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Syntheses of 1-(5′-Amino-5′-deoxy-β-D-xylofuranosyl)uracil and Its N_3-Methyl Derivative[1]

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1-(5′-Amino-5′-deoxy-β-D-xylofuranosyl)uracil (VIII) and N_3-methyl-1-(5′-amino-5′-deoxy-β-D-xylofuranosyl)uracil (IX) were synthesized by catalytic reduction of the respective 5′-azido nucleosides, which were obtained by nucleophilic attack of 1-(3,′5′-epoxy-β-D-xylofuranosyl)uracil (IV) or 1-(5′-halogeno-5′-deoxy-β-D-xylofuranosyl)uracils (II) and N_3-methyl-1-(3′,5′-epoxy-β-D-xylofuranosyl)uracil (V) or N_3-methyl-1-(5′-iodo-5′-deoxy-β-D-xylofuranosyl)uracil (III) by lithium azide in dimethylformamide. The structures of the products (VIII and XI) were firmly established.

Since the nucleoside antibiotic such as puromycin contains amino function at the sugar moiety and an analogue of the nucleoside part of this antibiotic, 9-(3′-amino-3′-deoxy-β-D-ribofuranosyl)adenine, is reported also to be active as antibiotic compound,[3] it is interesting to synthesize several amino-nucleosides and test their biological properties.

Recently, the present authors[4,5] found a convenient method to obtain 5′-halogeno-5′-deoxy-xylofuranosyluracils (II) and N_3-methyl-5′-iodo-5′-deoxyxylofuranosyluracil (III) from 2,3′-anhydro-1-(β-D-xylofuranosyl)uracil (I)[6] by respective treatment of I with hydrogen halides and methyl iodide. The products (II and III) were subsequently converted into the corresponding 3′,5′-epoxy compounds (IV and V) by treatment with alkali. By these reactions, the over-all yield of 3′,5′-epoxy compounds from uridine were improved to approx. 6—7% from that (approx. 1—2%) reported by Doerr, *et al.*[7] who obtained the compound (IV) from 1-(5′-O-mesyl-β-D-xylofuranosyl)uracil, a side product in acid hydrolysis of 1-(5′-O-mesyl-2′,3′-epoxy-β-D-lyxofranosyl)uracil to 1-(5′-O-mesyl-β-D-arabinofuranosyl)uracil.

As it has been reported[8,9] that the cleavage of epoxy ring of 1-(3′,5′-epoxy-2′-deoxy-β-D-xylofuranosyl)thymine with acid or iodide ion gave the products which were substituted at the 5′-carbon atom by hydroxyl or iodo group, respectively, it was thought possible to introduce nitrogen-containing function at the sugar moiety of IV and V by use of this type of reaction.

This time, the reaction of the epoxy compounds (IV and V) with several kinds of nucleophiles such as sodium thiocyanate, ammonia, lithium aluminum hydride, hydrogen sulfide, phthalimide, lithium azide and several nucleotides was investigated. Among these compounds only lithium azide reacted with IV and V and gave the nucleosides which were substituted

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3) N. N. Gerber and H. A. Lechevalier, *J. Org. Chem.*, **27**, 1731 (1962); H. T. Shigeura, G.E. Boxer, M.L. Meloni and S.D. Sampson, *Biochemistry*, **5**, 994 (1966).
4) K. Kikugawa and T. Ukita, *Chem. Pharm. Bull.*, (Tokyo), **17**, 775 (1969).
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6) N.C. Yung and J.J. Fox, *J. Am. Chem. Soc.*, **83**, 3060 (1961).
7) I.L. Doerr, J.F. Codington and J.J. Fox, *J. Org. Chem.*, **30**, 467 (1965).
8) J.P. Horwitz, J. Chua, J.A. Urbanski and M. Noel, *J. Org. Chem.*, **28**, 942 (1963).
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with azido group at the sugar moiety. It is noteworthy that the similar reaction of lithium azide with 1-(3′,5′-epoxy-2′-deoxy-β-D-xylofuranosyl)thymine did not afford the derivative substituted with azide group. The present authors also observed a similar difference in the reactivity of epoxy rings present in 2′-deoxy and 2′-hydroxy nucleosides, thus, halide ion reacted with 2′-deoxy-3′,5′-epoxy derivative very much slower than with 2′-hydroxy-3′,5′-epoxy compounds (IV and V).

