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Synthesis of a 'direct-linked' C-disaccharide from a pyranulose glycoside

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Abstract

Syntheses of five 'direct linked' C-disaccharides **8a–e** were reported. The ($Et_3SiH/BF_3{\cdot}Et_2O$) reduction of pyranulose glycoside **1** yielded (6*S*)- and (6*R*)-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one (**2a** and **2b**) in a ratio of ca. 2:1 and in 88% combined yield. The absolute stereochemistry of each was determined from its CD spectrum. The reduction of **2a** with $NaBH_4$ in methanol afforded two allylic alcohols **6a** and **6b** in 14 and 73% yield, respectively. The reduction of **2b** with $NaBH_4$ afforded **6c** and **6d** in 30 and 56% yield, respectively. Cis hydroxylation of the double bond in compounds **6a–d** with osmium tetroxide gave **7a–e**. The stereoisomers **7a–e** were separated and their configuration was established by ^1H NMR spectroscopy. Debenzoylation of compounds **7a–e** with aqueous sodium carbonate produced deprotected C-disaccharides **8a–e**.

Keywords: Synthesis; Pyranulose glycoside; C-Disaccharide; Direct-linked C-disaccharide

C-Disaccharides in which two sugar moieties are linked to a methylene group rather than to an interglycosidic oxygen atom have gained considerable attention due to their potential role in the inhibition of glycosidases [1] and as part of a treatment for metabolic diseases such as diabetes [2]. To the best of our knowledge, attention has been drawn in five instances [3] to the synthesis of disaccharides containing no spacer, i.e., compounds wherein the two sugar moieties are joined directly by a carbon–carbon bond. This paper describes the preparation of 'direct linked' C-disaccharides (**8a–e**) from pyranulose glycoside **1**, 6-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one, which can be obtained readily from glycosylfuran by our previously published procedure [4].

Reduction of **1** with Et_3SiH in the presence of $BF_3{\cdot}Et_2O$ afforded a mixture of diasteroisomeric 6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2*H*,6*H*)-one **2a** and **2b** in a ratio of ca. 2:1 and in 88% combined yield. These compounds were separated by preparative thin-layer chromatography (PTLC). Compounds **2a** and **2b** showed strong nuclear Overhauser enhancements (NOEs) between H-6 and H-2a (Scheme 1). To determine the absolute configuration of the chiral center created at C-6 in compounds **2a** and **2b**, we compared the CD spectra of the corresponding hydrazone compounds **4a** and **4b** with the spiro compounds **5a** and **5b**, whose absolute configurations are reported in our previous paper [5]. We prepared the hydrazone compounds **3a** and **3b** from **2a** and **2b** using

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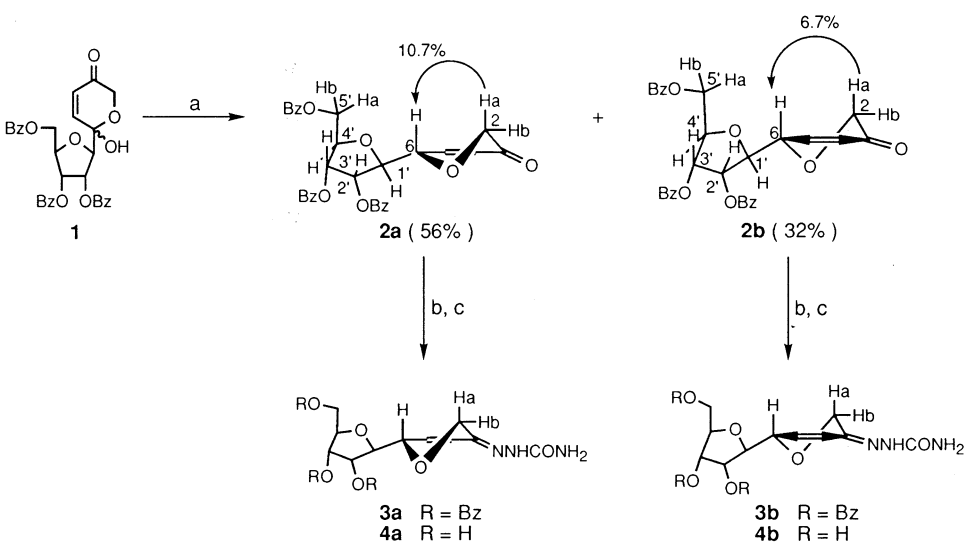
semicarbazide, followed by removal of the sugar protecting groups to give compounds **4a** and **4b** (Scheme 1). The CD spectrum of the (6*S*)-compound **5a** shows a positive Cotton effect at 277 nm, whereas a negative Cotton effect at 278 nm is observed for the (6*R*)-compound **5b** (Fig. 1). Since the longer wavelength Cotton effect of less polar compounds is negative, we have assigned this compound the 6*R* configuration (**4b**), while the more polar isomer is considered to be the 6*S*-isomer (**4a**).

Reduction of **2a** with $NaBH_4$ in methanol afforded two allylic alcohols **6a** and **6b** in 14 and 73% yield, respectively. The ^{1}H NMR spectrum of **6a** showed coupling constants of $J_{2a,3}$ 2.2 Hz and $J_{2b,3}$ 0 Hz, which indicated a pseudoequatorial position for H-3. The configuration at C-3 was established by an NOE experiment on **6a** (Scheme 2). Irradiation of H-6 (δ 4.47) enhanced the signal at δ 3.69 by 3.7%. Irradiation of the H-3 resonance (δ 3.83) in **6a** enhanced the signal at δ 3.69 by 3.8% and the signal at δ 3.98 by 1.8%. Consequently, it was concluded that **6a** has the structure of (3*S*,6*S*)-3-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-2,3-dihydro-6*H*-pyran. In turn, compound **6b**, with a lower R_f, was predominant; its ^{1}H NMR spectrum showed coupling constants of $J_{2a,3}$ 8.4 Hz and $J_{2b,3}$ 5.5 Hz, which pointed to a pseudoaxial position for H-3. Therefore, the structure of (3*R*)-3-hydroxy-(6*S*)-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-2,3-dihydro-6*H*-pyran was ascribed to **6b**. The reduction of **2b** with $NaBH_4$ in methanol afforded two allylic alcohols **6c** and **6d** in 30 and 56% yield, respectively. The ^{1}H NMR spectrum of **6c** showed coupling constants of $J_{2a,3}$ 2.2 Hz and $J_{2b,3}$ 0 Hz, indicating a pseudoequatorial position for H-3. In turn, compound **6d**, with a lower R_f, was predominant; its ^{1}H NMR spectrum showed coupling constants of $J_{2a,3}$ 6.6 Hz and $J_{2b,3}$ 4.4 Hz, which indicated a pseudoaxial position for H-3. The configuration at C-3 was established by an NOE experiment for **6d**. Irradiation of H-2a (δ 3.40) enhanced the signal at δ 4.14 by 9.2%. Irradiation of H-2b (δ 4.08) in **6d** enhanced the signal at δ 4.39 by 1.7%. These data indicate that the configuration of compounds **6c** and **6d** are 3*S* and 3*R*, respectively.

