Nucleosides. I. 5′-Amino-5′-deoxyuridine and 5′-Amino-5′-deoxythymidine[1a,b]

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The synthesis of 5′-amino-5′-deoxyuridine (IXa) and 5′-amino-5′-deoxythymidine (XII) from uridine and thymidine, respectively, are described.

Todd and co-workers[2] observed that 5′-O-acetyl-2′-O-tosyluridine (I), on treatment with sodium azide in acetonitrile, gave 2,2′-anhydro-1-(5′-O-acetyl-β-D-arabinosyl)uracil (IIa) instead of the expected azide derivative. The failure to effect cleavage of the 2,2′-anhydro bond in IIa by azide ion was ascribed to the low solubility of the alkali metal azide in acetonitrile.

2,2′-Anhydro bond formation readily occurs in the presence of a variety of bases as a result of a stereochemically controlled attack by the 2-carbonyl oxygen upon C-2′ with the expulsion of a secondary sulfonyloxy group.[3,4] Replacement of a primary sulfonyloxy group (C-5′) of uridine or thymidine, on the other hand, cannot be accomplished by intramolecular—(*i.e.*, 2,5′-anhydro bond formation) nucleophilic attack.[3,5] For this reason, it appeared of interest to undertake a study of the conditions necessary to promote the displacement of a 5′-sulfonyloxy group by azide ion as a possible route to pyrimidine aminonucleosides.

It has been shown in an unrelated study that both lithium azide and ammonium azide, generated *in situ*, serve as an excellent source of azide ion in N,N-dimethylformamide (DMF).[6] The interaction of 5′-O-tosyl-2′-,3′-O-isopropylideneuridine (III) and lithium azide in DMF gave a crystalline product (58% yield) which manifested a strong azide band (4.75 μ) in the infrared region of the spectrum. On the basis of elementary analysis, infrared and ultraviolet absorption spectra, the product was assigned the structure 5′-azido-5′-deoxy-2′,3′-O-isopropylideneuridine (IV). The latter, which exists in two crystalline modifications, on de-acetonation with acid, gave 5′-azido-5′-deoxyuridine (VI) in 81% yield.

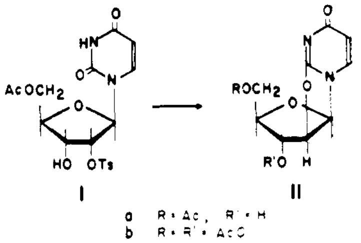

Figure 1

It was observed in accord with the above structural assignments that 5′-O-tosyluridine[7] (VII), on successive treatment with lithium azide (DMF) and acetic anhydride in pyridine produced 5′-azido-5′-deoxy-2′,3′-di-*O*-acetyluridine (VIII) in 73% over-all yield. The deacetylation of VIII with methanolic ammonia led to a product identical in every respect with VI. Catalytic hydrogenation transformed VI to 5′-amino-5′-deoxyuridine (IXa), which was obtained as an amorphous solid of indefinite melting point.[8] The latter was more carefully characterized as the N-acetyl derivative, IXb. Moreover, the same product (IXb) was obtained in 49% over-all yield from IV on successive catalytic reduction, acetylation, and de-acetonation.

Todd and associates[9] investigated the action of nucleophilic reagents on 2,5′-anhydro-1-(2′,3′-O-isopropylidene-β-D-ribosyl)uracil (V) and observed that anhydro bridge-opening is effectible in either direction, depending upon the reagent and reaction conditions. It appeared of interest, in connection with the present study, to ascertain the direction of attack of azide ion on the 2,5′-anhydro bond of V. Nucleophilic displacement at C-5′ of the sugar moiety (alkyl–oxygen fission) would lead to IV, whereas attack at C-2 of the aglycon could produce either a 2-azido-4(3*H*)-pyrimidinone derivative or the corresponding product of cyclization, a tetraazolo[1,5-*a*]pyrimidin-7-one.

