final pot temperature of 80° (2.5 mm.) recovered methyl chloride in Dry Ice traps and left 399 g. of slightly hazy, light yellow oil, $n^{25}D$ 1.4704. Distillation of a sample of this product gave 75.7%, b.p. 140–151° (0.55–0.21 mm.), $n^{25}D$ 1.4652, from which the yield was calculated as 71.7%. The product was molecularly distilled at 68° (0.05 mm.); 95.6 g. of distillate was collected leaving a rather large undistilled residue which contained about 30% of unchanged tetraethyl dithiodisuccinate. The distillate was found to contain about 2.6% chlorine corresponding to 25% of an O,O-dimethyl S-(1,2-dicarbethoxy)-*x*-chloroethyl phosphorothioate.

Anal. Calcd. for 75% $C_{10}H_{19}O_7PS$ plus 25% $C_{10}H_{18}ClO_7PS$: Cl, 2.54. Found: Cl, 2.60.

O,O-Dimethyl S-Carbethoxymethyl Phosphorothioate (V).—A mixture of 15.0 g. (0.063 mole) of diethyl dithiodiacetate and 15.6 g. (0.126 mole) of trimethyl phosphite in 35 ml. of toluene was heated at 110–112° for 5.5 hr. with stirring. Samples of the reaction mixture were taken at intervals for examination by g.l.c. [A Perkin-Elmer vapor fractometer, Model 154, with 2-ft. column of 20% Carbowax 20M on Chromosorb W, at 145°, with helium carrier gas at 200 ml./min. was used. Retention times were for IX, 0.9 min.; V, 29.5 min.; $(SCH_2CO_2C_2H_5)_2$, 33.0 min.] Reaction was estimated to be 50% complete in 1.5 hr. In a similar experiment in benzene at 80–82°, reaction was 50% complete in about 8 hr.

In an experiment in which no solvent was used, 27.0 g. (0.113 mole) of the disulfide was warmed to 97° on the steam bath. Addition of 28.1 g. (0.226 mole) of the phosphite caused an exothermic reaction which carried the temperature to 160° before cooling was applied. With steam on again, the temperature rose to only 105° for a few minutes, thus showing that the reaction was over. The products V and IX were isolated from this experiment. Yields were estimated by g.l.c. assay of the crude reaction product after distillation to remove excess phosphite.

O,O-Dimethyl S-(2-Carbethoxyethyl) Phosphorothioate (VI).—A reaction mixture containing 26.6 g. (0.1 mole) of diethyl 3,3′-dithiodipropionate and 24.8 g. (0.2 mole) of trimethyl phosphite without solvent was heated at 110–112° for 47 hr. with stirring. G.l.c., using the vapor fractometer with column described above at 165°, showed these retention times: X, 0.6 min.; VI, 16.7 min.; $(SCH_2CH_2CO_2C_2H_5)_2$, 28.1 min. Sampling for gas–liquid chromatography showed that the reaction was 50% complete in about 11 hr. After 28 hr., it was evident that residual disulfide was not reacting and that the phosphorothioate was being decomposed. From a similar experiment in which 13.3 g. (0.05 mole) of the disulfide and 12 g. (0.1 mole) of the phosphite were heated overnight on the steam bath, the products VI (76% pure by g.l.c.) and X (90%) were obtained by fractional distillation, washing, and redistillation. Their identities were confirmed by infrared spectra.

Reaction of Trimethyl Phosphite with Unsubstituted Alkyl Disulfides. A.—A mixture of 24.2 g. (0.2 mole) of ethyl disulfide and 49.6 g. (0.4 mole) of freshly distilled trimethyl phosphite (Matheson Coleman and Bell) was stirred and heated at 80–82° with sampling at 0, 22, and 42 hr. for examination by gas–liquid chromatography. An Aerograph gas chromatograph with a GE SF96 silicone column was used with helium carrier gas at 50 ml./min., column temperature 85–92°, injection port temperature 99°. At 22 hr., a component was observed which was found to cochromatograph with an authentic sample of trimethyl phosphorothionate. At 42 hr., this component appeared to have increased slightly in amount. No component was observed in the region in which an authentic sample of O,O,S-trimethyl phosphorothioate appeared. Thus, neither this material nor the S-ethyl homolog appeared to have been formed. After 42 hr., the major components were still unchanged starting materials. Ethyl sulfide was not positively identified. Quantitative estimates were not made.

