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Studies of Nucleosides and Nucleotides. LXXXIV.[1] Purine Cyclonucleosides. XL. Cyclonucleosides derived from 5′-Deoxyadenosine

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5′-Deoxyadenosine (I) was brominated at the 8-position and converted to 8,2′- (VI) and 8,3′-S-cyclonucleosides (VII) *via* the 2′,3′-dibutylstannylene compound by successive tosylation and heating with NaSH. When VI was treated with *tert*-butyl hypochlorite, an *exo* sulfoxide VIII was obtained. Desulfurization of VI and VII with Raney Ni gave 2′,5′- (IX) and 3′,5′-dideoxyadenosine (X), respectively. An 8,2′-O-cyclonucleoside (XII) was also obtained from V by a standard procedure. Rearrangement of XII to a ribo-type epoxide (XIII) in the presence of 0.1 N NaOH was observed.

Keywords——5′-chloro-5′-deoxyadenosine; 8-bromo-5′-deoxyadenosine; 8,2′-anhydro-8-thio-9-β-D-5-deoxyarabinofuranosyladenine; 8,3′-anhydro-8-thio-9-β-D-5-deoxyxylofuranosyladenine; 8,2′-anhydro-8-oxy-9-β-D-5-deoxyarabinofuranosyladenine; 8,2′-anhydro-8-thio-9-β-D-5-deoxyarabinofuranosyladenine sulfoxide; UV; CD; NMR; 5′-deoxy-2′,3′-anhydroadenosine

We have previously investigated various interconversion reactions of adenosine 8-cyclonucleoside.[3–6] These reactions involved the participation of the 5′-OH group, which is situated in the neighborhood of the reaction center. It therefore seemed of interest to study the reaction of cyclonucleoside bonds without participation of the 5′-OH group.

5′-Deoxyadenosine (I) might be a suitable starting material for this purpose. Synthesis of this compound has been performed *via* 8,5′-anhydro-8-mercaptoadenosine.[7] However, the overall yield from adenosine is rather low, and the route illustrated in Chart 1 was therefore adopted. Adenosine (II) was first chlorinated at the 5′-position with thionyl chloride in triethyl phosphate.[8] The yield was 65%. The resulting 5′-chloro-5′-deoxyadenosine (IIIa) was acetylated at 2′- and 3′-OH (IIIb) then reduced with tri-*n*-butyltin hydride in benzene solution. Deprotection with methanolic ammonia gave 5′-deoxyadenosine (I) in an overall yield of 52% calculated from adenosine. The UV absorption, chromatographic properties and nuclear magnetic resonance (NMR) signal at 1.30 ppm were consistent with this structure.

In order to obtain 8-S and -O-cyclonucleosides, compound I was first brominated as in the case of adenosine[9,10] and 8-bromo-5′-deoxyadenosine (IV) was obtained in a yield of 73%. Compound IV was treated with one equivalent of di-*n*-butyltinoxide,[11] then with tosyl chloride in dioxane at room temperature for 4 hr. The earlier procedure[10] required as much

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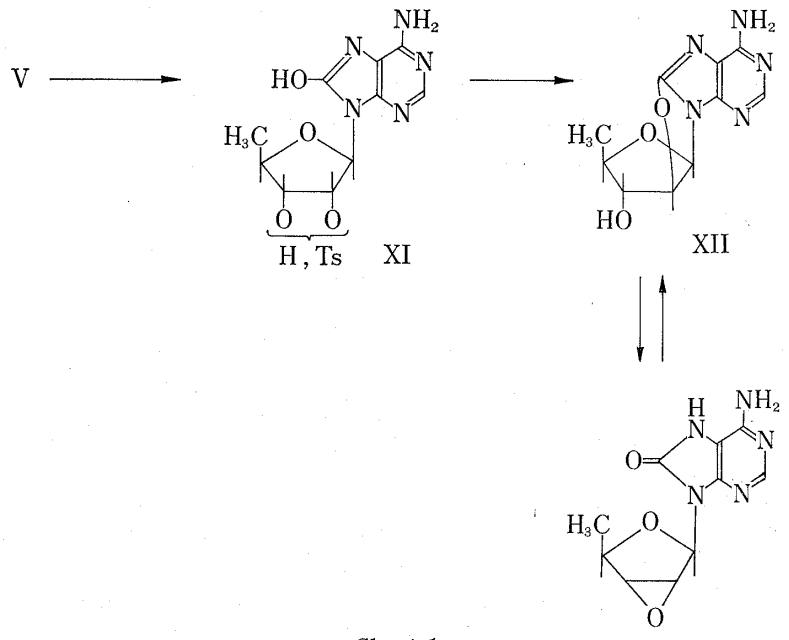

