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STUDIES OF NUCLEOSIDES AND NUCLEOTIDES—LXI[1]

PURINE CYCLONUCLEOSIDES 23 SYNTHESIS OF SULFOXIDES OF ADENINE S-CYCLONUCLEOSIDES[2]

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Abstract—8,2′ - Anhydro - 8 - mercapto - 9 - β - D - arabinofuranosyladenine, 8,3′ - anhydro - 8 - mercapto - 9 - β - D - xylofuranosyladenine and 8,5′ - anhydro - 8 - mercaptoadenosine were oxidized either with N-bromosuccinimide, t-butyl hypochlorite or performic acid to their 8-sulfoxides. Configuration of sulfoxides were determined to be *S* in former two cases. In the case of 8,5′-cyclonucleoside, both *S*- and *R*-compounds were obtained. UV, NMR and CD spectra of these sulfoxides were recorded.

In the course of study of purine 8-cyclonucleosides[3-5] we have found that cyclonucleosides having S-anhydro linkages were relatively stable against the treatment with acid or alkali in contrast to the O-cyclonucleosides. Some exceptions were observed as when a thiol group was positioned in proximity to the 8-carbon atom.[6] In order to find an effective method for cleaving the S-anhydro linkage leading to a new type of nucleoside, we attempted to oxidize S-cyclonucleosides of adenine with various oxidizing reagents, such as N-bromosuccinimide, t-butyl hypochlorite and performic acid. By the former two reagents 8,2′-(**1**), 8,3′-(**2**) and 8,5′-S-cycloadenosine (**3**) afforded only sulfoxides, but in the case of performic acid, 8,3′-isomer gave both sulfoxide and N^1-oxide. These oxidized compounds showed interesting properties in NMR and CD spectra and in the intramolecular rearrangement reaction.

Oxidation of 8,2′-S-*cycloadenosine*

When 8,2′-S-cycloadenosine[7] (**1**) was treated with N-bromosuccinimide (NBS), we could observe by TLC intramolecularly rearranged products in various ratios according to the reaction condition.

In order to obtain the desired sulfoxide, compound (**1**) was oxidized with t-butyl hypochlorite at −60 to −65°. After 3 hr a sulfoxide compound (**4**) was obtained in a yield of 88·5%. The UV absorption properties of (**4**) having λ_{max}'s at 273·5 nm in acidic and 282 nm in neutral solution suggested the sulfoxide structure. Elemental analysis gave a correct value. As shown in Fig. 2, a large negative Cotton band at around 280 nm of CD spectrum and a positive bands at 250 and 210 nm suggested the *S*-configuration as discussed in the case of 8,3′-cyclonucleoside. In the NMR spectrum 1′- and 3′-H signals shifted towards low field by the deshielding effect of the S–O group. These properties suggested the *S*-configuration of 8,2′-S-cycloadenosine sulfoxide (**4**). Therefore, it may be deduced that the oxidizing reagent attacked the S atom from the front side, but not from the sterically hindered rear side. The oxidation of **1** using performic acid gave the sulfoxide (**4**) in a yield of 75·5%. This sample was identical with that obtained by the oxidation by t-butylhypochlorite.

When the compound (**4**) was treated with dilute alkali, a compound (**5**) having UV λ_{max} at 261 nm was found by paper chromatography. This compound migrated on paper electrophoretogram at R_{AMP}1·0 and showed no reducing property by the fuchsinsulfite test. From this evidence the structure of compound (**5**) was assigned to be 8,5′ - anhydro - 8 - oxy - 9 - β - (2′ - deoxy - 2′ - sulfonato - D - arabinofuranosyl)adenine.

Oxidation of 8,3′-S-*cycloadenosine*

When 8,3′-S-cycloadenosine[8] (**2**) was allowed to react with two equivalents of NBS, a crystalline compound (**6**) precipitated. Elemental analysis and the molecular ion peak (*m/e* 297) in mass spectrum suggested the introduction of an O atom to the base moiety. This compound had UV absorption spectra having λ_{max}^{pH7} at 284 nm and a sulfoxide structure was suggested. Absorption band at 1070 cm^{-1} in IR spectrum supported this view. NMR spectrum of the compound **6** showed signals as listed in Table 1 together with those of 8,3′-cycloadenosine.[9] The signal of 2′-H shifted towards low field by 0·17 ppm and that of 5′-H shifted towards high field by 0·09 ppm from the original nucleoside (**2**). These values were consonant with the S-configuration of the sulfoxide, because the S–O atom directing to the 2′H and not to the 5′-H will cause these shifts as experienced by Rigav *et al.*[10] This S-configuration (Fig. 1) reflects in the sign of Cotton bands in the CD spectrum of the compound **6**. As shown in Fig. 2, the Cotton band at 283 nm showed a large negative value, which was inverted from that of compound **2**, and suggested the introduction of a new asymmetric center. The cause of this asymmetric attack of NBS may be interpreted as follows. The rear side of the S-atom may be sterically hindered by 5′-CH_2OH and the front side may be relatively free for the attack. This supposition may be supported by the fact that in the case of 8,5′-S-cyclonucleoside, in which no sterical distorsion exists, both sulfoxides of S- and R-configuration were obtained.