B.—A mixture of 25 g. (0.14 mole) of *n*-butyl disulfide and 34.8 g. (0.238 mole) of trimethyl phosphite (85% pure by g.l.c. assay) was heated on the steam bath for 17 hr. Distillation, redistillation, and combination of products on the basis of boiling points and refractive indexes gave five cuts which were assayed by g.l.c. The major components were unreacted trimethyl phosphite and *n*-butyl disulfide with estimated recoveries of 68.5 and 66.0%, respectively. Yields of trimethyl phosphorothionate and *n*-butyl sulfide of 20 and 22%, respectively, were estimated. No components were observed with retention times expected for O,O,S-trimethyl phosphorothioate or O,O-dimethyl S-*n*-butyl phosphorothioate.

Acknowledgment.—The author wishes to express his indebtedness to Mr. Walter Jura for polarographic determinations of maloxon purity and to Dr. R. Feinland and his associates for chromatographic determinations on the butyl disulfide reaction. Thanks are extended to Drs. R. J. Magee, B. Miller, R. Rabinowitz, R. W. Young, and G. A. Johnson for many helpful discussions. Elemental analyses were performed by Galbraith Laboratories.

Studies of Nucleosides and Nucleotides. XXVII.[1] Synthesis of α-Adenosine-5′-monophosphate

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A mixture of α and β anomers of N-benzoyl-9-(5′-diphenylphosphoryl)-D-ribofuranosyladenine 2′,3′ cyclic carbonate was obtained by the condensation of N^6-benzoyladenine chloromercury salt with 5-diphenylphosphoryl-D-ribofuranosyl bromide 2′,3′ cyclic carbonate. Removal of protecting groups by refluxing methoxide and subsequent incubation with snake venom gave α-adenosine-5′-monophosphate.

As part of a program of synthesizing various nucleoside phosphates for the investigation of substrate specificity of several enzyme systems[2,3] we synthesized α-adenosine-5′-monophosphate.

In 1958, Wright, *et al.*,[4] successfully synthesized α-adenosine, but did not attempt to phosphorylate this product. In their study cyclic carbonate protection on the 2′- and 3′-OH groups of ribofuranosyl bromide was shown to be suitable for obtaining the α anomer. In the synthetic work on α-D-ribofuranose-1-pyrophosphate-5-phosphate,[5] it was also found that a bulky substituent existing at C-5 position (on the upper side of the furanose ring) exerted an inhibitory effect against attack of the entering group at C-1 from the same side of the ring. Considering these

(1) Part XXVI: M. Ikehara and H. Uno, *Chem. Pharm. Bull.* (Tokyo), in press.

(2) M. Ikehara, E. Ohtsuka, S. Kitagawa, K. Yagi, and Y. Tonomura, *J. Am. Chem. Soc.*, **83**, 2679 (1961); M. Ikehara, E. Ohtsuka, S. Kitagawa, and Y. Tonomura, *Biochim. Biophys. Acta*, **82**, 74 (1964); M. Ikehara, E. Ohtsuka, H. Uno, K. Imamura, and Y. Tonomura, *ibid.*, in press.

(3) Y. Mizuno, M. Ikehara, A. Nomura, T. Ueda, E. Ohtsuka, F. Ishikawa, and Y. Kanai, *Chem. Pharm. Bull.* (Tokyo), **9**, 338 (1961).

(4) R. S. Wright, G. M. Tener, and H. G. Khorana, *J. Am. Chem. Soc.*; **80**, 2004 (1958).

