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56. Tyunosin Ukita,*1 Akira Hamada,*1 and Akira Kobata*2 : Organic Phosphates. XII.*3 Hydrobenzoin Cyclic Phosphorochloriodate as a Phosphorylating Agent.*4

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In the previous paper of this series, the authors reported the synthesis of hydrobenzoin cyclic phosphate (I) and its availability as a reagent for phosphorylation of several alcoholic compounds. This reaction consisted of alcoholysis of (I) followed by hydrolysis or hydrogenolysis of the phosphodiester-type compound produced. It was found that in the case of simple monofunctional primary alcohols these reactions occurred smoothly giving the final phosphate of the alcohol used in an excellent yield.[1] In the course of the synthesis of (I) by phosphorylation of hydrobenzoin with phosphoryl chloride, hydrobenzoin cyclic phosphorochloridate, an intermediate compound of this reaction, was not isolated.

In the present paper the isolation and purification of the chloridate (II) and its application to the phosphorylation of several hydroxylic compounds will be reported.

Hydrobenzoin (*meso*-type) was reacted with phosphoryl chloride in pyridine and, after removal of the solvent and excess reagent, the reaction mixture was extracted with benzene, and the product was precipitated from the extract with petroleum ether. After reprecipitation with the same solvents, the chloridate (II), $C_{14}H_{12}O_3ClP$, was obtained as colorless prisms in 70~90% yield. (II) is unstable to moisture and decomposes with liberation of hydrogen chloride.

Table I. Identification of the Reaction Products of Hydrobenzoin Cyclic Phosphorochloridate (II) with R-OH

R-OH	Neutral product (Cyclic triester)	Acidic product	Hydrobenzoin cyclic phosphate (I)	Hydrobenzoin phosphate
Benzyloxycarbonylaminoethanol (III)	(VI) S (55)	(VIII) M	M	F
1,2,3,4-Tetra-O-acetyl-β-D-glucose (IV)	(VII) S (30)	(IX) S	M	F
2',3'-O-Isopropylidene adenosine (V)	—	(X) S (43)	S	F

S, M, F represent the size and gradation of the tones of spots : S; strong, M; medium, F; faint. The figures given in parentheses are the yield (%) of the product isolated in preparative-scale experiments.

Three kinds of hydroxylic compounds, 2-benzyloxycarbonylaminoethanol (III), 1,2,3,4-tetra-O-acetyl-β-D-glucose (IV), and 2',3'-O-isopropylideneadenosine (V) were each reacted with (II) in pyridine while cooling and each reaction mixture used was subjected to paper chromatography and paper electrophoresis to detect the products. The results are summarized in Table I. In the case of (III) and (IV), four each phosphorus spots were detected and, as will be described below, these spots were found to correspond to hydrobenzoin cyclic phosphotriesters (VI and VII), hydrobenzoin phosphodiesters (VIII and IX), hydrobenzoin cyclic phosphate (I), and hydrobenzoin phosphate, the hydrolysis product of (I). Of these products, the main ones, (VI) and (VII), were isolated from the reaction mixture obtained by another run of experiment made on a preparative scale. Both (VI)

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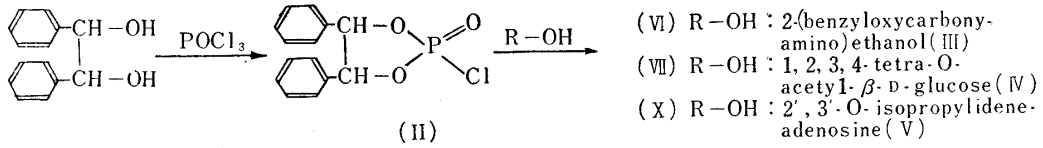
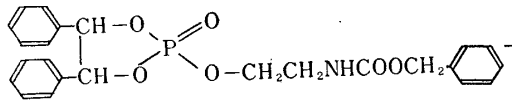
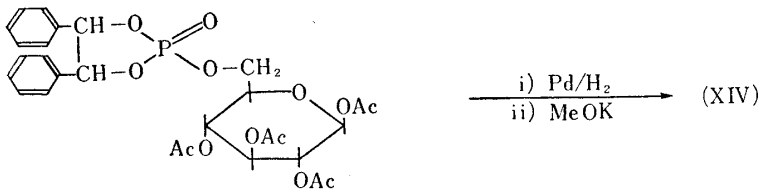
*3 Part XI : This Bulletin, **9**, 217 (1961).
*4 From the thesis of Akira Hamada for the degree of Doctor of Pharmaceutical Sciences, University of Tokyo, 1959.
1) T. Ukita, K. Nagasawa, M. Irie : J. Am. Chem. Soc., **80**, 1373 (1958).