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(1) (a) This work was supported in part by research grants CY-2903 and CY-5943 from the National Cancer Institute, Public Health Service, and in part by an institutional grant from the United Foundation of Greater Detroit allocated through the Michigan Cancer Foundation. (b) Presented before the Division of Medicinal Chemistry, 140th National Meeting, American Chemical Society, Chicago, Illinois, September, 1961.

(2) D. M. Brown, D. B. Parihar, and A. R. Todd, *J. Chem. Soc.*, 4242 (1958).

(3) D. M. Brown, A. R. Todd, and S. Varadarajan, *ibid.*, 868 (1957).

(4) J. F. Codington, R. Fecher, and J. J. Fox, *J. Am. Chem. Soc.*, **82**, 2794 (1960) and references cited.

(5) The formation of a 2,5-anhydronucleoside from the action of silver ion on, for example, 5′-iodo-5′-deoxyuridine is presumed to involve a carbonium ion intermediate. See ref. 3.

(6) W. G. Finnigan, R. A. Henry, and R. Loftquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).

(7) A. M. Michelson and A. R. Todd, *J. Chem. Soc.*, 816 (1955).

(8) H. M. Kissman and M. J. Weiss, *J. Am. Chem. Soc.*, **80**, 2575 (1958), have recorded similar physical properties for 1-(5′-amino-5′-deoxy-β-D-ribosyl)thymine as well as 5′-amino-5′-deoxycytidine.

(9) D. M. Brown, D. B. Parihar A. R. Todd, and S. Varadarajan, *J. Chem. Soc.*, 3028 (1958).

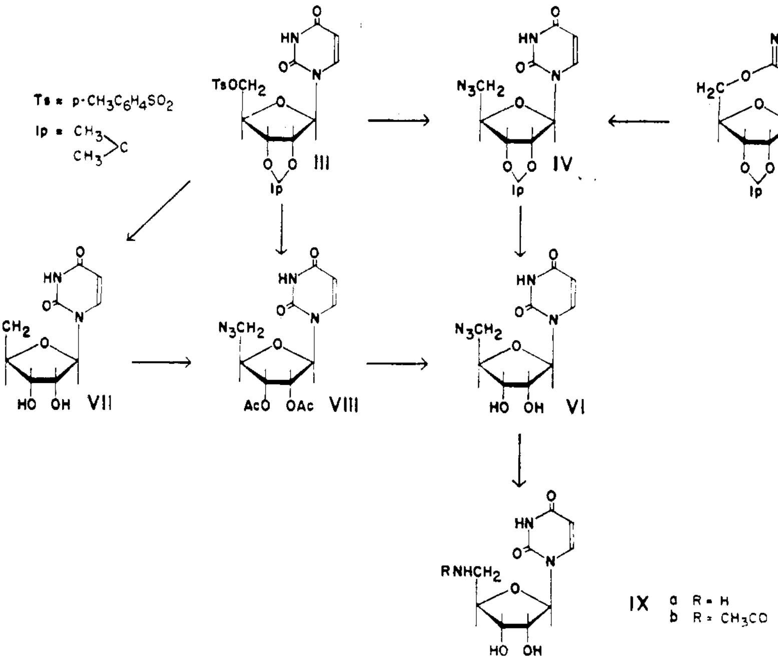

Figure 2

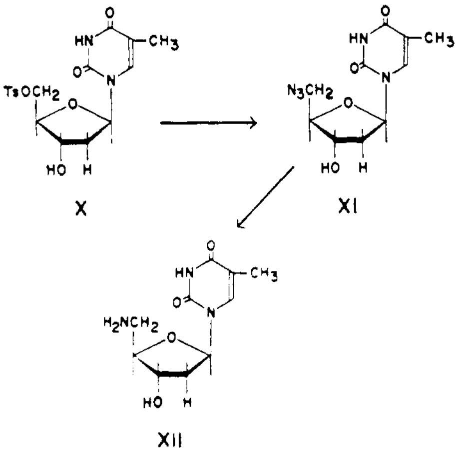

Figure 3

Reaction of V with lithium azide in DMF gave IV in 50% yield following reversed partition chromatography on Celite. No other product was detected in the course of spectrophotometric examination of the 120 fractions comprising the chromatogram. The same course of reaction was obtained by the action of ammonium azide, generated *in situ* in DMF, on V.