(5) G. M. Tener and H. G. Khorana, *ibid.*, **80**, 1999 (1958).

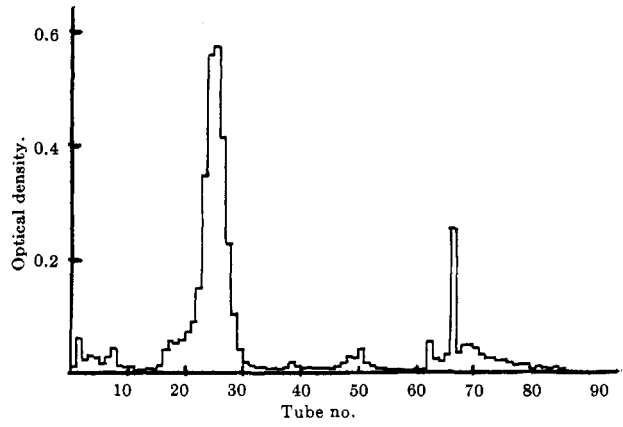


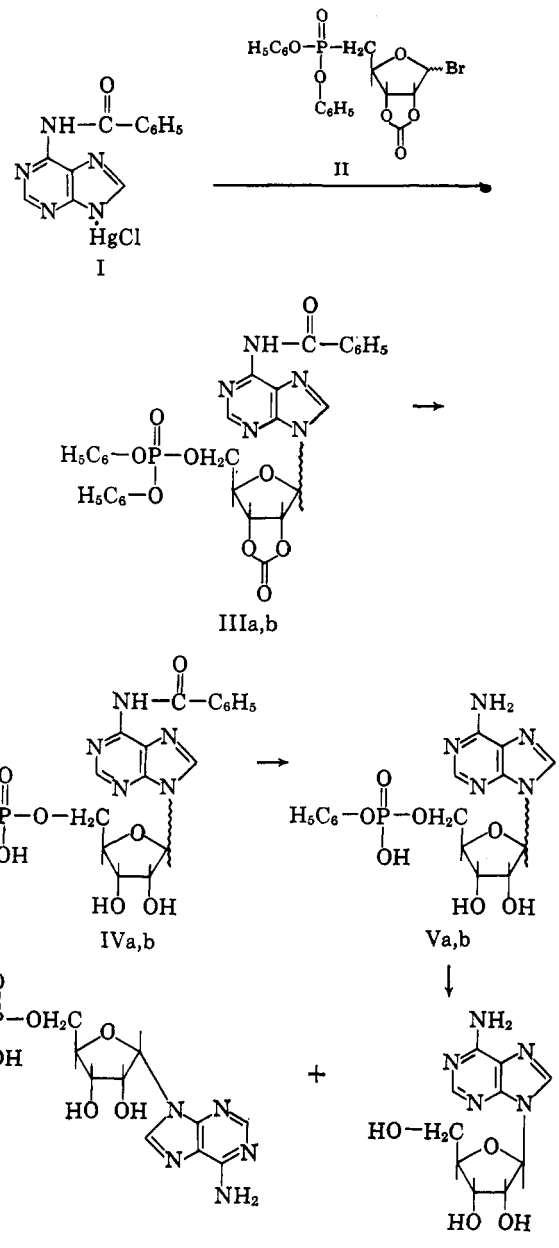
Figure 1.—Ion-exchange column chromatogram of the phosphodiesterase hydrolysate of 5′-phenyl-AMP. Eluting buffer: I, water (initial); II, 0.01 *N* formic acid and 0.03 *M* ammonium formate (beginning with tube no. 6); III, 0.2 *N* formic acid and 0.5 *M* ammonium formate (beginning with tube no. 37). See text for other conditions.

effects, together with the study of Ukita and Hayatsu,[6] we started with the condensation of N^6-benzoyladenine chloromercury salt (I) with 5′-diphenylphosphoryl-D-ribofuranosyl bromide 2′,3′-cyclic carbonate (II) (see Scheme I).