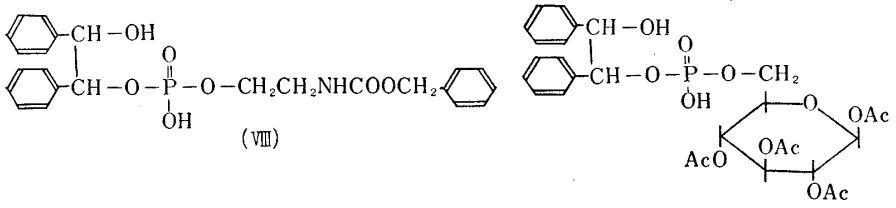
and (Ⅶ) were soluble in ether, chloroform, methanol, and ethanol, insoluble in water and petroleum ether, and they were found electrophoretically neutral. From these properties, their analytical data, $C_{24}H_{24}O_6NP$ for (Ⅵ) and $C_{28}H_{31}O_{13}P$ for (Ⅶ), and their behavior in further hydrolysis reactions, they were proved to be phosphotriesters represented by the structural formulae (Ⅵ) and (Ⅶ).

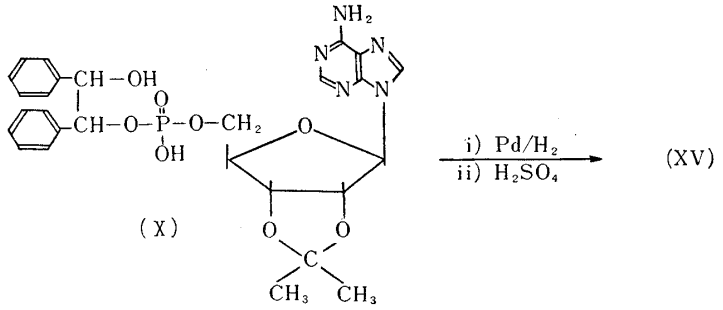
Other condensation products, (Ⅷ) and (Ⅸ), detected on paper chromatograms from these reaction mixtures showed electrophoretically acidic properties and, as will be described in the following paper of this series,[2] the product (Ⅷ) was identified as 2-(benzyloxycarbonylamino)ethyl hydrobenzoin phosphate, the hydrolysis product of the triester (Ⅵ). The product (Ⅸ) could analogously be represented by the structure of 1,2,3,4-tetra-O-acetyl-β-D-glucose 6-hydrobenzoin phosphate.











2) Part XIII. This Bulletin **9**, 639 (1961).

In the case of a similar condensation of (II) with 2′,3′-O-isopropylidene adenosine (V), however, the reaction mixture did not contain the neutral condensation product and the main product (X) was an acidic phosphorus compound, which was isolated by electrophoresis and purified as cyclohexylammonium salt, $C_{33}H_{43}O_8N_6P$. Similar to the products (VIII) and (IX), (X) showed the properties of a phosphodiester-type compound.

From these observations, it should be concluded that in the reaction of (II) with (V) the primary condensation product, 2′,3′-O-isopropylideneadenosine-5′-hydrobenzoin cyclic phosphate, is not stable enough to be detected by paper chromatography and paper electrophoresis, and only its hydrolysis product, phosphodiester-type compound (X) is detected, while the two cyclic phosphotriesters (VI and VII) are stable for detection and isolation.

