C-Nucleosides. Part 18.† Stereoselective Annulation of 6-Acetoxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one with Ethylene Glycol to Pyrano-[2,3-*b*]-1,4-dioxine Glycosides

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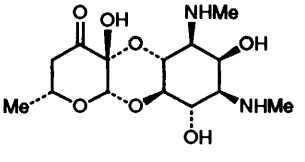
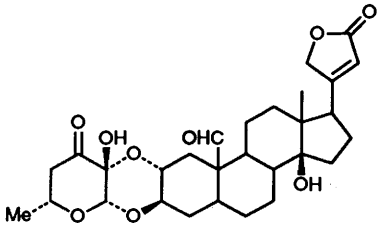
The synthesis of (4a*S*,8a*S*)- and (4a*R*,8a*R*)-4a-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-2,3,8,8a-tetrahydropyrano[2,3-*b*]-1,4-dioxin-7(4a*H*,6*H*)-one **9a** and **9b** is described. Treatment of the 6-acetoxypyranulose glycoside **2** with ethylene glycol in the presence of toluene-*p*-sulfonic acid in acetone for 1 h afforded the (6*S*)- and (6*R*)-6-(2-hydroxyethoxy)pyranulose glycosides **3a** and **3b** in 14 and 40% yield, respectively. The stereochemistry of compounds **3a** and **3b** was assigned as 6*S* and 6*R* by comparison of their CD spectra. When compounds **3a** and **3b** were treated with toluene-*p*-sulfonic acid at room temperature for 5 h, they reacted to give bicyclic compounds **9a** and **9b** in 65% yield, respectively. The stereochemistry of the bicyclic compounds **9a** and **9b** was established by nuclear Overhauser enhancement experiments.

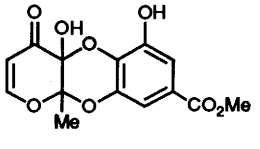
During our efforts to develop a general synthetic method for *C*-nucleosides, we have prepared an extremely useful intermediate, *viz.* 6-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one **1**, from which some novel ring transformations with a variety of amines have been reported.[1] Since our interest in compound **1** continues, we now describe the stereoselective annulation of 6-acetoxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one **2** with ethylene glycol to pyrano[2,3-*b*]-1,4-dioxine glycosides **9a** and **9b**. It is well known that the antibiotic spectinomycin,[2] the cardenolide uscharidin,[3] and the antimicrobial cercidin[4] contain the pyrano[2,3-*b*]-1,4-dioxine skeleton.