Chart 1

as 15 eq of the reagent, with methanol as a solvent. In contrast to the cases of adenosine[11] and bromoadenosine,[10] tosylation occurred at 2′- as well as 3′-OH, and 8-bromo-2′-O-tosyl-5′-deoxyadenosine and 8-bromo-3′-O-tosyl-5′-deoxyadenosine were obtained as a mixture V in a yield of 78%. The ratio of 2′- and 3′-O-tosylate was 7: 1. However, it was difficult to separate each compound from the product mixture.

The tosylate mixture V was then subjected to cyclization by heating with 2—3 eq of NaSH in aqueous dimethylformamide (DMF). The resulting cyclonucleosides were separated by column chromatography on Dowex 1×2 (OH^- form). Elution with 50% ethanol gave the 8,2′-S-cyclonucleoside (VI) as pale-yellow crystals, mp 225—226°, in a yield of 62%. Elution of the column with 1% aqueous acetic acid gave 8,3′-S-cyclo-5′-deoxyadenosine (VII) in a yield of 10.4%. Compound VI showed ultraviolet (UV) absorption characteristic of 8,2′-cycloadenosine, *i.e.*, $\lambda_{max}^{H_2O}$ at 276.5 nm and a large ε value (19300). In NMR spectra, the H-2′ signal appeared at 4.83 ppm and the H-1′ signal appeared as a doublet. In contrast, 8,3′-S-cyclonucleoside (VII) showed UV spectra with shoulders on the both sides of the absorption maximum at 281.5 nm; the NMR spectra of VII showed an H-3′ signal at 3.92 ppm and H-1′ appeared as a singlet. These spectral properties are characteristic of 2′- and 3′-cycloadenosines[12] respectively, and support the assigned structure. Elemental analysis also supported the correctness of the structure. Thus, both possible S-cyclonucleosides derived from 5′-deoxyadenosine were obtained.

When compound VI was oxidized with *tert*-butyl hypochlorite in methanol at −60°, a sulfoxide compound VIII was obtained in a yield of 60.5%. The UV absorption at 288 nm and a band at 1070 cm^{-1} in the infrared (IR) spectrum suggested VIII to be 8,2′-anhydro-8-thio-9-(5′-deoxyarabinofuranosyl)adenine S-oxide. The circular dichroism (CD) spectrum of this compound (Fig. 1) showed a large positive Cotton band at 288 nm. As discussed in the case of sulfoxides of S-cycloadenosine,[13] it must therefore be an *exo*-sulfoxide. This was further supported by NMR studies. The signal of 3′-proton was shifted towards lower field by 0.07 ppm and that of H-1′ was shifted towards higher field by 0.13 ppm. If the general rule derived from the cycloadenosine sulfoxides,[13] that the sugar proton on the S→O

12) M. Ikehara and T. Maruyama, *Tetrahedron*, **31**, 1369 (1975).
13) M. Ikehara, Y. Ogiso, and T. Morii, *Tetrahedron*, **32**, 43 (1976).

