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Nucleosides and Nucleotides. LIV. Synthesis of 6,6′-Cyclo-5′,6′-dideoxyhexofuranosyluracils *via* Radical Cyclization of a 6-Cyanouridine[1)]

TOMOHARU SANO, HIDEO INOUE, and TOHRU UEDA*

Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-12, Nishi-6, Kita-ku, Sapporo 060, Japan

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Synthesis of hexofuranosyluracil cyclonucleosides carbon-bridged between C-6 and C-6′ is described. Treatment of 6-cyano-5′-iodo-2′,3′-*O*-isopropylidene-5′-deoxyuridine with tri-*n*-butyltin hydride and 2,2′-azobisisobutyronitrile gave the 6′-imino-6,6′-cyclo-5′,6′-dideoxyallofuranosyluracil, which was converted to the 6′-oxo derivative. The 6′-oxo function was reduced with sodium borohydride and the 6′-hydroxyl group was eliminated to give the 5′,6′-unsaturated cyclodideoxyallofuranosyluracil, which was hydrogenated to furnish 6,6′-cyclo-5′,6′-dideoxyallofuranosyluracil, a uridine derivative fixed in the *anti* form.

Keywords——radical cyclization; tri-*n*-butyltin hydride; uridine; *C*-clouridine; conformationally fixed uridine; NMR; CD

Carbon-bridged cyclonucleosides are regarded as excellent models of nucleosides where the glycosyl torsion angles are fixed in appropriate angles. These compounds are useful for stereochemical investigations of the interactions of nucleosides and nucleotides with enzymes.[2)] Fox and co-workers have reported[3)] the synthesis of 6,5′-cyclouridine (**1**) *via* the intramolecular aldol reaction of 5-hydroxyuridine 5′-aldehyde and this was further led to a 5′-keto-6,6′-cyclouridine derivative.[4)] We have developed an intramolecular radical cyclization of 5′-deoxy-5′-iodo-5-chlorouridine initiated by tributyltin hydride and 2,2′-azobisisobutyronitrile (AIBN) to give 5′-deoxy-6,5′-cyclouridine (**2**).[5,6)] 5′-Deoxy-6,5′-cyclocytidine was also prepared by a similar approach.[6)] For the synthesis of cyclouridine bridged by one extra methylene unit as compared with **2** we utilized the reaction with a 6-cyanouridine, since radical addition to a nitrile group is also known. A preliminary account of the present work has appeared.[7)]

Treatment of 5-bromo-2′,3′-*O*-isopropylideneuridine (**3**) with sodium cyanide in dimethylformamide[8)] gave the 6-cyano derivative (**4**) in a crystalline form. The 5′-hydroxyl group of **4** was converted to the tosyloxy group (**5**) and then replaced with sodium iodide in 2-butanone to give the 5′-iodo derivative (**6**), which was crystallized as the monobenzene adduct. A mixture of tri-*n*-butyltin hydride and AIBN in toluene was added dropwise to a refluxing toluene solution of **6**. The nuclear magnetic resonance (NMR) spectrum of the crude product (**7**) exhibited a pair of ketimine proton signals at 11.00 and 11.20 ppm (br s, each) together with a multiplet due to the 5′-protons at 2.76—2.86 ppm. Without further purification, **7** was hydrolyzed in aqueous acetic acid to furnish crystalline 2′,3′-*O*-isopropylidene-6′-oxo-6,6′-cyclo-5′,6′-dideoxyallofuranosyluracil (**8**) in a yield of 35%. The signal due to the 5′-protons of **8** appeared as a double doublet, supporting the cyclo structure. Further, the red shift in the ultraviolet (UV) absorption maximum to 289 nm is characteristic of the extended conjugation of the uracil moiety in **8**. The yield of intramolecular cyclization of **6** was not satisfactory and the major by-product in this reaction was assumed to be the 5′-deoxy derivative (**9**). This may be due to the fact that compound **6** presumably adopts a *syn*

conformation in solution, since the X-ray diffraction analysis of **4** revealed a *syn* conformation (X=257.4°) of this 6-cyano compound.[9] Therefore, the 5′-radical generated from **6** would have more chance to be quenched to form the 5′-deoxy derivative (**9**) than to cyclize to give **7**. There is a possibility that the 5′-radical generated from **6** might add to the 6-position instead of the nitrile carbon. However, such a compound was not detected in the reaction mixture.

