ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 318 (1999) 180–185

CARBOHYDRATE RESEARCH

Note

Synthesis of 5-hydroxy-2-(β-D-ribofuranosyl)pyran-4-one from a pyranulose glycoside

Shigeyuki Kanazawa, Souhei Mizuno, Rie Yamauchi, Natsu Nishimura, Isamu Maeba *

Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

Received 23 February 1999; accepted 16 April 1999

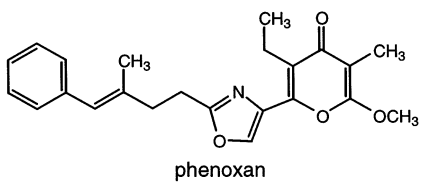
Abstract

The synthesis of 5-hydroxy-2-(β-D-ribofuranosyl)pyran-4-one (**9**) is described. Treatment of pyranulose glycoside with bromine in carbon tetrachloride afforded brompyranulose glycoside in 90% yield. The reaction of (6*S*)- and (6*R*)-4-bromo-6-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-6*H*-pyran-3-one (**2**) in acidic media was examined with the following results: the reaction of **2** with trifluoroacetic acid (TFA) in dioxane afforded a mixture of 5-hydroxy-2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-4-one (**3**) and its furan derivative 5-hydroxy-2-{5-(benzoyloxy)methyl]furan-2-yl}pyran-4-one (**4**), but the use of hydrochloric acid formed the bromofurfural, 3-bromo-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-2-furancarboxyaldehyde only. Acetylation of a mixture (**3** and **4**) with acetic anhydride facilitated product separation to give the corresponding acetates 5-acetoxy-2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-4-one (**5**) and 5-acetoxy-2-{5-[(benzoyloxy)methyl]furan-2-yl}pyran-4-one (**6**). Treatment of **5** with hydrazine afforded 3-hydroxymethyl-6-(β-D-ribofuranosyl)-1*H*-pyridazin-4-one in 43% yield. Debenzoylation of **5** with aq ammonia gave **9** in 50% yield.

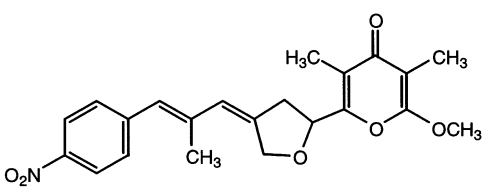
Keywords: Synthesis; Pyranulose glycoside; Pyran-4-one; Pyridazin-4-one; *C*-Nucleoside

1. Introduction

The pyran-4-one and benzopyran-4-one groups of naturally occurring compounds have aroused considerable interest due to their biological activities [1]. Phenoxan [2] and aureothin [3] are recently isolated natural products that have been shown to have anti-HIV activity.



phenoxan



aureothin

Hudecova and co-workers [4,5] have synthesized 5-hydroxy-2-azidomethylpyran-4-one

* Corresponding author. Tel.: +81-52-832-1781; fax: +81-52-834-8090.

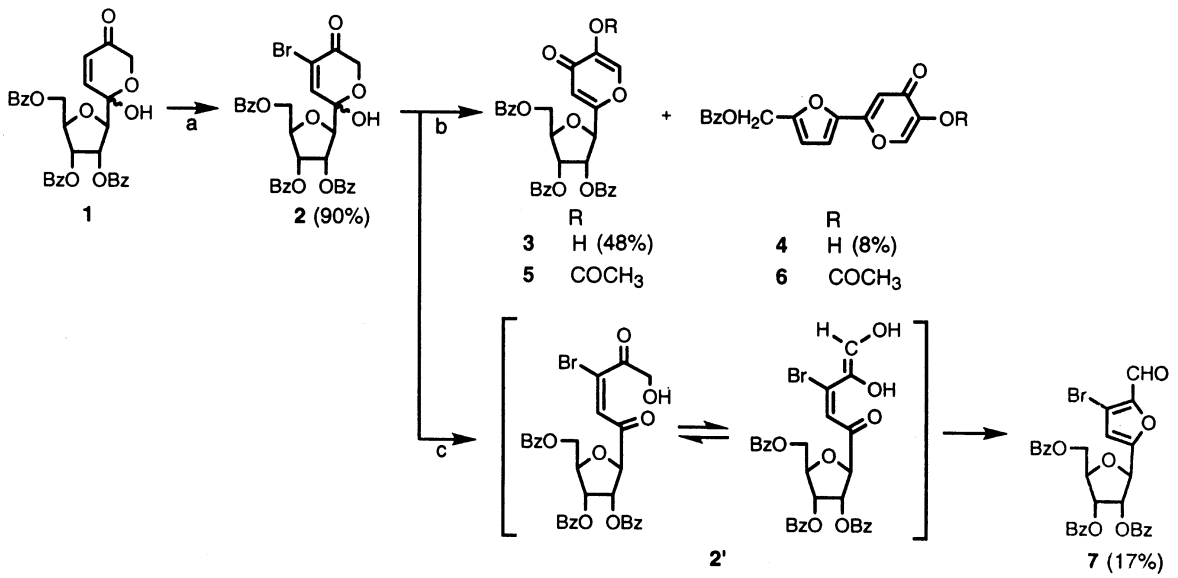
E-mail address: maeba@meijo-u.ac.jp (I. Maeba)