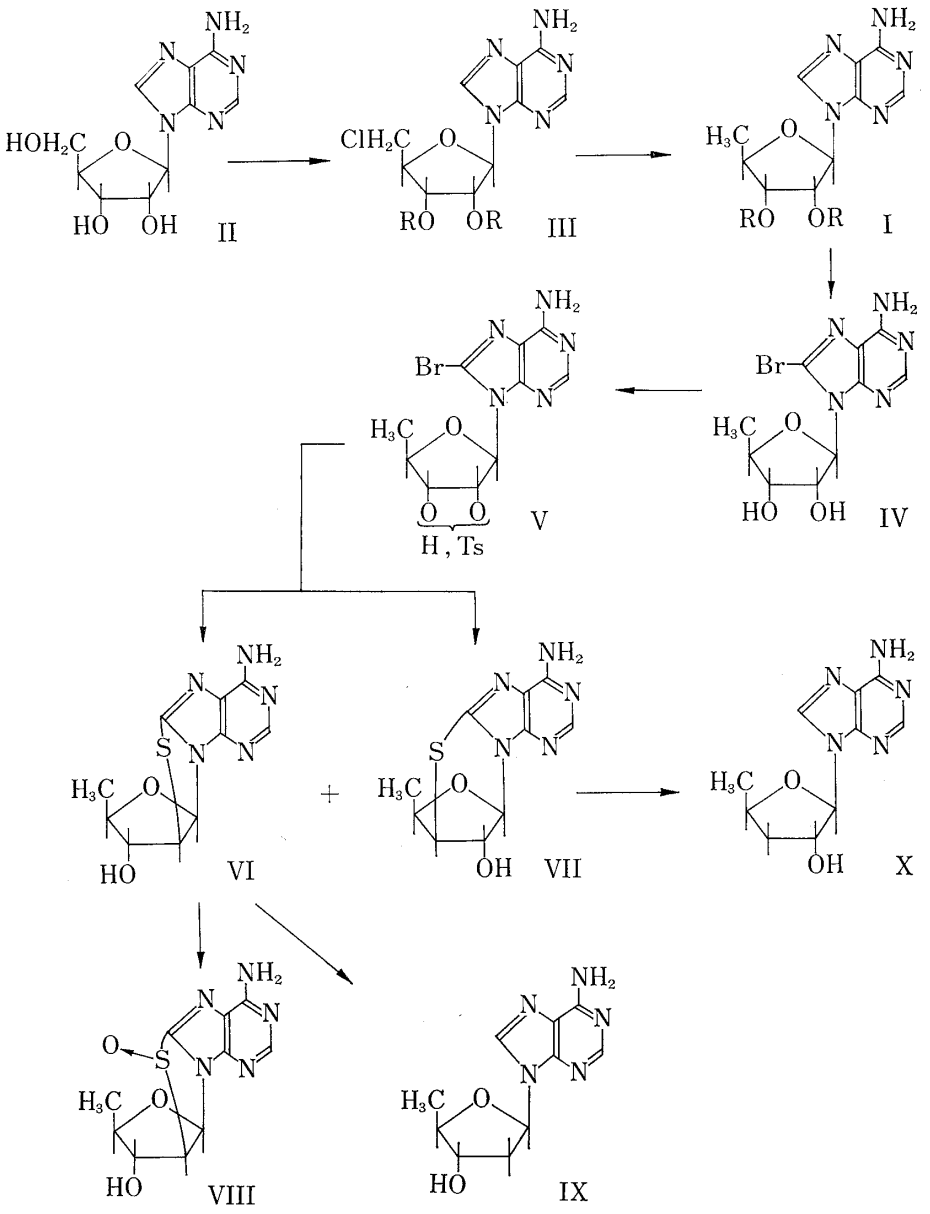

Chart 2

side shifts towards lower fields presumably due to the deshielding effect of the S→O group, while that on the opposite side shifts towards higher field, is valid in the present case, the structure of VIII should be *exo*-type sulfoxide. It is interesting that while in 8,2′- and 8,3′-S-cycloadenosine only *endo* sulfoxides were obtained, in the case of 5′-deoxyadenosine only the *exo* sulfoxide was obtained. This can be interpreted in terms of some steric interaction of the 5′-CH_2OH group in the former cases, which prevents access of the oxidizing agent from the *exo*-direction.