The reaction was carried out in xylene containing N,N-dimethylformamide (DMF)[7] at 125–130° for 1 hr. N-Benzoyl-9-(5′-diphenylphosphoryl)-D-ribofuranosyladenine 2′,3′-cyclic carbonate (III) was obtained as the mixture of α and β anomers. Since these anomers could not be separated effectively by paper chromatography, the mixture was subjected to alkaline hydrolysis in order to remove one phenyl group and the cyclic carbonate protection. Examination of the reaction mixture with paper chromatography, paper electrophoresis, and ultraviolet absorption properties showed the conversion of III to N-benzoyl-9-(5′-monophenylphosphoryl)-D-ribofuranosyladenine (IV) and benzoyladenine accompanied with a phosphorylated sugar. Removal of the N-benzoyl group by refluxing sodium methoxide and subsequent incubation of the mixture with *Trimeresurus flavoviridis* venom[3] gave only adenosine and adenine as ultraviolet-absorbing spots on the paper chromatogram. When the alkaline hydrolysate obtained above was incubated with the venom in the presence of Zn^{+2} (phosphodiesterase action[8]), only β-AMP (adenosine monophosphate) was isolated as the nucleotidyl material by ion-exchange column chromatography (see Figure 1).

These facts clearly showed the hydrolytic cleavage of the α anomer (IIIa) by treatment with sodium hydroxide solution. In order to avoid this destruction of the α anomer, the mixture containing IIIa and b was treated directly with sodium methoxide in methanol. After the reaction paper chromatographic and also electrophoretic examination indicated the simultaneous removal of the N^6-benzoyl and 2′,3′ cyclic carbonate groups as well as one phenyl group from the 5′-phosphoryl residue. Work-up of the reaction mixture

SCHEME I



gave 9-(5′-monophenylphosphoryl)-D-ribofuranosyladenine (V) as a cream-colored powder.

Incubation of this material with *Trimeresurus flavoviridis* venom for 3 hr. and subsequent chromatography on a Dowex IX8 column showed a pattern as in Figure 2. Peak I and II were nonnucleotidal material (presumably adenosine and adenine). Peak III contained a substance having R_f 0.22 (solvent A) and R_{AMP} 1.03 by paper chromatography and paper electrophoresis. Elemental analysis and ultraviolet absorption also suggested the 5′-AMP structure. Moreover, the resistance of this AMP to the 5′-nucleotidase of *Trimeresurus* venom indicates the structure of α-AMP to be correct. Metaperiodate consumption by this sample excluded the possibility of 2′- and 3′-phosphate.

This is another example of a ribonucleotide having a 5′-phosphate but resistant to the action of snake venom 5′-nucleotidase.[3,6,9] The ratio of the formation of α and β anomers in the condensation reaction was 4.5:1, estimated by the yield of α-AMP and β-

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(9) J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 1118 (1963).

adenosine. This fact is consistant with the hypothesis that a large group on C-5 inhibits β attack on the C-1 position. The ease with which α-AMP was hydrolyzed by alkaline treatment could be due to the larger separation of phosphate and base moieties than in the natural (β) AMP. Peak IV in Figure 2 proved to be a diphenylphosphoro derivative of AMP on examination by paper electrophoresis. The firm adsorption of phenyl-substituted nucleotides might be explained by the interaction of this group with the aromatic rings of the resin.[10]

Experimental

Paper Chromatography.—The eluents used were solvent A, 2-propanol–1% ammonium sulfate, 2:1; solvent B, 1-butanol–water, 86:14; solvent C, 2-propanol–28% ammonia–water, 7:2:1. Chromatography was performed by the ascending technique on Toyo filter paper no. 51A.

Paper electrophoresis was carried out in 0.05 *M* triethylammonium bicarbonate (pH 7.5, 20 v./cm., 1 hr.) using Toyo filter paper no. 51A.

