A Synthesis of New Coumarin *C*-Glycosyl Derivatives†

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The use of *C*-glycosyl compounds as chiral intermediates in the synthesis of aryl *C*-glycosides and more complex natural products is an ongoing interest over the years.[1] This has resulted into a number of synthetic strategies for the C−C bond formation that link the aliphatic or aromatic moiety with the sugar substrate. In general, there are two main streams of synthetic sequences. The first route involves stereoselective introduction of an alkyl or aryl moiety (α or *β*) at the anomeric carbon of the sugar substrate, while the second makes use of a preexisting alkyl appendage, at C-1 or C-4 of the furanose/C-5 of the pyranose, for the construction of the required moiety. Although a number of stereocontrolled syntheses of the former type are reported,[2] only stray cases of the latter type are known.[3] With the sugar *β*-keto esters **1** and **2** in hand,[4] we were interested in the second approach. We describe herein a methodology for the synthesis of the hitherto unknown coumarin *C*-glycosyl compounds, wherein the coumarin ring is at C-5 of the pyranose and the anomeric center of the sugar is free. A large number of coumarin derivatives including some with *O*-glycosidic linkages occur naturally.[5] However, the coumarin *C*-glycosides are rare in nature, and only two examples, namely dauroside D[6a] and mulberroside[6b] having spasmolytic and hypotensive activities but with mild toxicity, are known.[7] The first synthesis of coumarin *C*-glycosides was reported by Schmidt and Mahling.[8] However, no report of the *C*-glycosyl compounds with the coumarin ring at C-5 of the pyranose, with a free anomeric center, is known. To our visualization, the *β*-keto ester appendage at C-4 in **1**, with electrophilic and nucleophilic sites, appeared to be suitable for the construction of a coumarin ring at this end. The polyoxygenated carbon framework, with multiple avenues of chirality, would then portray the glycosidic part.

Results and Discussion

The sugar *β*-keto esters **1** and **2** were easily prepared from α-D-*xylo*-pentodialdo-1,4-furanose and α-D-*ribo*-pentodialdo-1,4-furanose derivatives, respectively, by the BF_3·etherate-catalyzed reaction with ethyl diazoacetate as described by us earlier.[4] One-pot Knoevenagel condensation[9] of the sugar *β*-keto esters **1** with 2-hydroxy benzaldehydes **3a**−**e** and **2** with **3a**−**c**, in ethanol using piperidine as a base, led to concomitant cyclization affording the corresponding coumarin sugar derivatives **4a**−**e** and **5a**−**c** in 55−65% yield (Scheme 1).[10] A characteristic feature, as in 3-acyl coumarin,[11] was observed in the ^{1}H NMR spectra of **4** and **5** wherein the chemical

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(10) The benzylidene adduct was isolated in ∼20−25% yield as a mixture of *E* and *Z* isomers. Attempts to improve the yield of **4/5** by making use of KF or weak bases such as Et_3N, isopropylamine, Cs_2CO_3, pyrrolidine, or DBU in different proportions under a variety of temperature and solvent conditions were unsuccessful. The solid-supported reactions using either silica gel or alumina or cadmium iodide also did not improve the yield. (a) Brillon, D.; Sauve, G. *J. Org. Chem.* **1992**, *57*, 1838−1842. (b) Kabalka, G. W.; Pagni, R. M. *Tetrahedron* **1997**, *53*, 7999−8065 and references therein. (c) Prajapati, D.; Sandhu, J. S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 739−740.

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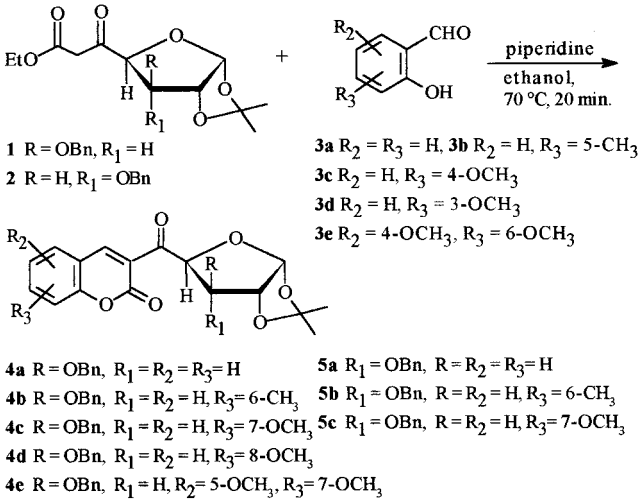
Scheme 1

