambda_{max}^{pH\ 11}$ 259 mμ (ε 16,100); tlc (S, 2) R_{20}/R_{15} = 1.15.

Anal. Calcd for $C_{10}H_{13}N_5O_3$: C, 47.80; H, 5.21; N, 27.87. Found: C, 48.01; H, 5.38; N, 27.85.

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