0008-6215/99/$ - see front matter
PII: S0008-6215(99)00098-1

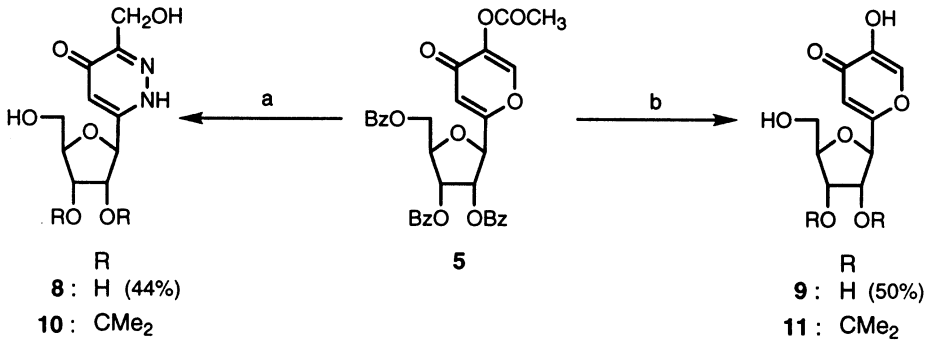
and 5-benzoyloxy-2-thiocyanatomethylpyran-4-one as potential antitumor agents. These findings prompted us to synthesize the 5-hydroxypyran-4-one glycoside (**9**). Two methods [6] have been reported for the synthesis of pyran-4-ones from pyran-3-one derivatives based on epoxidation to 6-alkoxypyran-3-one and subsequent hydrolysis in mild acid. Attempted epoxidation of a 6-alkoxypyran-3-one glycoside [7] under a variety of conditions, however, proved unsuccessful, leading to degradation of the starting material. Then, bromination of the pyranulose glycoside **1**, 6-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3[2*H*,6*H*]-one [8], followed by an in situ acid-(catalyzed) hydrolysis, was examined.

Bromination of pyranulose glycoside **1** with bromine and carbon tetrachloride at room temperature afforded pyranulose **2** as a mixture of diastereomers in 90% yield. These isomers could not be separated, but the mixture was purified by column chromatography, and the product mixture was entirely satisfactory for the next step. Treatment of bromo compound **2** with trifluoroacetic acid (TFA) in dioxane at room temperature for 6 days afforded two products, 5-hydroxy-2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-4-one (**3**, 48%), and the furan derivative **4** (8%), which resulted from elimination of two benzoyloxy groups. Separation of **3** and **4** was found to be impractical owing to slow elimination of the 2,3-dibenzoyloxy groups on the sugar moiety during chromatography on silica gel. Treatment of the mixture of **3** and **4** with acetic anhydride afforded the acetates **5** and **6** that could be easily separated by preparative thin-layer chromatography (PTLC). Structural determination of **3** was made via MS and NMR experiments. The ^{1}H NMR spectrum of **3** showed two singlets at δ 6.67 and 7.63 that are characteristic of the pyran-4-one moiety. When **2** was treated with hydrochloric acid in acetonitrile, it did not afford pyran-4-one **3** but instead gave bromofurfural **7** in 17% yield. We think that the formation of **7** proceeds through the formation of the ring-opened intermediate γ-diketone **2′**, which subsequently undergoes ring closure to the five-membered aldehyde (Scheme 1).