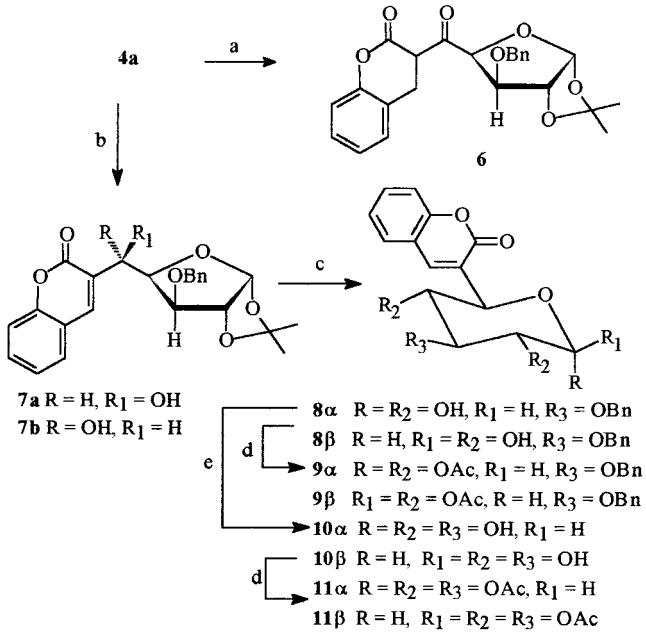


shifts of the olefinic protons in **4a**−**e** (δ ~8.4) and in **5a**−**c** (δ ~8.2) were downfield in contrast to that in the unsubstituted coumarin (δ ~7.7). This fact defined an *S-cis* conformation for the enone moiety leading to the structures **4** and **5** as shown in Scheme 1. In agreement with this, the chemical shifts of the H-4 of the furanose in **4** and **5** were deshielded, resonating at δ ~5.9 and ~5.4, respectively, as compared to the related sugar compounds appearing at δ ~4.3.[3a,4]

Aiming toward coumarin *C*-glycosyl derivatives, we chose **4a** as a model compound. In the next step, the reduction of the C-5 keto group in **4a** with $NaBH_4$ (0.5 equiv) in MeOH or in MeOH−THF,[12] at different temperatures, was attempted. This yielded a mixture of products from which two compounds were isolated. The spectral data revealed the reduction of the coumarin C=C as well as the C-5 keto group. However, when **4a** was reduced with $NaBH_4$ (0.5 equiv) in methoxyethanol at −78 °C the dihydrocoumarin **6** was isolated in 80% yield in which the C=C bond had been chemoselectively reduced, keeping the C-5 keto group intact (Scheme 2). The ^{1}H NMR spectrum of **6** exhibited the ABX pattern for the methine and the methylene protons of the dihydrocoumarin. The methine proton appeared at δ 4.39 as a doublet of doublet with J = 12.5, 6.4 Hz. This indicated the pseudoaxial−axial and pseudoaxial−equatorial relationship of the methine proton with the methylene protons. The preferential 1,4 reduction[13] of the C=C, over the C=O group, could be due to the increased reactivity of the C=C that is substituted at the same end by the C-5 keto group and the lactone carbonyl group. In another reaction, compound **4a** was reduced with $NaBH_4$−$CeCl_3$ in methanol at −78 °C.[14] This afforded carbinols **7a** and **7b** as a diastereomeric mixture in a ratio of 89:11, which on chromatography furnished the desired D-glucodiastereomer **7a** in 78% yield (Scheme 2).[15]

The assignment of the configuration at C-5 in carbinol **7a** was based on a comparison of its ^{1}H NMR with those

Scheme 2[a]



[a] Reaction conditions: (a) $NaBH_4$, methoxyethanol, −78 °C, 30 min; (b) $NaBH_4$−$CeCl_3$, MeOH, −78 °C, 30 min; (c) 3 N HCl/THF, 70 °C, 2 h; (d) Ac_2O, pyridine, DMAP, 25 °C; 20 h; (e) 10% Pd/C, ethanol−acetic acid, H_2, 1 atm, 24 h.