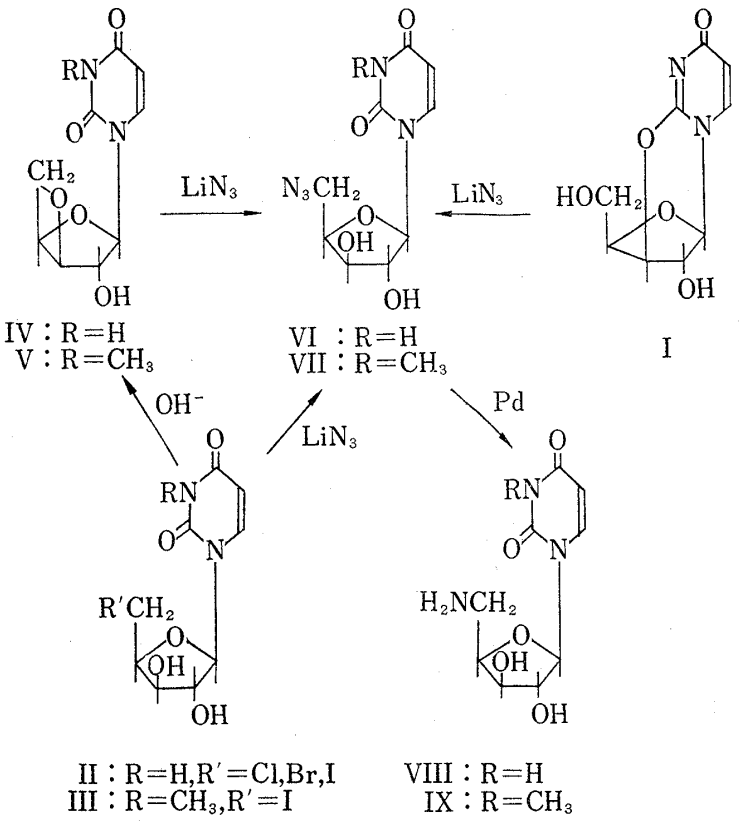

Chart 1

The reaction of IV and V with lithium azide gave crystalline products, VI and VII, respectively. Both the products (VI and VII) showed characteristic infrared absorption spectra of azido group at 2110 cm^{-1}. Metaperiodate titration suggested that these products have the structures of 1-(5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (VI) and N_3-methyl-1-(5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (VII), respectively. The following experiments unambiguously established the structure of the compound (VI). Thus, 1-(3′,5′-O-isopropylidene-β-D-xylofuranosyl)uracil (XI)[6] was benzoylated to give 1-(2′-O-benzoyl-3′,5′-O-isopropylidene-β-D-xylofuranosyl)uracil (XII) which was converted to 1-(2′-O-benzoyl-β-D-xylofuranosyl)-uracil (XIII) by treatment with acid. When XIII was allowed to react with one equimolar amount of *p*-toluenesulfonyl chloride at a low temperature, a monotosylated 2′-O-benzoyl derivative (XIV) was obtained in a good yield. The structure of the compound (XIV) was rigidly established to be 1-(2′-O-benzoyl-5′-O-tosyl-β-D-xylofuranosyl)uracil by its conversion to 1-(3′,5′-epoxy-β-D-xylofuranosyl)uracil (IV)[4] in a good yield by warming in aqueous alkali, which was subsequently hydrolyzed with acid to xylofuranosyluracil (X). If the compound (XIV) was 3′-O-tosyl derivative, the alkali treatment of XIV would afford 2,2′-anhydro-1-(β-D-arabinofuranosyl)uracil *via.* 2′,3′-epoxy-uridine as was reported by Reist, *et al.*[10] From these results the structure of the monotosylated compound (XIV) was confirmed to be 5′-tosylated compound. Further benzoylation of the tosylated compound (XIV) with 6 molar

10) E.J. Reist, J.H. Osiecki, L. Goodman and B.R. Baker, *J. Am. Chem. Soc.*, **83**, 2208 (1961).