It is worth noting that hydrazinolysis reactions of the γ-pyrone derivatives were found to give a mixture of derivatives of pyridazine and pyrazoles and not, as might have been expected, *N*-aminopyridines [9]. Reaction of the pyrone **5** with anhydrous hydrazine in *N*,*N*-dimethylformamide gave 3-hydroxymethyl-6-(β-D-ribofuranosyl)-1*H*-pyridazin-4-one (**8**) in 43% yield. However, the pyrazole



Scheme 1. Reagents and conditions: (a) Br_2/CCl_4, rt, 30 min; (b) TFA/dioxane, rt, 6 days; (c) HCl/MeCN, 60 °C, 8 h.



Scheme 2. Reagents and conditions: (a) NH_2NH_2/DMF, rt, 2 days; (b) aq. NH_3/MeOH, room temperature, 1 day.

derivative was not obtained. Structural assignment of **8** was supported by the ^{13}C NMR spectrum, which exhibited the signal of the amide carbonyl carbon at δ 172 ppm. Removal of the sugar protecting groups in compound **5** was readily accomplished with aqueous ammonia to afford 5-hydroxy-2-(β-D-ribofuranosyl)pyran-4-one (**9**) in 50% yield. We assigned the anomeric configuration of compounds **8** and **9** based on the difference in the chemical shifts of the two methyl signals of the corresponding 2,3-*O*-isopropylidene derivatives **10** and **11**. The ^1H NMR chemical shift differential value ($\Delta\delta$) of the methyl groups (0.19 and 0.22) is indicative of β stereochemistry in accordance with Imbach's rule [10] (< 0.15 and > 0.15 ppm for the α and β anomers, respectively). This indicates that the β-ribofuranoside configuration has been preserved during the reaction sequence (Scheme 2).

2. Experimental

Fast-atom bombardment MS spectra (FABMS) were run on a JMS-HX 110 spectrometer. ^1H and ^{13}C NMR spectra were measured with a JNM-A-400 or an A-600 (JEOL) spectrometer, with tetramethylsilane as an internal standard. UV spectra were recorded with a Shimazu UV-3100PC spectrophotometer. Specific rotations were measured with a JASCO DIP-370 polarimeter (10-cm cell). Elemental analyses were carried out by the microanalysis service of the University of Meijo. Analytical TLC was performed on glass plates coated with a 0.25-mm layer of Silica Gel GF_{254} (E. Merck). The compounds were detected by UV light (254 nm).

*(6S)- and (6R)-4-Bromo-6-hydroxy-6-(2,3,-5-tri-*O*-benzoyl-β-*D*-ribofuranosyl)-6H-pyran-3-one* (**2**).—To a solution of **1** [8] (515.2 mg, 0.9233 mmol) in CCl_4 (10 mL) at 0 °C was added CCl_4 (1 mL) containing 0.1 mL of bromine. The mixture was stirred at room temperatuer (rt) for 30 min, and excess bromine was decomposed by sodium thiosulfate. The reaction mixture was poured into ice-water, neutralized with satd aq $NaHCO_3$ and then extracted with $CHCl_3$ (3×10 mL). The extracts were combined, washed with water, dried over $MgSO_4$, and concentrated to dryness. The residue was chromatographed on a column of silica gel with $CHCl_3$ as eluent to give 529.4 mg (90%) of **2** as a pale-yellow foam; ^1H NMR ($CDCl_3$): δ 4.03, 4.14 (each d, each 0.5 H, $J_{2a,2b} = 16.8$ Hz, H-2a), 4.39, 4.40 (each d, each 0.5 H, $J_{1',2'} = 5.7$ and 6.7 Hz, H-1′), 4.51, 4.77 (each d, each 0.5 H, $J_{2a,2b} =$ 16.8 Hz, H-2b), 4.49–4.93 (m, 3 H, H-4′, 5′), 5.48 (dd, 0.5 H, $J_{2',3'} = J_{3',4'} = 6.4$ Hz, H-3′), 5.71–5.83 (m, 1.5 H, H-2′, 3′), 7.32–8.10 (m, 16 H, Ph, H-5); ^{13}C NMR ($CDCl_3$): δ 62.0, 63.1 (C-5′), 66.4, 66.8 (C-2), 71.7, 71.9, 72.0, 72.6, 79.0, 79.7, 86.1, 87.3 (C-1′, 2′, 3′, 4′), 94.6, 95.2 (C-6), 123.3, 124.5 (C-4), 128.3–134.1 (Ph), 145.4, 146.2 (C-5), 165.2, 165.3, 165.4, 166.0, 166.7, 167.1 (C=O), 186.7, 186.8 (C-3). Anal. Calcd for $C_{31}H_{25}BrO_{10}\cdot H_2O$: C, 56.81; H, 4.15. Found: C, 56.76; H, 4.09.