With this knowledge we turned our attention to 5′-O-tosylthymidine (X) as a possible route to 5′-amino-5′-deoxythymidine (XII). The conversion of thymidine to a 5′-tosylate *via* 3′-O-acetyl-5′-O-tritylthymidine has been recorded by Michelson and Todd.[7,10] This sequence of reactions was found to proceed in excellent yield in the present work. Reaction of X with lithium azide in DMF produced 5′-azido-5′-deoxythymidine (XI) in 76% yield. The constitution of this product followed from its composition and the detection of a strong azide absorption (4.81 μ) in the infrared region of the spectrum. Catalytic hydrogenation afforded the desired amino nucleoside (XII) in 79% yield.

The attempted replacement of the secondary sulfonyloxy function in I through the use of lithium azide in DMF led once again to 2,2′-anhydro bridge formation. In this case a mixture of IIa and the corresponding (5′-O) deacetylated product was obtained. The mixture, which evidently developed during the work-up, was reacetylated to give 2,2′-anhydro-1-(3′,5′-di-O-acetyl-β-D-arabinosyl)uracil (IIb) as the sole product. Attempts to open the 2,2′-anhydro bond in II with ammonium azide were unsuccessful.

These observations are, in essence, identical with the findings of Todd, *et al.*,[2] for the course of the same reaction with sodium azide in acetonitrile. Contrary, however, to the conclusion drawn in the prior study (*vide supra*), failure to effect cleavage of the 2,2′-anhydro bond in IIa by azide ion cannot be attributed to the low solubility of the salt. Rather, displacement at C-2, in IIa apparently requires a more potent nucleophile than azide ion in DMF or acetonitrile. Thus, iodide ion which is relatively more nucleophilic[11] than azide ion will open[2] this anhydronucleoside.

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[10] A. M. Michelson and A. R. Todd, *J. Chem. Soc.*, 951 (1953).

[11] J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, 1956.

Experimental[12]

5′-Azido-5′-deoxy-2′,3′-O-isopropylideneuridine (IV). a. From 5′-O-Tosyl-2′,3′-O-isopropylideneuridine (III).—A solution of 8.52 g. (19.6 mmoles) of crude III[13] and 2.4 g. (49.2 mmoles) of lithium azide[14] in dry DMF was stirred magnetically at 100° for 2.5 hr. under an atmosphere of nitrogen. The solvent was removed under diminished pressure and the gummy residue twice evaporated with ethanol. The residue was then dissolved in 50 ml. of water, the solution acidified with glacial acetic acid and then extracted (3 × 30 ml.) with chloroform. The extract was washed with dilute sodium bicarbonate and dried over magnesium sulfate. The filtered chloroform solution was evaporated under reduced pressure to a yellow sirup which was dissolved in 95% ethanol and treated with Norit. The product was deposited on storing the solution in a refrigerator overnight; wt. 3.51 g. (58% yield), m.p. 126–129°. Two recrystallizations from 95% ethanol afforded an analytical sample in the form of colorless thick needles, m.p. 132.5–133.5°; $[\alpha]^{26}\mathrm{D}$ +46° (95% EtOH, *c* 1), $\lambda^{95\%\ \mathrm{EtOH}}_{\mathrm{max,\ min}}$ (mμ) 258, 229 (ε 9600, 2400). $\lambda^{\mathrm{CHCl_3}}_{\mathrm{max}(\mu)}$ 4.76 (N_3); 5.83, 5.92 (CO); 16.68 (isopropylidene).

