Introduction of Carbon Substituents into Pyrimidine and Purine Nucleosides by Sulfur Extrusion (Nucleosides and Nucleotides. XXX)\(^{11}\)

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Treatment of 4-thiouridine with phenacyl bromide, bromoacetone, and ethyl bromo-acetate gave the corresponding 4-thioalkylcarbonyl derivatives. The sulfur extrusion reactions of these compounds afforded ribosides of 4-phenacylidene-2(3H)-pyrimidinone, 4-acetonylidene-2(3H)-pyrimidinone, and 2-pyrimidinone-4-acetic ester, respectively. The ease of sulfur extrusion depends on the electron-withdrawing ability of the carbonyl group attached to the 4-5-methylene group. Sulfur extrusion reactions starting from 6-thiinosine similarly gave the ribofuranosides of 6-phenacylpurine and 6-acetonylpurine. These purine ribosides exist mainly as the enol form rather than the keto form.

**Keywords**—sulfur extrusion reaction; thionucleosides; nucleosides; triphenylphosphine; UV; NMR

Few studies have been reported on the synthesis of nucleosides with carbon substituents in place of amino or oxo substituents on the base moieties of naturally occurring nucleosides. Procedures reported so far involve the glycosylation of 6-alkypurines\(^{30}\) or 4-methyl-2-pyrimidinone\(^{41}\) and the photo-addition of methanol to ribofuranosylpurine.\(^{5}\) \(9\beta\)-D-Ribofuranosyl-6-methylpurine and -1,6-dihydro-6-hydroxymethylpurine have been reported to be strong inhibitors of adenosine deaminases.\(^{5}\) In preceding papers we have reported facile substitutions of a methylsulfonyl group with various carbon nucleophiles at the 2, 6, or 8 position of purine nucleosides to give the corresponding C-substituted derivatives.\(^{1,6,7}\) We wish to report an alternative approach to the synthesis of C-substituted pyrimidine and purine nucleosides which utilizes the sulfur extrusion reaction established by Eschenmoser and co-workers.\(^{8}\) A preliminary report has already appeared.\(^{9}\) Essentially similar results were reported\(^{10}\) after the completion of our experiments. As 4-thiouridine and 6-thiinosine contain a thiaoamide group, these nucleosides may serve as substrates for the conversion of a thiaamide to a vinyllogous amide, as reported in the case of 4-\(\beta\)-bromophenacylthiouarcil, yielding 4-phenacyl-2-pyrimidinone.\(^{11}\) 4-Thiouridine (1), readily prepared by the sulfoxidolysis of cytidine,\(^{12}\) was treated with phenacyl bromide, bromoacetone, and ethyl bromoacetate in aqueous solution in the presence of sodium hydrogen carbonate to give the corresponding alkylthio derivatives (2—4) in high yields. 2',3'-O-Isopropylidene-4-thiouridine (1a) also gave the 4-thioacetate derivative (5).

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Heating the 4-phenacylthio derivative (2) in pyridine at reflux temperature gave a new product (6) which contained no sulfur. The ultraviolet (UV) absorption spectrum of the product exhibited a maximum at 375.5 nm, reflecting the elongation of the conjugation in the chromophore. In the nuclear magnetic resonance (NMR) spectrum an exchangeable proton at 13 ppm and a methine proton were observed instead of the methylene. Thus, the structure was assigned as 1-β-d-ribofuranosyl-4-phenacylidene-2(3H)-pyrimidinone. It should be noted that the sulfur extrusion in 2 occurred so readily that the addition of a sulfur trap, such as triethyl phosphate, was unnecessary. 4-Acetylthiouridine (3) was rather stable, and the elimination of sulfur took place on addition of triphenylphosphine and potassium t-butoxide in refluxing pyridine to give the 4-acetylidelene-2(3H)-pyrimidinone (7). The spectroscopic characteristics were similar to those of 6. The difference in the ease of elimination of sulfur between 2 and 3 is explained by the difference of the acidity of the methylene group, that of the former compound being more acidic. This is further exemplified in the reaction of 4-thiouridine and diethyl bromomalonate. Treatment of 1a with diethyl bromomalonate in dimethylformamide (DMF) in the presence of potassium carbonate at room temperature afforded 4-bis(ethoxycarbonyl)methylene-2(3H)-pyrimidinone riboside (8). The reaction conditions of S-alkylation led to simultaneous sulfur extrusion in this instance.