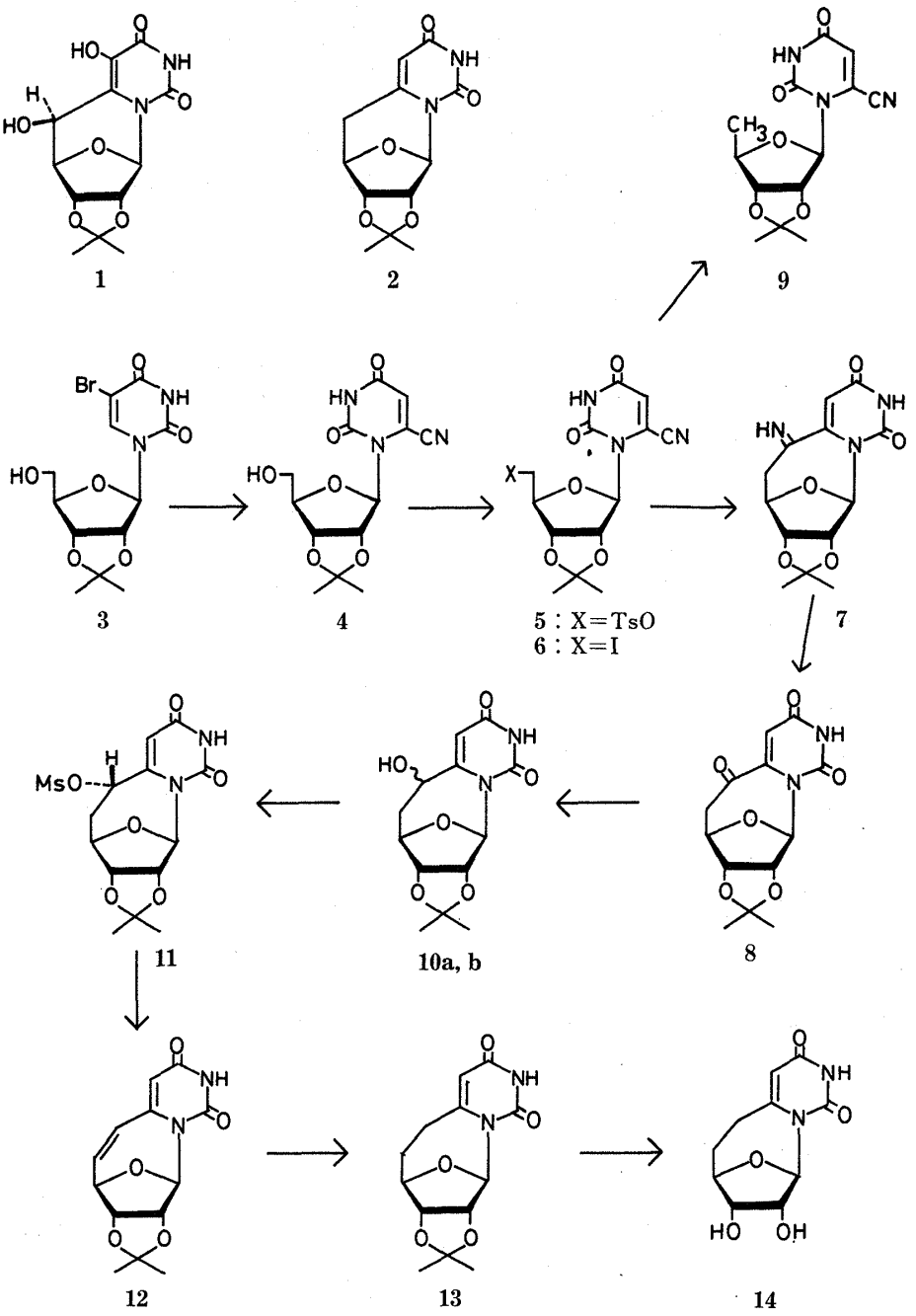

Chart 1

Reduction of **8** with sodium borohydride in methanol afforded two 6′-hydroxy products (**10a** and **10b**) which could be separated by preparative thin layer chromatography (PTLC). The products were assumed to be the 6′(*S*)- and 6′(*R*)-forms (**10a** and **10b**, respectively) in the 6′-*endo* conformation based on the NMR measurements. It should be noted that, whereas the

reduction of 5′-oxo-8,5′-cycloadenosine[10] and 5′-oxo-6,5′-cyclouridine[3b] with the borohydride gave the 5′(*S*)-isomer exclusively, the reduction of the 6′-oxo group in **8** proceeded without stereospecificity. Treatment of **10a** with mesyl chloride afforded the 6′(*S*)-mesyloxy derivative (**11**). The mesylation of **10b**, having a sterically hindered 6′-hydroxyl group, proceeded very slowly and, on heating during the reaction, the product was **11**, probably as a result of epimerization after the mesylation.