Spectinomycin



Uscharidin



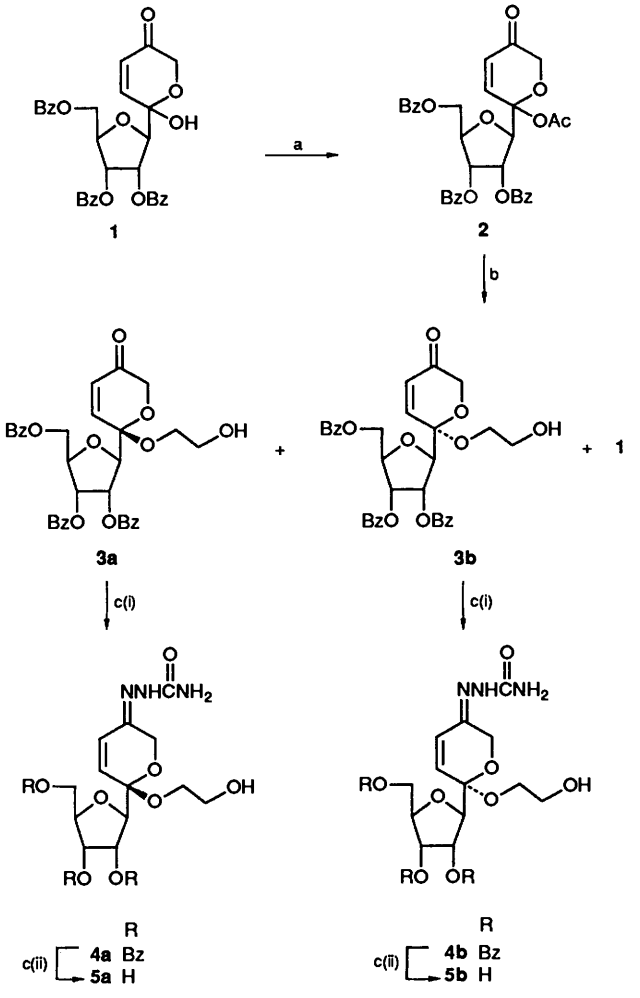
Cercidin

Treatment of hemiacetal **1** with acetic anhydride and pyridine at room temperature afforded acetate **2** in 71% yield after purification by silica gel column chromatography. Compound **2** is an inseparable mixture of diastereoisomers in a 4:1 ratio (^{1}H NMR spectroscopy). Compound **2** was treated with ethylene glycol in the presence of toluene-*p*-sulfonic acid (PTSA) at room temperature for 1 h. The reaction gave three products, deacetylated compound **1** and (6*S*)- and (6*R*)-6-(2-hydroxyethoxy)-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one **3a** and **3b** in 26, 14 and 40% yield, respectively. The similar chemical shifts of the anomeric protons in the NMR spectra of the individual isomers **3a** and **3b** indicated that both had the β configuration and thus were diastereoisomeric only at C-6. Compound **3a** was faster moving on TLC than was its isomer **3b**. In a recent report[5] from our laboratory, we described the stereochemistry at C-6 in 6-methoxy-6-(β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one by using the ratio of derived spiro compounds. We attempted to apply this method to the stereochemistry at C-6 in diastereoisomers **3a** and **3b**. However, debenzoylation of compounds **3a** and **3b** could not be employed because of the sensitivity and ease of decomposition of the enone on contact with alkaline solution. Then, treatment of compound **3a** and **3b** with semicarbazide was found to afford the corresponding semicarbazones **4a** and **4b** in good yield. The removal of the sugar protecting groups in compounds **4a** and **4b** was readily accomplished with methanolic sodium carbonate to afford the compounds **5a** and **5b** (Scheme 1).

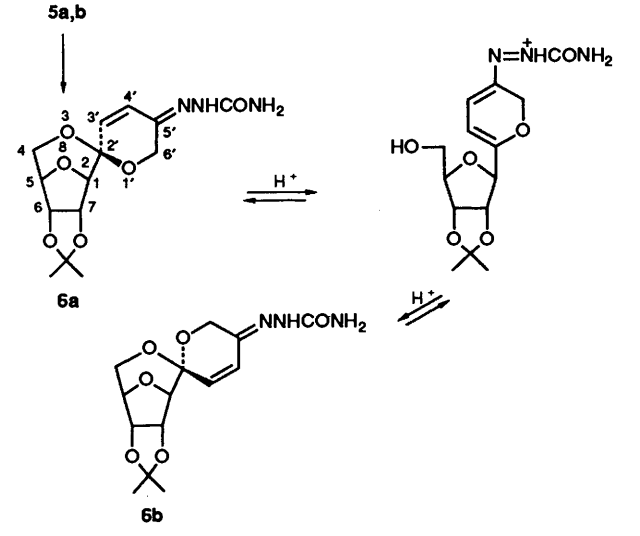
The spiro compounds **6a** and **6b** were synthesized from the tetraols **5a** and **5b** by using PTSA in acetone. The ratio of products **6a** and **6b** was 1:1 by ^{1}H NMR spectroscopy. The configuration of spiro compounds **6a** and **6b** at C-2 was established by ^{1}H NMR spectroscopy. The 3′-H signal of compound **6a** at δ 6.87 occurs at lower field than that of its isomer **6b** (δ 6.10). This chemical-shift difference can be attributed to the deshielding effect of a sugar oxygen atom in the chair conformation (dioxane ring) of the 2*R*-isomer **6a**.[6] Pure compound **6a** epimerized to diastereoisomer **6b** under the same conditions. At the equilibrium point the *R*:*S* ratio was approximately 1:1 (Scheme 2). This result was found to be impractical for the estimation of stereochemistry at C-6 in the precursors **3a** and **3b**. However, the formation of spiro compounds **6a** and **6b** showed that the β-ribofuranoside configuration had been preserved during the reaction sequence.

To determine the stereochemistry at C-6 in compounds **3a** and **3b**, we resorted to CD spectra. For the comparison of CD spectra, we prepared the (6*S*)- and (6*R*)-methoxyhydrazone compounds **8a** and **8b** from (6*S*)- and (6*R*)-6-methoxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one[5] by the method used for the preparation of compounds **5a** and **5b**. The CD spectrum of (6*S*)-compound **8a** shows a positive Cotton effect at 282 nm, whereas a negative Cotton effect at 276 nm is observed in the spectrum of (6*R*)-compound **8b** (Fig. 1). Since the longer-wavelength Cotton effect of the less polar compound is negative, we have assigned this compound the 6*S* configuration (**5b**) while the more polar isomer is considered to be the 6*R* isomer (**5a**).

† Part 17, M. Hayashi, A. Araki and I. Maeba, *Heterocycles*, in the press.