The triesters (VI and VII) and the diesters (IX and X) were catalytically hydrogenolyzed over palladium-charcoal to liberate their hydrobenzoin moieties (and benzyloxycarbonyl group in the case of (VI)) and to give the corresponding phosphomonoesters, phosphorylethanolamine (XI), 1,2,3,4-tetra-O-acetyl-β-D-glucose 6-phosphate (XII), and 2′,3′-O-isopropylidene adenosine 5′-phosphate (XIII), respectively. Further, the latter two phosphates, (XII) and (XIII), gave D-glucose 6-phosphate (XIV) and adenosine 5′-phosphate (XV) as final products by removal of the protective groups by ordinary procedures.

Generally, six-membered cyclic phosphotriesters have been known to be more stable than the five-membered ones.[3~5] Thus, phenyl 1,2-propanediol cyclic phosphate, the only five-membered cyclic phosphotriester hitherto isolated, decomposes by contact with water while phenyl 1,3-propanediol cyclic phosphate, a six-membered ester, is recrystallizable from boiling water.[6] This is the first time that these two cyclic phosphotriesters (VI and VII), which have comparably large substituents such as hydrobenzoin and benzyloxycarbonylaminoethyl, or 1,2,3,4-tetra-O-acetyl-β-D-glucose moiety, were found to have sufficient stability for their isolation and purification. These cyclic phosphotriesters should be useful for further research on chemical properties of five-membered cyclic phosphotriesters.

Experimental

Hydrobenzoin Cyclic Phosphorochloridate (II)——To an ice-cooled solution of 3.5 g. of freshly distilled $POCl_3$ in 15 cc. of dehyd. pyridine, 3 g. of hydrobenzoin (*meso*-type) dissolved in 60 cc. of dehyd. pyridine was added dropwise with vigorous stirring over a period of 2 hr. Stirring was continued for an additional 30 min. in an ice bath and 1 hr. at room temperature. The pyridine hydrochloride that precipitated was decanted off and the solvent was evaporated in a diminished pressure at 40°, bubbling dry air from a capillary. The residual mass thus obtained was repeatedly washed with 50 cc. of dehyd. petr. ether until complete removal of pyridine and filtered through a sintered glass filter. The residue on the filter was successively extracted with 10 and 5 cc. of dehyd. benzene at about 40°, and the combined extract was added slowly with 100 cc. of dehyd. petr. ether. White prisms separated on cooling were collected and recrystallized from the same solvents; m.p. 160~162°; yield, 70~90%. *Anal.* Calcd. for $C_{14}H_{12}O_3ClP$: C, 57.06; H, 4.16; P, 10.53. Found : C, 57.47; H, 4.24; P, 10.89.

The above process, especially concentration and extraction of the product, have to be carried out under complete exclusion of moisture, because of the unstability of (II) against moisture.

Paper Chromatography——A sample containing 10~40 γ of P was applied on Toyo Roshi No. 53 filter paper and run ascendingly for 15 hr., using the following solvent systems : (1) iso-PrOH-conc. NH_4OH-H_2O (7:1:2); (2) PrOH-conc. NH_4OH-H_2O (20:10:3); (3) iso-PrOH-*tert*-BuOH-conc. NH_4OH H_2O (40:20:1:39). The Rf values for each solvent system used are represented by abbreviations of Rf_1, Rf_2, and Rf_3, respectively. For the detection of spots, the Bandurski-Axelrod method[7] for phosphate, the periodate-Schiff reagent[8,9] for α-glycol group, Ninhydrin reagent for amino group,

3) T. Ukita, N. A. Bates, H. E. Carter : J. Biol. Chem., **216**, 867 (1955).
4) H. G. Khorana, G. M. Tener, R. S. Wright, J. G. Moffatt : J. Am. Chem. Soc., **79**, 430 (1957).
5) O. Bailly : Bull. soc. chim. France, **31**, 848 (1922).
6) D. C. Ayres, H. N. Rydon : J. Chem. Soc., **1957**, 1109.
7) R. S. Bandurski, B. Axelrod : J. Biol. Chem., **193**, 405 (1951).
8) J. G. Buchanan, C. A. Dekker, A. G. Long : J. Chem. Soc., **1950**, 3162.
9) J. Baddiley, J. G. Buchanan, R. E. Handschumacher, J. F. Prescott : *Ibid.*, **1956**, 2818.

aniline hydrogenphthalate reagent for reducing sugar, and ultraviolet absorption*5 for derivatives of adenosine were employed.