The sulfur extrusion of the ethoxycarbonylmethylthio derivative (4) proceeded sluggishly, so the sugar hydroxyl group was protected prior to the reaction. Compound 5 was acetylated and treated with triphenylphosphine and sodium hydride in tetrahydrofuran (THF). The product 9 was obtained as an amorphous material. On saponification and mild acid treatment of 9, 1-(2,3-0-isopropylidene-β-d-ribofuranosyl)-4-methyl-2-pyrimidinone (10) was obtained in an amorphous form. The parent nucleoside is already known(4) and the spectral data of 10 were in good accord with those of 4-methyl-2-pyrimidinone riboside.4)

Treatment of 6-thionosine with phenacyl bromide, bromoacetone, and ethyl bromoacetate gave the corresponding S-alkylated derivatives (11—13) in high yields. The extrusion reaction of the alkylthiopurines proceeded rather slowly. Treatment of 11 with triphenylphosphine did give the expected product, though it was difficult to isolate. Treatment of the benzoylated derivative (14) with triphenylphosphine and potassium t-butoxide in THF
gave the 6-phenacly derivative (15). The debenzylation of 15 with methanolic ammonia afforded 9-β-D-ribofuranosyl-6-phenacylpurine (16) in high yield. The tautomeric form of 16 was assigned as the enol form rather than the keto form, since 16 gave intense color with ferric chloride solution. The NMR spectrum of 16 showed a methine proton signal at 5.56 ppm. Although the enol proton could not be detected due to the presence of the sugar hydroxyls, the absence of an N3-proton signal (usually appearing at >10 ppm) indicates the structure 16.

The sulfur extrusion reaction of 12 with triphenylphosphine and potassium tert-butoxide in pyridine gave the 6-acetylpurine riboside (17), though in low yield. Compound 17 also exhibited intense coloration with ferric chloride solution. The NMR spectrum of 17 indicated the presence of the other tautomer with an N1-proton (see "Experimental"). Attempted sulfur extrusion of 13 under various conditions met with little success. The desired product, 6-ethoxycarbonylmethylpurine riboside, was obtained by the alternative route already reported.¹³

In conclusion, the extrusion of sulfur from alkylthio-nucleosides proceeded well when the carbonyl moiety attached to the thiomethylene group was strongly electron-withdrawing. The reduction of the keto group of the product should provide a new route for the preparation of alkylpyrimidines or -purine nucleosides. Reactions utilizing the keto group may yield various functionalized nucleosides. Studies along these lines are in progress. Biological tests of the newly synthesized C-substituted nucleosides are also under way, and preliminary tests of cytotoxic activity against leukemia L-5178Y cells indicated that 6-acetylpurines are moderately effective.¹³

Experimental

Melting points were determined with a Yanaco MP-3 melting point apparatus and are uncorrected. UV spectra were recorded on a Shimadzu UV-300 recording spectrophotometer. NMR spectra were taken with a JEOL JNM-FX 100FT NMR spectrometer. Mass spectra were taken with a Hitachi RMU-7 mass spectrometer. IR spectra were measured on a Hitachi 215 spectrophotometer. Thin-layer chromatography was carried out on Merck TLC plates (silica gel 60–F₂₅₄ pre-coated). Silica gel for column chromatography was Wakogel C-200. Ribonucleosides used in this work were purchased from Yamasa Shoyu Co., Ltd.