When the compound **6** was treated with dilute alkali at room temperature, a compound migrating at the same distance with 2′,3′-cyclic AMP on a paper electrophoretogram was formed. From the UV absorption properties this compound (**7c**) was assigned to be 8,5′ - O - cyclo - (3′ - deoxy - 3′ - sulfonato-xylofuranosyl)adenine, which might be formed via 3′ - deoxy - 3′ - sulfinato compound (**7a**). Another compound having R_{cAMP} 0·5 was

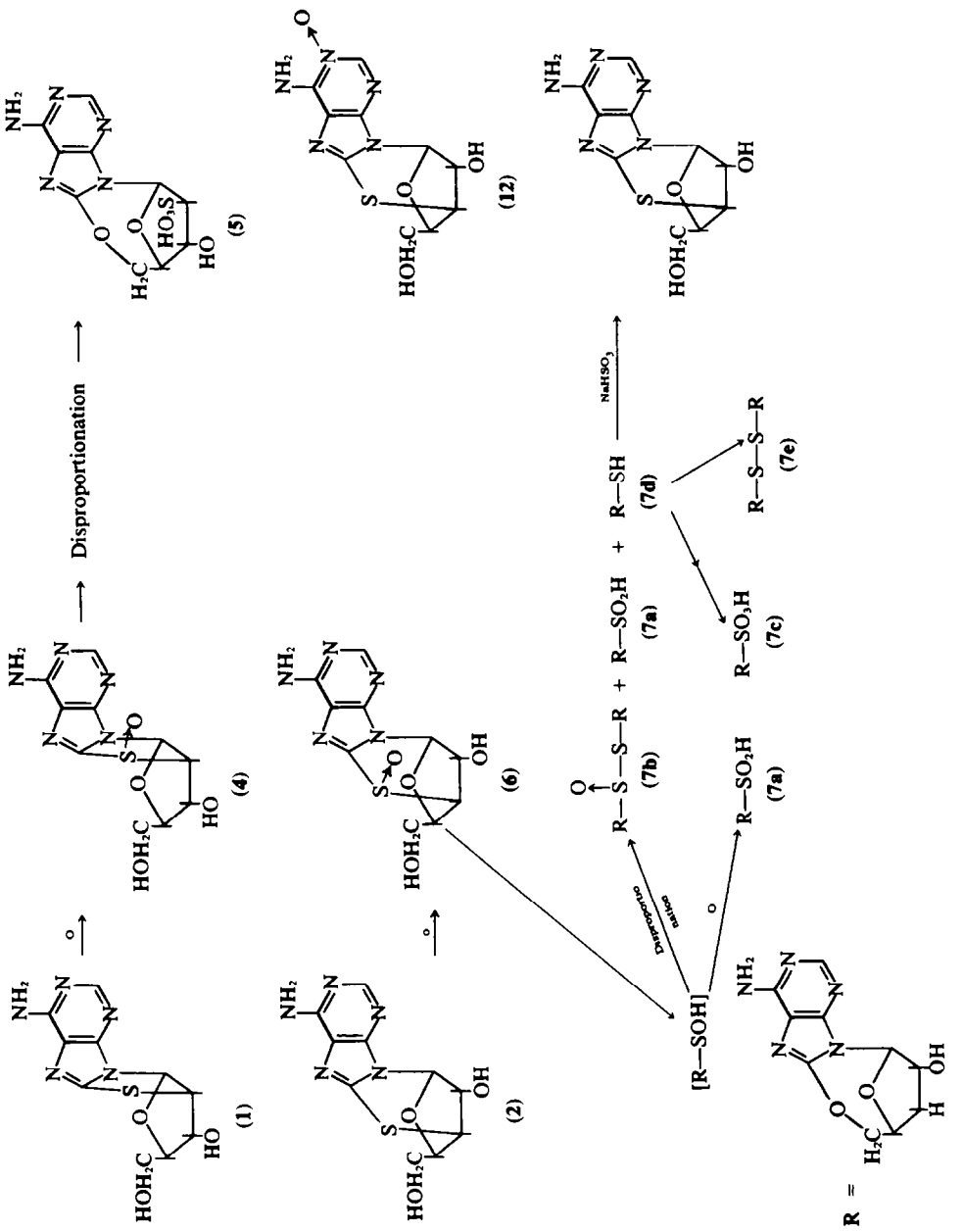

Chart 1.