Paper Electrophoresis——The sample was applied on a strip (26×12 cm.) of Toyo Roshi No. 53 filter paper (the start line placed 8 cm. from edge of the paper set on cathode side) and after being moistened with buffer solution of pH 5.6 (BuOH-AcOH-pyridine-H_2O=20:2:10:968) the strips were subjected to electrophoresis at a potential of 30 v/cm. for 60 min. The detection of the spots on paper was made by the same technique as that used in paper chromatography. Acetylated carbohydrate derivatives were detected by hydroxamic acid method.[10] The mobility (M) for each phosphorus spot was represented by the ratio of the distance of the spot from the start line to that of DNP-glutamic acid used as a standard.

2-(Benzyloxycarbonylamino)ethyl Hydrobenzoin Cyclic Phosphate (VI)——To a solution of 3.0 g. of (II) in 10 cc. of dehyd. pyridine chilled in an ice-salt bath, 1.5 g. of 2-(benzyloxycarbonylamino)ethanol[11] (III) in 5 cc. of dehyd. pyridine was added within 15 min. with vigorous stirring. Stirring was continued for additional 15 min. with cooling and 2 hr. at room temperature, and the mixture was set aside overnight. After concentration of the solution to 5 cc. in a reduced pressure at 40° (bath temperature), the concentrate was added with a small piece of ice, allowed to stand for 30 min., and then poured into 50 cc. of ice-water with stirring. The oil that separated was extracted three times with 30 cc. of Et_2O. The Et_2O solution after washing and drying was concentrated in a diminished pressure to a syrup, which was dissolved in 2 cc. of *tert*-BuOH and added with 5 cc. of H_2O to precipitate an oily product. After repeating this procedure twice, the oily product was collected by centrifugation, which solidified on addition of a drop of Et_2O and rubbing the glass wall; yield, 2.1 g. (55%). On recrystallization from the same solvents, the product was obtained as colorless microcrystals, which was dried over P_2O_5 *in vacuo* at room temperature, m.p. 90~92°. Rf_1 0.87, M 0. *Anal.* Calcd. for $C_{24}H_{24}O_6NP$: N, 3.09; P, 6.83. Found : N, 3.46; P, 7.15.

Phosphorylethanolamine (XI)——To 200 mg. of (VI) dissolved in 10 cc. of MeOH, 0.05 cc. of glacial AcOH and 100 mg. of anhyd. AcONa were added. The mixture was hydrogenated over 300 mg. of Pd-C (Pd 10%) added in three portions of 200 mg., 50 mg., and 50 mg. at intervals, as the absorption of H_2 tended to slacken, at room temperature. After 15 hr., when the consumption of H_2 was finished, the catalyst was removed by filtration and washed with boiling MeOH and H_2O. The filtrate and washings were combined and the mixture was extracted with Et_2O. The aqueous layer was concentrated to 20 cc., the concentrate was adjusted to pH 10 with saturated $Ba(OH)_2$ solution, and neutrallized with CO_2. The precipitate that formed was centrifuged off and barium salt of phosphorylethanolamine was precipitated from the supernatant by addition of 1.5 volumes of 95% EtOH. After reprecipitation with EtOH from aqueous solution, the barium salt was washed twice with 95% EtOH and once with dehyd. EtOH, yield; 89 mg. (73%). The sample for analysis was dried over P_2O_5 *in vacuo* at 80° for 5 hr. *Anal.* Calcd. for $C_2H_6O_4NBaP$: C, 8.69; H, 2.15; N, 5.07; P, 11.21. Found: C, 8.32; H, 2.31; N; 5.54; P, 10.98.

The sample obtained as above was identified with the authentic specimen by paper chromatography (Rf_1 0.10) and paper electrophoresis (M 0.28).