The α and β Anomers of N⁶-Benzoyl-9-(5′-diphenylphosphoryl)-D-ribofuranosyladenine 2′,3′ Cyclic Carbonate.—Benzyl-5-diphenylphosphoryl-β-D-ribofuranoside 2,3 cyclic carbonate[5] (3.0 g.) was dissolved in 30 ml. of acetic acid containing 10% acetic anhydride. On addition of acetic acid (30 ml.) containing 32% hydrobromic acid, the sugar dissolved completely and a yellow-orange solution was obtained. After allowing it to stand for 4 days at 25°, acetic acid was removed *in vacuo* and the residue was codistilled with three 10-ml. portions of xylene. The residue was finally taken up in 10 ml. of xylene. N⁶-Benzoyladenine chloromercury salt[11] (2.69 g.) was suspended in 150 ml. of xylene and azeotropically dried by the evaporation of one-third the volume of xylene. Into this mixture the xylene solution of the sugar derivative was added with mechanical stirring. After the addition of 1.0 g. of Celite and 10 ml. of DMF, the reaction mixture was refluxed on an oil bath (125–130°) for 1 hr. with stirring. The solution was diluted with *n*-hexane (250 ml.) and cooled, when an oily precipitate appeared. The supernatant was separated by decantation and concentrated *in vacuo*. The precipitate was extracted with chloroform (100 ml.) and the chloroform layer was washed with 30% potassium iodide solution (30 ml.) and two 30-ml. portions of water. Drying over sodium sulfate and subsequent evaporation of the solvent gave 3.08 g. of yellow glass: λ_{max}^{EtOH} 284 mμ; ν_{max}^{KBr} 1800 (cyclic carbonate), 1740 (ester carbonyl), 1280 (P=O), and 1215 cm.$^{-1}$ (P–O–C_6H_5); paper chromatography, R_f 0.89 (solvent B). The spot on the paper chromatogram did not consume metaperiodate[12] and was revealed by molybdate spray.[13]

Hydrolysis of Benzoyl-9-(5′-diphenylphosphoryl)-D-ribofuranosyladenine 2′,3′ Cyclic Carbonate with Sodium Hydroxide. A.—The fully protected nucleotide (167 mg.), obtained as above, was dissolved in 3 ml. of dioxane, followed by the addition of 3 ml. of 1 *N* sodium hydroxide. After allowing the reaction to stand for 3 hr. at room temperature, IRC-50 (H^+ form) resin was added, and the pH of the solution was adjusted to 4–4.5. The resin was removed by filtration and washed with dioxane (15 ml.). The solution was concentrated with the addition of three 20-ml. portions of ethanol and four 10-ml. portions of acetone. A cream-colored solid (99 mg.) was obtained: λ_{max}^{EtOH} 284 mμ; paper chromatography, R_f 0.71 (solvent, B), R_f 0.75 (solvent A) as the main spot corresponding to benzoylmonophenylphosphorylribofuranosyladenine (IO_4^- spray positive molybdate spray positive); paper electrophoresis, R_{AMP} 0.58. As the minor spots, adenine (R_f 0.38, solvent B) and a phosphorylated sugar (R_f 0.71, solvent A) were detected.

B.—Nucleotide III (50 mg.) was dissolved in 10 ml. of dioxane, followed by the addition of 1.0 ml. of 0.1 *N* sodium hydroxide.