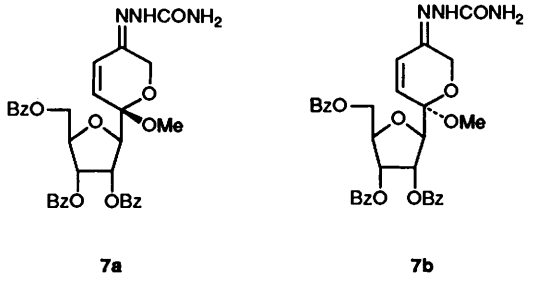


Scheme 1 *Reagents:* (a) Ac_2O, pyridine; (b) acetone, PTSA, ethylene glycol; (c) (i) 1,4-dioxane, semicarbazide, (ii) MeOH, aq. Na_2CO_3



Scheme 2

When compounds **3a** and **3b** were treated with PTSA at room temperature for 5 h, they reacted to give bicyclic compounds **9a** and **9b** by an intermolecular Michael reaction in 65% yield, respectively. The stereochemistry of products **9a** and **9b** was determined by nuclear Overhauser effect (NOE) experiments (Scheme 3). Irradiation of 8a-H (δ 4.40) in compound **9a** gave a 1% enhancement to 1′-H (δ 4.34), 1.6% enhancement to 2′-H (δ 6.16) and a 4% enhancement of the signal at δ 3.56 assignable to 2-H^a. Irradiation of 8a-H (δ 4.21) in compound **9b** gave a 9% enhancement to 1′-H (δ 4.42), 0.5% enhancement to 2′-H (δ 6.13) and a 3.5% enhancement of the signal at δ 3.73 assignable to 2-H^a. These data indicate that the configuration of compounds **9a** and **9b** is 4a*S*,8a*S* and 4a*R*,8a*R*, respectively.



Experimental

Mass spectra were taken on a Hitachi M-80 instrument by direct insertion at 70 eV; fast-atom bombardment (FAB) mass spectra were run on a JMS-HX 110 spectrometer. ^1H and ^{13}C NMR spectra were measured with JNM-GX-270 and GX-400 (JEOL) spectrometers, with tetramethylsilane as internal standard. *J*-Values are given in Hz. Analytical TLC was performed on glass plates coated with a 0.5-mm layer of silica gel GF_{254} (Merck). The compounds were detected by UV light (254 nm).

6-*Acetoxy*-6-(2′,3′,5′-*tri*-O-*benzoyl*-β-D-*ribofuranosyl*)*pyran*-3-(2H,6H)-*one* **2**.—To a solution of compound **1** (300 mg, 0.54 mmol) in acetic anhydride (2 cm^3) was added anhydrous pyridine (3 drops) at room temperature and the mixture was stirred for 12 h. The reaction mixture was poured into ice–water, then neutralized with aq. sodium hydrogen carbonate and extracted with chloroform (3 × 30 cm^3). The extracts were combined, washed with water, dried over magnesium sulfate, and evaporated under reduced pressure to afford a syrup. The residue was chromatographed over a column of silica gel with hexane–ethyl acetate (1:1) as eluent. This afforded the *title compound* **2** (230 mg, 71%) as a foam (Found: C, 65.6; H, 4.9. $C_{33}H_{28}O_{11}$ requires C, 65.99; H, 4.70%); $\delta_H(CDCl_3)$ 2.06 and 2.08 (3 H, each s, Me), 4.02 (0.8 H, d, *J* 17.1, 2-H^a), 4.17 (0.2 H, d, *J* 17.0, 2-H^a), 4.41–4.86 (4.2 H, m, 1′, 4′-H, 5′-H_2 and 2-H^b), 4.96 (0.8 H, d, *J* 2.7, 1′-H), 5.67 (0.8 H, t, *J* 5.4, 3′-H), 5.74 (0.2 H, t, *J* 5.4, 3′-H), 5.85 (0.2 H, dd, *J* 5.4 and 3.0, 2′-H), 6.01 (0.8 H, dd, *J* 5.4 and 2.7, 2′-H), 6.14 (0.8 H, d, *J* 10.4, 4-H), 6.24 (0.2 H, *J* 10.4, 4-H) and 7.26–8.10 (16 H, m, ArH and 5-H); $\delta_C(CDCl_3)$ 21.18 (Me), 62.83, 63.42, 67.75 and 68.33 (CH_2 and C-5′), 71.90, 72.38, 79.27, 79.51, 83.19 and 84.19 (C-1′, -2′, -3′ and -4′), 97.41 and 98.11 (C-6), 127.77–133.44 (Ar-C and C-4), 142.98 and 144.33 (C-5), 165.04, 165.33 and 169.72 (C=O) and 192.77 and 192.94 (C-3).

(6S)- *and* (6R)-6-(2-*Hydroxyethoxy*)-6-(2′,3′,5′-*tri*-O-*benzoyl*-β-D-*ribofuranosyl*)*pyran*-3(2H,6H)-*one* **3a** *and* **3b**.—To a solution of compound **2** (100 mg, 0.17 mmol) and ethylene glycol (1 cm^3) in acetone (1 cm^3) was added PTSA (10 mg), and the resulting solution was stirred at room temperature for 1 h. The reaction mixture was neutralized with aq. sodium hydrogen carbonate and extracted with chloroform (3 × 20 cm^3). The extracts were combined, washed with water, dried over magnesium sulfate, and evaporated under reduced pressure to afford a syrup. The residual syrup was separated by preparative TLC (PLC) with hexane–ethyl acetate (3:2) as developer.