Compounds VI and VII were then desulfridized by treatment with Raney nickel. 2′,5′-Dideoxyadenosine (X) was obtained from VI in a yield of 37%. Comparison of the UV absorption properties, which resemble those of adenosine, and mp with the literature data,[14] suggested the proposed structure to be correct. 3′,5′-Dideoxyadenosine (X) was obtained

14) M.J. Robins, J.R. McCarthy, Jr. and R.K. Robins, *Biochemistry*, **5**, 224 (1966).

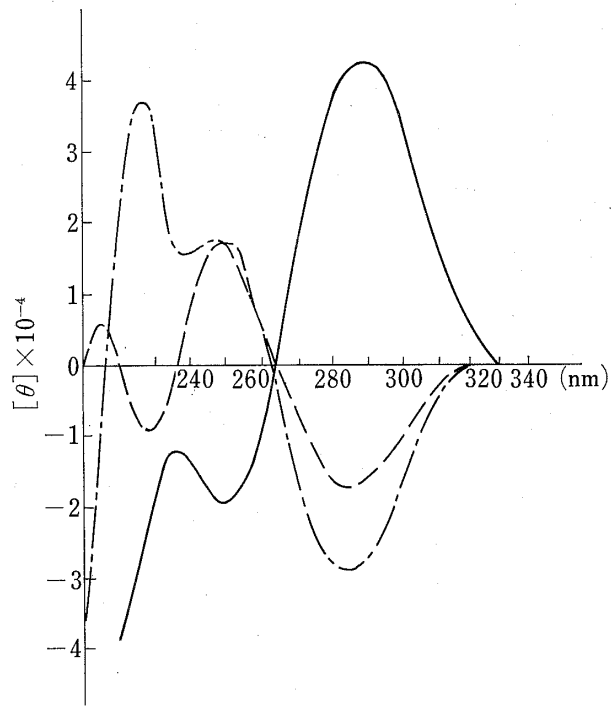

Fig. 1. CD Spectra of Sulfoxide VIIIX

———: VIII
———: 2′→SO of cycloadenosine.
———: 3′→SO of cycloadenosine.

analogously from VII in a yield of 40% as crystals having mp 188—190°. The UV and NMR spectral data of X supported the proposed structure.

In order to obtain O-cycloadenosines of 5′-deoxyadenosine, the 8-bromo-2′(or 3′)-tosyl derivative (V) was heated with acetic acid and acetic anhydride in the presence of sodium acetate. Appropriate work-up gave the 8-keto compound XI in a yield of 58%. Compound XI was then heated with methanolic ammonia at 70° in a sealed tube. A crystalline compound XII having mp around 190° was obtained in a yield of 65%. Its UV absorption properties, which resembled those of 8,2′-O-cycloadenosine,[11] and NMR data suggested the structure 8,2′-anhydro-8-oxy-9(β-D-5′-deoxyarabinofuranosyl)adenine for XII. The 8,3′-compound was not isolated. As found in the case of O-cycloadenosine formation, the 8,3′-cyclonucleoside may be decomposed during the reaction. Unlike 8,2′-O-cycloadenosine,[15] 8,2′-O-cyclo-5′-deoxyadenosine (XII) was stable in 0.01 N NaOH at 60°. However, when XII was kept at 30° in 0.1 N NaOH for 30 min a compound XIII having an 8-oxyadenine chromophore appeared. On prolonged standing the ratio XII: XIII became 1:3.4. The structure of XIII was assigned as 5′-deoxy-2′,3′-anhydro-8-oxyadenosine on the basis of the UV and NMR spectra, together with an analogous rearrangement reaction in the case of 8,2′-O-cycloadenosine.[15] Compound XIII was converted completely back to XII, on standing in 0.01 N NaOH at 30° for 10 hr. Therefore, it appears that a pH-dependent equilibrium exists between compounds XII and XIII. Reactions of the cyclonucleoside sulfoxides will be discussed in subsequent papers.