Treatment of **11** with 1,5-diazabicyclo[5.4.0]undecene (DBU) in dioxane gave the 5′,6′-unsaturated cyclodideoxyallofuranosyluracil (**12**) in a crystalline form. The presence of the unsaturation at the 5′,6′-position was readily confirmed by NMR measurements and from the red shift of the UV maximum of **12**.

Catalytic hydrogenation of **12** over Pd–carbon under atmospheric pressure gave 2′,3′-*O*-isopropylidene-6,6′-cyclo-5′,6′-dideoxyallofuranosyluracil (**13**). Deprotection of **13** by treatment with methanolic hydrogen chloride afforded 6,6′-cyclo-5′,6′-dideoxyallofuranosyluracil (**14**).

It should be emphasized that the circular dichroism (CD) spectrum of **14** showed a small, slightly negative band at the absorption maximum. As is well known, uridine and usual pyrimidine nucleosides show positive CD bands at their main absorption regions and they are regarded as adopting preferred *anti* conformations in solution. In fact, the CD spectrum of 5′-deoxy-6,5′-cyclouridine, a model of uridine fixed in an *anti* form, showed a strong positive band.[6] Therefore it follows that there is a transient torsion angle at which the sign of the CD band is reversed, which may be that in this 6,6′-cyclouridine, **14**. X-Ray diffraction studies of **14** for determination of the glycosyl torsion angle and further discussions on the sign of CD bands in relation to glycosyl torsion angles, based on comparison of various *C*-cyclouridines will be the subjects of a forthcoming paper.

Experimental

Melting points were determined on a Yanagimoto MP-3 micromelting point apparatus and are uncorrected. The proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL FX-100FT or FX-200FT spectrometer in $CDCl_3$ or dimethylsulfoxide (DMSO)-d_6 as the solvent with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm (δ), and signals are described as a (singlet), d (doublet), t (triplet), m (multiplet), or br (broad). All exchangeable protons were confirmed by addition of D_2O. UV absorption spectra were recorded with a Shimadzu UV-240 spectrophotometer. Mass spectra (MS) were measured on a JEOL D-300 spectrometer. CD were recorded on a JASCO J-40 spectropolarimeter at room temperature. Thin layer chromatography (TLC) was carried out on Merck pre-coated plates 60 F_{254}. Silica gel for column chromatography was Wako gel C-200. The starting nucleoside, uridine, was from Yamasa Shoyu Co., Ltd.

6-Cyano-2′,3′-*O*-isopropylideneuridine (4)——A solution of 5-bromo-2′,3′-*O*-isopropylideneuridine (**3**, 10.0 g, 27.8 mmol) and NaCN (2.0 g, 1.5 eq) in 50 ml of dimethylformamide (DMF) was stirred for 24 h at room temperature. After addition of 1.0 ml of AcOH, the solvent was removed at low temperature *in vacuo* and the residue was taken up in $CHCl_3$. This solution was applied to a column of silica gel (300 g, 4.4 × 36 cm) and elution was performed with 4% MeOH–$CHCl_3$. The eluate was concentrated and the foamy residue was crystallized from MeOH–ether to give 6.5 g (76%) of **4**, mp 166—167 °C. MS *m/z*: 309 (M^+), 294 (M − 15). NMR (DMSO-d_6): 12.03 (br s, 1, H-3), 6.74 (s, 1, H-5), 5.86 (d, 1, H-1′), 5.22 (dd, 1, H-2′), 4.90 (t, 1, HO-5′), 4.70 (dd, 1, H-3′), 4.00 (m, 1, H-4′), 3.56 (dd, 2, H-5′), 1.50, 1.30 (s each, 6, Me_2C). $J_{1',2'}$ = 2.3 Hz, $J_{2',3'}$ = 6.8 Hz, $J_{3',4'}$ = 4.4 Hz, $J_{4',5'}$ = 5.9 Hz, $J_{5',5'OH}$ = 5.9 Hz. UV λ_{max}^{MeOH}: 279 nm. *Anal.* Calcd for $C_{13}H_{15}N_3O_6$: C, 50.48; H, 4.89; N, 13.59. Found: C, 50.27; H, 4.80; N, 13.51.