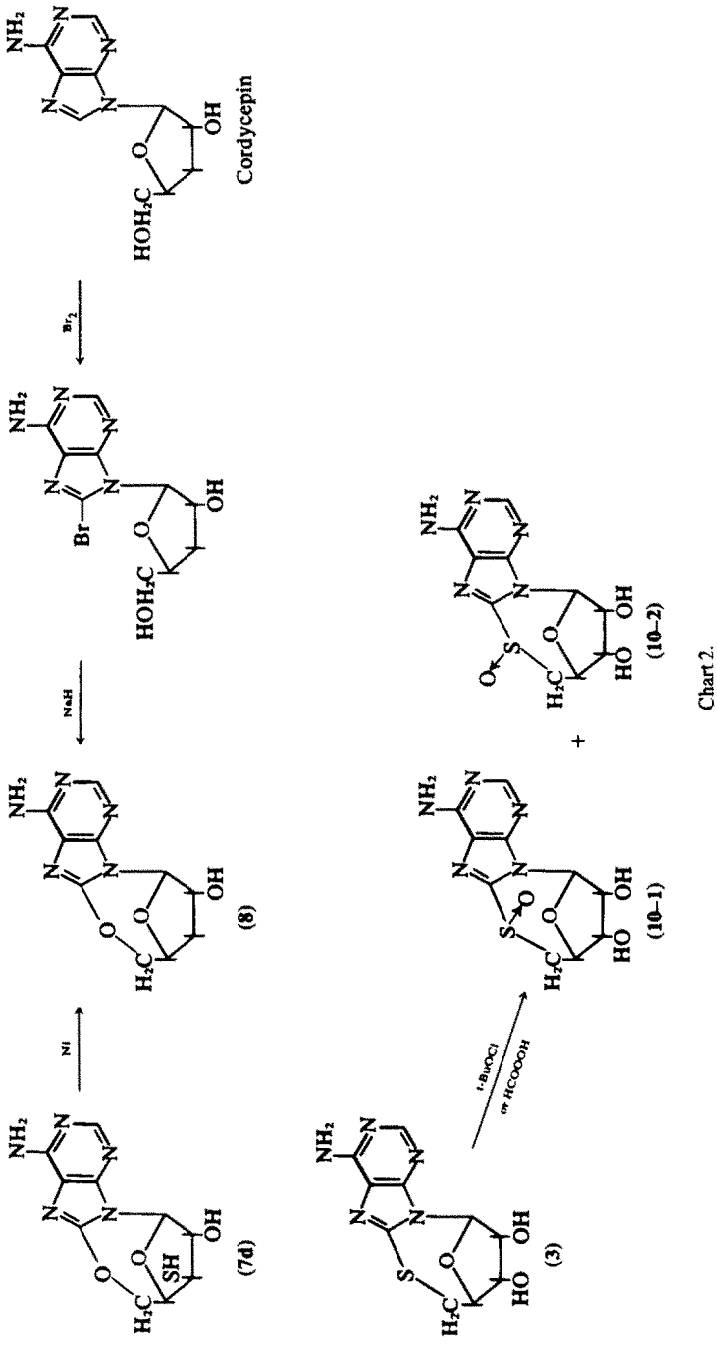

Chart 2.

Table 1. NMR spectra of S-cycloadenosine and its sulfoxide (δ)