Anal. Calcd. for $C_{12}H_{15}N_5O_5$: C, 46.60; H, 4.89; N, 22.65. Found: C, 46.72; H, 5.01; N, 22.59.

b.—From 2,5′-Anhydro-1-(2′,3′-O-isopropylidene-β-D-ribosyl)uracil (V) and Lithium Azide.—A solution of 530 mg. (2 mmoles) of V and 300 mg. (6.2 mmoles) of lithium azide in 20 ml. of dry DMF was stirred magnetically at 100° for 1 hr. under an atmosphere of nitrogen. The yellow solution was evaporated to dryness under diminished pressure at 50° and the residual gum dissolved in *ca.* 50 ml. of water containing a few drops of glacial acetic acid. The gummy precipitate was extracted with chloroform (3 × 25 ml.) and the extract washed successively with cold dilute sodium bicarbonate and water. The dried extract was evaporated to a frothy glass under reduced pressure. The crude product was purified by reverse-phase partition chromatography on Celite[15] with an ethyl acetate–water system. The material (0.5 g.) was dissolved in 2 ml. of the upper phase of the solvent system and 2 g. of the treated Celite was thoroughly mixed with this solution. This wet Celite was added to the top of a column containing 20 g. of Celite which had been mixed well with the 20 ml. of the lower phase of the solvent system. The column (2.5 × 12 cm.) was washed with equilibrated water and the effluent was examined regularly in the spectrophotometer[12] set at 260 mμ. A total of 120 samples (*ca.* 960 ml.) was collected. Fractions 50–102 were recombined and, on slow evaporation in a stream of air, a solid, in the form of fine colorless needles, was deposited; wt. 310 mg. (50% yield), m.p. 116–117°. A single recrystallization from dilute ethanol provided an analytical sample, m.p. 116.5–117.5°; $[\alpha]^{26}\mathrm{D}$ +45° (95% EtOH, *c* 1), $\lambda^{\mathrm{CHCl_3}}_{\mathrm{max}(\mu)}$ 4.75 (N_3), 5.83, 5.92 (CO), 11.65 (isopropylidene), $\lambda^{95\%\ \mathrm{EtOH}}_{\mathrm{max,\ min}}$ (mμ), 258, 229 (ε 9600, 2400).

Anal. Calcd. for $C_{12}H_{15}N_5O_5$: C, 46.60; H, 4.89; N, 22.65. Found: C, 46.86; H, 5.11; N, 22.54.

Mixture melting point with the product obtained in procedure a, 131–132°. When the lower melting crystalline modification was recrystallized from 95% ethanol and a seed crystal of the higher melting modification was added, clusters of colorless thick needles were obtained, m.p. 132.5–133.5°.

c. From III and Ammonium Azide.—To a stirred mixture of 1.22 g. (18.8 mmoles) of sodium azide and 1.21 g. (22.6 mmoles) of ammonium chloride in 50 ml. of DMF was added 0.5 g. (1.88 mmoles) of III and the mixture stirred at 90° for 14.5 hr. The inorganic salts were removed by filtration and the solution evaporated to dryness under reduced pressure. The residue was partitioned between chloroform and water, the organic layer drawn off, and the aqueous phase extracted (3 × 25 ml.) with chloroform. The combined dried extract was evaporated to dryness under reduced pressure and oily residue solidified on standing; wt. 0.325 g. (56% yield), m.p. 125–128°. A single recrystallization from ethanol gave thick colorless needles (0.235 g.), m.p. 132.5–133.5° alone or when admixed with an authentic sample of IV.

5′-Azido-5′-deoxyuridine (VI).—A solution of 1.69 g. (5.3 mmoles) of IV in 100 ml. of 90% ethanol containing 2 ml. of concentrated hydrochloric acid was refluxed for 1 hr. The clear solution was evaporated to dryness under reduced pressure at < 50°. The residue was evaporated twice with benzene and twice with ethanol. The solid crystallized from absolute ethanol in the form of fine colorless needles; wt. 1.07 g. (73% yield), m.p. 148–150°. An additional crop of the same material; wt. 0.12 g. (8% yield), m.p. 148–150°, was obtained after concentrating the alcohol filtrate to *ca.* 0.5 the original volume. A second recrystallization from alcohol provided an analytical sample, m.p. 151.5–152.5°; $[\alpha]^{25}\mathrm{D}$ +69° (95% ethanol, *c* 0.6), $\lambda^{\mathrm{Nujol}}_{\mathrm{max}(\mu)}$ 4.78 (azide); $\lambda^{95\%\ \mathrm{EtOH}}_{\mathrm{max,\ min}}$ (mμ) 262, 232 (ε 9950, 2540).