*5-Hydroxy-2-(2,3,5-tri-*O*-benzoyl-β-*D*-ribofuranosyl)pyran-4-one* (**3**) *and 5-hydroxy-2-{5-[(benzoyloxy)methyl]furan-2-yl}pyran-4-one* (**4**).—To a solution of **2** (106.2 mg, 0.1667

mmol) in dioxane (3 mL) at 0 °C was added TFA (2 mL). The mixture was stirred at rt for 6 days, and then the reaction mixture was poured into ice-water, neutralized with satd aq $NaHCO_3$ and extracted with $CHCl_3$ (3 × 10 mL). The extracts were combined, washed with water, and dried over $MgSO_4$. The extracts, on evaporation of the solvent, afforded a brownish oil that was separated by PTLC with 99:1 $CHCl_3$–MeOH as eluent.

Compound **3**. Yield 43.9 mg (48%); colorless foam; ^{1}H NMR ($CDCl_3$): δ 4.59 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'a} = 3.7$ Hz, H-5′a), 4.73–4.76 (m, 1 H, H-4′), 4.87 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'b} = 3.3$ Hz, H-5′b), 5.04 (d, 1 H, $J_{1',2'} = 5.5$ Hz, H-1′), 5.79 (t, 1 H, $J_{2',3'} = J_{3',4'} = 5.5$ Hz, H-3′), 5.88 (dd, 1 H, $J_{1',2'} = J_{2',3'} = 5.5$ Hz, H-2′), 6.70 (s, 1 H, H-5), 7.37–8.13 (m, 16 H, Ph, H-2); ^{13}C NMR ($CDCl_3$): δ 63.3 (C-5′), 72.2, 74.0, 79.9, 80.6 (C-1′, 2′, 3′, 4′), 111.4 (C-5), 128.3–133.7 (Ph), 138.2 (C-3), 145.9 (C-2), 163.5 (C-6), 165.0, 165.2, 166.0 (C=O), 173.8 (C-4). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{25}O_{10}$: 557.1448 [MH]. Found: m/z 557.1429 $[MH]^+$.

Compound **4**. Yield 3.9 mg (8%); colorless foam; ^{1}H NMR ($CDCl_3$): δ 5.36 (s, 2 H, CH_2), 6.65 (d, 1 H, $J_{3,4} = 3.7$ Hz, furan H-4), 6.85 (s, 1 H, H-5), 6.95 (d, 1 H, $J_{3,4} = 3.7$ Hz, furan H-3), 7.84 (s, 1 H, H-2), 7.43–8.07 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$): δ 58.1 (CH_2), 106.3 (C-5), 113.1, 116.1 (furan C-3, 4), 128.4–133.5 (Ph), 145.7, 146.1, 152.8, 155.7 (C-3, 6, and furan C-2, 5), 166.0 (C=O), 173.6 (C-4). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{17}H_{13}O_6$: 313.0712 [MH]. Found: m/z 313.0721 $[MH]^+$.

5-Acetoxy-2-(2,3,5-tri-O-*benzoyl-β*-D-*ribofuranosyl)pyran-4-one* (**5**) *and 5-acetoxy-2-{5-(benzoyloxy)methyl]furan-2-yl}pyran-4-one* (**6**).—To a solution of **2** (172.4 mg, 0.2706 mmol) in dioxane (3 mL) at 0 °C was added TFA (2 mL). The mixture was stirred at rt for 6 days, and the reaction mixture was concentrated. To the residue was added acetic anhydride (5 mL) containing one drop of anhydrous pyridine, and the mixture was stirred at rt for 2 h. The reaction mixture was poured into ice-water, then neutralized with satd aq $NaHCO_3$ and extracted with $CHCl_3$ (3 × 10 mL). The extracts were combined, washed with water, dried over $MgSO_4$, and concentrated in vacuo to a syrup. This syrup was separated by PTLC with 3:1 EtOAc–$CHCl_3$ as eluent.