Compound **1** (24.0 mg, 26%); R_f 0.31; syrup; identification was confirmed by comparing the ^1H NMR spectrum with that of the product previously prepared by the reported procedure.[1]

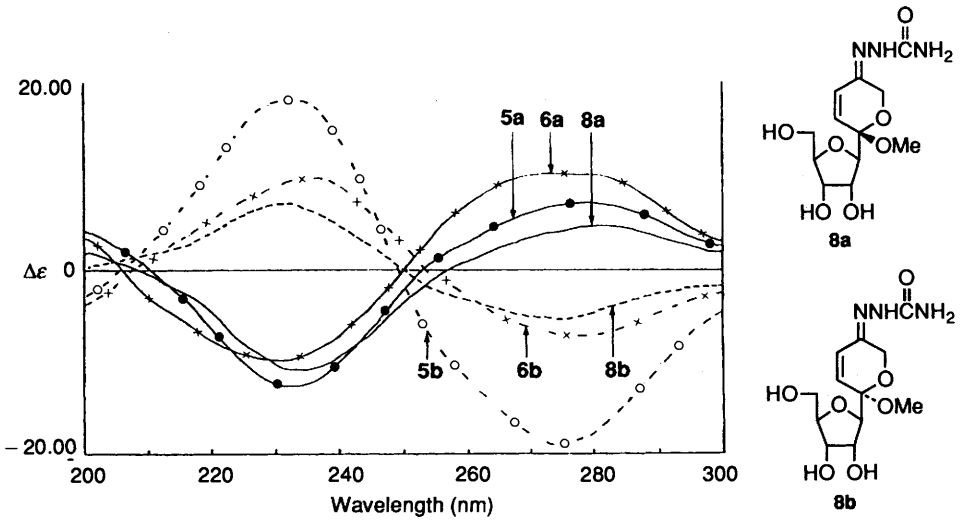
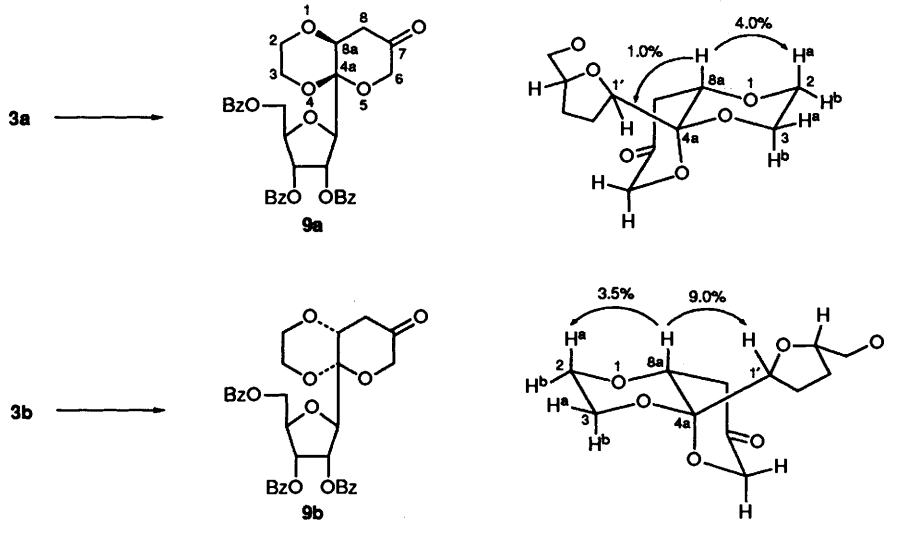


Fig. 1 CD spectra of semicarbazone *c*-nucleosides in methanol



Scheme 3 NOE experiments with diastereoisomers **9a** and **9b**

Compound **3a** (10.3 mg, 14%); R_f 0.26; foam; $\delta_H(CDCl_3)$ 3.65 (4 H, s, CH_2CH_2OH), 4.37 (2 H, s, 2-H_2), 4.53–4.61 (1 H, m, 5′-H^a), 4.57 (1 H, d, *J* 3.7, 1′-H), 4.66 (1 H, m, 4′-H), 4.77 (1 H, dd, *J* 3.4 and 11.5, 5′-H^b), 5.80 (1 H, dd, *J* 5.4 and 8.7, 3′-H), 5.99 (1 H, dd, *J* 3.7 and 5.4, 2′-H), 6.27 (1 H, d, *J* 10.4, 4-H), 7.05 (1 H, d, *J* 10.4, 5-H) and 7.25–8.17 (15 H, m, ArH); δ_C ($CDCl_3$) 61.81, 63.68, 66.45 and 68.71 (CH_2, C-5′ and -2), 72.34, 72.48, 79.64 and 85.32 (C-1′, -2′, -3′ and -4′), 96.38 (C-6), 128.29–133.57 (Ar-C and -4), 146.09 (C-5), 165.36, 165.42 and 166.19 (C=O) and 192.99 (C-5) Found: M^+, 602.1809. $C_{33}H_{30}O_{11}$ requires M, 602.1786).