Compound	H-2	6-NH_2	1'-H	2'-H	3'-H	4'-H	5'-H	2'-OH	3'-OH	5'-OH
8,2'-S-Cyclo-adenosine	8·04(s)	7·03(s)	6·49(d) $J_{1'H-2'H}=7$	4·86(q) $J_{2'H-3'H}=2.5$	4·38(q) $J_{3'H-4'H}=3.5$	3·99(q)	3·43(m)		5·86(d)	4·85
8,2'-S-Cyclo-adenosine sulfoxide	8·29(s)	7·95(b)* $J_{1'H-2'H}=6$	7·02(d)	4·32(q) $J_{2'H-3'H}=2.5$	4·77(q) $J_{3'H-4'H}=2.5$	4·19(q) $J_{4'H-5'H}=2.5$	a 3·32(q) b 3·21(q) $J_{5'a,b}=12.5$			
8,3'-S-Cyclo-adenosine	8·05(s)	7·07(s)	5·81(s)	4·87(d) $J_{2'H\ 2'OH}=3.5$	3·92(d) $J_{3'H-4'H}=4$	4·63(q) $J_{4'H-5'H}=5.5$	3·67(t)	6·36(d)		4·89
8,3'-S-Cyclo-adenosine sulfoxide	8·20(s)	7·53(s)	6·00(s)	5·04(d) $J_{2'H-2'OH}=3$	4·12(d) $J_{3'H-4'H}=5$	4·68(q) $J_{4'H-5'H}=3$	3·58(d)	6·44(d)		5·04
8,5'-S-Cyclo-adenosine	8·12(s)	7·27(s)	6·17(d) $J_{1'H-2'H}=1.5$	4·71(m) $J_{2'H-3'H}=6$	4·39(m) $J_{4'H-5'H}=2.5$	4·80(t)	3·15(q)	5·61(d) $J_{2'H-2'OH}$	5·27(d) $J_{3'H-3'OH}=4.5$	
8,5'-S-Cyclo-adenosine sulfoxide (1)	8·23	7·71	6·16 $J_{1'H-2'H}=1.5$							
(2)	8·19	7·62	6·08(s)							

*b, broad.

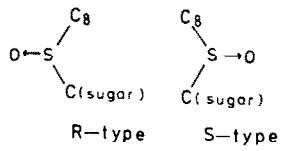

Fig. 1.

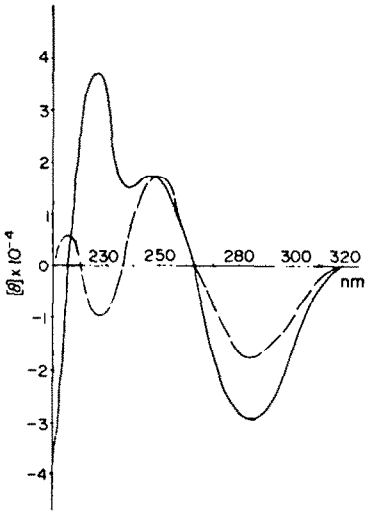

Fig. 2. CD spectra of sulfoxide of 8,2'-S and 8,3'-S-cycloadenosine. pH 7·4 0·01 M potassium phosphate buffer. ——, 3'-S·O; --, 2'-S·O.

assumed to be 3'-thiol compound (**7d**) and that remaining at the origin was 3',3'-thiolsulfinate compound (**7b**). The compound **7b** was isolated as a crystalline material and the structure was confirmed by elemental analyses. This intramolecular conversion of **6** by the alkali treatment may be interpreted as shown in the chart. The activated C^8–SO–C^3 bond was cleaved by the attack of 5'-OH and the resulting 3'-xylosulfenyl compound disproportionated to the thiolsulfinate (**7b**), sulfinate (**7a**) and thiol compounds (**7d**). The compound (**7d**) might be further oxidized to disulfide (**7e**) and sulfonate (**7c**). This type of rearrangement through the attack of the 5'-CH_2OH in the alkali solution have been reported previously in the case of O-cycloadenosines.[11]

The CD spectra of thiolsulfinate (**7b**) and thiol compound (**7d**) are shown in Fig. 3. Large positive Cotton bands at around 260 nm resembling those of 8,5'-O-cyclonucleoside[12] suggested the structure of **7b** and **7d** to be correct. The 8,5'-O-cyclo structure of **7** was confirmed as follows. The thiol compound (**7d**) was desulfurized to give 8,5' - anhydro - 8 - oxycordycepin (**8**). This compound could also be synthesized from cordycepin[13] by the bromination at C-8 and the cyclization using NaH in dioxane as performed previously with adenosine.[14] Compound **8** is the first example of cordycepin 8-cyclonucleoside.[15] When **7d** was heated with aqueous $NaHSO_3$ at 100° for 1 hr, 8,3'-S-cycloadenosine (**2**) was obtained. This reaction was also suggestive for the structure of **7a-e** as 8,5'-O-cyclonucleoside.