1,2,3,4-Tetra-O-acetyl-β-D-glucose 6-Hydrobenzoin Cyclic Phosphate (VII)——A solution of 2.0 g. of (IV)[12] dissolved in 6 cc. of dehyd. pyridine was chilled in an ice-salt bath. To this solution 2.3 g. of (II) in 5 cc. of dehyd. pyridine was added with vigorous stirring during 15 min. The mixture was stirred for additional 15 min. with cooling and set aside overnight at 0°. After addition of a small piece of ice and standing for 30 min., the mixture was poured slowly into 100 cc. of ice-water with mechanical stirring which was continued until the precipitate solidified. The precipitate, which was washed with 100 cc. of ice-water, was dissolved in 2 cc. of $CHCl_3$ and the solution was filtered. To the filtrate, 4 cc. of petr. ether was added and the mixture was kept at 0° overnight. White needles (1.06 g., 30%) thus obtained were recrystallized from MeOH, m.p. 168~169°. The sample for analysis was dried over P_2O_5 *in vacuo* for 5 hr. $[\alpha]_D^{23}$ +18.8° (c=1.62, $CHCl_3$), Rf_1 0.65, M 0. *Anal.* Calcd. for $C_{28}H_{31}O_{13}P$: C, 55.45; H, 5.12; P, 5.12. Found : C, 55.69; H, 5.33; P, 5.00.

D-Glucose 6-Phosphate (XIV)——i) From the triester (VII) : A solution of 500 mg. of (VII) and 200 mg. of anhyd. AcONa in 20 cc. of MeOH was hydrogenolyzed with 300 mg. of Pd-C (Pd 10%), which was added in three portions of 150 mg., 100 mg., and 50 mg. at intervals, at room temperature. After 12 hr., when the consumption of H_2 was over, the catalyst was removed by filtration and successively washed with boiling MeOH, 50% MeOH, and H_2O. The filtrate was combined with washings and concentrated *in vacuo* to 10 cc. The concentrate was extracted with Et_2O, the aqueous layer was again concentrated *in vacuo* to 5 cc., and lyophilized.

*5 Manaslu-light (type UV-Sl) was used.

10) M. Abdel-Akher, F. Smith : J. Am. Chem. Soc., **73**, 5859 (1951).

11) W. G. Rose : *Ibid.*, **69**, 1384 (1947).

12) D. D. Reynolds, W. L. Evans : Org. Syntheses, **22**, 56 (1942).

The glassy residue (XII) (Rf_1 0.15, ca. 200 mg.) thus obtained was dissolved in 4 cc. of cold dehyd. MeOH. To the solution, 2 cc. of 1*N* MeOK in anhyd. MeOH was added and the mixture was allowed to stand overnight in a refrigerator. The precipitate formed was collected by centrifugation, washed four times with dehyd. MeOH, dissolved in 10 cc. of H_2O, and filtered. The filtrate was decationized with Dowex-50 (H^+), the acidic solution thus obtained was neutralized with saturated $Ba(OH)_2$ solution, and the solution was concentrated to 5 cc. To the concentrate 20 cc. of dehyd. EtOH was added, the precipitate (barium D-glucose 6-phosphate) (95 mg.) was collected by centrifugation, and dissolved in 5 cc. of H_2O. The solution was again decationized with Dowex-50 (H^+) and filtered. After adjusting to pH 5.0 with 0.05*N* NaOH, 35 mg. of solid crystalline $(AcO)_2Ba$ was added to the filtrate. Soon after the disappearance of $(AcO)_2Ba$, the solution was filtered and 4 volumes of EtOH was added to the filtrate. The precipitated product was collected by centrifugation, washed twice with 80% EtOH and once with dehyd. EtOH, and then dried over P_2O_5 *in vacuo* at 80° for 6 hr. Yield, 82 mg. (25%). This product was identified with the authentic specimen by paper chromatography (Rf_1 0.07, Rf_2 0.40) and paper electrophoresis (M 0.82). $[\alpha]_D^{23}$ +19.5° (c=1.56, 0.1*N* HCl) (authentic specimen showed $[\alpha]_D^{16}$ +19.9°[13]). *Anal.* Calcd. for $C_6H_{11}O_9BaP$: C, 18.22; H, 2.80; P, 7.83. Found: C, 18.25; H, 3.55; P, 7.87.