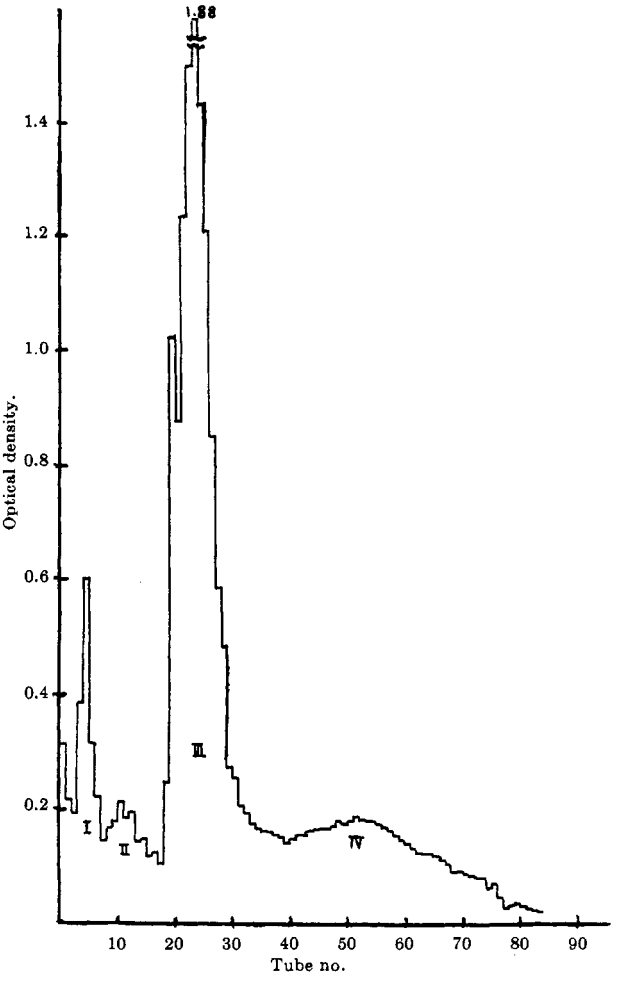

Figure 2.—Ion-exchange column chromatography of α-AMP. Eluting buffer: I, water (initial); II, 0.006 *N* hydrochloric acid and 0.2 *M* lithium chloride (beginning with tube no. 7); III, 0.06 *N* hydrochloric acid and 0.2 *M* lithium chloride (beginning with tube no. 38). See text for other conditions.

Examination of the reaction mixture by paper electrophoresis, after allowing it to stand for 40 hr., showed three spots: R_{AMP} 0.82, (A), R_{AMP} 0.45 (B), and R_{AMP} 0.18 (C). The ratio of A:B estimated by ultraviolet absorption was 1:4. Spot C was detected only by molybdate spray and was assumed to be a phenylphosphoryl sugar.

Hydrolysis of the Alkaline Hydrolysate of III with Snake Venom. A. Hydrolysis in the Presence of Zn^{+2} (Phosphodiesterase).—The reaction mixture contained 25 mg. of substrate (the above alkaline hydrolysate), 1.0 ml. of 0.1 *M* Tris buffer (pH 8.9), 0.2 ml. of 0.1 *M* magnesium chloride, 0.05 ml. of 0.2 *M* zinc chloride, and 1.0 ml. of enzyme solution[14] (total volume 3.0 ml.). After incubation of this mixture for 2 hr. at 37°, the reaction was quenched by heating at 100° for 3 min. A part of the solution (0.2 ml., $TOD_{260\ m\mu}$ 24.3) was diluted with water to 5 ml., adjusted to pH 8.0, and applied to an ion-exchange chromatographic column of Dowex IX8 (formate, 0.8 × 5 cm.) (Figure 1). Water washing gave nucleoside, $TOD_{260\ m\mu}$ 1.15 (4.7%); elution with 0.01 *N* formic acid plus 0.03 *M* ammonium formate gave unknown material, $TOD_{260\ m\mu}$ 1.01 (4.2%), and AMP, $TOD_{260\ m\mu}$ 12.81 (52.8%); and elution with 0.2 *N* formic acid plus 0.5 *M* ammonium formate gave phenyl-AMP, $TOD_{260\ m\mu}$ 2.17 (8.9%). AMP fractions ($TOD_{260\ m\mu}$ 12.75) were combined with authentic AMP[15] ($TOD_{260\ m\mu}$ 7.81) and chromatographed again on the column of Dowex I X8 resin. The main fraction ($TOD_{260\ m\mu}$ 12.39, 60.4%) was recovered as a single symmetrical peak and was identical with authentic AMP by paper chromatographic and electrophoretic tests.