6-Cyano-2′,3′-*O*-isopropylidene-5′-*O*-tosyluridine (5)——Compound **4** (5.00 g, 16.2 mmol) was dissolved in 32 ml of pyridine, then TsCl (3.70 g, 1.2 eq) was added and the mixture was stirred for 26 h at room temperature. After addition of 1 ml of H_2O, the solution was poured into 1.8 l of ice water with stirring. The precipitate was collected, washed with ice water, and air-dried overnight. The product was dissolved in hot EtOH, decolorized with active charcoal, and kept at room temperature. The separated crystals were collected to give 5.87 g (78%) of **5**, mp 167—168 °C. MS *m/z*: 463 (M^+), 448 (M − 15). NMR ($CDCl_3$): 8.97 (br s, 1, H-3), 7.8—7.3 (m, 4, Ph), 6.30 (s, 1, H-5), 5.97 (d, 1, H-1′), 5.16 (dd, 1, H-2′), 4.80 (dd, 1, H-3′), 4.33—4.23 (m, 3, H-4′,5′), 2.44 (s, 3, Me–Ts), 1.54, 1.33 (s each, 6, Me_2C). $J_{1',2'}$ = 1.5 Hz, $J_{2',3'}$ = 6.5 Hz, $J_{3',4'}$ = 3.8 Hz. *Anal.* Calcd for $C_{20}H_{21}N_3O_8S$: C, 51.83; H, 4.57; N, 9.07; S, 6.92. Found: C, 51.56; H, 4.46; N, 8.79; S, 7.02.

6-Cyano-5′-deoxy-5′-iodo-2′,3′-*O*-isopropylideneuridine (6)——A solution of **5** (7.00 g, 15.1 mmol) and NaI (5.67 g, 2.5 eq) in 100 ml of 2-butanone was refluxed for 21 h. After the solution had cooled, the precipitate was removed and the filtrate was concentrated. The residue was partitioned between AcOEt and H_2O, and the organic layer was separated, dried over Na_2SO_4, and evaporated to leave a foamy residue. This was crystallized from benzene to give **6** (6.64 g, 88%) as the mono-benzene adduct, mp 85—87 °C. MS *m/z*: 419 (M^+), 418 (M−1), 404 (M−15). NMR ($CDCl_3$): 9.07 (br s, 1, H-3), 7.36 (s, 6, benzene), 6.33 (s, 1, H-5), 6.05 (d, 1, H-1′), 5.21 (dd, 1, H-2′), 4.88 (dd, 1, H-3′), 4.39 (m, 1, H-4′), 3.42 (dd, 1, Ha-5′), 3.29 (dd, 1, Hb-5′), 1.59, 1.37 (s each, 6, Me_2C). $J_{1',2'}=2.0$ Hz, $J_{2',3'}=6.8$ Hz, $J_{3',4'}=3.9$ Hz, $J_{5'a,b}=9.8$ Hz, $J_{4',5'}=8.3$ and 6.6 Hz. *Anal.* Calcd for $C_{13}H_{14}IN_3O_5+C_6H_6$: C, 45.89; H, 4.05; N, 8.45; I, 25.52. Found: C, 45.69; H, 4.13; N, 8.56; I, 25.59.