Compound **3b** (30.0 mg, 40%); R_f 0.17; foam; $\delta_H(CDCl_3)$ 3.71 (4 H, s, CH_2CH_2OH), 4.19 (1 H, d, *J* 11.4, 2-H^a), 4.40 (1 H, d, *J* 11.4, 2-H^b), 4.55 (1 H, m, 5′-H^a), 4.57 (1 H, d, *J* 5.7, 1′-H), 4.63 (1 H, m, 4′-H), 4.77 (1 H, dd, *J* 3.0 and 12.1, 5′-H^b), 5.70 (1 H, t, *J* 5.7, 3′-H), 5.96 (1 H, t, *J* 5.7, 2′-H), 6.18 (1 H, d, *J* 10.4, 4-H), 6.96 (1 H, d, *J* 10.4, 5-H) and 7.31–8.10 (15 H, m, ArH); $\delta_C(CDCl_3)$ 61.68, 63.54, 65.13 and 67.89 (CH_2, C-5′ and -2), 71.25, 72.29, 79.99 and 82.42 (C-1′, -2′, -3′ and -4′), 96.24 (C-6), 128.24–133.45 (Ar-C and C-4), 144.05 (C-5), 165.02, 165.29 and 166.08 (C=O) and 193.11 (C-3) (Found: M^+, 602.1807).

(6R)- *and* (6S)-6-(2-*Hydroxyethoxy*)-6-(2′,3′,5′-*tri*-O-*benzoyl*-β-D-*ribofuranosyl*)*pyran*-3(2H,6H)-*one Semicarbazones* **4a** *and* **4b**.—To a solution of compound **3a** (9 mg, 0.014 mmol) in 1,4-dioxane (0.5 cm^3) was added semicarbazide (2 mg, 0.027 mmol), and the resulting solution was stirred at room temperature for 12 h and then evaporated. The residue was chromatographed over a column of silica gel with chloroform–methanol (97:3) as eluent. This afforded *compound* **4a** (5.4 mg, 61%) as a foam; $\delta_H(CDCl_3)$ 3.63 (4 H, s, CH_2CH_2OH), 4.47 (1 H, d, *J* 3.7, 1′-H), 4.53 (1 H, dd, *J* 5.0 and 11.4, 5′-H^a), 4.63 (1 H, m, 4′-H), 4.66 (2 H, s, 2-H_2), 4.73 (1 H, dd, *J* 5.0 and 11.4, 5′-H^b), 5.75 (1 H, t, *J* 5.4, 3′-H), 5.98 (1 H, dd, *J* 3.7 and 5.4, 2′-H), 6.24 (1 H, d, *J* 10.4, 5-H), 6.41 (1 H, d, *J* 10.4, 4-H) and 7.31–8.02 (15 H, m, ArH) {Found: $[M + Na]^+$ (FAB, *m*-nitrobenzyl alcohol as matrix), 682.1996. $C_{34}H_{33}N_3NaO_{11}$ requires (M + Na), 682.2014}.

In the same manner, *compound* **4b** (26.3 mg, 55%) was obtained as a foam from substrate **3b** (43.7 mg); $\delta_H(CDCl_3)$ 3.69 (4 H, s, CH_2CH_2OH), 4.46 (1 H, d, *J* 5.4, 1′-H), 4.50–4.72 (4 H, m, 2-H_2, 4′-H and 5′-H^a), 4.76 (1 H, dd, *J* 3.4 and 11.8, 5′-H^b), 5.78 (1 H, t, *J* 5.4, 3′-H), 5.95 (1 H, t, *J* 5.4, 2′-H), 6.18 (1 H, d, *J* 10.42, 5-H), 6.39 (1 H, d, *J* 10.4, 4-H) and 7.29–8.09 (15 H, m, ArH) {Found: $[M + Na]^+$ (FAB, *m*-nitrobenzyl alcohol as matrix), 682.2012}.