(10) The adsorption tendency of various nucleotides having aromatic character was briefly discussed (M. Ikehara and H. Uno, Abstracts of Papers presented at the 18th Annual Meeting of Pharmaceutical Society of Japan, 1963, p. 66).

(11) M. W. Bullock, J. J. Hand, and E. L. R. Stockstad, *J. Org. Chem.*, **22**, 568 (1957).

(12) M. Viscontini, D. Hoch, and P. Karrer, *Helv. Chim. Acta*, **38**, 642 (1955).

(13) C. S. Hanes and F. A. Isherwood, *Nature*, **164**, 1107 (1949).

(14) Crude snake venom was passed through a DEAE cellulose column and contained *ca.* 10 mg. of protein.

(15) Purchased from Sigma Chemical Co., St. Louis, Mo.

B. Hydrolysis with Whole Snake Venom (Phosphodiesterase and 5′-Nucleotidase).—The reaction mixture containing 30 mg. of substrate, 200 mmoles of glycine buffer (pH 8.6), 50 mmoles of magnesium chloride, and 1 ml. of enzyme solution (total volume 2 ml.) was incubated at 37° for 4 hr. Examination of reaction mixture by paper chromatography (solvent B) together with authentic adenosine (R_f 0.19) and α-adenosine (R_f 0.12) showed no differentiation (R_f 0.15) and no spot corresponding to AMP was detected.

Treatment of N-Benzoyl-9-(5′-diphenylphosphoryl)-D-ribofuranosyladenine 2′,3′ Cyclic Carbonate with Sodium Methoxide.—The fully protected nucleotide III (90 mg.) was dissolved in 10 ml. of anhydrous methanol, followed by the addition of 1.5 ml. of 1 *N* sodium methoxide. After refluxing the reaction mixture for 70 min., the pH was adjusted to 4.0–4.5 with IRC-50 (H^+) resin. The resin was removed by filtration and the solvent was evaporated *in vacuo*. The traces of solvent were removed by codistillation with two 20-ml. portions of ethanol and three 30-ml. portions of acetone. A brownish solid material was obtained: 48 mg.; $\lambda_{max}^{H_2O}$ 260 mμ; paper chromatography, R_f 0.48 (solvent A, IO_4^- consuming); paper electrophoresis, R_{AMP} 0.68. This material was slightly contaminated with adenine (R_f 0.32, solvent A).

Enzymatic Hydrolysis of 9-(5′-O-Monophenylphosphoryl)-D-ribofuranosyladenine.—The brownish solid obtained above (30 mg.) was dissolved in a solution consisting of 200 mmoles of glycine–NaCl–NaOH buffer (pH 8.5), 60 mmoles of magnesium chloride, and 0.5 mg. of enzyme.[16] The total volume of the reaction mixture was 2.5 ml. This was incubated at 37° for 30 min. and the reaction was quenched by heating at 100° for 3 min. The whole solution was diluted with 20 ml. of water and one-third of the solution was applied to an ion-exchange column (Dowex IX8, chloride form, 0.8 × 10 cm). Washing with water gave nucleoside (adenosine), $TOD_{260\ m\mu}$ 22.9 (11.9%); elution with 0.006 *N* HCl and 0.2 *M* LiCl gave AMP, $TOD_{260\ m\mu}$ 5.9 (3.1%), and α-AMP, $TOD_{260\ m\mu}$ 54.3 (28.2%) (see Figure II). α-AMP fractions were collected and neutralized with 1 *N* LiOH solution and evaporated *in vacuo* to a small bulk below 25°. Further elution of the column with 0.06 *N* HCl and 0.2 *M* LiCl gave monophenyl-AMP, $TOD_{260\ m\mu}$ 54.3 (28.2%). To the sirupy solution of α-AMP was added 2 vol. of methanol and 30 vol. of acetone. The white precipitate, which appeared after storing the solution in a refrigerator at 0–5° for 3 hr., was collected by centrifugation and washed with ethanol and ether. The dried (3 mm. over P_2O_5 for 5 hr.) material weighed 5.8 mg. The purity estimated photometrically on the weight basis (calculated as having $\epsilon_{260\ m\mu}$ 14,500) was 72.8%. The main contaminant was water of crystallization and lithium chloride: paper chromatography, R_f 0.22 (solvent A), R_{AMP} 0.92; paper electrophoresis, $R_{adenosine}$ 1.5, R_{AMP} 1.03.