Compound **5**. Yield 55.5 mg (34%); R_f 0.70; colorless foam; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3 H, CH_3), 4.59 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'a} = 4.0$ Hz, H-5′a), 4.72–4.76 (m, 1 H, H-4′), 4.84 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'b} = 3.3$ Hz, H-5′b), 5.03 (d, 1 H, $J_{1',2'} = 5.5$ Hz, H-1′), 5.78 (dd, 1 H, $J_{2',3'} = J_{3',4'} = 5.5$ Hz, H-3′), 5.88 (dd, 1 H, $J_{1',2'} = J_{2',3'} = 5.5$ Hz, H-2′), 6.67 (s, 1 H, H-5), 7.69 (s, 1 H, H-2), 7.36–8.11 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 20.4 (CH_3), 63.4 (C-5′), 72.3, 73.9, 79.7, 80.7 (C-1′, 2′, 3′, 4′), 115.5 (C-5), 128.4–133.5 (Ph, C-4), 141.3 (C-3), 147.9 (C-2), 163.1 (C-6), 165.1, 165.3, 166.1, 167.6 (C=O), 172.2 (C-4). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{33}H_{27}O_{11}$; 599.1553 [MH]. Found: m/z 599.1554 $[MH]^+$. Anal. Calcd for $C_{33}H_{26}O_{11}\cdot 0.7H_2O$: C, 64.92; H, 4.51. Found: C, 64.86; H, 4.52.

Compound **6**. Yield 6.1 mg (6%); R_f 0.55; colorless foam; ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3 H, CH_3), 5.35 (s, 2 H, CH_2), 6.65 (d, 1 H, $J_{3,4} = 3.3$ Hz, furan H-4), 6.84 (s, 1 H, H-5), 6.95 (d, 1 H, $J_{3,4} = 3.3$ Hz, furan H-3), 7.88 (s, 1 H, H-2), 7.43–8.07 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$): δ 20.4 (CH_3), 58.0 (CH_2), 110.2 (C-5), 113.1, 113.4 (furan C-3, 4), 128.4–133.3 (Ph), 145.5, 146.9, 153.1, 155.1 (C-3, 6, and furan C-2, 5), 166.0, 167.8 (C=O), 172.3 (C-4). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{19}H_{15}O_7$; 355.0818 [MH]. Found: m/z 355.0823 $[MH]^+$.

3-Bromo-5-(2,3,5-tri-O-*benzoyl-β*-D-*ribofuranosyl)-2-furancarboxyaldehyde* (**7**).—A solution of **2** (134.0 mg, 0.2104 mmol) in CH_3CN (10 mL) containing five drops of conc HCl was allowed to stir at 60 °C for 8 h. The reaction mixture was neutralized with satd aq $NaHCO_3$ and extracted with $CHCl_3$ (3 × 10 mL). The extracts were combined, washed with water, dried over $MgSO_4$, and the solvent was evaporated in vacuo to give a syrup. This syrup was purified by PTLC with 99:1 $CHCl_3$–MeOH as eluent. This afforded 22.3 mg (17%) of **7** as a foam; ^{1}H NMR ($CDCl_3$): δ 4.60 (dd, 1 H, $J_{5'a,5'b} = 12.5$, $J_{4',5'a} = 3.8$ Hz, H-5′a), 4.71–4.74 (m, 1 H, H-4′), 4.83 (dd, 1 H, $J_{5'a,5'b} = 12.5$, $J_{4',5'b} = 3.1$ Hz, H-5′b), 5.32 (d, 1 H, $J_{1',2'} = 5.3$ Hz, H-1′), 5.83 (t, 1 H,

$J_{2',3'} = J_{3',4'} = 5.3$ Hz, H-3′), 5.89 (dd, 1 H, $J_{1',2'} = J_{2',3'} = 5.3$ Hz, H-2′), 6.63 (s, 1 H, H-4), 7.36–8.11 (m, 15 H, Ph), 9.65 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$): δ 63.4 (C-5′), 72.2, 74.5, 77.2, 80.4 (C-1′, 2′, 3′, 4′), 112.8 (C-3), 115.0 (C-4), 128.5–134.0 (Ph), 148.2 (C-5), 156.7 (C-2), 165.1, 165.3, 166.2 (C=O), 176.2 (CHO). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{24}^{79}BrO_9$, $C_{31}H_{24}^{81}BrO_9$; 619.0604, 621.0589 [MH]. Found: m/z 619.0586, 621.0565 $[MH]^+$.