(6R)- *and* (6S)-6-(2-*Hydroxyethoxy*)-6-(β-D-*ribofuranosyl*)-*pyran*-3(2H,6H)-*one Semicarbazones* **5a** *and* **5b**.—To a solution

of compound **4a** (5.4 mg, 0.008 mmol) in methanol (1.5 cm^3) at 0 °C was added aq. sodium carbonate and the mixture was kept at room temperature for 1 h, then evaporated. The residue was purified by PLC with chloroform–methanol (4:1) as developer. This afforded *compound* **5a** (1.0 mg, 36%) as a foam; CD (MeOH)/nm 233 ($\Delta\varepsilon$ −12.93) and 278 ($\Delta\varepsilon$ +7.41); $\delta_H(CD_3OD)$ 3.57–3.84 (7 H, m, 4′-H, 5′-H_2 and CH_2CH_2OH), 3.93 (1 H, t, *J* 5.4, 3′-H), 4.03 (1 H, d, *J* 2.7, 1′-H), 4.30 (1 H, dd, *J* 2.7 and 5.4, 2′-H), 4.61 (1 H, d, *J* 10.8, 2-H^a), 4.67 (1 H, d, *J* 10.8, 2-H^b), 6.25 (1 H, d, *J* 10.4, 5-H) and 6.37 (1 H, d, *J* 10.4, 4-H) {Found: $[M + Na]^+$ (FAB, glycerol as matrix), 370.1231. $C_{13}H_{21}N_3NaO_8$, requires (M + Na), 370.1227}.

In the same manner, *compound* **5b** (5.0 mg, 36%) was obtained as a foam from substrate **4b** (26.3 mg); CD (MeOH)/nm 234 ($\Delta\varepsilon$ +18.03) and 274 ($\Delta\varepsilon$ −19.35); $\delta_H(CD_3OD)$ 3.57–3.87 (7 H, m, 4′-H, 5′-H_2, and CH_2CH_2OH), 3.92 (1 H, t, *J* 7.1, 3′-H), 4.02 (1 H, dd, *J* 3.7 and 7.1, 2′-H), 4.10 (1 H, d, *J* 3.7, 1′-H), 4.55 (1 H, d, *J* 15.8, 2-H^a), 4.58 (1 H, d, *J* 15.8, 2-H^b), 6.26 (1 H, d, *J* 10.4, 5-H) and 6.43 (1 H, d, *J* 10.4, 4-H) {Found: $[M + Na]^+$ (FAB, glycerol as matrix), 370.1235}.

(1R,2R,5R,6R,7R)- *and* (1R,2S,5R,6R,7R)-6,7-(*Isopropylidenedioxy*)-3,8-*dioxabicyclo*[3.2.1]*octane*-2-*spiro*-2′-*pyran*-5′(2′H,6′H)-*one Semicarbazones* **6a** *and* **6b**.—To a solution of compound **5b** (10 mg, 0.029 mmol) in acetone (0.5 cm^3) was added PTSA (3 mg), and the resulting solution was stirred at room temperature for 1 h. The reaction mixture was neutralized with aq. sodium hydrogen carbonate and evaporated under reduced pressure. TLC [chloroform–methanol (97:3)] showed that the syrup contained two major compounds (R_f 0.30 and 0.24). The ratio of products **6a**:**6b** was 1:1 by ^1H NMR spectroscopy. The mixture was separated by PLC with chloroform–methanol (97:3) as developer, to afford the spiro compounds **6a** (3.4 mg, 36%) and **6b** (3.5 mg, 36%).

Compound **6a**: needles; m.p. 235–236 °C; CD (MeOH)/nm 230 ($\Delta\varepsilon$ −10.20) and 277 ($\Delta\varepsilon$ +9.96); R_f 0.30; $\delta_H(CDCl_3)$ 1.36 and 1.50 (6 H, each s, Me), 3.60 (1 H, d, *J* 11.8 Hz, 4-H^b), 3.82 (1 H, dd, *J* 1.7 and 11.8, 4-H^a), 3.95 (1 H, s, 1-H), 4.21 (1 H, d, *J* 1.7, 5-H), 4.58 (1 H, d, *J* 16.1, 6′-H^a), 4.71 (1 H, d, *J* 16.1, 6′-H^b), 4.79 (1 H, d, *J* 5.7, 6-H), 5.10 (1 H, d, *J* 5.7, 7-H), 6.36 (1 H, d, *J* 10.4, 4′-H) and 6.87 (1 H, d, *J* 10.4, 3′-H) (Found: M^+, 325.1300 $C_{14}H_{19}N_3O_6$ requires M, 325.1272).

Compound **6b**: needles; m.p. 230–232 °C; CD (MeOH)/nm 237 ($\Delta\varepsilon$ +9.36) and 278 ($\Delta\varepsilon$ −7.02); R_f 0.24; $\delta_H(CDCl_3)$ 1.37 and 1.51 (6 H, each s, Me), 3.47 (1 H, d, *J* 11.4, 4-H^b), 4.05 (1 H, s, 1-H), 4.16 (1 H, dd, *J* 1.7 and 11.1, 4-H^a), 4.21 (1 H, d, *J* 1.7, 5-H), 4.44 (1 H, d, *J* 16.1, 6′-H^a), 4.83 (1 H, d, *J* 5.7, 6-H), 4.88 (1 H, d, *J* 16.1, 6-H^b), 4.92 (1 H, d, *J* 5.7, 7-H), 6.10 (1 H, d, *J* 10.4, 3′-H) and 6.38 (1 H, d, *J* 10.4, 4′-H) (Found: M^+, 325.1277).