4-Phenaclythiouridine (2)—4-Thiouridine (1, 590 mg) and NaHCO₃ (184 mg, 1 eq) were dissolved in 3 ml of H₂O and phenacyl bromide (597 mg, 1.5 eq) in 3 ml of EtOH was added. The solution was stirred for 20 min while 20 ml of EtOH was added. The separated crystals were collected and recrystallized from MeOH to give 582 mg (77%) of 2, mp 161.5—162.5°. Anal. Calcd for C₁₇H₁₈N₄O₃S: C, 53.97; H, 4.80; N, 13) The tests were performed by Dr. H. Yoshino and co-workers, Yamasa Shoyu Co.
4-Acetylthiothiourilide (3) — A solution of 10.40 g of 1 and 3.67 g of NaHCO₃ in H₂O (150 ml) — EtOH (20 ml) was treated with 8.22 g of bromoacetone (80% purity, 1.2 eq), and the solution was stirred for 1 hr at room temperature. The solvent was concentrated in vacuo and the residue was crystallized from EtOH to give 10.50 g (83%) of 3, mp 142—144°. Anal. Calcld. for C₁₅H₁₉N₂O₄S: C, 45.57; H, 5.10; N, 8.86; S, 10.26. Found: C, 45.58; H, 5.12; N, 8.81; S, 10.36. UV λ max (nm) (e): 301 (13900), 265 (63900). λ max: 237 (2600). NMR (DMSO-d₆): δ: 8.32 (d, 1, 6-H, J = 8 Hz), 6.55 (d, 1, 5-H, J = 2.3 Hz), 5.80 (d, 1, 1’-H, J = 2.3 Hz), 4.13 (s, 2, -SCH₂), 2.29 (s, 3, COCH₃).

4-Ethoxycarbonylthiothiourilide (4) — Ethyl bromoacetate (334 mg, 1.3 eq) was added to a solution of 390 mg of 1 and 138 mg of NaHCO₃ in H₂O (3 ml) — EtOH (2 ml), and the solution was stirred for 2 hr at room temperature. After adding 86 mg of the bromoacetate and stirring for another 2 hr, the solvent was removed in vacuo and the residue was taken up in a minimum amount of EtOH. The solution was applied to a column of silica gel (20 g) and the product was eluted with 8—10% MeOH in CHCl₃. The eluate was concentrated and the residue was crystallized from EtOH to give 278 mg (73%) of 4, mp 135—136.5°. Anal. Calcld. for C₁₆H₁₈N₂O₄S: C, 45.09; H, 5.26; N, 8.09; S, 9.26. Found: C, 44.91; H, 5.26; N, 7.86; S, 9.07. UV λ max: 330 nm shoulder at 265 nm. λ max: 237 nm. NMR (DMSO-d₆): δ: 8.46 (d, 1, 6-H), 6.96 (d, 1, 5-H, J = 7 Hz), 6.15 (d, 1, 1’-H, J = 3 Hz), 4.54 (q, 2, -OCH₂CH₃), 4.31 (s, 2, -SCH₂), 1.53 (t, 3, -OCH₂CH₂), 5.7 (t, 7 Hz).

2’,3’-O-Isopropylidene-4-thiourilide (1a) — Cytidine (34.15 g) was suspended in 1400 ml of aceton, and 20 ml of 60% HClO₄ was added. The suspension was stirred for 2 hr and the clear solution was neutralized with anhydrous K₂CO₃. The filtrate was concentrated, and the residue was dissolved in 240 ml of H₂O. The solution (40 ml) was added to a mixture of 50 ml of pyridine and 80 ml of liquid H₂S in a tube under cooling with ice-acetone. The tube was sealed and kept for 3 days at 50°. After removal of H₂S by evaporation and bubbling the residue through with N₂ gas, the solution was concentrated and the residue was taken up in EtOH. The insoluble material was removed by filtration and the filtrate was concentrated. The residue was crystallized from EtOH to give 1a. Six runs of this reaction gave 1a in a yield of 31.85 g (75.7%), mp 182—183° (mp 170—183°).