To the combined MeOH mother liquor and washings, left after collection of the foregoing potassium D-glucose 6-phosphate, a slight excess of $(AcO)_2Ba$ was added. The barium salt (36 mg.) that precipitated was collected by centrifugation and purified as above to obtain additional 25 mg. of barium D-glucose 6-phosphate. Thus the total yield of crude barium D-glucose 6-phosphate was 40.3% calculated from the triester (VII).

ii) From the diester (IX) produced as a by-product in the synthesis of (VII): Barium D-glucose 6-phosphate was also isolated from the aqueous filtrate obtained after filtration of the triester (VII) in the synthesis of the latter. The filtrate was extracted with three 30-cc. portions of $CHCl_3$, the organic layer was washed with H_2O, and dried. The $CHCl_3$ solution was concentrated to 10 cc., filtered, and, after addition of equal volume of Et_2O, the mixture was kept at 0°. The precipitate (450 mg.) that appeared was dissolved in 20 cc. of MeOH and filtered. The hydrogenation and deacetylation were carried out on this filtrate with the same technique as in the case of (VII). The resulting crude barium D-glucose 6-phosphate crystallized from aqueous solution as sparingly soluble heptahydrate and then purified as described above. Yield, 135 mg.

Reaction of 2′,3′-O-Isopropylideneadenosine (V) with Hydrobenzoin Cyclic Phosphorochloridate (II)——A solution of 500 mg. of (V)[14] dissolved in 3 cc. of dehyd. pyridine was frozen in dry ice-Me_2CO bath. To this solution, a cooled solution of 1.0 g. of (II) in 2.5 cc. of dehyd. pyridine was added at once. After 5 min., the cooling bath was removed and when the solid mixture was warmed up to semi-solid suspension, the reaction flask was again immersed in an ice-salt bath of ca. −30°, the mixture was stirred for 2 hr., and set aside overnight at 0°. From this reaction mixture, 0.02 cc. was withdrawn and examined by paper electrophoresis. There was no neutral spot, which revealed both ultraviolet absorption and P,*6 and only one acidic phosphodiester-type compound (X) with Rf_1 0.80 and M 0.62 was detected as the reaction product.

To the above reaction mixture, a piece of ice was added and after 30 min. the mixture was poured into 70 cc. of ice-water with stirring. The aqueous solution was extracted thoroughly with $CHCl_3$ to remove a neutral compound, the extract was washed once with H_2O, and dried. On removal of $CHCl_3$, a pale yellow residue was obtained which was recrystallized from boiling H_2O and identified with unreacted 2′,3′-O-isopropylideneadenosine (V) (yield, 90 mg.).

One-quarter of the aqueous layer, obtained after extraction with $CHCl_3$, was streaked on 4 sheets of Toyo Roshi No. 27 filter paper (30×30 cm.) and submitted to paper electrophoresis. The zones of the paper which contained the diester (X) were cut out and the cuttings were extracted with a small volume of dil. NH_4OH (conc. NH_4OH 2+H_2O 100). The extracts were combined, passed through a column (2×10 cm.) of Amberlite IRC-50 (cyclohexylammonium form) and the total effluent and washings were lyophilized. The residual white powder was dissolved in 30 cc. of MeOH and filtered. On addition of Et_2O to the filtrate and keeping at 0°, fine powdery precipitate was obtained; yield, 120 mg. (43%). Reprecipitation from iso-PrOH-Et_2O gave a pure product of m.p. 208~209°(decomp.). The sample for analysis was dried over P_2O_5 *in vacuo* at 80° for 5 hr. *Anal.* Calcd. for $C_{33}H_{42}O_8N_6P$ (cyclohexylammonium salt of the diester (X)): C, 58.06; H, 6.30; N, 12.32; P, 4.55. Found: C, 57.82; H, 6.25; N, 11.89; P, 5.01. Rf_1 0.80, M 0.62.