Cis hydroxylation of the double bond in compounds **6a** and **6c** with osmium tetroxide in dry pyridine gave **7a** and **7d** in 78 and 85% yield, respectively. These results show the predictable sensitivity of cis hydroxylation with osmium tetroxide in relation to steric hindrance. With compounds **6a** and **6c**, which have both substituents (C-6-ribose and C-3-OH) on the same side of the ring, the reaction is fully stereoselective. By assuming that the hydroxylating agent attacked from the side with less steric hindrance, we assigned to the products the configurations of 3*R*,4*S*,5*S*,6*S*



Scheme 1. Reagents and conditions: (a) Et_3SiH, $BF_3{\cdot}Et_2O$, 0 °C, 20 s; (b) semicarbazide, dioxane, rt, 1.5 h; (c) concd aq Na_2CO_3, MeOH, 5 h.

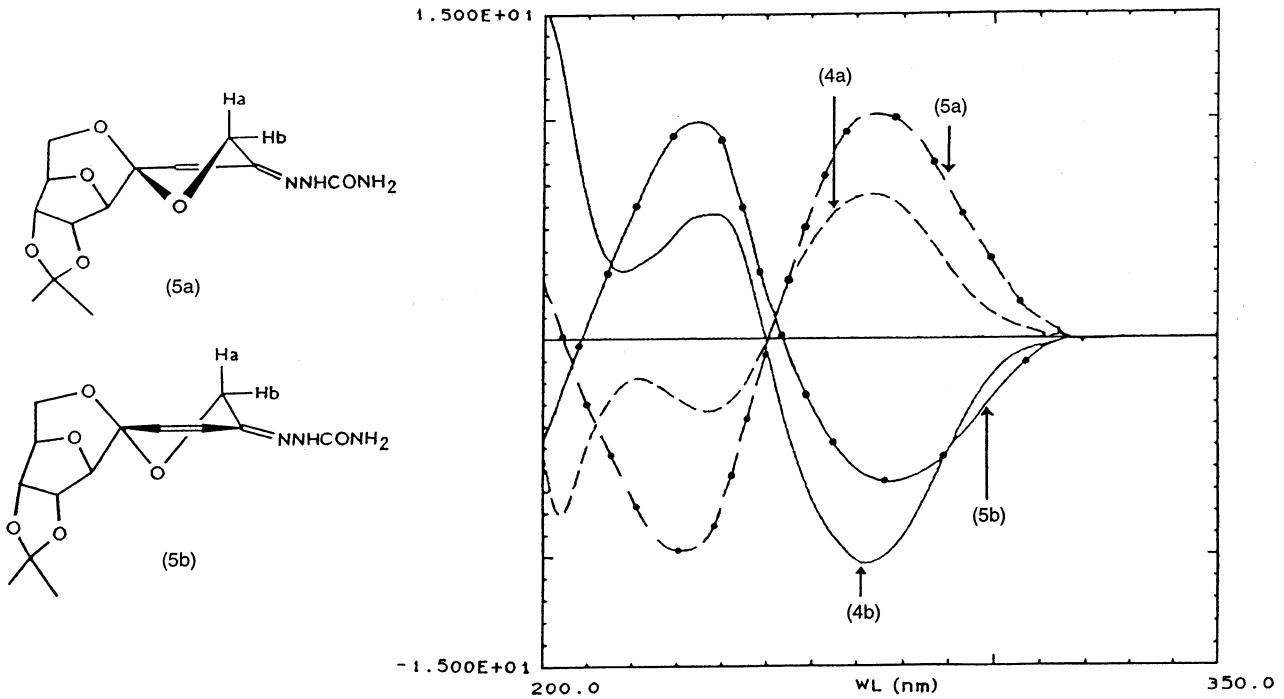


Fig. 1. CD spectra of the semicarbazones of the C-glycosides in MeOH.

(**7a**) and 3*S*,4*R*,5*R*,6*R* (**7d**). Cis hydroxylation of compound **6b** with osmium tetroxide gave mixtures of two compounds **7b** and **7c** in a ratio of ca. 1:5 and in 61% combined yield. Both compounds were isolated by PTLC. Hydroxylation of **6b**, in which the steric hindrance due to substituents at the C-6-ribose and C-3-OH acts in opposite directions, results in a mixture of two products. The configuration at C-4 and C-5 was established by an NOE experiment with **7b**. Irradiation of H-6 (δ 3.46) enhanced the signal at δ 4.09 by 4.0% and the signal at δ 3.36 by 1.9%.

These data indicate that the configurations of compounds **7b** and **7c** are 3*S*,4*R*,5*R*,6*S* and 3*S*,4*S*,5*S*,6*S*, respectively. On the other hand, treatment of **6d** under the same reaction conditions also afforded an 83% yield of **7e** with no trace of the other isomer. The ^{1}H NMR spectrum of **7e** shows a large H-5 and H-6 coupling constant (9.5 Hz), confirming the trans diaxial relationship for this set of hydrogens. Consequently, it was concluded that **7e** has the structure (3*R*,4*R*,5*R*)-3,4,5-trihydroxy-(6*R*)-6-(2,3,5-tri-*O*-benzoy-β-D-ribofuranosyl)-tetrahydropyran. Debenzoylation of compounds (**7a–e**) with aqueous sodium carbonate produced deprotected disaccharides (**8a–e**). Studies to evaluate the biological activity of the disaccharides will be reported elsewhere.

1. Experimental

Fast-atom-bombardment mass spectra (FABMS) were run on a JMS-HX 110 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured with a JNM-A-400 or an A-600 (JEOL) spectrometer, with tetramethylsilane as an internal standard. Optical rotations were measured with a Jasco DIP-370 polarimeter (10-cm cell) at 25 °C. Analytical TLC was performed on glass plates coated with a 0.5-mm layer of Silica Gel GF_{254} (E. Merck). The compounds were detected by UV light (254 nm).