Experimental[16]

5′-Chloro-5′-deoxyadenosine (II, R=H)——Adenosine (534 mg, 2 mmol) was dissolved in triethyl phosphate (15 ml) and thionyl chloride (0.8 ml) was added. The solution was stirred at room temperature for 40 hr. After checking the extent of reaction by thin-layer chromatography (TLC), the mixture was added dropwise to ether (100 ml) with stirring. The resulting powder was dissolved in H_2O and neutralized with 1 N NaOH. Upon concentration of the solution, 5′-chloro-5′-deoxyadenosine (370 mg, 1.3 mmol, 65%) was obtained. UV: $\lambda_{max}^{H_2O}$ 259 nm. TLC (5:1: *Rf* 0.39. mp 110—111° (decomposed at 205°). These properties are identical with those reported previously.[8]

5′-Deoxyadenosine (I, R=H)——Compound II (R=H) (285.5 mg, 1 mmol) was dissolved in pyridine (5 ml) and acetic anhydride (2.5 ml). The solution was heated at 80° for 5 hr. The solution was evaporated

15) J.B. Chattopadhya and C.B. Reese, *J. Chem. Soc. Chem. Comm.*, **860** (1976).
16) UV absorption spectra were taken with a Hitachi 200-10 spectrophotometer. ^{1}H-NMR spectra were recorded on a Hitachi R-22 spectrometer (90 MHz, ambient probe temperature 34°). Chemical shifts were measured from an external tetramethylsilane (TMS) capillary. Paper chromatography was performed on Toyo filter paper No. 51A by the descending technique. Solvents used were: A, *n*-BuOH–H_2O, 84:16; B, iso-PrOH-conc. ammonia–water (7:1:2); C, *n*-BuOH–AcOH–H_2O, 5:2:3. conc. NH_4OH–H_2O, 7:1:2. TLC was performed on Merck Kieselgel G (type 60). Elution was performed with $CHCl_3$–EtOH mixture at a specified ratio.

off several times *in vacuo* with added EtOH. The resulting glass was dissolved in benzene (5 ml) and a benzene (10 ml) solution of $(n\text{Bu})_3\text{SnH}$ [prepared from $(n\text{-Bu})_3\text{SnCl}$, 10 mmol] was added. After addition of 2,2′-isobutyronitrile (15 ml), the mixture was refluxed for 3 hr. The solvent was removed by evaporation several times with added MeOH. The residue was taken up in 9 N methanolic ammonia (10 ml) at room temperature. The solvent was evaporated off and residue dissolved in H_2O–MeOH mixture (6: 1, v/v, 70 ml). The solution was extracted with hexane (30 ml × 2), then the H_2O–MeOH layer was concentrated and applied to a column (1.7 × 20 cm) of Dowex 1 × 2 (OH^- form). After washing with water, the column was eluted with 50% MeOH. Concentration of the eluants gave a powder, which was recrystallized from EtOH to give 199.3 mg (0.8 mmol, 80%) of 5′-deoxyadenosine, mp 199—201°. UV: $\lambda_{max}^{H_2O}$ 259 nm. NMR: δ 1.30 (d, 3H, H-5′). TLC (5: 1): *Rf* 0.30. The sample was identical with an authentic sample.[7]

5′-Deoxy-8-bromoadenosine (IV)——5′-Deoxyadenosine (1.50 g, 6.9 mmol) was dissolved in a mixture of H_2O (30 ml) and 0.5 M sodium acetate buffer (30 ml). Saturated bromine–H_2O (40 ml) was added and the mixture was kept at room temperature for 3 hr. After checking completion of the reaction by TLC (3: 1), the color of Br_2 was removed with $NaHSO_3$, and the solution was neutralized with 5 N NaOH. The mixture was concentrated and the resulting crystals were collected by filtration. Compound IV was obtained in a yield of 1.44 g (4.9 mmol, 73%). The sample became colored at 180° and melted at 187° with decomposition. *Anal.* Calcd. for $C_{10}H_{12}BrN_5O_3$: C, 36.38; H, 3.67; N, 21.22; Br, 24.20. Found: C, 36.32; H, 3.47; N, 21.39; Br. 24.48. UV: $\lambda_{max}^{H_2O}$ (ε) 265.5 nm (13200), $\lambda_{max}^{0.1\ NCl}$ 263 nm (14800), $\lambda_{max}^{0.1N\ NaOH}$ 265.5 (13000). NMR (δ): 8.15 (s, 1, H-2), 7.37 (s, 2, N^6–H), 5.82 (d, 1, H-1′), 5.20 (t, 1, H-2′), 4.17 (t, 1, H-3′), 3.98 (m, 1, H-4′), 1.33 (d, 3, H-5′). TLC (7: 1): *Rf* 0.38.