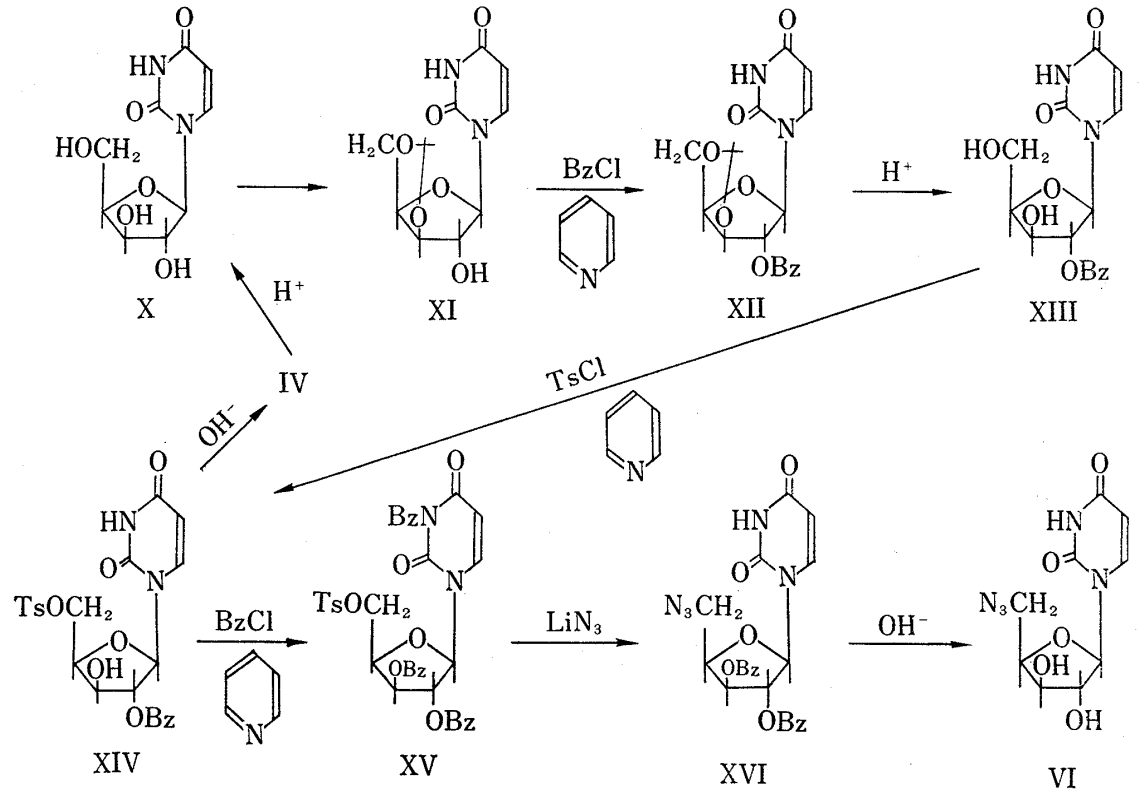

Chart 2

excess of benzoyl chloride gave N_3-benzoyl-1-(5′-O-tosyl-2′,3′-di-O-benzoyl-β-D-xylofuranosyl)-uracil (XV). The reaction of XV with lithium azide in dimethylformamide gave 1-(5′-azido-5′-deoxy-2′,3′-di-O-benzoyl-β-D-xylofuranosyl)uracil (XVI), thus the benzoyl group attached at the base moiety was released during this reaction. The structure of XVI was confirmed by elemental analysis, ultraviolet absorption spectra and infrared absorption spectra. Debenzoylation of the compound (XVI) in aqueous ammonia afforded 1-(5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (VI) and the 5′-azido product thus synthesized was identical with the azido derivative that was obtained by the reaction between lithium azide and 3′,5′-epoxy compound (IV), in mixed melting point test, infrared absorption spectra and *Rf* values.