3-Hydroxymethyl-6-(β-D-ribofuranosyl)-1H-pyridazin-4-one (**8**).—To a solution of **5** (29.5 mg, 0.04933 mmol) in DMF (0.5 mL) at 0 °C was added DMF (0.5 mL) containing one drop of anhydrous hydrazine. The mixture was stirred at rt for 24 h, and the reaction mixture was concentrated. The residue was purified by PTLC with 4:1 $CHCl_3$–MeOH as eluent. This afforded 5.5 mg (44%) of **8** as a foam: λ_{max} (MeOH) 270 nm (log ε 3.8); $[\alpha]_D$ −7.26° (c 0.9, MeOH); ^{1}H NMR (CD_3OD): δ 3.73 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'a} = 3.3$ Hz, H-5′a), 3.86 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'b} = 3.3$ Hz, H-5′b), 4.02 (dd, 1 H, $J_{1',2'} = 6.2$, $J_{2',3'} = 5.5$ Hz, H-2′), 4.04–4.07 (m, 1 H, H-4′), 4.12 (dd, 1 H, $J_{3',4'} = 4.1$, $J_{2',3'} = 5.5$ Hz, H-3′), 4.64 (s, 2 H, CH_2), 4.71 (d, 1 H, $J_{1',2'} = 6.2$ Hz, H-1′), 6.52 (s, 1 H, H-5); ^{13}C NMR (CD_3OD): δ 60.8, 62.6 (CH_2), 72.5, 78.4, 81.1, 87.3 (C-1′, 2′, 3′, 4′), 112.5 (C-5), 156.1, 158.5 (C-3, 6), 172.4 (C-4). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{10}H_{15}N_2O_6$; 259.0930 [MH]. Found: m/z 259.0937 $[MH]^+$.

5-Hydroxy-2-(β-D-ribofuranosyl)pyran-4-one (**9**).—To a solution of **5** (39.5 mg, 0.066 mmol) in MeOH (1 mL) was added 28% aq NH_4OH (0.2 mL) at rt for 1 day, and the reaction mixture was concentrated. The residue was purified by PTLC with 4:1 $CHCl_3$–MeOH as eluent. This afforded 8.1 mg (50%) of **9** as a foam; λ_{max} (MeOH) 220 and 271 nm (log ε 3.8 and 3.5); $[\alpha]_D$ −13.1° (c 0.8, MeOH); ^{1}H NMR (CD_3OD): δ 3.66 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'a} = 4.8$ Hz, H-5′a), 3.76 (dd, 1 H, $J_{5'a,5'b} = 12.1$, $J_{4',5'b} = 3.3$ Hz, H-5′b), 3.96–3.99 (m, 1 H, H-4′), 4.03 (dd, 1 H, $J_{2',3'} = J_{3',4'} = 5.1$ Hz, H-3′), 4.14 (dd, 1 H, $J_{1',2'} = J_{2',3'} = 5.1$ Hz, H-2′), 4.57 (d, 1 H, $J_{1',2'} = 5.1$ Hz, H-1′), 6.65 (s, 1 H, H-5), 7.93 (s, 1 H, H-2); ^{13}C NMR (CD_3OD): δ 63.0 (C-5′), 72.7, 76.7, 82.6, 86.3 (C-1′, 2′, 3′, 4′), 111.7 (C-5), 141.3 (C-3), 147.6 (C-2), 168.6 (C-6), 176.7 (C-4). HREIMS Calcd for $C_{10}H_{12}O_7$: 244.0583. Found: m/z 244.0570.