Epimerization of Compound **6a** *by PTSA*.—To a solution of pure **6a** (13 mg) in acetone was added PTSA (3 mg), and the resulting solution was stirred at room temperature for 5 h. Evaporation of the reaction mixture under reduced pressure gave a syrup, shown by ^1H NMR spectroscopy to consist of epimers **6a** and **6b** in the ratio 1:1. Also, compound **6b** could be epimerized to compound **6a** under the same conditions. The ratio **6a**:**6b** was 1:1 by ^1H NMR spectroscopy.

(6S)- *and* (6R)-6-*Methoxy*-6-(2′,3′,5′-*tri*-O-*benzoyl*-β-D-*ribofuranosyl*)*pyran*-3(2H,6H)-*one Semicarbazones* **7a** *and* **7b**.—Compound **7a** was prepared from (6*S*)-6-methoxy-6-(2′,3′,5′-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one[5] and semicarbazide as described above for compound **4a**.

Compound **7a**: yield 75%; foam; $\delta_H(CDCl_3)$ 3.30 (3 H, s, OMe), 4.46 (2 H, s, 2-H), 4.48 (1 H, m, 5′-H^a), 4.60 (1 H, m, 4′-H), 4.66 (1 H, d, *J* 3.0, 1′-H), 4.75 (1 H, dd, *J* 3.4 and 11.4, 5′-H^b), 5.76 (1 H, dd, *J* 5.4 and 7.1, 3′-H), 5.94 (1 H, dd, *J* 3.0 and 7.1, 2′-H), 6.21 (1 H, d, *J* 10.4, 5-H), 6.38 (1 H, d, *J* 10.4, 4-H) and 7.26–8.09 (15 H, m, ArH) {Found: $[M + Na]^+$ (FAB, *m*-nitrobenzyl alcohol as matrix), 652.1880. $C_{33}H_{31}N_3NaO_{10}$, requires (M + Na), 652.1908}.

Compound **7b** was prepared from (6*R*)-6-methoxy-6-(2′,3′,5′-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one[5] and semicarbazide as described above for compound **4a**.

Compound **7b**: yield 85%; foam; $\delta_H(CDCl_3)$ 3.40 (3 H, s, OMe), 4.43–4.63 (4 H, m, 2-H_2, 4′-H and 5′-H^a), 4.56 (1 H, d, *J* 4.7, 1′-H), 4.70 (1 H, dd, *J* 3.7 and 11.8, 5′-H^b), 5.72 (1 H, t, *J* 6.1, 3′-H), 5.83 (1 H, dd, *J* 4.7 and 6.1, 2′-H), 6.22 (1 H, d, *J* 10.4, 5-H), 6.38 (1 H, d, *J* 10.4, 4-H) and 7.26–8.08 (15 H, m, ArH) {Found: $[M + Na]^+$ (FAB, *m*-nitrobenzyl alcohol as matrix), 652.1960}.

(6S)- *and* (6R)-6-*Methoxy*-6-(β-D-*ribofuranosyl*)*pyran*-3-(2H,6H)-*one Semicarbazones* **8a** *and* **8b**.—Compound **8a** was prepared from **7a** as described above for compound **5a**. *Compound* **8a**: yield 63%; foam; CD (MeOH)/nm 233 ($\Delta\varepsilon$ −11.23) and 282 ($\Delta\varepsilon$ +4.65); $\delta_H(CDCl_3)$, 3.39 (3 H, s, OMe), 3.56 (1 H, dd, *J* 5.4 and 11.7, 5′-H^a), 3.73 (1 H, dd, *J* 2.7 and 11.7, 5′-H^b), 3.84 (2 H, m, 2′- and 4′-H), 4.02 (1 H, d, *J* 3.4, 1′-H), 4.17 (1 H, dd, *J* 3.0 and 5.0, 3′-H), 4.57 (1 H, d, *J* 16.1, 2-H^a), 4.72 (1 H, d, *J* 16.1, 2-H^b), 6.22 (1 H, d, *J* 10.4, 5-H) and 6.48 (1 H, d, *J* 10.4, 4-H) {Found: $[M + Na]^+$ (FAB, glycerol as matrix), 340.1131. $C_{12}H_{19}N_3NaO_7$, requires (M + Na), 340.1121}.