1-(2,2-0-Isopropylidene-2,5-difluoro-4-ethoxycarbonylmethylthiothiouracil (5) — A solution of 4.50 g of 1a in 80 ml of DMF was treated with 1.38 g of NaHCO₃ in 10 ml of H₂O and 2.75 g of ethyl bromoacetate. The solution was stirred for 2 hr at room temperature. The solvent was removed in vacuo and the residue was dissolved in 100 ml of CHCl₃ and washed with H₂O. The organic layer was concentrated and the residue was crystallized from EtOH to give 5.21 g (90%) of 5, mp 178—180°. Anal. Calcld. for C₁₃H₁₁F₂N₂O₄S: C, 49.74; H, 5.74; N, 7.25; S, 8.28. Found: C, 49.65; H, 5.70; N, 7.14; S, 8.20. NMR (DMSO-d₆): δ: 8.08 (d, 1, 6-H), 6.50 (d, 1, 5-H, J = 8.3 Hz), 5.82 (s, 1, 1’-H), 4.12 (q, 2, OCH₂CH₃), 4.02 (s, 2, SCH₂), 1.48, 1.30 (s, 3, 3’-CMe₂), 1.22 (t, 3, OCH₂CH₂), J = 6.8 Hz.

1-p-Ribofuranosyl-4-phenaclidene-2(3H)-pyridimione (6) — Compound 2 (3.78 g) was dissolved in 20 ml of pyridine and the solution was refluxed for 1 hr. The solvent was then removed in vacuo and the residue was taken up in H₂O and concentrated again. Concentration from H₂O was repeated several times and the final residue was taken up in a minimum amount of MeOH. Silica gel was added to the solution and the solvent was removed to leave a powder. This was applied to the top of a silica gel column (120 g) and the column was eluted with 10% MeOH in CHCl₃. The eluate containing the product was concentrated and the residue was crystallized from EtOH to give 4.00 g (46%) of 6, mp 180—187°. Anal. Calcld. for C₁₃H₁₇F₂N₂O₄S: C, 58.85; H, 5.24; N, 8.09. Found: C, 58.22; H, 5.32; N, 7.99. UV λ max nm (e): 375.5 (15200), 262.5 (2800), 310 (780), 242 (2100). 312 nm (e): 388 (17000), 250 (4600). 312 nm (e): 320 (1200). 234 (4000). NMR (DMSO-d₆): δ: 13.12 (bs, 1, N₂H), 7.82 (d, 1, 6-H), 8.10—7.45 (m, 5, Ph), 6.25 (s, 1, 4-CH₃), 6.16 (d, 1, 5-H, J = 7.5 Hz), 5.88 (d, 1, 1’-H, J = 4.5 Hz). MS m/e: 346 (M⁺), 257 (M—9), 214 (B+1), 213 (B).

1-p-Ribofuranosyl-4-acetylimino-2(3H)-pyrimidimione (7) — A solution of 1.58 g of 3 and 3.93 g of triphenylphosphine in 100 ml of pyridine was treated with 244 mg of t-BuOK in 20 ml of t-BuOH, and the solution was refluxed for 5 min. After cooling, the solution was neutralized by the addition of AcOH and the solvent was removed in vacuo. The residue was taken up in 100 ml of H₂O and washed with CHCl₃. The aqueous layer was concentrated and the residue was applied to a column of silica gel (60 g). The eluent with 10% MeOH in CHCl₃ was collected and concentrated, then the residue was crystallized from EtOH—AcOEt to give 717 mg (50%) of 7, mp 168—170°. Anal. Calcld. for C₁₃H₁₇N₂O₄: C, 50.70; H, 5.67; N, 9.86. Found: C, 50.71; H, 5.66; N, 9.83. UV λ max (nm) (e): 370 (sh, 20700), 351 (26500), 338 (sh, 23400), 265 (3900). 312 nm (e): 284 (3000). 312 nm (e): 361 (38500), 280—200 (plateau, 5600). NMR (DMSO-d₆): δ: 12.60 (bs, 1, N₂—H), 7.60 (d, 1, 6-H), 5.94 (d, 1, 5-H, J = 8.3 Hz), 5.84 (d, 1, 1’-H, J = 4.5 Hz), 5.38 (s, 1, 4-CH₃), 2.06 (s, 3, CH₃). MS m/e: 284 (M⁺), 152 (B+1), 151 (B).