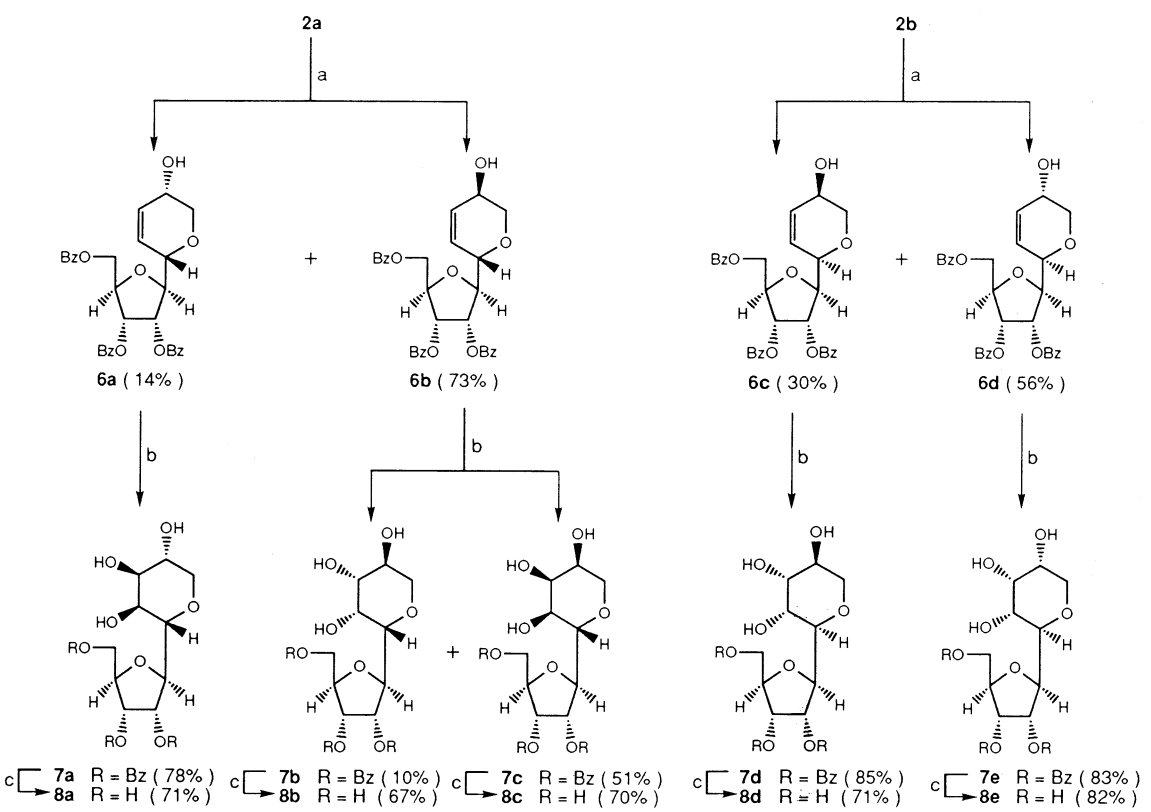
*(6*S*)- and (6*R*)-6-(2,3,5-Tri-*O*-benzoyl-β-*D*-ribofuranosyl)pyran-3(2*H*,6*H*)-one* (**2a**) *and* (**2b**).—To a solution of **1** (1.28 g, 2.30 mmol) and Et_3SiH (0.5 mL) in acetonitrile (20 mL) was added $BF_3{\cdot}Et_2O$ (0.56 g, 3.95 mmol), and the mixture was stirred at 0 °C for 20 s. The reaction mixture was neutralized with saturated $NaHCO_3$ and then extracted with $CHCl_3$ (3 × 10 mL). The extracts were com-

bined, washed with water, dried over $MgSO_4$, and evaporated to dryness. The residual syrup was separated by PTLC with $CHCl_3$ as eluent after three elutions.

Compound **2a**. Yield: 695.9 mg (56%); R_f 0.38; ^{1}H NMR ($CDCl_3$): δ 4.04 (dd, 1 H, $J_{2a,2b}$ 16.5, $J_{2a,4}$ 2.0 Hz, H-2a), 4.21 (d, 1 H, $J_{2a,2b}$ 16.5 Hz, H-2b), 4.49 (dd, 1 H, $J_{5'a,5'b}$ 12.1, $J_{4',5'a}$ 4.1 Hz, H-5′a), 4.53 (m, 2 H, H-6,1′), 4.67 (m, 1 H, H-4′), 4.83 (dd, 1 H, $J_{5'a,5'b}$ 11.7, $J_{4',5'b}$ 3.3 Hz, H-5′b), 5.70 (dd, 1 H, $J_{2',3'}$ 5.5, $J_{3',4'}$ 7.1 Hz, H-3′), 5.75 (dd, 1 H, $J_{1',2'}$ 2.8, $J_{2',3'}$ 5.5 Hz, H-2′), 6.24 (dd, 1 H, $J_{4,5}$ 10.6, $J_{2a,4}$ 2.0 Hz, H-4), 7.16 (dd, 1 H, $J_{4,5}$ 10.6, $J_{5,6}$ 1.8 Hz, H-5), 7.34–8.09 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 63.5 (C-5′), 71.5 (C-2), 72.2, 72.6, 74.1, 79.3, 83.6 (C-6,1′,2′,3′,4′), 128.3–133.5 (Ph, C-4), 146.7 (C-5), 165.3, 165.3, 166.1 (C=O), 193.9 (C-3). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{27}O_9$; [MH] 543.1655. Found: $[MH]^+$ m/z 543.1680.

Compound **2b**. Yield: 397.7 mg (32%); R_f 0.32; mp 129–130 °C; ^{1}H NMR ($CDCl_3$): δ 4.12 (dd, 1 H, $J_{2a,2b}$ 16.3, $J_{2a,4}$ 2.0 Hz, H-2a), 4.22 (d, 1 H, $J_{2a,2b}$ 16.3 Hz, H-2b), 4.49 (dd, 1 H, $J_{5'a,5'b}$ 12.1, $J_{4'a,5'b}$ 3.7 Hz, H-5′a), 4.54 (dd, 1 H, $J_{6,1'} = J_{1',2'}$ 3.7 Hz, H-1′), 4.62 (m, 1 H, H-4′), 4.69 (dd, 1 H, $J_{6,1'}$ 3.7, $J_{5,6}$ 1.8 Hz, H-6), 4.78 (dd, 1 H, $J_{5'a,5'b}$ 12.1, $J_{4',5'b}$ 3.3 Hz, H-5′b), 5.67 (dd, 1 H, $J_{2',3'} = J_{3',4'}$ 6.4 Hz, H-3′), 5.84 (dd, 1 H, $J_{2',3'}$ 6.4, $J_{1',2'}$ 3.7 Hz, H-2′), 6.21 (dd, 1 H, $J_{4,5}$ 10.3, $J_{2a,4}$ 2.4 Hz, H-4), 7.07 (dd, 1 H, $J_{4,5}$ 10.3, $J_{5,6}$ 1.8 Hz, H-5), 7.35–8.06 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 63.0 (C-5′), 71.6 (C-2), 72.1, 72.7, 73.0, 79.4, 83.4 (C-6,1′,2′,3′,4′), 128.4–133.5 (Ph, C-4), 147.2 (C-5), 165.3, 165.5, 166.1 (C=O), 193.7 (C-3). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{27}O_9$ [MH] 543.1655. Found: $[MH]^+$ m/z 543.1631.