Adenosine 5′-Phosphate (XV)——i) From the diester (X): A mixture of 250 mg. of cyclohexylammonium salt of the diester (X) and 300 mg. of Pd-C (Pd 10%) in 10 cc. of 50% EtOH was

*6 The origin and neutral areas on the paper were cut off to inset for P by the Allen method (Biochem. J., **34**, 858 (1940)).

13) T. Ukita, K. Nagasawa: Unpublished data.

14) "Methods in Enzymology," Vol. III, 812 (1957).

shaken in H_2 atmosphere at 30°. After 8 hr. of hydrogenation, the catalyst was filtered and extracted with warm 50% EtOH and H_2O. The filtrate and extracts were combined, extracted twice with Et_2O, and the aqueous layer was concentrated to 10 cc. To the concentrate, 20 cc. of 0.1*N* H_2SO_4 was added and the solution was set aside at room temperature for 2 days. The solution was adjusted to pH 2.8 with saturated solution of $Ba(OH)_2$ and, after removal of $BaSO_4$ by centrifugation, the supernatant was concentrated to 5 cc. *in vacuo*. After removal of Ba^{2+} with Dowex-50 (H^+), the acid solution was poured into Me_2CO. The precipitated adenosine 5′-phosphate weighed 83 mg. (65%). On recrystallization from H_2O, adenosine 5′-phosphate was obtained as colorless needles, m.p. 192.5~194°. This product was identified with the authentic specimen by paper chromatography (Rf_1 0.08, Rf_2 0.25) and paper electrophoresis (M 0.60). The sample for analysis was dried over P_2O_5 *in vacuo* at 100~105° for 5 hr. *Anal.* Calcd. for $C_{10}H_{14}O_7N_5P$: C, 34.59; H, 4.06; P, 8.92. Found: C, 34.44; H, 4.01; P, 8.63.

ii) Adenosine 5′-phosphate directly from the reaction mixture of (V) and (II): To the reaction mixture of (V) and (II), prepared by similar procedure as described above, a solution of 1 g. of $NaHCO_3$ in 7 cc. of H_2O was added with cooling and the mixture was shaken until the evolution of CO_2 ceased. The solvent was removed in a reduced pressure, and the residual pyridine was completely removed in a reduced pressure by repeated evaporation of H_2O added. The final residue was dissolved in 20 cc. of H_2O and extracted with $CHCl_3$ to remove the unreacted starting material (V). The aqueous layer was neutralized with Dowex-50 (H^+), passed through a column (2×15 cm.) of Amberlite IRC-50 (NH_4^+ form), and the column was washed with H_2O. Total effluent and washings were lyophilized, the resulting powder (1.4 g.) was dissolved in 20 cc. of 50% EtOH, and hydrogenated over 500 mg. of Pd-C (Pd 10%) which was added, as described above, in portions of 300 mg., 100 mg., and 100 mg. at intervals. After 12 hr. of hydrogenation, the catalyst was removed by filtration and washed with warm 50% EtOH and H_2O. The combined filtrate and washings were extracted with Et_2O and the separated aqueous layer was concentrated to 10 cc. The concentrate was adjusted to pH 8.0 with saturated solution of $Ba(OH)_2$ and neutralized with CO_2. The precipitate was removed by centrifugation and the supernatant was lyophilized. To the solution of 424 mg. of powdery residue in 10 cc. of H_2O, 30 cc. of 0.1*N* H_2SO_4 was added, the mixture was filtered, and set aside at room temperature for 2 days. Adenosine 5′-phosphate was obtained from the mixture by the similar procedure as described in (i). Yield, 216 mg. (39% calculated from isopropylidene adenosine (V)).

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Summary

Hydrobenzoin cyclic phosphorochloridate was synthesized and isolated in a pure state. This compound was reacted with 2-(benzyloxycarbonylamino)ethanol, 1,2,3,4-tetra-O-acetyl-β-D-glucose, and 2′,3′-O-isopropylideneadenosine, and the reaction products were submitted to hydrogenolysis to obtain the respective O-phosphate of the above three alcoholic compounds. Removal of the protective group from the phosphates thus obtained gave phosphorylethanolamine, D-glucose 6-phosphate, and adenosine 5′-phosphate, respectively.

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