of structurally analogous compounds. It is known that, for a given pair of C-5 epimeric carbinols, derived from α-D-*gluco*-furanose, the chemical shift of H-3 is reported to be diagnostic such that in the L-idoconfiguration the H-3 resonates significantly upfield (δ ~3.6) as compared to that in the D-glucoconfiguration (δ ~4.0).[16] In carbinol **7a**, H-3 appeared considerably downfield at δ 4.17 supporting the D-glucoconfiguration at C-5.[17] The observed good diastereoselectivity in favor of the *erythro*-carbinol **7a** could be explained on the basis of Felkin−Anh's model.[18a] In case of $CeCl_3$-mediated reduction processes, the Ce^{3+} enhances the formation of nonchelation-controlled products.[18b] Therefore, for compound **4a**, two conformations **A** and **B** (Scheme 3) were considered. In conformation **A**, the electron-withdrawing C−O group of furanose, whereas in **B** the largest C-3-benzyloxy substituent, both at Cα to the carbonyl, was placed at a right angle to the C=O group. Although conformation **A** is preferred[18c] over **B**, the attack of the hydride from the opposite face of the C−O group (*Re* face) is disfavored by the C-3-benzyloxy substituent explains why *threo*-

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(14) Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454−5459 and references therein.

(15) The isolation of **7a** was possible due to the higher R_f value of **7a** than **4a**; however, our attempts to isolate **7b** in pure form were unsuccessful.

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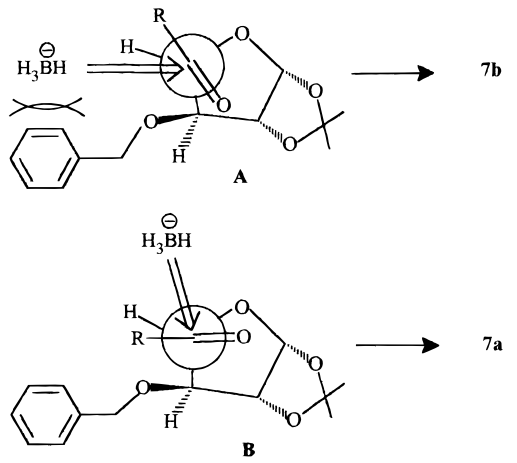
(17) In the ^{1}H NMR spectrum of **7a**, the H-4 of furanose appeared at the usual value of δ 4.5, indicating the absence of the diamagnetic deshielding effect of a lactone carbonyl. Probably, the intramolecular hydrogen bonding with −OH at C-5 holds the coumarin ring as shown in conformational structure **7a**.

(18) (a) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199−2204. Anh, N. T.; Einsenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61. (b) Marcantoni, E.; Cingolani, S.; Bartoli, G.; Bosco, M.; Sambri, L. *J. Org. Chem.* **1998**, *63*, 3624−3630. (c) Conformation **A** has less steric impedance of the substituents than **B**. In addition, the nucleophilic attack in **A** seeks the LUMO of the carbonyl, which is stabilized through the mixing of the π^* C=O orbital with the lowest energy σ^* orbital associated with the electronegative oxygen of the furanose; see: Houk, K. N.; Paddon-Row: M. N.; Rondan, N. G.; Wu, Y.-D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science* **1986**, *231*, 1108−1117. We are thankful to one of the reviewers for his comments.

Scheme 3



carbinol **7b** is obtained as a minor product. However, in the alternate conformation **B**, the hydride addition from the opposite face of the bulky C-3-benzyloxy group (*Si* face) is strongly favored due to the minimized steric nonbonded interactions, leading to the preferential formation of the *erythro*-carbinol **7a** as the major product.

In the next step, the hydrogenolysis of **7a** using H_2/Pd−C was attempted, which resulted in a mixture of products.[19] Alternately, when **7a** was hydrolyzed with 3 N HCl−THF at 70 °C for 2 h, the 3-*O*-benzyl-5-*C*-(3-coumarin)-D-*xylo*-pyranose **8** (α:β = 3:2) was isolated as a pale brown solid in 80% yield. The compound **8** on acetylation and separation of the anomeric mixture gave the triacetate derivatives **9**α and **9**β as pale yellow solids. Hydrogenolysis of **8**, using H_2−Pd/C in EtOH−AcOH at 1 atm for 24 h, afforded an anomeric mixture of 5-C-(3-coumarin)-D-*xylo*-pyranose **10** as a solid in 79% yield. The acetylation of **10** gave the tetraacetate derivative **11**, which was characterized by spectroscopic techniques.