2′(or 3′)-O-Tosyl-5′-deoxy-8-bromoadenosine (V)——Compound IV (577 mg, 1.75 mmol) and $(n\text{Bu})_2\text{SnO}$ (436 mg, 1.75 mmol) were dissolved in MeOH (15 ml) and refluxed for 3 hr. The resulting crystals were collected by filtration, giving the crude di-*n*-butylstannylene derivative in a yield of 769 mg (1.37 mmol, 78%). This material was dissolved in dioxane (20 ml), then TsCl (492 mg, 2.60 mmol) and Et_3N (0.44 ml, 2.60 mmol) were added, and the mixture was refluxed for 4 hr. After checking for completion of the reaction by TLC (7: 1), the solvent was removed *in vacuo*. The residue was shaken with *n*-hexane–H_2O mixture and the insoluble material was recrystallized from EtOH–H_2O. Compound V was obtained in a yield of 489.7 mg (1.0 mmol, 78%). UV: $\lambda_{max}^{50\%\ EtOH}$ 265.5 nm. IR (KBr): 1174, 1187 cm^{-1} (covalnet tosylate).

8,2′-Anhydro-8-thio-9-(β-D-5′-deoxyarabinofuranosyl)adenine (VI) and 8,3′-Anhydro-8-thio-9-(β-D-5′-deoxyxylofuranosyl)adenine (VII)——A mixture of 2′- and 3′-tosylates (V) (2.26 g, 4.7 mmol) was dissolved in DMF (60 ml) and H_2O (5 ml). N_2 gas was bubbled through the solution and NaSH (14.4 mmol) was added. The flask was stoppered and heated at 70° for 7 hr. On TLC (7: 1), two spots (*Rf* 0.15 and 0.20) were detected in a ratio of 7: 1. The reaction mixture was neutralized with 1 N HCl and the solvent was evaporated off *in vacuo*. The residue was taken up in H_2O and the insoluble material was filtered off. The filtrate was concentrated *in vacuo* and applied to a column of Dowex 1 × 2 (OH^- form). Elution with 50% MeOH gave compound VI plus a small amount of VII. The eluates were concentrated *in vacuo* and the residue was recrystallized from EtOH. Compound VI was obtained in a yield of 770.5 mg (291 mmol, 62%). The column was then eluted with 1% AcOH to give compound VII in a yield of 130 mg (0.49 mmol, 10.4%) after recrystallization from EtOH. 8,2′-Cyclocompound VI: mp 225—226°. *Anal.* Calcd. for, $C_{10}H_{11}N_5O_2S$: C, 45.27; H, 4.19; N, 26.40; S, 12.08. Found: C, 45.14; H, 4.19; N, 26.27; S, 11.92. UV: $\lambda_{max}^{H_2O}$ 276.5 (ε 19300), $\lambda_{max}^{0.1N\ HCl}$ 278 (19000), $\lambda_{max}^{0.1N\ NaOH}$ 278 (19500). NMR (δ): 8.05 (s, 1H, H-2), 7.02 (s, 2H, N^6–H), 6.47 (d, 1H, H-1′), 5.90 (b, 1H, 3′-OH), 4.83 (q, 1H, H-2′), 4.16 (m, 1H, H-3′), 4.08 (m, 1H, H-4′), 1.21 (d, 3H, H-5′). Paper chromatography: *Rf* (B) 0.65, *Rf* (C) 0.71. TLC (7: 1): *Rf* 0.15. 8,3′-Cyclo compound VII: mp over 300°. *Anal.* Calcd. for $C_{10}H_{11}N_5O_2S\cdot 1/2H_2O$: C, 43.78; H, 4.42; N, 25.53; S, 11.69. Found: C, 43.65; H, 4.28; N, 25.47; S, 11.59. NMR (δ): 8.09 (s, 1H, K-2), 7.09 (s, 2H, N^6–H), 5.81 (s, 1H, H-1′), 4.93 (s, 1H, H-2′), 3.92 (d, 1H, H-3′), 1.43 (d, d, 3H, H-5′). PPC: *Rf* (B) 0.69, *Rf* (C) 0.74. TLC (7: 1): *Rf* 0.20.