6′-Imino-2′,3′-*O*-isopropylidene-6,6′-cyclo-5′,6′-dideoxy-1-(β-D-allofuranosyl)uracil (7), 2′,3′-*O*-Isopropylidene-6′-oxo-6,6′-cyclo-5′,6′-dideoxy-1-(β-D-allofuranosyl)uracil (8), and 6-Cyano-5′-deoxy-2′,3′-*O*-isopropylideneuridine (9)——Compound **6** (2.11 g, 4.25 mmol) was refluxed in 100 ml of toluene under an argon atmosphere, and a mixture of Bu_3SnH (1.68 ml, 1.5 eq) and AIBN (150 mg) in 6 ml of toluene was added dropwise through an injection syringe over a period of 3 h. Heating was continued for 30 min after the end of the addition, then the solution was concentrated and the residue was partitioned between *n*-hexane and CH_3CN. The CH_3CN layer was concentrated to leave **7** as a syrup. This was dissolved in 10 ml of tetrahydrofuran, the 50 ml of 50% AcOH–H_2O was added and the mixture was kept at room temperature for 90 min. The solvent was removed and the residue was partitioned between AcOEt and H_2O, the aqueous layer being neutralized by addition of $NaHCO_3$. The organic layer was separated, dehydrated through a Whatman 1PS filter paper, and concentrated. The residue was dissolved in $CHCl_3$ and applied to a column of silica gel (50 g, 2.8 × 20 cm). The eluate with 1% MeOH–$CHCl_3$ was concentrated and the residue was crystallized from EtOH to give 435.2 mg (35%) of **8**, mp 205—206 °C.

Physical constants of **7** are as follows. UV λ_{max}^{MeOH}: 281 nm. MS *m/z*: 293 (M^+), 278 (M−15). NMR (DMSO-d_6): 11.60 (br s, 1, H-3), 11.20 and 11.00 (br s each, 1, NH=), 6.32 (d, 1, H-1′), 5.70 (d, 1, H-5), 4.72—4.57 (m, 3, H-2′,3′,4′), 2.86—2.76 (m, 2, H-5′), 1.42, 1.25 (d each, 6, Me_2C).

Compound **8**. UV λ_{max}^{MeOH}: 289 nm. MS *m/z*: 294 (M^+), 279 (M−15). NMR (DMSO-d_6): 8.57 (br s, 1, H-3), 6.49 (s, 1, H-1′), 5.97 (d, 1, H-5), 4.78—4.68 (m, 3, H-2′,3′,4′), 3.20 (dd, 1, H-5′a), 2.93 (dd, 1, H-5′b), 1.54, 1.33 (s each, 3+3, Me_2C). $J_{5,N^3H}=1.7$ Hz, $J_{4',5'a}=5.5$ Hz, $J_{4',5'b}=4.6$ Hz, $J_{5'a,b}=13.4$ Hz. *Anal.* Calcd for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52. Found: C, 52.84; H, 4.70; N, 9.43.

The faster eluting fraction of the above column with 1% MeOH–$CHCl_3$ was concentrated to obtain 344 mg (28%) of **9** as a foam. MS *m/z*: 278 (M−15), 157 (sugar), 138 (B+1). NMR ($CDCl_3$): 10.0 (br s, 1, H-3), 6.34 (d, 1, H-5), 6.07 (d, 1, H-1′), 5.13 (dd, 1, H-2′), 4.69 (dd, 1, H-3′), 4.3—4.0 (m, 1, H-4′), 1.43 (d, 3, H-5′), 1.58, 1.36 (s each, 6, Me_2C). $J_{1',2'}=2.4$ Hz, $J_{2',3'}=6.7$ Hz, $J_{3',4'}=5.1$ Hz, $J_{4',5'}=6.4$ Hz.

2′,3′-*O*-Isopropylidene-6,6′(*S*)-cyclo-5′-deoxy-1-(β-D-allofuranosyl)uracil (10a) and 2′,3′-*O*-Isopropylidene-6,6′(*R*)-cyclo-5′-deoxy-1-(β-D-allofuranosyl)uracil (10b)——Compound **8** (300 mg, 1.02 mmol) was dissolved in 30 ml of MeOH, and 10.3 ml of 0.1 M $NaBH_4$ in MeOH (4 eq) was added with stirring. After 30 min at room temperature, the solution was neutralized with 1.0 N HCl and the solvent was removed *in vacuo*. The residue was partitioned between AcOEt and H_2O saturated with NaCl, and the organic layer was passed through a Whatman 1 PS filter paper. The filtrate was evaporated and the residue was taken up in hot MeOH; the solution was applied to a preparative thin layer plate (20 × 20 cm). The plate was developed twice with $CHCl_3$–MeOH (8 : 1). The appropriate bands were excised and eluted with the same solvent. From the band having higher *Rf* value **10b** (74 mg, 24%) was obtained as crystals from EtOH. The band with lower *Rf* value gave **10a** (121.3 mg, 40%).