*(6S)-6-(2,3,5-Tri-*O*-benzoyl-β-*D*-ribofuranosyl)pyran-3(2H,6H)-one semicarbazone* (**3a**). —To a solution of **2a** (74.0 mg, 0.137 mmol) in dioxane (2 mL) was added semicarbazide hydrochloride (24 mg, 1 mmol), and the mixture was stirred at room temperature (rt) for 1.5 h. Water was added and the mixture was extracted with $CHCl_3$ (3 × 10 mL). The extracts were combined, washed with water, dried over $MgSO_4$, and evaporated to



Scheme 2. Reagents and conditions: (a) $NaBH_4$, 20 °C, 20 min; (b) OsO_4, dry pyridine, rt, 2 h; (c) concd aq Na_2CO_3, MeOH, rt, 5 h.

dryness. The residual syrup was purified by PTLC with 49:1 $CHCl_3$–MeOH as eluent.

Compound **3a**. Yield: 65.2 mg (80%); R_f 0.33; colorless prisms; mp 137–138 °C; ^{1}H NMR ($CDCl_3$): δ 4.19 (d, 1/2 H, $J_{2a,2b}$ 13.7 Hz, H-2a), 4.21 (d, 1/2 H, $J_{2a,2b}$ 15.9 Hz, H-2a), 4.31 (d, 1/2 H, $J_{2a,2b}$ 13.7 Hz, H-2b) 4.43 (m, 3/2 H, H-6,1′), 4.53 (m, 3/2 H, H-6,5′a), 4.64 (m, 1 H, H-4′), 4.76 (m, 1 H, H-5′b), 4.84 (d, 1/2 H, $J_{2a,2b}$ 15.9 Hz, H-2b), 5.72 (m, 2 H, H-2′,3′), 6.27 (dd, 1/2 H, $J_{4,5}$ 10.5, $J_{5,6}$ 1.2 Hz, H-5), 6.31 (dd, 1/2 H, $J_{4,5}$ 10.5, $J_{4,6}$ 1.6 Hz, H-4), 6.44 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{5,6}$ 2.0 Hz, H-5), 6.85 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{4,6}$ 2.4 Hz, H-4), 7.30–8.09 (m, 15 H, Ph), 9.35, 9.60 (each s, each 1/2 H, NH, exchanged with D_2O). Anal. Calcd for $C_{32}H_{29}N_3O_9 \cdot 0.5\ H_2O$ C, 63.15; H, 4.97; N, 6.90. Found: C, 63.09; H, 5.00; N, 6.78.

*(6*R*)-6-(2,3,5-Tri-*O*-benzoyl-β-*D*-ribofuranosyl)pyran-3(2*H*,6*H*)-one semicarbazone* (**3b**). —This compound was prepared from **2b** as described above for **3a**.

Compound **3b**. Yield: 82%; R_f 0.30; colorless prisms; mp 137–138 °C; ^{1}H NMR ($CDCl_3$): δ 4.24 (d, 1/2 H, $J_{2a,2b}$ 13.5 Hz, H-2a), 4.26 (d, 1/2 H, $J_{2a,2b}$ 15.9 Hz, H-2a), 4.36 (d, 1/2 H, $J_{2a,2b}$ 13.5 Hz, H-2b), 4.48 (m, 3 H, H-6,1′,5′a), 4.59 (m, 3/2 H, H-4′,5′b), 4.73 (d, 1/2 H, $J_{2a,2b}$ 15.9 Hz, H-2b), 4.81 (dd, 1/2 H, $J_{5'a,5'b}$ 12.1, $J_{4',5'b}$ 3.5 Hz, H-5′b), 5.70 (m, 1 H, H-3′), 5.83 (m, 1 H, H-2′), 6.23 (dd, 1/2 H, $J_{4,5}$ 10.4, $J_{5,6}$ 1.8 Hz, H-5), 6.29 (dd, 1/2 H, $J_{4,5}$ 10.4, $J_{4,6}$ 2.1 Hz, H-4), 6.38 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{5,6}$ 2.1 Hz, H-5), 6.85 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{4,6}$ 2.4 Hz, H-4), 7.32–3.06 (m, 15 H, Ph), 9.36, 9.55 (each s, each 1/2 H, NH, exchanged with D_2O). Anal. Calcd for $C_{32}H_{29}N_3O_9 \cdot 0.5\ H_2O$: C, 63.15; H, 4.97; N, 6.90. Found: C, 63.35; H, 4.86; N, 6.74.

*(3*S*)- and (3*R*)-3-Hydroxy-(6*S*)-6-(2,3,5-tri-*O*-benzoyl-β-*D*-ribofuranosyl)-2,3-dihydro-6*H*-pyran* (**6a**) *and* (**6b**). —To a solution of **2a** (111.3 mg, 0.21 mmol) in MeOH (4 mL) was slowly added $NaBH_4$ (10.4 mg, 0.27 mmol) at 0 °C for 20 min. Water was added and the mixture was extracted with $CHCl_3$ (3×10 mL). The extracts were combined, washed with water, dried over $MgSO_4$, and evaporated to dryness. The residual syrup was separated by PTLC with 8:1 $CHCl_3$–EtOAc as eluent.

Compound **6a**. Yield: 15.8 mg (14%); R_f 0.18; ^{1}H NMR ($CDCl_3$): δ 2.85 (br d, 1 H, OH, exchanged with D_2O), 3.69 (dd, 1 H, $J_{2a,2b}$ 12.1. $J_{2a,3}$ 2.2 Hz, H-2a), 3.83 (br, 1 H, H-3), 3.98 (d, 1 H, $J_{2a,2b}$ 12.1 Hz, H-2b), 4.39 (dd, 1 H, $J_{1',2'}$ 6.1, $J_{6,1'}$ 2.7 Hz, H-1′), 4.47 (apparent s, 1 H, H-6), 4.58 (dd, 1 H, $J_{5a',5b'}$ 11.7, $J_{4',5a'}$ 3.5 Hz, H-5′a), 4.66 (m, 1 H, H-4′), 4.71 (dd, 1 H, $J_{5a',5b'}$ 11.7, $J_{4',5b'}$ 3.3 Hz, H-5′b), 5.70 (dd, 1 H, $J_{2',3'}$ 6.1, $J_{3',4'}$ 3.8 Hz, H-3′), 5.77 (dd, 1 H, $J_{4,5}$ 10.2, $J_{5,6}$ 1.5 Hz, H-5), 5.95 (apparent t, 1 H, H-4), 6.21 (dd, 1 H, $J_{1',2'} = J_{2',3'}$ 6.1 Hz, H-2′), 7.29–8.20 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 62.1 (C-3), 64.1 (C-5′), 70.8 (C-2), 73.0 (C-6), 69.9, 73.6, 80.0, 83.1 (C-1′,2′,3′,4′), 128.3–133.5 (Ph, C-4,5), 165.5, 165.6, 166.3 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{29}O_9$; [MH] 545.1812. Found: $[MH]^+$ m/z 545.1797.