The oxidation of the cyclonucleoside (**2**) with t-butyl hypochlorite could be conducted at −70 to −80°. This reagent may be preferable for obtaining the sulfoxide because further oxidation to the sulfone or the intramolecular rearrangement could be avoided. Moreover epimerization of the sulfoxide might be prohibited at this

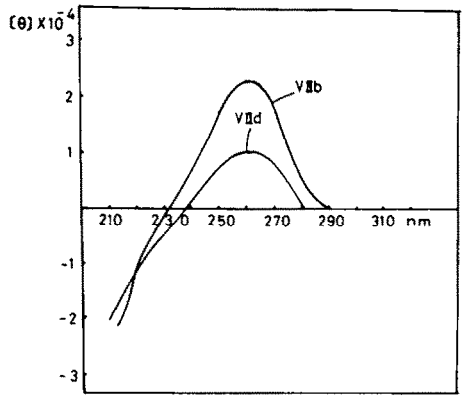

Fig. 3.

low temperature. When compound (2) was treated with t-butyl hypochlorite at −70 to −80° for 1 hr, almost the complete conversion to the sulfoxide (6) was observed. Isolated yield of (7) was 71·5% and the product was identical with that obtained as above by the NBS oxidation.

The oxidation of the compound (2) using performic acid of perphthalic acid gave the sulfoxide (7) in 42 and 34%, respectively. In the latter case (7) was accompanied by N^1-oxide[16] (9) in a ratio of 9:1. The compound (7) obtained in this case was identical with that obtained above.

By the use of oxidizing reagents, the compound (2) gave only the sulfoxide having *S*-configuration and none of the *R*-configuration. This fact may be interpreted by assuming that the S-atom of the anhydro bond of 8,3'-cyclonucleoside could be approached only from the front side and not from the rear side which may be sterically hindered by the 5'-CH_2OH group.

Oxidation of 8,5'-S-*cycloadenosine*

When 8,5'-S-cycloadenosine (3) was oxidized with NBS at room temperature, no reaction occurred. The compound (3) was then oxidized with t-butyl hypochlorite at −60° for 3 hr. In this instance a sulfoxide compound (10) was obtained in a yield of 71·5%. The structure of (10) has been thought to be elucidated by elemental analysis, IR band at 1060 cm^{-1}, UV absorption properties as described in the Experimental, and migration as one spot in paper chromatography as well as in TLC. However, the NMR spectrum of the compound (10) (Fig. 4) showed the two peaks corresponding to H-2', NH_2-6 and H-1', respectively. The ratios of the two peaks corresponding to (1) and (2) was 1:2, suggesting that this sample contained sulfoxide isomers, *S*- and *R*-types in 1:2 ratio. The assignment of these two isomers was done by CD spectra as described later. The separation of these two isomers by recrystallization or chromatography has so far failed.

Treatment of the compound (3) with performic acid at room temperature for 1–2 hr also gave the sulfoside compound (10) in a yield of 68·8%. Further oxidation gave only fluorescent compounds and no N-oxide. This species of (10) could not be discriminated by TLC and PC from that obtained by the oxidation with t-butyl hypochlorite. Nevertheless, NMR spectrum of this sample (Fig. 4) showed the existence of two isomers (1) and (2) in the ratio of 8:3.

The CD spectra of these two specimen, i.d. sample obtained by t-butyl hypochlorite oxidation and by the performic acid oxidation, were investigated. As shown in

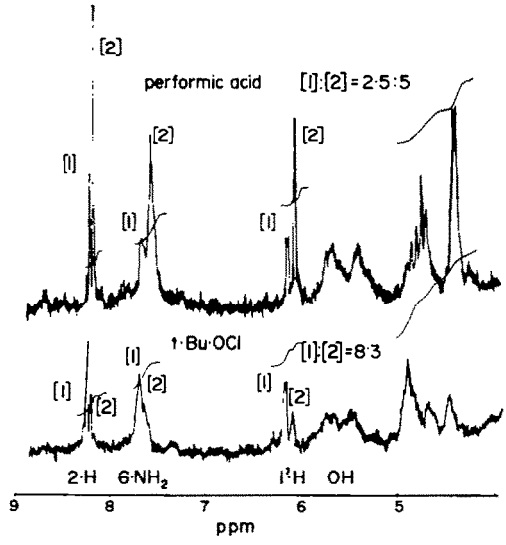

Fig. 4. NMR spectra of sulfoxide of 8,5'-S-cycloadenosine.