The azido nucleoside (VI) was also synthesized by treatment of 1-(5′-chloro-5′-deoxy-β-D-xylofuranosyl)uracil (II: R′=Cl) with lithium azide, but in this case the difficulty in the purification of the product prevented the isolation of the pure compound. N_3-Methyl-1-(5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (VII) was analogously synthesized by the reaction of lithium azide with N_3-methyl-1-(5′-iodo-5′-deoxy-β-D-xylofuranosyl)uracil (III) in a high yield.

These 5′-azido nucleosides (VI and VII) were catalytically reduced with palladium–barium sulfate and hydrogen into 5′-amino derivatives. The aminonucleosides, 1-(5′-amino-5′-deoxy-β-D-xylofuranosyl)uracil (VIII) and N_3-methyl-1-(5′-amino-5′-deoxy-β-D-xylofuranosyl)uracil (IX) thus synthesized strongly colored with ninhydrin reagent, whereas the 3′-amino-3′-deoxy analogs were reported to be negative in coloration with the reagent.[11] The studies on the biological activities of these amino nucleosides are under progress.

It was reported earlier that the 2,2′-anhydro-1-(β-D-arabinofuranosyl)uracil did not react with azide ion,[12,13] but 2,5′-anhydrouridine reacted with azide ion to produce 5′-azide substituted compound.[13] The authors tested whether the 2,3′-anhydro-1-(β-D-xylofuranosyl)-

11) C.W. Waller, *J. Am. Chem. Soc.*, **75**, 2025 (1953); B.R. Baker, R.E. Schaub and J.H. Williams, *J. Am. Chem. Soc.*, **77**, 7 (1955).
12) D.M. Brown, A.R. Todd and S. Varadarajan, *J. Chem. Soc.*, **1958**, 4242.
13) J.P. Horwitz, A.J. Tomson, J.A. Urbanski and J. Chua, *J. Org. Chem.*, **27**, 3045 (1962).

uracil (I) reacted with lithium azide or not. Under the same conditions reported by Horwitz, *et al.*,[13] no reaction occurred, but when a large excess of the reagent in a high concentration of 3M was present in the mixture, the compound (I) reacted with lithium azide in dimethylformamide and gave an azido nucleoside,[14] in a very low yield, whose *Rf* values were quite identical with those of the compound (VI). The azido nucleoside thus formed was reduced into amino nucleoside which colored with ninhydrin reagent. Therefore the reaction of azide ion with 2,3′-anhydro compound (I) to yield 5′-substituted derivative might be analogous to that in the reaction of halogen ion with the compound (I).[4,5]

Experimental[15]

Methods

Paper chromatography was performed on Toyo Roshi No. 53 filter paper using solvent systems, (1) iso-PrOH–conc. NH_4OH–H_2O (7:1:2), (2) BuOH–H_2O (84:16), (3) BuOH–AcOH–H_2O (4:1:2). Thin-layer chromatography was carried out using solvent system, (4) AcOEt–benzene (1:3). The *Rf* value of the spot obtained for individual solvent was represented by the symbol (*Rf*) with suffix corresponding to the number of the solvents.

Paper electrophoresis was run in 0.02M sodium borate buffer (pH 9.2) at 30 V/cm and 25° for 1 hr. Cellulose powder (200—300 mesh) and silica gel were used for column chromatography.