Anal. Calcd. for $C_9H_{11}N_5O_5$: C, 40.15; H, 4.12; N, 26.02. Found: C, 40.31; H, 4.19; N, 25.82.

5′-Azido-5′-deoxy-2′,3′-di-O-acetyluridine (VIII).—A solution of 0.65 g. (1.6 mmoles) of 5′-O-tosyluridine[3] and 0.16 g. (3.2 mmoles) of lithium azide in 10 ml. of DMF was stirred magnetically at 100° under an atmosphere of nitrogen for 2.5 hr. The solvent was removed under reduced pressure and the residue twice evaporated with ethanol. The residual gum was dissolved in 2 ml. of dry pyridine to which was added 5 ml. of freshly distilled acetic anhydride. After holding the solution overnight at room temperature, 10 ml. of methanol was added to the chilled reaction mixture and the clear solution evaporated to dryness under diminished pressure. The residue was then dissolved in a mixture of chloroform and water, the organic layer drawn off, and the aqueous phase extracted with chloroform (3 × 50 ml.). The dried extract was evaporated to dryness under reduced pressure and the residue crystallized from 5 ml. of 95% ethanol; wt. 0.42 g. (73% yield), m.p. 97–99°. Recrystallization from ethyl acetate–petroleum ether (b.p. 30–60°) afforded colorless plates, m.p. 101–103°; $[\alpha]^{24}\mathrm{D}$ +85° (ethanol, *c* 1), $\lambda^{\mathrm{CHCl_3}}_{\mathrm{max}}$ 4.75 (azide), 5.73 (acetate), $\lambda^{\mathrm{EtOH}}_{\mathrm{max,\ min}}$ (mμ) 257, 229 (ε 9950, 2660).

Anal. Calcd. for $C_{13}H_{15}N_5O_7$: C, 44.19; H, 4.28; N, 19.83. Found: C, 44.44; H, 4.53; N, 20.36.

A solution of 0.1 g. (0.28 mmole) of crude VIII (m.p. 97–99°) was dissolved in 10 ml. of cold methanol which had previously been saturated with ammonia. After 18 hr. at room temperature, the solution was evaporated to dryness under reduced pressure and the residue crystallized from ethanol; wt. 0.04 g. (53% yield), m.p. 149–151°. Mixture melting point with an authentic sample of VI, 149–151°. Infrared and ultraviolet absorption spectra, as obtained with the two samples, were essentially superimposable.

5′-Amino-5′-deoxyuridine (IXa).—A solution of 0.27 g. (1 mmole) of VI in 100 ml. of absolute ethanol containing 0.1 g. platinum oxide was shaken under 45 lb. of hydrogen for 3 hr. The catalyst was removed by filtration and the solution evaporated to dryness under reduced pressure. The residue was dissolved in 10 ml. of water to afford a cloudy solution which was treated with Norit and Celite and filtered. The filtrate was evaporated to dryness under diminished

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(12) All melting points are uncorrected. Analytical determinations were performed by Micro-Tech Laboratories, Skokie, Illinois. Ultraviolet absorption measurements were made with a Cary recording spectrophotometer, Model 11. Infrared absorption spectra were measured both in chloroform and Nujol using a Perkin-Elmer, Model 21, recording spectrophotometer.

(13) P. A. Levene, and R. S. Tipson, *J. Biol. Chem.*, **106**, 113 (1934); obtained III in the form of a pink flaky glass which is the material obtained and used in the present study.

(14) N. Hofman-Bang, *Acta Chem. Scand.*, **11**, 581 (1957).