Compound **6b**. Yield: 81.6 mg (73%); R_f 0.13; ^{1}H NMR ($CDCl_3$): δ 1.67 (br d, 1 H, OH, exchanged with D_2O), 3.33 (dd, 1 H, $J_{2a,2b}$ 10.8, $J_{2a,3}$ 8.4 Hz, H-2a), 4.09 (dd, 1 H, $J_{2a,2b}$ 10.8, $J_{2a,3}$ 5.5 Hz, H-2b), 4.37 (m, 3 H, H-3,6,1′), 4.51 (dd, 1 H, $J_{5a',5b'}$ 11.9, $J_{4',5'a}$ 4.6 Hz, H-5′a), 4.62 (m, 1 H, H-4′), 4.75 (dd, 1 H, $J_{5a',5b'}$ 11.9, $J_{4',5b'}$ 3.7 Hz, H-5b), 5.70 (dd, 1 H, $J_{2',3'}$ 5.6, $J_{3',4'}$ 6.8 Hz, H-3′), 5.75 (dd, 1 H, $J_{1',2'}$ 3.2, $J_{2',3'}$ 5.6 Hz, H-2′), 5.85 (dd, 1 H, $J_{5,6}$ 1.6, $J_{4,5}$ 10.6 Hz, H-5), 5.97 (dd, 1 H, $J_{3,4}$ 1.0, $J_{4,5}$ 10.6 Hz, H-4), 7.03–8.09 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 62.8 (C-3), 63.9 (C-5′), 69.2 (C-2), 72.6 (C-6), 72.4, 73.9, 79.0, 84.3 (C-1′,2′,3′,4′), 127.0 (C-5), 128.3–133.3 (Ph, C-4), 155.2, 165.4, 166.2 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{29}O_9$; [MH] 545.1812. Found: $[MH]^+$ m/z 545.1808.

*(3*R*)- and (3*S*)-3-Hydroxy-(6*R*)-6-(2,3,5-tri-*O*-benzoyl-β-*D*-ribofuranosyl)-2,3-dihydro-6*H*-pyran* (**6c**) *and* (**6d**). —The same procedure was used as for the reduction of **2a** with $NaBH_4$.

Compound **6c**. Yield: 30%; R_f 0.23; ^{1}H NMR ($CDCl_3$): δ 3.16 (br d, 1 H, OH, exchanged with D_2O), 3.63 (dd, 1 H, $J_{2a,2b}$ 12.1, $J_{2a,3}$ 2.2 Hz, H-2a), 3.81 (m, 2 H, H-2b,3), 4.36 (apparent s, 1 H, H-6), 4.41 (dd, 1 H, $J_{1',2'}$ 6.2, $J_{6',1'}$ 3.1 Hz, H-1′), 4.62 (m, 2 H, H-4′,5′a), 4.78 (dd, 1 H, $J_{5'a,5'b}$ 12.0, $J_{4',5'b}$ 3.1 Hz, H-5′b), 5.72 (dd, 1 H, $J_{2',3'}$ 6.2, $J_{3',4'}$ 4.2 Hz, H-3′), 5.86 (dd, 1 H, $J_{1',2'} = J_{2',3'}$ 6.2 Hz, H-2′), 5.90 (dd, 1 H,

$J_{4,5}$ 10.0, $J_{5,6}$ 1.1 Hz, H-5), 6.15 (apparent t, 1 H, H-4), 7.29–8.14 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 62.2 (C-3), 64.1 (C-5′), 71.0 (C-2), 71.5, 73.0, 73.2, 80.6, 82.4 (C-6,1′,2′,3′,4′), 128.4–133.4 (Ph, C-4,5), 165.5, 165.7 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{29}O_9$; [MH] 545.1812. Found: $[MH]^+$ m/z 545.1813.

Compound **6d**. Yield: 56%; R_f 0.15; ^{1}H NMR ($CDCl_3$): δ 1.82 (br d, 1 H, OH, exchanged with D_2O), 3.40 (dd, 1 H, $J_{2a,2b}$ 11.0, $J_{2a,3}$ 6.6 Hz, H-2a), 4.08 (dd, 1 H, $J_{2a,2b}$ 11.0, $J_{2b,3}$ 4.4 Hz, H-2b), 4.14 (apparent s, 1 H, H-6), 4.39 (m, 2 H, H-3,1′), 4.51 (dd, 1 H, $J_{5'a,5'b}$ 11.7, $J_{4',5'a}$ 4.4 Hz, H-5′a), 4.56 (m, 1 H, H-4′), 4.75 (dd, 1 H, $J_{5'a,5'b}$ 11.7, $J_{4',5'b}$ 3.7 Hz H-5′b), 5.71 (dd, 1 H, $J_{2',3'} = J_{3',4'}$ 5.5 Hz, H-3′), 5.80 (dd, 1 H, $J_{1',2'} = J_{2',3'}$ 5.5 Hz, H-2′), 5.85 (dd, 1 H, $J_{4,5}$ 10.3, $J_{5,6}$ 1.6 Hz, H-5), 6.05 (apparent d, 1 H, H-4), 7.31–8.10 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 62.4 (C-3), 63.9 (C-5′), 69.2 (C-2), 72.3, 72.6, 72.6, 79.5, 83.5 (C-6,1′,2′,3′,4′), 127.4 (C-5), 128.4–133.4 (Ph, C-4), 165.4, 165.4, 166.2 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{29}O_9$; [MH] 545.1812. Found: $[MH]^+$ m/z 545.1801.

*(3*R,*4*S,*5*S*)-3,4,5-Trihydroxy-(6*S*)-6-(2,3,5-tri-*O*-benzoyl-β-*D*-ribofuranosyl)tetrahydropyran* (**7a**).—Osmium tetroxide (18 mg, 0.01 mmol) in 0.2 mL of dry pyridine was added to a solution of 34.0 mg (0.063 mmol) of **6a** in 0.5 mL of pyridine at rt. The solution was stirred for 2 h at rt and then treated with a solution of 34 mg of sodium bisulfite in a mixture of 0.2 mL of pyridine and 0.3 mL of water and then stirred for an additional 1 h. The solution was extracted with dichloromethane (3×10 mL). The extracts were combined, washed with water, dried over $MgSO_4$, and evaporated to dryness. The residual syrup was separated by PTLC with 19:1 $CHCl_3$–MeOH as eluent.