1-(2,3-O-Isopropylidene-β-D-ribofuranosyl)-4-bis(ethoxy carbonyl)methylene-2(3H)-pyrimidinone (8) — A mixture of 2.0g of 1a, 966g of K₂CO₃, and 1.91g of diethyl bromomalonate in 20ml of DMF was stirred for 1.5hr at room temperature. AcOEt (80ml) was added to the mixture and the solution was partitioned with 50ml of H₂O. The organic layer was dried over Na₂SO₄, concentrated in vacuo, and the residue was crystallized from EtOH-AcOEt to give 1.30g (46%) of 8, mp 123—124°. Anal. Calcd for C₉H₇NO₃S: C, 53.51; H, 6.15; N, 6.57. Found: C, 53.42; H, 6.19; N, 6.43. UV λₘₐₓ nm (ε): 355 (sh, 14000), 336 (22800), 325 (sh, 22000), 237 (63000). λₘₐₓ ¹H NMR cm⁻¹ (δ): 344 (162700), 257 (72000). λₘₐₓ ¹³C NMR cm⁻¹ (δ): 296 (3600). NMR (CDCl₃) δ: 11.88 (bs, 1, N₂⁻), 7.06 (dd, 1, 1'-H, J = 8.3 and 1.5 Hz), 5.52 (dd, 1, 1'-H, J = 2.3 Hz), 4.22 (q, 4, -OCH₂CH₂), 1.54, 1.34 (s, 3, 3', CMe₂), 1.38 (t, 6, -OCH₂CH₃).

1-(5-O-Acetyl-2,3-O-Isopropylidene-β-D-ribofuranosyl)-4-ethoxy carbonylmethyl-2-pyrimidinone (9) — Compound 5 (100mg) and Ac₂O (0.5ml) in 3ml of pyridine were kept overnight at room temperature. The solvent was then removed and the residue was taken up in CHCl₃, washed with H₂O, and dried over Na₂SO₄. After removal of the solvent, the residue dissolved in 5ml of THF, then 136mg of triphenylphosphine and 25mg of 50% NaH were added and the mixture was heated under reflux for 1hr. After neutralization of the solution with AcOH the solution was removed in vacuo and the residue was applied to a column of silica gel (10g). The eluent with 10% AcOEt in CH₂Cl₂ was concentrated to leave 58mg (56%) of 9 in an amorphous form. UV λₘₐₓ nm: 321, 267. λₘₐₓ ¹H NMR cm⁻¹: 277, 227. λₘₐₓ ¹³C NMR cm⁻¹: 338, 267. λₘₐₓ ¹⁹F NMR cm⁻¹: 272, 235. NMR (CDCl₃) δ: 10.86 (bs, N₂⁻), 6.68 (dd, 1, 6', H), 5.68 (dd, 1, 5'-H, J = 7.5 Hz), 5.52 (bs, 1, 1'-H). 5.1—4.8 (m, 2, 2',3', 4', 5'). 4.71 (s, 1, 4-CH₂), 1.41 (q, 2, -OCH₂CH₂), 0.26 (s, 3, Ac), 1.54, 1.34 (s, 3, 3', CMe₂), 1.26 (t, 3, -OCH₂CH₃).