Anal. Calcd. for $C_{10}H_{12}LiN_5O_7P \cdot 6H_2O$: P, 6.63. Found: P, 6.91.

(16) Purified as in ref. 13 and tested for its activity to hydrolyze AMP totally to adenosine and inorganic phosphate.

Acknowledgment.—The authors wish to thank Mrs T. Tohma and Miss A. Maeda for elemental analyses

Synthesis and Characterization of 3,6-Diamino-3,6-dideoxy-D-idose[1]

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The stereoselective synthesis of the title compound utilizing the azide group as a potential amine function is described. Versatile intermediates such as methyl 2,3-anhydro-6-azido-6-deoxy-α-D-talopyranoside and 3,6-diazido-3,6-dideoxy-D-idose were synthesized. It is shown that the 3,6-diaminohexose gives a positive reaction in the Elson–Morgan color test and produces 10% the color of D-glucosamine. A study of the opening of epoxides with azide ion in model compounds in the D-talose series is included.

The discovery of several antibiotic and other biological substances possessing substantial therapeutic value has led to the unveiling of some unique types of amino sugars as their components.[2] With the advent of modern techniques, the constitution and gross structural elucidation of many of these new substances has become greatly facilitated. The proof of structure, stereochemistry, and mode of linkage of novel types of amino sugars found in such substances represents a challenge to the chemical investigator.

The present synthesis of 3,6-diamino-3,6-dideoxy-D-idose was undertaken for two purposes: firstly, to initiate a synthetic program involving the synthesis of several members of this novel class of diaminohexoses in anticipation of their eventual discovery in biological substances, and, secondly, to study the chemical properties of this representative member of 3,6-diamino-3,6-dideoxyhexoses. The synthesis of a 3,6-diamino-3,6-dideoxyhexose derivative has been recently described.[3] It is noteworthy to mention that the antibiotic kanamycin contains 3-amino-3-deoxy-D-glucose as well as 6-amino-6-deoxy-D-glucose among its components[4] and that the combination of amine functions in one molecule to produce a 3,6-diamino-3,6-dideoxyhexose is biogenetically possible. Furthermore, 3-amino-3-deoxyhexose derivatives are common constitutents of several antibiotics.[2]

The only diaminohexoses of biological origin are 2,6-diamino-2,6-dideoxy-D-glucose (neosamine C),[5–8] 2,6-diamino-2,6-dideoxy-L-idose (neosamine B, paromose),[9–11] and a 2,4-diamino-2,4,6-trideoxyhexose.[12] Owing to the unavailability of 2,6-diamino-2,6-dideoxyhexoses other than the D-gluco analog,[5] considerable time

(1) Preliminary communication, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 2D.

(2) For a recent comprehensive review on this subject, see J. D. Dutcher, "Advances in Carbohydrate Chemistry," Vol. 18, Academic Press, Inc., New York, N. Y., 1963, p. 259.

(3) M. L. Wolfrom, D. Horton, and Y.-L. Hung, ref. 1, p. 3D. The D-*altro* stereochemistry has been assigned to this diamino sugar derivative by degradative studies (personal communication by Dr. D. Horton).

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