Compound **7a**. Yield: 28.1 mg (78%); ^{1}H NMR ($CDCl_3$): δ 1.71, 2.63, 3.35 (each br, each 1 H, OH, exchanged with D_2O), 3.67 (d, 1 H, $J_{2a,2b}$ 12.2 Hz, H-2a), 3.72 (dd, 1 H, $J_{5,6}$ 10.0, $J_{6,1'}$ 4.3 Hz, H-6), 3.83 (apparent s, 1 H, H-3), 3.86 (d, 1 H, $J_{2'a,2'b}$ 12.2 Hz, H-2b), 4.06 (dd, 1 H, $J_{3,4} = J_{4,5}$ 3.2 Hz, H-4), 4.12 (dd, 1 H, $J_{5,6}$ 10.0, $J_{4,5}$ 3.2 Hz, H-5), 4.53 (dd, 1 H, $J_{5'a,5'b}$ 12.2, $J_{4',5'a}$ 4.9 Hz, H-5′a), 4.58 (dd, 1 H, $J_{6,1'}$ 4.3, $J_{1',2'}$ 2.6 Hz, H-1′), 4.64 (m, 1 H, H-4′), 4.78 (dd, 1 H, $J_{5'a,5'b}$ 12.2, $J_{4',5'b}$ 3.2 Hz, H-5′b), 5.64 (dd, 1 H, $J_{3',4'}$ 7.9, $J_{2',3'}$ 5.4 Hz, H-3′), 5.88 (dd, 1 H, $J_{2',3'}$ 5.4, $J_{1',2'}$ 2.6 Hz, H-2′), 7.26–8.09 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 63.6, 67.4 (C-5′, 2), 66.4, 69.6, 70.0, 72.3, 73.2, 75.4, 78.3, 83.9 (C-3,4,5,6,1′,2′,3′,4′), 128.4–133.5 (Ph), 165.6, 166.0, 166.4 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{31}O_{11}$; [MH] 579.1866. Found: $[MH]^+$ m/z 579.1851.

*(3*S,*4*R,*5*R*)- and (3*S,*4*S,*5*S*)-3,4,5-Trihydroxy-(6*S*)-6-(2,3,5-tri-*O*-benzoyl-β-*D*-ribofuranosyl)tetrahydropyran* (**7b**) *and* (**7c**).—The same procedure was used as for the oxidation of **6a** with osmium tetroxide.

Compound **7b**. Yield: 10%; R_f 0.38; ^{1}H NMR ($CDCl_3$): δ 1.68 (br, 3 H, OH, exchanged with D_2O), 3.05 (dd, 1 H, $J_{2a,2b} = J_{2a,3}$ 10.6 Hz, H-2a), 3.36 (dd, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 3.4 Hz, H-4), 3.46 (d, 1 H, $J_{5,6}$ 3.4 Hz, H-6), 3.92 (m, 1 H, H-3), 3.99 (dd, 1 H, $J_{2a,2b}$ 10.6, $J_{2b,3}$ 5.4 Hz, H-2b), 4.09 (dd, 1 H, $J_{4,5} = J_{5,6}$ 3.4 Hz, H-5), 4.47 (m, 2 H, H-1′,5′a), 4.61 (m, 1 H, H-4′), 4.81 (dd, 1 H, $J_{5'a,5'b}$ 12.1, $J_{4',5'b}$ 3.3 Hz, H-5′b), 5.67 (dd, 1 H, $J_{3',4'}$ 8.2, $J_{2',3'}$ 5.1 Hz, H-3′), 5.93 (dd $J_{2',3'}$ 5.1 $J_{1',2'}$ 1.7 Hz, H-2′), 7.35–8.08 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 63.4, 69.8 (C-2,5′), 67.7, 69.0, 72.3, 74.3, 75.2, 77.8, 79.5, 83.1 (C-3,4,5,6,1′,2′,3′,4′), 128.4–133.6 (Ph), 165.4, 166.2, 166.5 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{31}O_{11}$; [MH] 579.1866. Found: $[MH]^+ m/z$, 579.1864.

Compound **7c**. Yield: 51%; R_f 0.32; ^{1}H NMR ($CDCl_3$): 1.78, 2.63, 3.05 (each br, each 1 H, OH, exchanged with D_2O), 3.41 (dd, 1 H, $J_{2a,2b} = J_{2a,3}$ 10.5 Hz, H-2a), 3.70 (m, 2 H, H-2b,6), 3.77 (m, 1 H, H-3), 3.84 (dd, 1 H, $J_{5,6}$ 10.0, $J_{4,5}$ 2.7 Hz, H-5), 4.20 (dd, 1 H, $J_{3,4} = J_{4,5}$ 2.7 Hz, H-4), 4.54 (dd, $J_{5'a,5'b}$ 12.2, $J_{4',5'a}$ 3.2 Hz, H-5′a), 4.58 (dd, 1 H, $J_{6,1'}$ 2.9, $J_{1',2'}$ 2.4 Hz, H-1′), 4.64 (m, 1 H, H-4′), 4.77 (dd, 1 H, $J_{5'a,5'b}$ 12.2, $J_{4',5'b}$ 3.2 Hz, H-5′b), 5.62 (dd, 1 H, $J_{3',4'}$ 8.1, $J_{2',3'}$ 5.4 Hz, H-3′), 5.80 (dd, 1 H, $J_{2',3'}$ 5.4, $J_{1',2'}$ 2.4 Hz, H-2′), 7.33–8.09 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 63.5, 65.7 (C-2,5′), 67.0, 68.8, 70.5, 72.2, 73.1, 74.5, 78.3, 83.9 (C-3,4,5,6,1′,2′,3′,4′), 128.4–133.5 (Ph), 165.5, 166.1, 166.4 (C=O). FABMS (nitrobenzyl al-

cohol as matrix): Calcd for $C_{31}H_{31}O_{11}$; [MH] 579.1866. Found: $[MH]^+$ *m/z* 579.1857.

(3S,4R,5R)-3,4,5-Trihydroxy-(6R)-6-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)tetrahydropyran (**7d**).—The same procedure was used as for the oxidation of **6a** with osmium tetroxide.