Compound **10a**. mp 276—279 °C (dec.). UV λ_{max}^{MeOH}: 262 nm. MS *m/z*: 296 (M^+), 281 (M−15). NMR (DMSO-d_6): 11.42 (br s, 1, H-3), 6.46 (s, 1, H-1′), 5.97 (d, 1, HO-6′), 5.84 (s, 1, H-5), 5.04 (d, 1, H-2′), 4.92 (d, 1, H-3′), 4.49 (m, 1, H-4′), 4.33 (m, 1, H-6′), 2.12 (m, 1, H-5′a), 1.83 (m, 1, H-5′b), 1.42, 1.29 (s each, 6, Me_2C). $J_{2',3'}=5.9$ Hz, $J_{4',5'a}=2.9$ Hz, $J_{4',5'b}=3.4$ Hz, $J_{5'a,b}=14.2$ Hz, $J_{5'a,6'}=2.4$ Hz, $J_{5'b,6'}=10.3$ Hz. *Anal.* Calcd for $C_{13}H_{16}N_2O_6$: C, 52.70; H, 5.44; N, 9.46. Found: C, 52.53; H, 5.39; N, 9.38.

Compound **10b**. mp 284—286 °C (dec.). UV λ_{max}^{MeOH}: 265 nm. MS *m/z*: 296 (M^+), 281 (M−15). NMR (DMSO-d_6): 11.47 (br s, 1, H-3), 6.33 (s, 1, H-1′), 6.10 (d, 1, HO-6′), 5.79 (s, 1, H-5), 5.05 (s, 2, H-2′,3′), 4.65 (m, 1, H-6′), 4.50 (m, 1, H-4′), 2.2—1.9 (m, 2, H-5′), 1.41, 1.26 (s each, 6, Me_2C). $J_{4',5'}=2.7$ and 4.6 Hz, $J_{5',6'}=3.4$ and 3.9 Hz, $J_{6',HO\text{-}6'}=3.4$ Hz. *Anal.* Calcd for $C_{13}H_{16}N_2O_6$: C, 52.70; H, 5.44; N, 9.46. Found: C, 52.71; H, 5.44; N, 9.42.

2′,3′-*O*-Isopropylidene-6′(*S*)-*O*-mesyl-6,6′-cyclo-5′-deoxy-1-(β-D-allofuranosyl)uracil (11)——Compound **10a** (100.5 mg, 0.34 mmol) was dissolved in 3 ml of pyridine, and MsCl (30 μl, 1.2 eq) was added under cooling in an ice bath. After 6 h at room temperature a drop of H_2O was added and the solvent was evaporated off. The residue was partitioned between AcOEt and H_2O and the organic layer was dehydrated through a Whatman 1 PS filter paper. The solvent was evaporated off and the residue was crystallized from EtOH to give **11** (100.1 mg, 79%), mp 223—224 °C. MS *m/z*: 374 (M^+), 359 (M−15). NMR (DMSO-d_6): 11.68 (br s, 1, H-3), 6.47 (s, 1, H-1′), 5.81 (s, 1, H-5), 5.24 (d, 1, H-2′), 5.15 (dd, 1, H-6′), 4.92 (d, 1, H-3′), 4.59 (m, 1, H-4′), 3.43 (s, 3, Me-Ms), 2.4 (m, 1, H-5′a), 2.2 (m, 1, H-5′b), 1.44, 1.33 (s each, 6, Me_2C), $J_{2',3'}=5.6$ Hz, $J_{4',5'a}=2.9$ Hz, $J_{4',5'b}=4.0$ Hz, $J_{5'a,b}=13.7$ Hz. $J_{5'b,6'}=10$ Hz. *Anal.* Calcd for $C_{14}H_{18}N_2O_8S$: C, 44.91; H, 4.85; N, 7.48; S, 8.56. Found: C, 45.10; H, 4.66; N, 7.44; S, 8.53. Mesylation of a mixture of **10** proceeded slowly at room temperature and finally with warming to give **11** in a similar yield.