The configurations at the anomeric carbon and at C-5 in **8**−**11** were assigned on the basis of the ^{1}H NMR data of the glycosidic part. The anomers with low $J_{1,2}$ (3.0−4.0 Hz) were assigned the α-configuration, while those with high $J_{1,2}$ (8.0−9.0 Hz) were assigned the β-configuration.[20] This assignment was supported by the greater deshielding of the H-1 in the α-anomers as compared to the β-anomers.[21] In fixing the configuration at C-5, the crucial factor was the coupling constant between H-5 and H-4.[22] The H-5 proton in **8**α−**11**α appeared as a doublet at δ ∼5.0 with $J_{4,5} \approx 9.7$ Hz and in **8**β−**11**β at δ ∼5.14 with $J_{4,5} \approx 10.0$ Hz. The large value of the $J_{4,5}$ was in accordance with the axial−axial relationship of the H-5 and H-4. This confirmed the equatorial orientation of the coumarin ring in **8**−**11**.[23] The presence of two sets of triplets for H-3 and H-4, with large coupling constants, indicated that the substituents at C-2, C-3, and C-4 of the pyranose, in compounds **8**−**11**, were equatorially oriented with a $^4C_1$ conformation for the pyranose ring.

In conclusion, we have developed a convenient approach for the synthesis of the unnatural C-5 coumarin glycosyl compounds by making use of the sugar β-keto ester **1**. The three-step simple reaction sequence of Knoevenagel condensation and lactonization, the hydride reduction of the ketone, and the acid-mediated acetal exchange forms a practical strategy. The freely available anomeric position in these compounds could be used as a handle for further conversion to *O*-/*C*-glycosides, *C*-nucleosides, and disaccharides. Work in this direction is in progress.

Experimental Section

^{1}H NMR (300 MH_Z, 500 MHz) and ^{13}C NMR (75 MHz, 125 MHz) spectra were recorded using $CDCl_3$ as a solvent unless otherwise stated. Chemical shifts are reported in ppm (δ) relative to internal standard Me_4Si. IR spectra of samples were measured as thin films in Nujol mull on KBr plates. Optical rotations were recorded at ambient temperature. Whenever required, the reactions were carried out in oven-dried glassware under dry N_2. On workup, the solvents were evaporated at reduced pressure with a rotary evaporator. Thin-layer chromatography was performed on 0.25 mm precoated silica gel, and flash chromatography was carried out on silica gel (200−400 mesh). The organic solvents such as *n*-hexane, THF, diethyl ether, methylene chloride, petroleum ether (pet. ether, 60−70 °C fraction), ethyl acetate, pyridine, and acetic anhydride were purified and dried before use. Piperidine, anhydrous cerous chloride, DMAP, sodium borohydride, and phosphorus oxychloride were purchased from Aldrich and/or Fluka. Ethyl-3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-heptofuranuronate-5-ulose **1** and ethyl-3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-heptofuranuronate-5-ulose **2** were prepared from D-glucose in 70% and 65% yield, respectively, as reported previously.[4] 4-Methoxy-2-hydroxy benzaldehyde, 5-methyl-2-hydroxy benzaldehyde, 3-methoxy-2-hydroxy benzaldehyde, and 4,6-dimethoxy-2-hydroxy benzaldehyde were prepared from reported procedures.[24]

General Procedure for the Knoevenagel Condensation and Cyclization for Compounds 4a−d and 5a−c. The reaction procedure given for **4a** is representative:

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*xylo*-pentofuran-5-ulose)]-2*H*-1-benzopyran-2-one (4a). To a solution of sugar β-keto ester **1** (1.0 g, 2.75 mmol), piperidine (0.28 g, 3.3 mmol), and molecular sieves (1.0 g) in ethanol (6 mL) at 25 °C was added 2-hydroxy benzaldehyde **3a** (0.40 g, 3.3 mmol) in ethanol (4 mL) over a 10 min period, and the reaction was heated at 70 °C for 20 min in an oil bath. On cooling, the reaction mixture was neutralized with 2 N HCl (2 mL), concentrated, and extracted with Et_2O (5 × 20 mL). The combined extract was washed with water and brine and dried (Na_2SO_4). Removal of the solvent followed by chromatography (elution with pet. ether/EtOAc = 8/2) gave **4a** as a pale yellow solid (0.753 g, 65%): mp 123−124 °C; R_f = 0.56 (hexane/EtOAc = 2/3); $[\alpha]_D = -80.34$ (*c* 0.42, $CHCl_3$); IR (cm^{-1}) 1710, 1690, 1595; ^{1}H NMR (500 MHz) δ 1.36 (s, 3H), 1.55 (s, 3H), 4.25 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 3.7 Hz, 1H), 4.69 (d, J = 4.2 Hz, 1H), 5.89 (d, J = 4.2 Hz, 1H), 6.16 (d, J = 3.7 Hz, 1H), 6.90−7.21 (m, 5H), 7.32 (dd, J = 8.2, 1.5 Hz, 1H), 7.36 (dt, J = 7.6, 1.5 Hz, 1H), 7.60 (dd, J = 7.6, 1.5 Hz, 1H), 7.68 (dt, J = 8.2, 1.5 Hz, 1H), 8.46 (s, 1H); ^{13}C NMR (125 MHz) δ 26.9, 27.5, 72.1, 82.5, 83.0, 85.8, 105.7, 112.8, 116.9, 118.5, 123.0, 125.3, 128.1, 128.3, 128.5, 130.5, 134.8, 136.5, 148.6, 155.3, 158.8, 190.8. Anal. Calcd for $C_{24}H_{22}O_7$: C, 68.24; H, 5.25. Found: C, 68.02; H, 5.35.

(19) Debenzylation in glucofuranose derivatives require high pressure under which C=C was found to be reduced. Starting compound was recovered even after 48 h at 4 bar.

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(21) The chemical shifts of H-1: **8**α/**10**α ≈ δ 5.2, $J_{1,2} \approx 3.3$ Hz; **8**β/**10**β ≈ δ 5.1, $J_{1,2} \approx 9.0$ Hz. For acetates **9**α/**11**α ≈ δ 6.4, $J_{1,2} \approx 3.7$ Hz; **9**β/**11**β ≈ δ 5.8, $J_{1,2} \approx 8.2$ Hz).

(22) Lemieux, R. U.; Howard, J. *Can. J. Chem.* **1963**, *41*, 308−316. The characterization of structures **8**−**11** supported our earlier assignment for the carbinol **7a** with the D-gluco configuration at C-5.

(23) The ^{1}H NMR data for all these compounds and in particular for **9**β thus confirms the D-gluco configuration of **7a**. The H-5 appeared as a doublet with a coupling constant of ∼9.7 Hz, indicating the axial−axial relation with H-4.