(15) The material used for partition chromatography was treated in accordance with the method described by G. A. Howard and A. J. P. Martin, *Biochem. J.*, **46**, 532 (1950). Celite 545 was dried at 110° and when cool, was allowed to stand in a desiccator with dimethyldichlorosilane (Dow). The treated material, which should all float when shaken with water, was washed with methanol until the washings were no longer acid to Bromthymol Blue, dried at 110°, and stored for use.

pressure and residue evaporated several times from ethanol to eliminate the last traces of moisture. The residue was dissolved in a mixture of methanol and ethanol, then concentrated to *ca.* 10 ml. on a hot plate. An amorphous off-white solid was deposited on standing which was collected and dried *in vacuo*, wt. 0.11 g., softening at 60–80° and gradually decomposing up to 150°. Attempts to remove the apparent solvent of crystallization by drying at 80° (10^{-3} mm.) led to decomposition. A second crop of material of the same melting point behavior was obtained by concentrating the alcohol filtrate to 0.5 the original volume; wt. 0.04 g. (total yield 62%); $[\alpha]^{25}\text{D}$ +14°, $\lambda^{H_2O}_{\text{max, min}}$ (mμ) 262, 230 (ϵ 10,060, 2340).

Anal. Calcd. for $C_9H_{13}N_3O_5 \cdot CH_3OH$: C, 43.63; H, 6.23; N, 15.27. Found: C, 43.74; H, 5.89; N, 15.56.

5′-Acetamido-5′-deoxyuridine (IXb). **a. From VI.**—A solution of 0.270 g. (1 mmole) of VI was reduced in ethanol (100 ml.) and in the presence of platinum oxide under 3 atm. of hydrogen in the manner described in the preceding section. After removal of the catalyst, the filtrate was evaporated to dryness under reduced pressure, the white residue redissolved in 50 ml. of dry methanol, and 0.11 ml. of freshly distilled acetic anhydride was added at 10°. After stirring the reaction mixture at room temperature for 5 hr., the solvent was removed at 20–25° under reduced pressure. The residue was triturated with ether, the supernatant liquid decanted, and the residue dissolved in methanol. The solution was treated with Norit, the filtrate concentrated to *ca.* 10 ml. and a colorless solid, rosettes of needles, was deposited on standing overnight at room temperature; wt. 0.185 g. (65% yield), m.p. 225–228° with sintering at 215°. A second recrystallization from the same solvent raised the melting point to 230–231°; $[\alpha]^{24}\text{D}$ + 27° (H_2O, *c* 0.4), $\lambda^{H_2O}_{\text{max, min}}$ (mμ) 262, 231 (ϵ 9830, 2060).

Anal. Calcd. for $C_{11}H_{15}N_3O_6$: C, 46.31; H, 5.30; N, 14.73. Found: C, 46.16; H, 5.50; N, 14.69.

b. From IV.—A solution of 0.63 g. (2.04 mmoles) of IV in 100 ml. of absolute ethanol containing 0.1 g. of platinum oxide was shaken under 3 atm. of hydrogen for 1 hr. The catalyst was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The glassy residue was dissolved in 5 ml. of dry pyridine and 0.6 ml. of freshly distilled acetic anhydride was added. After 4 hr. at room temperature, 15 ml. of methanol was added to the chilled reaction mixture. Evaporation at reduced pressure below 50° followed by two evaporations with absolute ethanol gave a frothy glass which was immediately dissolved in 12 ml. of 98% formic acid and held at room temperature for 3 hr. Removal of the acid under reduced pressure, followed by repeated evaporation of the residue with ethanol gave a product which crystallized from methanol as rosettes of colorless needles; wt. 0.284 g. (49% yield), m.p. 229–230° alone or when admixed with a sample of IXb obtained according to procedure **a**.