Metaperiodate titration was carried out as described in the preceeding papers.[4,5]

1-(5′-Azido-5′-deoxy-β-D-xylofuranosyl)uracil (VI)——Method A: From 1-(3′,5′-Epoxy-β-D-xylofuranosyl)-uracil (IV): A sealed tube containing 100 mg of 1-(3′,5′-epoxy-β-D-xylofuranosyl)uracil (IV),[4,7] 150 mg of lithium azide and 1 ml of dimethylformamide (DMF) was heated at 100° overnight. The tube was opened and the solvent was removed *in vacuo*. The resulting syrup was applied onto a cellulose column (2 cm × 28 cm) and solvent system, BuOH–H_2O (84:16) was passed through the column. The product (VI), separated from the starting material was isolated from the fractions which gave an ultraviolet absorbing spot having Rf_2 0.64. The product was crystallized from acetone–benzene (1:1) mixture to give 90 mg (yield, 78%) of colorless plates, having mp 80°. Recrystallization from the same solvent afforded pure sample, mp 105—108°. Rf_1 0.71, Rf_2 0.64, Rf_3 0.70. UV $\lambda_{max}^{H_2O}$ mμ (ε): 261 (11200), $\lambda_{min}^{H_2O}$: 231 (2700), $\lambda_{max}^{0.1N\ NaOH}$: 261 (9000), $\lambda_{min}^{0.1N\ NaOH}$: 242 (5700). IR ν_{max}^{KBr} cm^{-1}: 2120 (N_3). $[\alpha]_D^{12°}$:+81° (c=0.13 in H_2O). *Anal.* Calcd for $C_9H_{11}O_5N_5$: C, 40.15; H, 4.12; N, 26.02. Found: C, 40.26; H, 4.38; N, 25.77.

The product consumed 1 equivalent mole of metaperiodate slowly as xylofuranosyluracil did.

Method B: From 1-(5′-Chloro-5′-deoxy-β-D-xylofuranosyl)uracil (II: R′=Cl) and Method C: From 2,3′-Anhydro-1-(β-D-xylofuranosyl)uracil (I): 5′-Chloro derivative (II: R′=Cl)[4] (187 mg) was dissolved in 5 ml of DMF containing 1.5 g of lithium azide, and the mixture was heated at 100° overnight. The reaction mixture was evaporated to dryness *in vacuo* and the residue was applied onto a cellulose column (3 cm × 44 cm) and eluted with the solvent of BuOH–H_2O mixture. But the product was not entirely purified because of the close location of its spot to that of the starting material. The product which gave a single spot in paper chromatogram was obtained as 100 mg of gum. Rf_1 0.71, Rf_2 0.64, Rf_3 0.70. The product was catalytically reduced with hydrogen and palladium catalyst to an amino nucleoside (Rf_2 0.02) which showed positive reaction to ninhydrin reagent.

2,3′-Anhydro-1-(β-D-xylofuranosyl)uracil (I)[6] (100 mg) was dissolved in 1 ml of DMF containing 300 mg of lithium azide and the mixture was heated in a sealed tube at 100° for 20 hr. The heavily colored reaction mixture was evaporated *in vacuo* and the residue was applied to a preparative paper chromatography. The spot having Rf_2 0.64 was extracted with H_2O, and the extract was evaporated to dryness to leave a small amount of colored gum which showed Rf_1 0.71, Rf_2 0.64 and Rf_3 0.70. The product was reduced to amino nucleoside (Rf_2 0.02) by catalytic hydrogenation with palladium catalyst, which gave positive reaction to ninhydrin reagent.

N_3-Methyl-1-(5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (VII)——Method A. From N_3-Methyl-1-(3′,5′-epoxy-β-D-xylofuranosyl)uracil (V): A sealed tube containing 135 mg of N_3-methyl-1-(3′,5′-epoxy-β-D-xylofuranosyl)uracil (V),[5] 150 mg of lithium azide and 5 ml of DMF was heated 115—130° for 20 hr. The tube was opened and the solvent was removed *in vacuo*. The residue was dissolved in H_2O and passed through the Dowex 50 (H^+) and Dowex 1 (HCO_3^-) columns successively to remove inorganic salt. The eluate was evaporated to dryness, and recrystallization of the residue afforded 7 mg of pure VII as colorless needles,

14) 2,2′-Anhydro-1-(β-D-arabinofuranosyl)uracil was also found to react with lithium azide when a large excess of the reagent in a high concentration was present and to yield an azido nucleoside which was subsequently converted to ninhydrin-positive aminonucleoside.