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3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*xylo*-pentofuran-5-ulose)]-6-methyl-2*H*-1-benzopyran-2-one (4b). The reaction of **1** (1.0 g, 2.75 mmol) and 2-hydroxy-5-methylbenzaldehyde **3b** (0.449 g, 3.3 mmol) using piperidine (0.28 g, 3.3 mmol) and molecular sieves (1.0 g) in ethanol (10 mL) gave **4b** as a yellow solid (0.743 g, 62%): mp 81−82 °C; R_f = 0.58 (hexane/EtOAc = 2/3); $[\alpha]_D$ = −66.06 (*c* 0.44, $CHCl_3$); IR (cm^{-1}) 1720, 1698, 1616; ^1H NMR (300 MHz) δ 1.37 (s, 3H), 1.56 (s, 3H), 2.45 (s, 3H), 4.26 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.67 (d, *J* = 3.9 Hz, 1H), 4.70 (d, *J* = 4.1 Hz, 1H), 5.90 (d, *J* = 4.1 Hz, 1H), 6.17 (d, *J* = 3.9 Hz, 1H), 6.90−7.05 (m, 5H), 7.23 (d, *J* = 8.9 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 1H), 7.49 (dd, *J* = 8.9, 1.5 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (75 MHz) δ 20.8, 26.8, 27.3, 71.9, 82.3, 82.8, 85.6, 105.5, 112.6, 116.4, 118.1, 122.7, 127.9, 128.1, 128.3, 129.9, 134.9, 135.9, 136.4, 148.5, 153.4, 158.9, 190.7. Anal. Calcd for $C_{25}H_{24}O_7$: C, 68.80; H, 5.54. Found: C, 68.52; H, 5.76.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*xylo*-furan-5-ulose)]-7-methoxy-2*H*-1-benzopyran-2-one (4c). The reaction of **1** (1.0 g, 2.75 mmol) and 2-hydroxy-4-methoxybenzaldehyde **3c** (0.502 g, 3.3 mmol) using piperidine (0.28 g, 3.3 mmol) and molecular sieves (1.0 g) in ethanol (10 mL) gave **4c** as a yellow solid (0.664 g, 62%): mp 142−143 °C; R_f = 0.48 (hexane/EtOAc = 2/3); $[\alpha]_D$ = −103.54 (*c* 0.45, $CHCl_3$); IR (cm^{-1}) 1710, 1680, 1590; ^1H NMR (500 MHz) δ 1.34 (s, 3H), 1.53 (s, 3H), 3.91 (s, 3H), 4.24 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 3.7 Hz, 1H), 4.68 (d, *J* = 4.1 Hz, 1H), 5.87 (d, *J* = 4.1 Hz, 1H), 6.15 (d, *J* = 3.7 Hz, 1H), 6.76 (d, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.92−7.15 (m, 5H), 7.50 (d, *J* = 8.7 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (125 MHz) δ 26.9, 27.4, 56.4, 72.1, 82.4, 83.1, 85.7, 100.5, 105.7, 112.4, 112.7, 114.1, 119.9, 127.9, 128.3, 128.5, 131.9, 136.8, 148.9, 158.8, 159.2, 165.7, 190.5. Anal. Calcd for $C_{25}H_{24}O_8$: C, 66.36; H, 5.35. Found: C, 66.19; H, 5.06.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*xylo*-pentofuran-5-ulose)]-8-methoxy-2*H*-1-benzopyran-2-one (4d). The reaction of **1** (1.0 g, 2.75 mmol) and 2-hydroxy-3-methoxybenzaldehyde **3d** (0.502 g, 3.3 mmol) using piperidine (0.28 g, 3.3 mmol) and molecular sieves (1.0 g) in ethanol (10 mL) gave **4d** as a yellow solid (0.675 g, 63%): mp 105−106 °C; R_f = 0.49 (hexane/EtOAc = 2/3); $[\alpha]_D$ = −101.0 (*c* 0.42, $CHCl_3$); IR (cm^{-1}) 1715, 1700, 1610; ^1H NMR (300 MHz) δ 1.37 (s, 3H), 1.56 (s, 3H), 4.0 (s, 3H), 4.26 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 3.9 Hz, 1H), 4.71 (d, *J* = 4.2 Hz, 1H), 5.92 (d, *J* = 4.2 Hz, 1H), 6.16 (d, *J* = 3.9 Hz, 1H), 6.90−7.10 (m, 5H), 7.14−7.35 (m, 3H), 8.40 (s, 1H); ^{13}C NMR (75 MHz) δ 26.8, 27.3, 56.4, 72.0, 82.6, 82.8, 85.6, 105.5, 106.5, 112.6, 116.1, 118.9, 121.4, 124.9, 127.8, 127.9, 128.2, 128.4, 136.4, 147.0, 148.6, 158.2, 190.7. Anal. Calcd for $C_{25}H_{24}O_8$: C, 66.36; H, 5.35. Found: C, 66.48; H, 5.40.