Compound **7d**. Yield: 85%; ^{1}H NMR ($CDCl_3$): δ 1.80, 2.80, 3.05 (each br, each 1 H, OH, exchanged with D_2O), 3.48 (d, 1 H, $J_{2a,2b}$ 11.8 Hz, H-2a), 3.65 (dd, 1 H, $J_{5,6}$ 9.8, $J_{6,1'}$ 1.7 Hz, H-6), 3.71 (apparent s, 1 H, H-3), 3.83 (d, 1 H, $J_{2a,2b}$ 11.8 Hz, H-2b), 4.07 (apparent s, 1 H, H-4), 4.12 (d, 1 H, $J_{5,6}$ 9.8 Hz, H-5), 4.62 (m, 1 H, H-4′), 4.67 (dd, 1 H, $J_{1',2'}$ 4.1, $J_{6,1'}$ 1.7 Hz, H-1′), 4.72 (m, 2 H, H-5′), 5.74 (dd, 1 H, $J_{2',3'} = J_{3',4'}$ 5.6 Hz, H-3′), 5.81 (dd, 1 H, $J_{2',3'}$ 5.6, $J_{1',2'}$ 4.1 Hz, H-2′), 7.33–8.09 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 64.0, 67.2 (C-2,5′), 64.2, 69.9, 70.2, 73.1, 73.4, 74.4, 80.0, 80.9 (C-3,4,5,6,1′,2′,3′,4′), 128.4–133.4 (Ph), 165.5, 165.7, 166.7 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{31}O_{11}$: [MH] 579.1866. $[MH]^+$ *m/z* 579.1843.

(3R,4R,5R)-3,4,5-Trihydroxy-(6R)-6-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)tetrahydropyran (**7e**).—The same procedure was used as for the oxidation of **6a** with osmium tetroxide.

Compound **7e**. Yield: 83%; ^{1}H NMR ($CDCl_3$): δ 2.10, 2.52, 2.60 (each br, each 1 H, OH, exchanged with D_2O), 3.42 (m, 2 H, H-2a,3), 3.54 (dd, 1 H, $J_{2a,2b}$ 9.9, $J_{2b,3}$ 4.8 Hz, H-2b), 3.65 (dd, 1 H, $J_{5,6}$ 9.5, $J_{6,1'}$ 1.5 Hz, H-6), 3.76 (dd, 1 H, $J_{5,6}$ 9.5, $J_{4,5}$ 2.6 Hz, H-5), 4.14 (d, 1 H, $J_{4,5}$ 2.6 Hz, H-4), 4.42 (dd, 1 H, $J_{5'a,5'b}$ 12.5, $J_{4',5'a}$ 3.7 Hz, H-5′a), 4.60 (m, 2 H, H-4′,1′), 4.84 (dd, 1 H, $J_{5'a,5'b}$ 12.5, $J_{4',5'b}$ 3.7 Hz, H-5′b), 5.69 (dd, 1 H, $J_{3',4'}$ 7.7, $J_{2',3'}$ 5.5 Hz, H-3′), 5.79 (dd 1 H $J_{2',3'}$ 5.5 $J_{1',2'}$ 2.6 Hz, H-2′), 7.32–8.10 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 63.1, 65.7 (C-2,5′), 66.7, 67.0, 70.8, 72.2, 73.9, 74.3, 78.5, 81.4 (C-3,4,5,6,1′,2′,3′,4′), 128.3–133.4 (Ph), 165.4, 165.8, 166.4 (C=O). FABMS (nitrobenzyl alcohol as matrix): Calcd for $C_{31}H_{31}O_{11}$; [MH] 579.1866. Found: $[MH]^+$ *m/z* 579.1908.

General procedure for the deprotection.—Sufficient methanolic sodium carbonate (0.5 mL, 0.4 mmol) was added to the protected C-nucleoside (0.04 mmol) in MeOH (2 mL). The mixture was kept at rt for 5 h and evaporated under reduced pressure. The residue was purified by PTLC to afford the free C-nucleoside.

(6S)-6-(β-D-Ribofuranosyl)pyran-3-(2H,6H)-one semicarbazone (**4a**). Yield: 89%; CD (MeOH)/nm 237.0 (Δε −3.33), 273.4 (Δε +6.52); ^{1}H NMR (CD_3OD): δ 3.57 (dd, 1 H, $J_{5'a,5'b}$ 12.0, $J_{4',5'b}$ 5.4 Hz, H-5′a), 3.73 (dd, 1 H, $J_{5'a,5'b}$ 12.0, $J_{4',5'b}$ 3.1 Hz, H-5′b), 3.83 (m, 1 H, H-4′), 3.91 (m, 2 H, H-6,2′), 4.06 (dd, 1 H, $J_{2',3'}$ 5.4, $J_{3',4'}$ 3.7 Hz, H-3′), 4.23 (m, 3/2 H, H-2a,1′), 4.36 (d, 1/2 H, $J_{2a,2b}$ 13.9 Hz, H-2b), 4.82 (m, 1 H, H-2a,2b), 6.33 (dd, 1/2 H, $J_{4,5}$ 10.5, $J_{4,6}$ 1.8 Hz, H-4), 6.37 (dd, 1/2 H, $J_{4,5}$ 10.5, $J_{5,6}$ 1.5 Hz, H-5), 6.53 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{5,6}$ 2.0 Hz, H-5), 6.80 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{4,6}$ 2.4 Hz, H-4). FABMS (nitrobenzyl alcohol as matrix): *m/z* 288 $[MH]^+$.

(6R)-6-(β-D-Ribofuranosyl)-pyran-3(2H,6H)-one semicarbazone (**4b**). Yield: 76%; CD (MeOH)/nm 238.2 (Δε +5.66), 271.8 (Δε −1.03); ^{1}H NMR (CD_3OD): δ 3.59 (m, 1 H, H-5′a), 3.69 (dd, 1 H, $J_{5'a,5'b}$ 12.0, $J_{4',5'b}$ 3.4 Hz, H-5′b), 3.81 (dd, 1 H, $J_{2',3'}$ 8.5, $J_{1',2'}$ 5.4 Hz, H-2′), 3.92 (m, 2 H, H-3′,4′), 4.05 (t, 1 H, $J_{6,1'} = J_{1',2'}$ 5.4 Hz, H-1′), 4.27 (d, 1/2 H, $J_{2a,2b}$ 13.8 Hz, H-2a), 4.28 (d, 1/2 H, $J_{2a,2b}$ 15.7 Hz, H-2a), 4.33 (m, 1/2 H, H-6), 4.41 (d, 1/2 H, $J_{2a,2b}$ 13.8 Hz, H-2b), 4.44 (m, 1/2 H, H-6), 4.82 (d, 1/2 H, $J_{2a,2b}$ 15.7 Hz, H-2b), 6.34 (dd, 1/2 H, $J_{4,5}$ 10.5, $J_{5,6}$ 1.7 Hz, H-5), 6.38 (dd, 1/2 H, $J_{4,5}$ 10.5, $J_{4,6}$ 1.7 Hz, H-4), 6.52 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{5,6}$ 2.2 Hz, H-5), 6.82 (dd, 1/2 H, $J_{4,5}$ 10.7, $J_{4,6}$ 2.6 Hz, H-4). FABMS (nitrobenzyl alcohol as matrix): *m/z* 288 $[MH]^+$.