5′-Deoxy-8,2′-S-cycloadenosine Sulfoxide (VIII)——The 8,2′-S-cyclo compound (VI) (50 mg, 0.19 mmol) was dissolved in MeOH (20 ml), and *tert*-BuOCl (0.1 ml) was added at −60—70°. The mixture was kept at this temperature for 7 hr. The reaction mixture yielded 32 mg of VIII (0.12 mmol, 60.5%). *Anal.* Calcd. for $C_{10}H_{11}N_5O_3S$: C, 42.66; H, 3.91; N, 24.88, S, 11.37. Found: C, 42.53; H, 3.67; N, 24.53; S. 11.20. UV: $\lambda_{max}^{H_2O}$ 288 nm, $\lambda_{max}^{0.1N\ HCl}$ 278 nm, $\lambda_{max}^{0.1N\ NaOH}$285.5 nm. IR (KBr): 1070 cm^{-1} (sulfoxide). NMR (δ): 8.23 (s, 1H, H-2), 7.65 (b, 2H, N^6–H), 6.34 (d, 1H, H-1′), 4.78 (q, 1H, H-2′), 4.23 (m, 1H, H-3′), 4.18 (m, 1H, H-4′), 1.22 (d, 3H, H-5′). CD: shown in Fig. 1. Paper chromatography: *Rf* (B) 0.54, *Rf* (C) 0.61. TLC (4:1): *Rf* 0.25.

N^6,O-Diacetyl-2′-O-tosyl-5′-deoxyadenosine (XI)——Anhydrous sodium acetate (1.5 g) was dissolved in a mixture of AcOH (14 ml) and Ac_2O (7 ml) by slight heating. The tosylate mixture V (400 g, 0.83 mmol) was added and the reaction mixture was refluxed for 3 hr. After checking completion of the reaction by TLC (25: 1), the solvent was evaporated off *in vacuo* and the residue was evaporated down several times with added EtOH. The residue was taken up in $CHCl_3$–H_2O mixture, then the $CHCl_3$ layer was washed with aq. $NaHCO_3$ and dried over $MgSO_4$. The residue obtained by removal of $CHCl_3$ was dissolved in EtOH and the resulting crystals were collected. Compound XI was obtained in a yield of 238.9 mg (0.48 mmol, 48%). mp 239—238.5°. UV: $\lambda_{max}^{95\%\ EtOH}$ 281 nm, $\lambda_{max}^{0.1N\ HCl}$ 280 nm, $\lambda_{max}^{0.1N\ NaOH}$304 nm.

8,2′-Anhydro-8-oxy-9-(β-D-5′-deoxyarabinofuranosyl)adenine (XII)——Compound XI (275.3 mg, 0.55

mmol) was heated with 9 N methanolic ammonia (5 ml) in a steel tube at 70° for 7 hr. After cooling, the resulting crystals were collected by filtration. Compound XII was obtained in a yield of 88.8 mg (0.36 mmol, 65%). This sample became colored at 190° and melted slowly with decomposition. UV: $\lambda_{max}^{H_2O}$ 257 nm (ε 13600), $\lambda_{max}^{0.1N\ HCl}$ 259 (13700), $\lambda_{max}^{0.1N\ NaOH}$ 265 (11900). NMR (δ): 8.02 (s, 1H, H-2), 6.74 (6, 2H, N^6–H), 6.45 (d, 1H, H-1′, $J_{1'-2'}$=5.5 Hz), 5.83 (b, 1H, 3′-OH), 5.63 (d, 1H, H-2′), 4.21 (m, 2H, H-3′ and 4′), 1.02 (d, 3H, H-5′). Paper chromatography: *Rf* (B) 0.72, *Rf* (C) 0.71.