Fig. 5, (10) obtained by t-BuOCl showed a large negative band at 273 nm and a positive band at 230 nm. In contrast, (10) obtained by performic acid gave a positive band at 285 nm and a negative band at 232 nm. This indicated that the former sample contained larger amounts of the isomer having the *S*-configuration, which was analogous to 2'- or 3'-S-cycloadenosine sulfoxide, than the counterpart *R*-isomer. The sample obtained by performic acid oxidation, however, contained larger amounts of *R*- than *S*-isomer. Since the former sample contained (1) and (2) in a ratio of 1:2 and the latter contained in 8:3, *S*-isomer should be assigned to the compound (2) and *R*-isomer to the compound (1). The CD spectra of the pure (1) and (2) could be estimated by calculation as shown in Fig. 5 (· · · · · ·). The amplitude of the Cotton effect of these two isomers (± 3–4×10^4) is comparable to that of other cyclonucleoside sulfoxides. These findings suggest that in the case of 8,5'-S-cycloadenosine (3), the attacking oxidative reagent may have access to the S-atom rather freely from both sides and gave rise to isomers of *S*- and *R*-configuration in certain ratios.

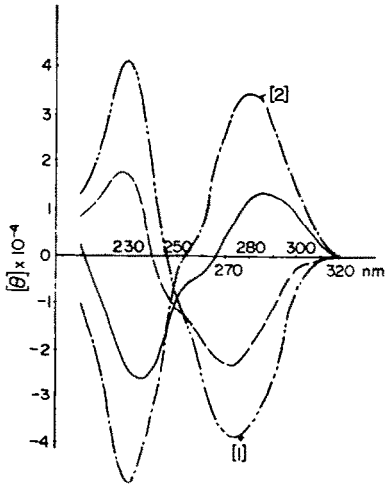

Fig. 5. CD spectra of sulfoxide of 8,5'-S-cycloadenosine. pH 7·4 0·01 M potassium phosphate buffer. ——, performic acid; – – – t-BuOCl; –·–, –···–, calcd.

The sulfoxide of 8,2'-, 8,3'- and 8,5'-S-cycloadenosine was thus synthesized and the labilization of S-cyclo bond by the introduction of a sulfoxide group was confirmed. Further reactions of cyclonucleoside sulfoxides will be reported in subsequent papers.

EXPERIMENTAL†

8,2' - Anhydro - 8 - mercapto - 9 - β - D - arabinofuranosyladenine sulfoxide

(i) 8,2'-S-Cycloadenosine (112 mg, 0·4 mmole) was dissolved in MeOH (30 ml) and t-BuOCl (0·1 ml) was added under cooling to −60 to −65° with a dry ice-acetone bath. The mixture was kept at this temp for 3 hr. The mixture was added dropwise in ether–pentane (1:3, vol/vol, 400 ml) and the ppt was collected and washed with ether (10 ml × 3), 0·05 M triethylammonium bicarbonate buffer (pH 7·5, 1 ml), and finally with water (1 ml × 2). The mother liquor was evaporated and the residue was washed similarly. 8,2'-S-Cycloadenosine sulfoxide was obtained in a yield of 117 mg (88·5%). (Found: c, 38·37; H, 3·95; N, 22·08; S, 9·81. Calcd. for $C_{10}H_{11}N_5O_4S \cdot H_2O$: C, 38·10; H, 4·16; N, 22·23; S, 10·12%.) UV: nm (ε) $\lambda_{max}^{H^+}$ 273·5 (16,000), $\lambda_{max}^{pH7.4}$ 282 (12,500). λ_{max} in alkaline soln could not be determined because of a rapid rearrangement to the 8,5'-O-cyclo compound. ν_{max}^{KBr} 1070 cm^{-1} (sulfoxide).

(ii) 8,2'-S-Cycloadenosine (140 mg, 0·5 mmole) was dissolved in formic acid (1 ml) and 30% H_2O_2 (0·5 ml). The mixture was kept at room temp for 3 hr and added dropwise to ether–pentane (400 ml, v/v). The ppt was collected and washed with water (1 ml × 2). 8,2'-S-Cycloadenosine sulfoxide was obtained in a yield of 112 mg (54%). This sample was identical with that obtained in (i).

8,3' - Anhydro - 8 - mercapto - 9 - β - D - xylofuranosyladenine sulfoxide

(i) 8,3'-S-Cycloadenosine (281 mg, 1 mmole) was dissolved in 80% aqueous MeOH and NBS (356 mg, 2 mmoles) was added. The mixture was kept at room temp for 5–6 hr. A crystalline ppt was collected by filtration, yield was 175 mg (59%). The analytical sample was recrystallized from MeOH. (Found: C, 40·48; H, 3·94; N, 23·47; S, 10·19. Calc. for $C_{10}H_{11}O_4N_5S$: C, 40·40; H, 3·73; N, 23·56; S, 10·78%). UV: $\lambda_{max}^{0.1N\,HCl}$ nm (ε) 223, 274 (12,500); $\lambda_{max}^{pH7.4}$ 284 (16,100); $\lambda_{max}^{0.1N\,NaOH}$ 261 (15,900). The last value is due to the alkali rearrangement to 8,5'-O-cyclo derivative. IR: ν_{max}^{KBr} 1070 cm^{-1} (sulfoxide). NMR signals are listed in Table 1. TLC: ($CHCl_3$–EtOH, 7:4) R_f 0·55.