3-Hydroxymethyl-6-(2,3-O-isopropylidene-β-D-ribofuranosyl)-1H-pyridazin-4-one (**10**).—To a solution of deprotected *C*-nucleoside **8** (47.1 mg, 0.1826 mmol) in acetone (5 mL) was added PTSA (10 mg), and the mixture was stirred at rt for 5 h. The reaction mixture was neutralized with satd aq $NaHCO_3$, and the solvent was evaporated. The residue was purified by PTLC with 93:7 $CHCl_3$–MeOH as eluent. This afforded 9.5 mg (18%) of **10** as a foam; ^{1}H NMR (CD_3COCD_3): δ 1.33, 1.55 (each s, each 3 H, CH_3), 3.82 (dd, 1 H, $J_{5'a,5'b} = 11.7$, $J_{4',5'a} = 2.9$ Hz, H-5′a), 3.89 (dd, 1 H, $J_{5'a,5'b} = 11.7$, $J_{4',5'b} = 2.9$ Hz, H-5′b), 4.31 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 2.9$ Hz, H-4′), 4.51 (s, 2 H, CH_2), 4.80 (dd, 1 H, $J_{1',2'} = 4.4$, $J_{2',3'} = 6.0$ Hz, H-2′), 4.88 (d, 1 H, $J_{1',2'} = 4.4$ Hz, H-1′), 4.91 (dd, 1 H, $J_{2',3'} = 6.0$, $J_{3',4'} = 4.4$ Hz, H-3′), 6.29 (s, 1 H, H-5); FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{25}N_2O_6$; 299.1243 [MH]. Found: m/z 299.1254 $[MH]^+$.

5-Hydroxy-2-(2,3-O-isopropylidene-β-D-ribofuranosyl)pyran-4-one (**11**).—This compound was prepared from **9** as described above for **10**; foam, 32%; ^{1}H NMR (CD_3COCD_3): δ 1.33, 1.52 (each s, each 3 H, CH_3), 3.65–3.72 (m, 2 H, H-5′), 4.16–4.19 (m, 1 H, H-4′), 4.70 (d, 1 H, $J_{1',2'} = 3.9$ Hz, H-1′), 4.78 (dd, 1 H, $J_{1',2'} = 3.9$, $J_{2',3'} = 4.4$ Hz, H-2′), 4.82 (dd, 1 H, $J_{2',3'} = 4.4$, $J_{3',4'} = 6.2$ Hz, H-3′), 6.52 (s, 1 H, H-5), 7.99 (s, 1 H, H-2); FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{13}H_{17}O_7$; 285.0974 [MH]. Found: m/z 285.0980 $[MH]^+$.

Acknowledgements

This work was partly supported by the Ministry of Education Science, Sports and Culture of Japan (High-Tech Research Center Project).

References

[1] G.R. Geen, J.M. Evans, A.K. Vong, *Comprehensive Heterocyclic Chemistry II*, Vol. 5, Pergamon, Oxford, 1996, pp. 469–500.
[2] R. Jansen, B. Kunze, V. Wray, H. Reichenbach, E. Jurkiewicz, G. Hunsmann, G. Hofle, *Liebigs Ann. Chem.*, (1991) 707–708.
[3] (a) Y. Hirata, H. Nakata, K. Yamada, K. Okuhara, T. Naito, *Tetrahedron*, 14 (1961) 252–274. (b) Y, Shizuri, K. Uchida, S. Yamamura, *Chem. Lett.*, (1987) 1381–1384.
[4] D. Hudecova, S. Jantova, M. Melnik, M. Uher, *Folia Microbiol.*, 41 (1996) 473–476.
[5] M. Uher, J. Bransova, J. Brtko, D. Hudecova, J. Dobias, and P. Filipcik, Slovakia Patent SK 278075, December 1995.
[6] (a) T. Shono, Y. Matsumura, *Tetrahedron Lett.*, 17 (1976) 1363–1364. (b) H. Takao, Y. Endo, T. Horie, *Heterocycles* 34 (1992) 1803–1812.
[7] I. Maeba, K. Osaka, N. Morisita, K. Fujioka, C. Ito, *J. Chem. Soc., Perkin Trans. 1*, (1991) 939–944.
[8] I. Maeba, T. Takeuchi, T. Iijima, H. Furukawa, *J. Org. Chem.*, 53 (1988) 1401–1405.
[9] H.C. van der Plas, *Ring Transformation of Heterocycles*, Vol. 2-1, Academic Press, New York, 1973, pp. 35–37.
[10] J.-L. Imbach, B.L. Kam, *J. Carbohydr. Nucleosides Nucleotides*, 1 (1974) 271–273.