2′,3′-*O*-Isopropylidene-5′,6′-dehydro-6,6′-cyclo-5′,6′-dideoxy-1-(β-D-allofuranosyl)uracil (12)——A solution of compound **11** (302 mg, 0.8 mmol) and DBU (0.3 ml, 2.5 eq) in 10 ml of dioxane was heated at 90 °C for 60 min. The solvent was evaporated off and the residue was partitioned between $CHCl_3$ and H_2O, the aqueous layer being neutralized with 1 N HCl. The organic layer was passed through a Whatman 1 PS filter paper and the filtrate was concentrated. The residue was taken up in $CHCl_3$ and applied to a column of silica gel (9 g, 1.7 × 9 cm). The eluate with 1% MeOH–$CHCl_3$ was evaporated and the residue was crystallized from EtOH to give 131.4 mg (59%) of **12**, mp 274—276 °C. UV λ_{max}^{MeOH}: 298 nm. MS *m/z*: 278 (M^+), 263 (M − 15), 220 (M − 58). NMR (DMSO-d_6): 11.48 (br s, 1, H-3), 6.44 (dd, 1, H-5′), 6.42 (d, 1, H-1′), 6.22 (d, 1, H-6′), 5.48 (s, 1, H-5), 4.95—4.90 (m, 2, H-2′,4′), 4.81 (d, 1, H-3′), 1.45, 1.27 (s each, 6, Me_2C). $J_{2',3'}$ = 5.5 Hz, $J_{4',5'}$ = 4.9 Hz, $J_{5',6'}$ = 12.2 Hz. *Anal.* Calcd for $C_{13}H_{14}N_2O_5$: C, 56.11; H, 5.07; N, 10.07. Found: C, 55.97; H, 5.03; N, 9.98.

2′,3′-*O*-Isopropylidene-6,6′-cyclo-5′,6′-dideoxy-1-(β-D-allofuranosyl)uracil (13)——Compound **12** (212.2 mg, 0.763 mmol) was dissolved in 6 ml of tetrahydrofuran and hydrogenated over Pd–C (20 mg) at room temperature under atmospheric pressure. A small volume of benzene was added and the catalyst was filtered off, then the filtrate was concentrated. The residue was crystallized from EtOH to give 175.1 mg (82%) of **13**. mp: sublimed on heating over 280 °C. UV λ_{max}^{MeOH}: 263 nm (ε, 11000). CD in MeOH θ (nm): 0 (290), +2900 (275), 0 (267), −13000 (245), −9400 (230). MS *m/z*: 280 (M^+), 265 (M − 15). NMR (DMSO-d_6): 11.36 (br s, 1, H-3), 6.41 (s, 1, H-1′), 5.64 (s, 1, H-5), 5.06 (d, 1, H-2′), 4.85 (d, 1, H-3′), 4.48 (m, 1, H-4′), 2.69 (m, 1, H-6′), 2.00 (m, 1, H-5′a), 1.74 (m, 1, H-5′b), 1.43, 1.29 (s each, 6, Me_2C). $J_{2',3'}$ = 5.4 Hz. *Anal.* Calcd for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 10.00. Found: C, 55.70; H, 5.77; N, 10.04.

6,6′-Cyclo-5′,6′-dideoxy-1-(β-D-allofuranosyl)uracil (14)——Compound **13** (84.8 mg, 0.3 mmol) was suspended in a mixture of 1.7 ml of MeOH and 1.7 ml of 1 N HCl and the mixture was heated at 90 °C for 2 h, then cooled. EtOH was added, and the solvent was evaporated off. The addition and evaporation of the solvent were repeated several times while crystalline **14** precipitated; total yield, 63.9 mg (88%). Recrystallization of **14** from hot water containing a small amount of MeOH afforded a pure sample. mp: sublimed on heating over 270 °C. UV $\lambda_{max}^{H_2O}$: 266 nm (ε, 11300). CD in H_2O θ (nm): 0 (270), −10300 (240), −9200 (230). MS *m/z*: 240 (M^+). NMR (DMSO-d_6): 11.29 (br s, 1, H-3), 6.33 (d, 1, H-1′), 5.62 (s, 1, H-5), 5.38 (d, 1, HO-2′), 5.16 (d, 1, HO-3′), 4.51 (m, 1, H-2′), 4.31 (m, 1, H-4′), 4.12 (dd, 1, H-3′), 2.67 (m, 2, H-6′), 1.90 (m, 1, H-5′a), 1.70 (m, 1, H-5′b). $J_{1',2'}$ = 2.0 Hz, $J_{2',3'}$ = 5.9 Hz. *Anal.* Calcd for $C_{10}H_{12}N_2O_5$: C, 50.00; H, 5.04; N, 11.66. Found: C, 49.80; H, 4.93; N, 11.59.

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