1-(2,3-O-Isopropylidene-β-D-ribofuranosyl)-4-methyl-2-pyrimidinone (10) — Compound 9 (58mg) was dissolved in a mixture of 0.1N NaOH (2ml) and EtOH (3ml), and kept overnight at room temperature. The solution was acidified by the addition of 0.1N HCl and kept overnight at 10°C. The solution was then neutralized with 1N NaOH, and the solvent was evaporated off. The residue was applied to a column of silica gel (10g). The eluent with 5% EtOH in CHCl₃ was concentrated to give an amorphous residue 10 (23mg, 56%). UV λₘₐₓ nm: 297nm. λₘₐₓ ¹H NMR cm⁻¹: 309nm. λₘₐₓ ¹³C NMR cm⁻¹: 260nm. NMR (DMSO-d₆) δ: 8.12 (d, 1, 6'-H), 6.39 (d, 1, 5'-H, J = 7.2 Hz), 5.92 (d, 1, 1'-H, J = 1.5 Hz), 2.28 (s, 3, 4-CH₂), 1.49, 1.29 (s, 3, 3', CMe₂).

6-Phenylthioniosine (11) — 6-Thioniosine(6) (2.84g) was dissolved in H₂O (50ml) and EtOH (10ml) containing 924mg of NaHCO₃ by warming. Phenacylbromide (2.39g) was added to the cooled solution and the mixture was stirred for 2 days at room temperature. After removal of the solvent, the residue was added in a minimum amount of AcOH and the solution was brought to pH 10. The eluent with 10—15% MeOH in CHCl₃ was collected and concentrated. The residue was crystallized from EtOH to give 3.06g (76%) of 11, mp 103—105°. Anal. Calcd for C₉H₈N₂O₈S: C, 53.73; H, 4.43; N, 13.93; S, 7.95. Found: C, 53.45; H, 4.43; N, 13.76; S, 8.13. UV λₘₐₓ nm (ε): 292 (sh, 20300), 284 (21500), 252 (14300), 226 (13700).

6-Acetonothioniosine (12) — 6-Thioniosine (3.41g) was dissolved in H₂O (50ml) and EtOH (5ml) containing 1.11g of NaHCO₃ by warming. Bromoaacetone (2.41g) was added to the solution and the mixture was stirred overnight. After work-up as described above, a crystalline product 12 (3.48g, 85%) was obtained from EtOH, mp 138—140°. Anal. Calcd for C₉H₈N₂O₈S: C, 45.88; H, 4.74; N, 16.47; S, 9.40. Found: C, 45.82; H, 4.64; N, 16.32; S, 9.31. UV λₘₐₓ nm (ε): 281 (12700), 218 (8300). λₘₐₓ ¹H NMR cm⁻¹: 240 (1800), 208 (7500). NMR (DMSO-d₆) δ: 8.82 (s, 1, 8'-H), 8.76 (s, 1, 2'-H), 6.08 (d, 1, 1'-H, J = 5.5 Hz), 4.38 (s, 2, CH₂), 2.54 (s, 3, COCH₃), 1R (KBr): 1720 cm⁻¹ (COCH₃).

6-Ethoxy carbonylmethylthioniosine (13) — 6-Thioniosine (4.26g) and 3.0g of ethyl bromoacetate were treated as described above and the product 13 (4.26g, 77%) was crystallized from EtOH, mp 131—133°. Anal. Calcd for C₁₀H₁₀N₂O₄S: C, 45.40; H, 4.90; N, 15.13; S, 8.64. Found: C, 45.32; H, 4.86; N, 15.15; S, 8.71. UV λₘₐₓ nm (ε): 287 (sh, 11800), 280 (13000), 227 (85000). λₘₐₓ ¹H NMR cm⁻¹: 239 (1600). NMR (DMSO-d₆) δ: 8.76 (s, 1, 8'-H), 8.72 (s, 1, 2'-H), 6.05 (d, 1, 1'-H, J = 5.3 Hz), 4.26 (s, 2, CH₂), 4.15 (q, 2, -OCH₂CH₃), 1.20 (t, 3, -OCH₂CH₃, J = 6.9 Hz).