15) All melting points are uncorrected.

mp 149—151°. Rf_1 0.93, Rf_2 0.78, Rf_3 0.82. IR ν_{max}^{KBr} cm^{-1}: 2110. *Anal.* Calcd for $C_{10}H_{13}O_5N_5$: C, 42.40; H, 4.63; N, 24.73. Found: C, 42.93; H, 4.65; N, 24.30.

Method B: From N_3-Methyl-1-(5′-iodo-5′-deoxy-β-D-xylofuranosyl)uracil (III): A sealed tube containing 300 mg of N_3-methyl-1-(5′-iodo-5′-deoxy-β-D-xylofuranosyl)uracil (III), 300 mg of lithium azide and 12 ml of DMF was heated at 100° for 3 hr. The mixture was evaporated *in vacuo* and the resulting gum was dissolved in 50% EtOH. The solution was passed through Dowex 50 (H^+) and Dowex 1 (HCO_3^-) columns successively to remove inorganic salts. The effluent was evaporated again to dryness *in vacuo*. Crystallization from EtOH–H_2O mixture (1:1) gave 160 mg (68%) of the product as colorless needles, mp 152—154°. Rf_1 0.93, Rf_2 0.78, Rf_3 0.82. UV $\lambda_{max}^{H_2O}$ mμ (ε): 261 (8500), $\lambda_{min}^{H_2O}$: 233 (2200), $\lambda_{max}^{0.1N\ NaOH}$: 265 (8700), $\lambda_{min}^{0.1N\ NaOH}$: 236 (2600). $[\alpha]_D^{12°}$:+23° (c=0.13 in H_2O). IR ν_{max}^{KBr} cm^{-1}: 2110 (N_3). *Anal.* Calcd for $C_{10}H_{13}O_5N_5$: C, 42.40; H, 4.63; N, 24.73. Found: C, 42.10; H, 4.62; N, 24.69.

The product consumed slowly 1 equivalent mole of metaperiodate as xylofuranosyluracil did. The product was coincided with that obtained by method A in every respect: mixed melting point test, infrared spectra and *Rf* values on paper chromatograms.

1-(2′-O-Benzoyl-3′,5′-O-isopropylidene-β-D-xylofuranosyl)uracil (XII)—To a 35 ml pyridine solution containing 700 mg of 1-(3′,5′-O-isopropylidene-β-D-xylofuranosyl)uracil (XI)[6] was added 0.41 ml of benzoyl chloride at 0°. The mixture was kept at 5° for 20 hr and several milliliters of water were added to stop the reaction. After standing the mixture at room temperature for about 30 minutes, pyridine was removed *in vacuo*. The residue was extracted with 20 ml of $CHCl_3$ and the extract was washed several times with $NaHCO_3$ solution and water successively. The chloroform layer was dried over Na_2SO_4 and evaporated to dryness, and the residue was crystallized from EtOH–ligroin (3:16) mixture and recrystallized from EtOH to give 803 mg (84%) of the product as colorless needles, mp 171—173°. UV λ_{max}^{EtOH} mμ (ε): 230 (20500), 260 (14900), λ_{min}^{EtOH}: 216.5 (17800), 246.5 (13000). $[\alpha]_D^{17°}$:−53° (c=0.11 in $CHCl_3$). *Anal.* Calcd for $C_{19}H_{20}O_7N_2 \cdot 1/2\ C_2H_5OH$; C, 57.48; H, 5.33; N, 7.06. Found; C, 57.40; H, 5.73; N, 7.25.