Compound **8b** was prepared from compound **7b** as described above for compound **5a**. *Compound* **8b**: yield 58%; foam; CD (MeOH)/nm 230 ($\Delta\varepsilon$ +7.10) and 276 ($\Delta\varepsilon$ −6.16); $\delta_H(CDCl_3)$ 3.38 (3 H, s, OMe), 3,62 (1 H, dd, *J* 4.0 and 11.7, 5′-H^a), 3.75–3.95 (4 H, m, 2′-, 3′-, 4′-H and 5′-H^b), 4.12 (1 H, d, *J* 3.4, 1′-H), 4.43 (1 H, d, *J* 15.8, 2-H^a), 4.72 (1 H, d, *J* 15.8, 2-H^b), 6.25 (1 H, d, *J* 10.4, 5-H) and 6.36 (1 H, d, *J* 10.4, 4-H) {Found: $[M + Na]^+$ (FAB, glycerol as matrix), 340.1144}.

(4aS,8aS)- *and*(4aR,8aR)-4a-(2′,3′,5′-*Tri*-O-*benzoyl*-β-D-*ribofuranosyl*)-2,3,8,8a-*tetrahydropyrano*[2,3-b]-1,4-*dioxin*-7(4aH,6H)-*one* **9a** *and* **9b**.—To a solution of compound **3a** (10 mg, 0.017 mmol) in acetone (0.5 cm^3) was added PTSA (3 mg), and the resulting solution was stirred at room temperature for 5 h. The reaction mixture was neutralized with aq. sodium hydrogen carbonate and evaporated to give a syrup. The residue was purified by PLC with hexane–ethyl acetate (3:2) as developer.

Compound **9a** (6.7 mg, 65%); foam; $\delta_H(CDCl_3)$ 2.62 (1 H, dd, *J* 3.4 and 17.5, 8-H^a), 2.74 (1 H, dd, *J* 3.4 and 17.5, 8-H^b), 3.42 (1 H, dd, *J* 2.0 and 11.8, 3-H^a), 3.56 (1 H, td, *J* 2.0 and 11.8, 2-H^a), 3.66 (1 H, dd, *J* 3.0 and 11.8, 2-H^b), 4.08 (1 H, td, *J* 3.0 and 11.8, 3-H^b), 4.23 (1 H, d, *J* 17.5, 6-H^a), 4.34 (1 H, d, *J* 2.0, 1′-H), 4.40 (1 H, t, *J* 3.4, 8a-H), 4.48 (1 H, dd, *J* 5.0 and 12.1, 5′-H^a), 4.58 (1 H, m, 4′-H), 4.63 (1 H, d, *J* 17.5, 6-H^b), 4.86 (1 H, dd, *J* 3.4 and 12.1, 5′-H^b), 5.83 (1 H, dd, *J* 5.7 and 8.1, 3′-H), 6.16 (1 H, dd, *J* 2.0 and 5.7, 2′-H) and 7.24–8.21 (15 H, m, ArH); $\delta_C(CDCl_3)$ 41.56 (C-8), 61.24, 63.38 and 65.35 (C-2, -3 and -6), 69.86, 72.02, 72.56, 79.34 and 84.12 (C-1′, -2′, -3′, -4 and -8a), 72.36 (C-5′), 93.55 (C-4a), 128.27–133.32 (Ar-C), 165.07, 165.18 and 166.06 (C=O) and 205.83 (C-7) (Found: M^+, 602.1765. $C_{33}H_{30}O_{11}$ requires M, 602.1786).

In the same manner, compound **9b** (6.0 mg, 65%) was obtained as a foam from substrate **3b** (10 mg); $\delta_H(CDCl_3)$ 2.59 (1 H, dd, *J* 3.4 and 17.1, 8-H^a), 3.28 (1 H, dd, *J* 3.4 and 17.1, 8-H^b), 3.65 (1 H, dd, *J* 2.7 and 11.8, 3-H^a), 3.73 (1 H, td, *J* 2.7 and 11.8, 2-H^a), 3.84 (1 H, dd, *J* 3.4 and 11.8, 2-H^b), 4.08 (1 H, td, *J* 3.4 and 11.8, 3-H^b), 4.12 (1 H, d, *J* 11.4, 6-H^a), 4.21 (1 H, t, *J* 3.4, 8a-H), 4.42 (1 H, t, *J* 3.4, 1′-H), 4.39–4-47 (1 H, m, 5′-H^a), 4.55–4.64 (1 H, m, 4′-H), 4.60 (1 H, d, *J* 11.4, 6-H^b), 4.73 (1 H, dd, *J* 3.4 and 11.8, 5′-H^b), 5.71 (1 H, dd, *J* 5.4 and 7.1, 3′-H), 6.13 (1 H, dd, *J* 3.4

and 5.4, 2′-H) and 7.25–8.11 (15 H, m, ArH); δ_C($CDCl_3$) 41.56 (C-8), 61.11, 63.45 and 65.12 (C-2, -3 and -6), 71.89, 72.20, 73.06, 79.35 and 85.66 (C-1′, -2′, -3′, -4′ and -8a), 72.30 (C-5′), 92.98 (C-4a), 128.26–133.25 (Ar-C), 165.07, 165.16 and 166.03 (C=O) and 206.08 (C-7) (Found: M^+, 602.1811).

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