(ii) 8,3'-S-Cycloadenosine (70 mg) was dissolved in anhyd MeOH (25 ml). The soln was cooled to −70 to −80° by dry ice-acetone and t-BuOCl (0·05 ml) was added. After keeping the mixture at −70° for 3 hr, it was poured in ether–pentane (2:8, v/v, 300 ml). The ppt was collected and washed with $NaHCO_3$ aq (1 ml), water (1 ml × 2), and finally recrystallized from EtOH, yield was 41 mg (51·4%). When the mixture was neutralized with TEAE-cellulose at −70°, the yield was raised to 59%. This sample was identical with that obtained in (i).

(iii) 8,3'-S-Cycloadenosine (14 mg) was dissolved in a mixture of formic acid (0·1 ml) and 30% H_2O_2 (0·05 ml). After stirring the soln at room temp for 1 hr, excess H_2O_2 was decomposed with MnO_2. MnO_2 was filtered off and the filtrate was evaporated *in vacuo*. The residue was washed with H_2O (0·2 ml). The sulfoxide was obtained in a yield of 6 mg (42%). This sample was identical with that obtained in (i). In the mother liquor a trace amount of N^1-oxide[16] was found by TLC.

†UV absorption spectra were measured with a Hitachi EPS-3T spectrophotometer, IR spectra with a Hitachi EPI-L spectrophotometer, and NMR spectra with a Hitachi R22 (90 MHz) spectrometer in d_6-DMSO with TMS as external standard. CD was measured with a JASCO ORD/UV-5 spectropolarimeter installed with a CD attachment. Paper chromatography was performed on Whatman 3 MM paper in following convent systems: A, water adjusted to pH 10 with conc. ammonia; B, i-PrOH–conc ammonia–water (7:1:2); C, n-BuOH–AcOH–water (5:2:3). TLC was performed on Kieselgel HF 254. Paper electrophoresis was performed in 0·05 M triethylammonium bicarbonate (pH 7·4) at 600–900 V/40 cm for 1 hr.

8,5' - Anhydro - 8 - oxy - 9 - β - (3' - deoxy - 3' - mercapto - D - xylofuranosyl) adenine, disulfide, sulfonic acid and thiolsulfinate

8,3'-S-Cycloadenosine sulfoxide (74 mg) was dissolved in MeOH (20 ml) and conc ammonia aq (1 ml) was added. The ppt was collected and recrystallized from EtOH. The thiolsulfinate compound was obtained in a yield of 30 mg (42%), m.p. 260° (dec). (Found: C, 41·89; H, 3·74; N, 23·92; S, 10·82. Calcd. for $C_{20}H_{20}N_{10}O_7S_2$: C, 41·66; H, 3·50; N, 24·29; S, 11·12%). UV: (nm) $\lambda_{max}^{H^+}$ 261, $\lambda_{max}^{H_2O}$ 261, $\lambda_{max}^{OH^-}$ 260. NMR: (δ) 8·10 (s, H-2), 7·00 (s, 6-NH_2), 5·93 (s, H-1'). In the mother liquor were detected 3'-mercapto compound, sulfonic acid, and disulfide. The sulfonic acid showed R_{AMP} 1·0 in PEP and negative in IO_4-benzidine test for *cis*-diol. By the fuchsin-decolorizing test for reducing $-SO_2H$ residue this material showed negative results. 3'-Mercapto compound showed R_{AMP} 0·2 and positive IO_4-benzidine test, but negative in fuchsin test. The disulfide remained at the origin of the paper electrophoresis.

8,5'-Anhydro-8-oxy-3'-deoxyadenosine

(i) 8,5' - Anhydro - 3' - thio-xylofuranosyladenine disulfide (5 mg) was dissolved in MeOH (5 ml) and refluxed with Raney nickel (W-2, 0·5 ml) for 2 hr. Paper chromatography (solvent A) showed a spot at R_f 0·39. This material was revealed by cystein-H_2SO_4 reagent as a pink spot showing the existence of 3'-deoxyribose.