1-(2′-O-Benzoyl-β-D-xylofuranosyl)uracil (XIII)——A 90% ethanolic solution (230 ml) of 1.2 g of XII and 1.5 ml of conc. HCl was refluxed for 15 min. The mixture was evaporated to dryness, and the residue was recrystllized from isopropanol to furnish 866 mg (yield, 80.5%) of the product as colorless needles, mp 140—145°. UV λ_{max}^{EtOH} mμ (ε): 230 (16400), 260 (12000), λ_{min}^{EtOH}: 216.5 (15400), 246.5 (10700). $[\alpha]_D^{16.5°}$: −68° (c=0.07 in CH_3OH). *Anal.* Calcd for $C_{16}H_{16}O_7N_2 \cdot 1/2\ C_2H_5OH$: C, 55.53; H, 5.34; N, 7.47. Found: C, 55.66; H, 5.31; N, 7.43.

1-(2′-O-Benzoyl-5′-O-tosyl-β-D-xylofuranosyl)uracil (XIV)——To a solution of 11.5 ml of pyridine containing 1.4 g (4.02 mmoles) of XIII was added 875 mg (4.6 mmoles) of *p*-toluenesulfonyl chloride at 0°. The mixture was kept at 0° for 1 hr and additionaly at room temperature overnight. To the mixture was added small amount of water to stop the reaction and the mixture was evaporated to dryness *in vacuo*. The residue was washed with cold water and dissolved in EtOH and evaporated to dryness. Crystallization from $CHCl_3$ afforded 1.3 g (yield, 62%) of the product, mp 107—110°. Recrystallization from absolute MeOH gave pure sample as colorless needles, mp 131—133°. UV λ_{max}^{EtOH} mμ (ε): 226.2 (29000), 258.5 (13000), λ_{min}^{EtOH}: 212.4 (22500), 247.6 (12000). $[\alpha]_D^{16°}$:−42° (c=0.07 in CH_3OH). *Anal.* Calcd for $C_{23}H_{22}O_9N_2S$: C, 54.98; H, 4.42; N, 5.58. Found: C, 55.21; H, 4.35; N, 5.84.

1-(3′,5′-Epoxy-β-D-xylofuranosyl)uracil (IV)——A solution of 265 mg of XIV in 15 ml of 0.2N NaOH was heated at 60−90° for 4 hr, and then passed through Dowex 50 (H^+) and Dowex 1 (HCO_3^-)columns successively to remove salts. The effluent from the final column was evaporated to dryness, and recrystallization of the residue from EtOH afforded the product IV as colorless prisms, mp 219—223°. Rf_1 0.60, Rf_2 0.33, Rf_3 0.60. *Anal.* Calcd for $C_9H_{10}O_5N_2$: C, 47.83; H, 4.46; N, 12.40. Found: C, 47.62; H, 4.65; N, 12.69.

The product was quite coincided with the authentic 1-(3′,5′-epoxy-β-D-xylofuranosyl)uracil[4] in mixed melting point test, infrared spectra and *Rf* values.

The product was changed into 1-(β-D-xylofuranosyl)uracil when it was heated at 100° for 2 hr in 0.4N H_2SO_4, which gave the mobility of 5.0 cm towards anode in electrophoresis, while 1-(β-D-arabinofuranosyl)-uracil moved 2.0 cm to the anode.

N-Benzoyl-1-(2′,3′-di-O-benzoyl-5′-O-tosyl-β-D-xylofuranosyl)uracil (XV)——To a solution of 6 ml of pyridine containing 426 mg (0.84 mmole) of XIV was added 0.6 ml (5.2 mmoles) of benzoyl chloride, and the mixture was kept at 40—45° overnight. To the mixture was added small amount of water and it was evaporated to dryness. The resulting syrup was extracted with $CHCl_3$ and the extract was washed three times with water saturated with $NaHCO_3$ and then with water successively. The dried chloroform layer was evaporated to dryness and the residue was recrystallized from MeOH to afford 380 mg (63%) of the product as colorless needles, mp 137.5—141.5°. UV λ_{max}^{EtOH} mμ (ε): 230 (47800), shoulder 260 (23200), λ_{min}^{EtOH}: 215 (34000). $[\alpha]_D^{17°}$: +68° (c=0.08 in $CHCl_3$). *Anal.* Calcd for $C_{37}H_{30}O_{11}N_2S$: C, 62.53; H, 4.26; N, 3.95. Found: C, 62.23; H, 4.41; N, 4.55.