2',3',5'-Tri-O-benzoyl-6-phenylthioniosine (14) — 2',3',5'-Tri-O-benzoyl-6-thioniosine(8) (5.96g) was dissolved in 60ml of DMF, then 1.52g of K₂CO₃ and 2.09g of phenyl bromide were added. The solution was stirred for 2hr at room temperature and poured into ice-water. The precipitate was separated and dried to give 6.68g (94%) of crude 14, which was used directly for the next step.

9-(2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl)-6-phenacylpurine (15) — Crude 14 (500mg), triphenylphosphate (367mg) and 50% NaH (67mg) were taken up in 20ml of THF. After heating under reflux for 2hr, the solution was concentrated and the residue was taken up in a small amount of CH₂Cl₂. This solution was applied to a column of silica gel (20g) and eluted with 10% AcOEt in CH₂Cl₂. The product 15 was obtained as a foam, 250mg (74%). UV λₘₐₓ nm: 373, 230nm. λₘₐₓ ¹H NMR cm⁻¹: 297nm. This was used for the next step without purification.

9-β-α-Ribofuranosyl-6-phenacylurine (16) — Compound 15 (350 mg) was dissolved in 20 ml of MeOH saturated with NH₃, and kept overnight at room temperature. Nitrogen was bubbled through the solution for 20 min while crystals separated. The precipitate was collected and washed well with MeOH–CHCl₃ to give 179 mg (93%) of 16, mp 238–240°. Anal. Calcd for C₁₃H₁₄N₄O₅: C, 58.37; H, 4.90; N, 15.13. Found: C, 58.37; H, 4.87; N, 15.04. UV λₑₓᵧ₀ₓ nm (ε): 386 (7500), 252 (3500). ½max: 305 (600). ½max ¹H NMR: 384 (10500), 245 (3900). ½max ¹H NMR: 305 (600), 240 (3800). NMR (DMSO-d₆) δ: 8.62 (s, 1, 8-H), 8.54 (s, 1, 2-H), 8.0–7.5 (m, 5, Ph), 6.56 (s, 1, 6-CH=), 6.02 (d, 1, 1′-H, J = 5.3 Hz). MS m/z: 370 (M⁺), 239 (B + 2), 238 (B + 1), 237 (B). Compound 16 gave a violet color with FeCl₃ solution.

9-β-α-Ribofuranosyl-6-acetonylurine (17) — Compound 12 (1.70 g) and triphenylphosphine (3.93 g) were taken up in 100 ml of pyridine, then 560 mg of t-BuOK in 30 ml of t-BuOH was added. The solution was refluxed for 30 min, neutralized with AcOH, and concentrated. The residue was partitioned with H₂O and CHCl₃. The aqueous layer was concentrated and the residue was applied to a column of silica gel (60 g). The eluent with 10% MeOH in CHCl₃ was concentrated and the residue was crystallized from EtOH–H₂O to give 445 mg (28%) of 17, mp 163–165°. Anal. Calcd for C₁₃H₁₄N₄O₄·1/4H₂O: C, 49.91; H, 5.27; N, 17.90. Found: C, 49.86; H, 5.35; N, 17.80. UV λₑₓᵧ₀ₓ nm (ε): 360 (15000), 345 (sh, 9000), 288 (7200). ½max ¹H NMR: 288 (15000), 226 (3800). ½max ¹H NMR: 359 (25700), 241 (8800). ½max ¹H NMR: 283 (2600), 226 (8200). NMR (DMSO-d₆) δ: 10.72 (s, 0, N-OH), 8.94, 8.56 (each s, 1, 8-H, ratio 1:2.5), 8.86, 8.47 (each s, 1, 2-H, ratio 1:2.5), 6.09, 5.90 (each d, 1, 1′-H, J = 5.3 Hz, ratio 1:2.5), 2.29, 2.11 (each s, 3, CH₃, ratio 1:2.5). The presence of a minor tautomer resulted in complex signals for other protons, and assignment was impossible. MS m/z: 308 (M⁺), 210 (M – 99), 205 (B + 30), 176 (B + 1). Compound 17 showed a violet coloration with FeCl₃ solution.

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