8-Oxy-2′,3′-anhydro-5′-deoxyadenosine (XIII)——O-Cyclonucleoside (XIII) (25 mg, 0.1 mmol) was dissolved in 0.1 N NaOH (15 ml) and kept at room temperature for 60 min. Checking by TLC (6: 1) showed spots corresponding to the starting material (*Rf* 0.15) and a new compound (*Rf* 0.30) in a ratio of 1: 3.4. The mixture was rapidly neutralized with cooling and the solvent was coevaporated off *in vacuo*. Compound XIII was isolated by preparative TLC (6: 1). UV: $\lambda_{max}^{50\%\ EtOH}$ 259 (sh), 267 nm, $\lambda_{max}^{0.1N\ HCl}$ 285 (1h), 263 nm; $\lambda_{max}^{0.1N\ NaOH}$ 280.5 nm. NMR (δ): 7.92 (s, 1H, H-2), 6.75 (b, 2H, N^6–H), 5.88 (s, 1H, H-1′), 4.27 (m, 1H, H-2′), 4.22 (m, 1H, H-4′), 3.98 (m, 1H, H-3′), 1.27 (d, 3H, H-5′). Paper chromatography: *Rf* (C) 0.77.

When a mixture of XII and XIII was dissolved in 0.01 N NaOH and kept at 30° for 1 hr, only a single spot corresponding to O-cycloadenosine (XII) appeared on TLC (6: 1).

2′,5′-Dideoxyadenosine (IX)——The 8,2′-S-cyclonucleoside (VI) (50 mg, 0.19 mmol) was dissolved in dioxane (5 ml) and H_2O (1 ml). Raney Ni (0.5 ml) was added to the solution, which was refluxed for 1 hr with stirring. Raney Ni was filtered off and washed with hot dioxane several times. The filtrate and washings were combined and evaporated down *in vacuo*. The residue was recrystallized from ethyl acetate to give IX in a yield of 16.5 mg (0.09 mmol, 37%). mp 185—189°. UV: $\lambda_{max}^{50\%\ EtOH}$ 259 nm, $\lambda_{max}^{0.1N\ HCl}$ 257 nm, $\lambda_{max}^{0.1N\ NaOH}$ 259 nm. Paper chromatography: *Rf* (B) 0.76, *Rf* (C) 0.70. These properties are identical to those reported previously.[13]

3′,5′-Dideoxyadenosine (X)——The 8,3′-S-cyclonucleoside (VII) (100 mg, 0.37 mmol) was dissolved in dioxane (6 ml) and H_2O (3 ml). Raney Ni (0.5 ml) was added and the mixture was refluxed for 1 hr with stirring. Raney Ni was filtered off and the filtrate and washings were combined and concentrated *in vacuo*. The residue was recrystallized from ethyl acetate to give X in a yield of 35 mg (0.15 mmol, 40%). *Anal.* Calcd. for $C_{10}H_{13}N_5O_2$: C, 51.04; H, 5.57; N, 29.77. Found: C, 50.83; H, 5.36; N, 29.55. UV $\lambda_{max}^{50\%\ EtOH}$ 260 nm, $\lambda_{max}^{0.1N\ HCl}$ 257.5 nm, $\lambda_{max}^{0.1N\ NaOH}$ 260.5 nm. NMR (δ): 8.15 (s, 2H, H-8 and 2), 7.16 (b, 2H, N^6–H), 5.84 (d, 1H, H-1′), 4.64 (m, 1H, H-2′), 4.44 (m, 1H, H-4′), 2.06 (q, 2H, H-3′), 1.33 (d, 3H, H-5′). Paper chromatography: *Rf* (B) 0.78, *Rf* (C) 0.75.