1-(2′,3′-Di-O-benzoyl-5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (XVI)——A solution of 620 mg of XV and 108 mg of lithium azide in 6.2 ml of DMF was heated at 100° for 3 hr in nitrogen atmosphere. The solvent was removed *in vacuo* to dryness and the residue was dissolved in $CHCl_3$ and washed with water. The dried chloroform layer was evaporated to dryness and applied onto a silicagel column (containing 10 g

of silicagel) and eluted with solvent mixture, AcOEt–benzene (1:3.5). The fractions which contained the product having Rf_4 0.35 were pooled and evaporated to dryness. Water was added to the residue to give 270 mg (yield, 65%) of powdery crystals of XVI, mp 88—92°. Rf_4 0.35. UV λ_{max}^{EtOH} mμ (ε): 230 (33000), 260 (13000), λ_{min}^{EtOH}: 215 (24000). *Anal.* Calcd for $C_{23}H_{19}O_7N_5$: C, 57.86; H, 4.01; N, 14.67. Found: C, 58.48; H, 4.39; N, 14.59.

Debenzoylation of the Product XVI——1-(2′,3′-Di-O-benzoyl-5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (XVI) (150 mg) was dissolved in 30 ml of a mixed solvent, $CHCl_3$–MeOH (1:1), and to the solution 0.2 ml of conc. NH_4OH was added. The mixture was kept at room temperature overnight and then at 37° overnight. The solvent was removed *in vacuo* and the residue was recrystallized from acetone–benzene mixture (1:1) to afford 35 mg of the compound (VI) as colorless plates. Further recrystallization gave pure sample which melted at 103—104°. Rf_1 0.71, Rf_2 0.64, Rf_3 0.70.

This product was identical with the compound which was obtained by the reaction of 1-(3′,5′-epoxy-β-D-xylofuranosyl)uracil (IV) with lithium azide, in mixed melting point test, infrared absorptions and *Rf* values.

1-(5′-Amino-5′-deoxy-β-D-xylofuranosyl)uracil (VIII)——An ethanolic solution (10 ml) of 100 mg of 1-(5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (VI) and 500 mg of palladium on $BaSO_4$ were shaken in a hydrogen atmosphere at 760 mmHg and 25° for 12 hr. The catalyst was removed by centrifugation and the supernatant was evaporated *in vacuo*. The residue was applied onto a Dowex 50 (H^+) column (1 cm×2 cm) and the column was washed with water and then the product was eluted with 1N NH_4OH. The effluent was evaporated to dryness to furnish 65 mg of colorless gum. Rf_2 0.02.

The product was colored light orange with ninhydrin reagent.

N_3-Methyl-1-(5′-amino-5′-deoxy-β-D-xylofuranosyl)uracil (IX)——An ethanolic solution (10 ml) of 120 mg of N_3-methyl-1-(5′-azido-5′-deoxy-β-D-xylofuranosyl)uracil (VII) and 750 mg of palladium on $BaSO_4$ were shaken in a hydrogen atmosphere at 760 mmHg and 25° for 3 hr. The catalyst was removed by centrifugation and the supernatant was evaporated to dryness. Recrystallization of the residue from EtOH gave 74 mg (yield, 70%) of the product as colorless needles which melted at 174—178°. Rf_1 0.68, Rf_2 0.07. UV $\lambda_{max}^{H_2O}$ mμ (ε): 261 (8100), $\lambda_{min}^{H_2O}$: 231 (2100), $\lambda_{max}^{0.1N\ NaOH}$: 264 (8400), $\lambda_{min}^{0.1N\ NaOH}$: 234 (2300). $[\alpha]_D^{12°}$: +11° (c=0.2 in H_2O). *Anal.* Calcd for $C_{10}H_{15}O_5N_3$: C, 46.78; H, 5.89; N, 16.33 Found: C, 46.78; H, 5.93; N, 16.11.

The product was colored light violet with ninhydrin reagent.

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