(ii) Cordycepin (3'-deoxyadenosine) (30 mg) was dissolved in H_2O (0·5 ml) and 0·5 M acetate buffer (0·5 ml). Saturated bromine-water (0·75 ml) was added and the soln was kept at room temp for 1 hr. The color of the mixture was discharged with small amount of $NaHSO_3$. The mixture was neutralized with N NaOH, the solvent was evaporated *in vacuo*, and the residue was recrystallized from H_2O. 8-Bromocordycepin was obtained in a yield of 19 mg (61%), m.p. 197–200°. UV: (nm) $\lambda_{max}^{H^+}$ 261, $\lambda_{max}^{H_2O}$ 261, $\lambda_{max}^{OH^-}$ 261. PPC: R_f (A) 0·39 (same with the sample obtained in (1)).

8,5' - Anhydro - 8 - mercaptoadenosine sulfoxide S- and R-isomers

(i) 8,5'-S-Cycloadenosine (70 mg) was dissolved in anhyd MeOH (30 ml) and cooled to −60 to −65° with dry ice-acetone. At this temp t-BuOCl (0·05 ml) was added and the mixture was kept at −60° for 3 hr. The mixture was added dropwise to EtOH containing TEAE-cellulose (bicarbonate form). After the cellulose was filtered off, the filtrate was evaporated to give a residue, which was recrystallized from EtOH. 8,5'-S-Cycloadenosine sulfoxide was obtained in a yield of 53 mg (71·5%). (Found: C, 40·47; H, 3·94; N, 22·05; S, 9·74. Calcd. for $C_{10}H_{11}N_5O_4S \cdot 1/2CH_3OH$: C, 40·25; H, 4·18; N, 22·36; S, 10·22%). UV: nm (ε) $\lambda_{max}^{H^+}$ 225, 273 (17,500); $\lambda_{max}^{pH7.4}$ 281 (13,700); $\lambda_{max}^{OH^-}$ 279 (13,900). IR: ν_{max}^{KBr} 1060 cm^{-1} (sulfoxide). Paper chromatography: R_f(A) 0·45, R_f(B) 0·40, R_f(C) 0·22.

(ii) 8,5'-S-Cycloadenosine (140 mg, 0·5 mmole) was dissolved in formic acid (1 ml) and 30% H_2O_2 (0·5 ml). After stirring at room temp for 2 hr, the mixture was worked up as in (i). The residue was recrystallized from EtOH to give the sulfoxide in a yield of 95 mg (68·8%). This sample was identical with that obtained in (i).

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REFERENCES

[1]Part LX: M. Ikehara and Y. Ogiso, *Chem. Pharm. Bull.* **23**, 1114 (1975).
[2]A part of this study has been reported: *Tetrahedron Letters* 2965 (1971).
[3]M. Ikehara and H. Tada, *J. Am. Chem. Soc.* **87**, 606 (1965).
[4]M. Ikehara and H. Tada, *Purines—Theory and Experiment* (Edited by B. Pullman), p. 455. The Israel Academy of Sciences and Humanities (1972).
[5]M. Ikehara, *Accounts Chem. Res.* **2**, 47 (1969).
[6]M. Ikehara and Y. Ogiso, *J. Carbohyd. Nucleosides. Nucleotides.* **2**, in press.
[7]M. Ikehara and T. Tezuka, *Tetrahedron Letters* 1169 (1972).
[8]M. Ikehara and M. Kaneko, *Tetrahedron* **26**, 4251 (1970).

[9]The tentative assignment of NMR signals in Ref. 2 should be corrected.
[10]J. T. Rigav, C. C. Bacon and C. R. Johnson, *J. Org. Chem.* **35**, 3655 (1970).
[11]M. Ikehara and Y. Ogiso, *Tetrahedron* **28**, 3695 (1972).
[12]M. Ikehara, M. Kaneko, Y. Nakahara, S. Yamada and S. Uesugi, *Chem. Pharm. Bull.* **19**, 1381 (1971).
[13]E. A. Kaczka, N. R. Trenner, B. Arison, R. W. Walker and K. Folkers, *Biochem. Biophys. Res. Commun.* **14**, 456 (1964).
[14]M. Ikehara, M. Kaneko and R. Okano, *Tetrahedron* **26**, 5675 (1970).
[15]Recently, 2',5'-cyclic phosphate of cordycepin was synthesized: M. Ikehara and J. Yano, *Nucleic Acid Res.* **1**, 1783 (1974).
[16]M. Ikehara and Y. Ogiso, *Chem. Pharm. Bull.*, in press.