5′-Azido-5′-deoxythymidine (XI).—A solution of 1.5 g. (3.8 mmoles) of 5′-O-tosylthymidine[7] (X) in 30 ml. of DMF containing 0.45 g. (9.2 mmoles) of lithium azide was stirred magnetically at 100° for 2.5 hr. under an atmosphere of nitrogen. Removal of the solvent under diminished pressure followed by several evaporations from ethanol left a gummy residue, which was dissolved in 75 ml. of 50% methanol and stirred batchwise with 7.0 g. of Amberlite IR-120 (H^+) for 0.5 hr. The resin was removed by filtration and the filtrate, on evaporation to near dryness under reduced pressure at < 50°, afforded a white crystalline mass which was washed into a filter funnel with a minimum of ice water; wt. 0.53 g., m.p. 163–165°. Concentration of the washings in an air stream gave additional crop of solid; wt. 0.23 g. (total yield 75%), m.p. 162–165°. The combined solid, on recrystallization from isopropyl alcohol, gave colorless plates, m.p. 165–166°; $[\alpha]^{25}\text{D}$ +98° (methanol, *c* 1); $\lambda^{\text{Nujol}}_{\text{max}(\mu)}$ 4.80 (azide), $\lambda^{95\%\ \text{EtOH}}_{\text{max, min}}$ (mμ) 266, 235 (ϵ 9900, 2700).

Anal. Calcd. for $C_{10}H_{13}N_5O_4$: C, 44.91; H, 4.90; N, 26.21. Found: C, 45.11; H, 5.21; N, 26.37.

5′-Amino-5′-deoxythymidine (XII).—A solution of 0.155 g. (0.6 mmole) of XI in 50 ml. of absolute ethanol containing 50 mg. of platinum oxide was shaken for 0.5 hr. under 30 lb. of hydrogen. The mixture was filtered through Celite and the filtrate evaporated to dryness under diminished pressure. The product crystallized from benzene–methanol as microscopic needles; wt. 0.11 g. (79% yield), m.p. 173–174°. Recrystallization from the same mixture of solvents provided an analytical sample; m.p. 173.5–174.5°; $[\alpha]^{26}\text{D}$ +39° (MeOH, *c* 1), $\lambda^{\text{Nujol}}_{\text{max}}$ (μ) 3.02 (NH, OH), 5.85, 5.94 (CO), $\lambda^{H_2O}_{\text{max, min}}$ (mμ) 266, 233 (ϵ 9300, 2100).

Anal. Calcd. for $C_{10}H_{15}N_3O_4$: C, 49.78; H, 6.28; N, 17.42. Found: C, 49.77; H, 6.62; N, 17.12.

2,2′-Anhydro-1-(3′,5′-di-*O*-acetyl-β-D-arabinosyl)uracil (IIb).—A mixture of 0.35 g. (0.8 mmole) of 5′-O-acetyl-2′-O-tosyluridine[2] (I) and 0.11 g. (2.2 mmoles) lithium azide in 10 ml. DMF was stirred magnetically at 100° under an atmosphere of nitrogen for 2.5 hr.[16] The solvent was removed under diminished pressure and the residue evaporated several times from ethanol. The gummy mixture was dissolved in 10 ml. of water and the solution stirred batchwise successively with 2.0 g. of Amberlite IR-120 (H^+) and 1.0 g. of Amberlite IR-4B (OH^-). The filtered solution was evaporated to dryness and the last traces of moisture were removed by repeated evaporations with absolute ethanol. The residue was dissolved in 5 ml. of dry pyridine and 2.0 ml. of freshly distilled acetic anhydride was added. After standing overnight at room temperature, 10 ml. of methanol was added to the chilled reaction mixture and clear solution evaporated to dryness under reduced pressure. Several evaporations of the residue from ethanol gave a crystalline mass which was collected and recrystallized from a small volume (*ca.* 5 ml.) of ethanol, to give colorless prisms; wt. 0.115 g. (47% yield), m.p. 183–185° (lit.[2] 186–187°), $\lambda^{95\%\ \text{EtOH}}_{\text{max}}$ (mμ) 248, 225 (ϵ 7750, 9560), $\lambda^{95\%\ \text{EtOH}}_{\text{min}}$ (mμ) 237 (ϵ 7360) (lit.[2] in 95% EtOH), λ_{max} (mμ) 248, 224 (ϵ 8030, 9725), λ_{min} (mμ) 238 (ϵ 7450).

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(16) Longer reaction times gave intractable tars.