(3R,4S,5S)-3,4,5-Trihydroxy-(6S)-6-(β-D-ribofuranosyl)tetrahydropyran (**8a**). Yield: 71%; $[\alpha]_D$ +3.8° (*c* 0.43, MeOH); ^{1}H NMR (CD_3OD): δ 3.58 (dd, 1 H, $J_{2a,2b}$ 12.0, $J_{2a,3}$ 5.1 Hz, H-2a), 3.66 (m, 3 H, H-4′,5′), 3.73 (dd, 1 H, $J_{2a,2b}$ 12.0, $J_{2b,3}$ 3.1 Hz, H-2b), 3.79–3.92 (m, 5 H, H-3,4,5,6,1′), 4.14 (dd, 1 H, $J_{2',3'}$ 4.8, $J_{3',4'}$ 2.8 Hz, H-3′), 4.27 (dd, 1 H, $J_{1',2'} = J_{2',3'}$ 4.8 Hz, H-2′); ^{13}C NMR (CD_3OD): δ 63.8, 67.9 (C-2,5′), 67.0, 71.4, 71.6, 72.2, 73.1, 76.7, 84.9, 85.7 (C-3,4,5,6,1′,2′,3′,4′). FABMS (triethanolamine as matrix): Calcd for $C_{10}H_{17}O_8$; [M − H] 265.0923. Found: $[M-H]^-$ *m/z* 265.0882.

(3S,4R,5R)-3,4,5-Trihydroxy-(6S)-6-(β-D-ribofuranosyl)tetrahydropyran (**8b**). Yield: 67%; $[\alpha]_D$ +37.2 (*c* 0.45, MeOH); ^{1}H NMR

(CD_3OD): δ 3.10 (t, 1 H, $J_{2a,2b} = J_{2a,3}$ 10.7 Hz, H-2a), 3.28 (m, 1 H, H-6), 3.56 (dd, 1 H, $J_{5'a,5'b}$ 11.7, $J_{4',5'a}$ 5.4 Hz, H-5′a), 3.72 (dd, 1 H, $J_{5'a,5'b}$ 11.7, $J_{4',5'b}$ 2.9 Hz, H-5′b), 3.81 (m, 2 H, H-1′,4′), 3.91–4.03 (m, 4 H, H-2b,3,5,2′), 4.14 (dd, 1 H, $J_{2',3'}$ 5.4, $J_{3',4'}$ 3.9 Hz, H-3′); ^{13}C NMR (CD_3OD): δ 63.4, 71.5 (C-2,5′), 68.3, 70.3, 72.7, 73.8, 76.3, 80.9, 83.6, 84.6 (C-3,4,5,6,1′,2′,3′,4′). FABMS (triethanolamine as matrix): Calcd for $C_{10}H_{17}O_8$; $[M-H]$ 265.0923. Found: $[M-H]^-$ m/z 265.0806.

*(3*S,*4*S,*5*S*)-3,4,5-Trihydroxy-(6*S*)-6-(β*-D-*ribofuranosyl)tetrahydropyran* (**8c**). Yield: 70%; $[\alpha]_D$ +9.1° (*c* 1.11, MeOH); ^1H NMR (CD_3OD): δ 3.50–3.66 (m, 6 H, H-2a,3,5,6,5′), 3.72 (dd, 1 H, $J_{2a,2b}$ 12.0, $J_{2b,3}$ 3.2 Hz, H-2b), 3.83 (m, 1 H, H-4′), 3.89 (dd, 1 H, $J_{6,1'}$ 5.7. $J_{2',1'}$ 4.8 Hz, H-1′), 4.03 (m, 1 H, H-4), 4.11 (dd, 1 H, $J_{2',3'}$ 4.8, $J_{3',4'}$ 2.3 Hz, H-3′), 4.19 (dd, 1 H, $J_{1',2'} = J_{2',3'}$ 4.8 Hz, H-2′); ^{13}C NMR (CD_3OD): δ 63.8, 66.3 (C-2,5′), 68.7, 69.7, 72.2, 72.3, 73.1, 75.7, 85.0, 85.6 (C-3,4,5,6,1′,2′,3′,4′). FABMS (triethanolamine as matrix): Calcd for $C_{10}H_{17}O_8$: $[M-H]$ 265.0923. Found: $[M-H]^-$ m/z 265.0902.

*(3*S,*4*R,*5*R*)-3,4,5-Trihydroxy-(6*R*)-6-(β*-D-*ribofuranosyl)tetrahydropyran* (**8d**). Yield: 71%; $[\alpha]_D$ −22.2° (*c* 0.32, MeOH); ^1H NMR (CD_3OD): δ 3.58 (m, 2 H, H-2a,5′a), 3.67 (m, 2 H, H-4′,5′b), 3.73 (dd, 1 H, $J_{2a,2b}$ 12.2, $J_{2a,3}$ 2.9 Hz, H-2b), 3.83 (m, 2 H, H-5,6), 3.92 (dd, 1 H, $J_{6,1'} = J_{1',2'}$ 3.2 Hz, H-1′), 3.99 (m, 2 H, H-3,4), 4.11 (m, 2 H, H-2′,3′); ^{13}C NMR (CD_3OD): δ 63.0, 68.2 (C-2,5′), 65.8, 71.4, 71.6, 72.5, 72.7, 75.8, 82.6, 85.5 (C-3,4,5,6,1′,2′,3′,4′). FABMS (triethanolamine as matrix): Calcd for $C_{10}H_{17}O_8$; $[M-H]$ 265.0923. Found; $[M-H]^-$ m/z 265.0960.

*(3*R,*4*R,*5*R*)-3,4,5-Trihydroxy-(6*R*)-6-(β*-D-*ribofuranosyl)tetrahydropyran* (**8e**). Yield: 82%; $[\alpha]_D$ −20.5° (*c* 1.00, MeOH); ^1H NMR (CD_3OD): δ 3.52–3.69 (m, 7 H, H-2,5,6,4′,5′), 3.83 (m, 1 H, H-3), 3.94 (dd, 1 H, $J_{6,1'} = J_{1',2'}$ 5.1 Hz, H-1′), 4.09 (m, 3 H, H-4,2′,3′); ^{13}C NMR (CD_3OD): δ 64.0, 66.6 (C-2,5′), 68.6, 68.7, 72.5, 73.1, 73.2, 75.2, 82.6, 85.6 (C-3,4,5,6,1′,2′,3′,4′). FABMS (triethanolamine as matrix): Calcd for $C_{10}H_{17}O_8$; $[M-H]$ 265.0923. Found: $[M-H]^-$ m/z 265.0914.

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