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*xylo*-furan-5-ulose)]-5,7-dimethoxy-2*H*-1-benzopyran-2-one (4e). The reaction of **1** (1.0 g, 2.75 mmol) and 2-hydroxy-4,6-dimethoxybenzaldehyde **3e** (0.601 g, 3.3 mmol) using piperidine (0.28 g, 3.3 mmol) and molecular sieves (1.0 g) in ethanol (10 mL) gave **4e** as a yellow solid (0.821 g, 62%): mp 182−183 °C; R_f = 0.26 (hexane/EtOAc = 1/1); $[\alpha]_D$ = −49.13 (*c* 1.245, $CHCl_3$); IR (cm^{-1}) 1718, 1691, 1588; ^1H NMR (300 MHz) δ 1.37 (s, 3H), 1.56 (s, 3H), 3.92 (s, 3H), 3.94 (s, 3H), 4.27 (d, *J* = 12.08 Hz, 1H), 4.57 (d, *J* = 12.08 Hz, 1H), 4.64 (d, *J* = 3.84 Hz, 1H), 4.69 (d, *J* = 4.03 Hz, 1H), 5.89 (d, *J* = 4.03 Hz, 1H), 6.17 (d, *J* = 3.84 Hz, 1H), 6.29 (d, *J* = 2.01 Hz, 1H), 6.38 (d, *J* = 2.01 Hz, 1H), 7.00−7.05 (m, 5H), 8.85 (s, 1H); ^{13}C NMR (75 MHz) δ 26.84, 27.31, 56.23, 71.90, 82.34, 83.05, 85.48, 92.62, 95.21, 104.51, 105.52, 112.49, 116.85, 127.71, 128.11, 128.28, 136.80, 144.56, 158.52, 159.35, 166.90, 190.12. Anal. Calcd for $C_{26}H_{26}O_9$: C, 64.72; H, 5.43. Found: C, 64.57; H, 5.33.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*ribo*-pentofuran-5-ulose)]-2*H*-1-benzopyran-2-one (5a). The reaction of **2** (1.0 g, 2.75 mmol) and 2-hydroxybenzaldehyde **3a** (0.40 g, 3.3 mmol) using piperidine (0.28 g, 3.3 mmol) and molecular sieves (1.0 g) in ethanol (10 mL) gave **5a** as a pale yellow solid (0.637 g, 55%): mp 87−88 °C; R_f = 0.51 (hexane/EtOAc = 2/3); $[\alpha]_D$ = −37.5 (*c* 0.11, $CHCl_3$); IR (cm^{-1}) 1718, 1695, 1598; ^1H NMR (300 MHz) δ 1.39 (s, 3H), 1.66 (s, 3H), 4.32 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.64 (dd, *J* = 4.4, 3.3 Hz, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 5.42 (d, *J* = 8.8 Hz, 1H), 5.83 (d, *J* = 3.3 Hz, 1H), 7.20−7.42 (m, 6H), 7.60−7.73 (m, 2H), 8.20 (s, 1H); ^{13}C NMR (75 MHz)) δ 26.9, 27.2, 72.5, 78.6, 79.5, 82.4, 105.2, 113.9, 116.8, 118.1, 124.9, 125.4, 127.9, 128.0, 128.3, 129.8, 134.3, 137.3, 146.9, 155.0, 158.5, 196.2. Anal. Calcd for $C_{24}H_{22}O_7$: C, 68.24; H, 5.25. Found: C, 68.12; H, 5.40.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*ribo*-pentofuran-5-ulose)]-6-methyl-2*H*-1-benzopyran-2-one (5b). The reaction of **2** (1.0 g, 2.75 mmol) and 2-hydroxy-5-methylbenzaldehyde **3b** (0.449 g, 3.3 mmol) using piperidine (0.28 g, 3.3 mmol) and molecular sieves (1.0 g) in ethanol (10 mL) gave **5b** as a yellow solid (0.682 g, 57%): mp 95−96 °C; R_f = 0.58 (hexane/EtOAc = 2/3); $[\alpha]_D$ = −6.79 (*c* 0.21, $CHCl_3$); IR (cm^{-1}) 1720, 1690, 1610; ^1H NMR (300 MHz) δ 1.39 (s, 3H), 1.66 (s, 3H), 2.42 (s, 3H), 4.34 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.63 (dd, *J* = 4.0, 3.3 Hz, 1H), 4.75 (d, *J* = 12.1 Hz, 1H), 5.41 (d, *J* = 8.6 Hz, 1H), 5.83 (d, *J* = 3.3 Hz, 1H), 7.22−7.40 (m, 7H), 7.43−7.46 (dd, *J* = 8.6, 2.0 Hz 1H), 8.20 (s, 1H);^{13}C NMR (75 MHz) δ 20.7, 26.9, 27.2, 72.5, 78.6, 79.5, 82.5, 105.2, 113.9, 116.5, 117.9, 126.0, 127.9, 128.1, 128.3, 129.4, 134.8, 135.5, 137.3, 147.1, 153.1, 158.2, 196.4. Anal. Calcd for $C_{25}H_{24}O_7$: C, 68.80; H, 5.54. Found; C, 68.91; H, 5.78.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*ribo*-pentofuran-5-ulose)]-7-methoxy-2*H*-1-benzopyran-2-one (5c). The reaction of **2** (1.0 g, 2.75 mmol) and 2-hydroxy-4-methoxybenzaldehyde **3c** (0.502 g, 3.3 mmol) using piperidine (0.28 g, 3.3 mmol) and molecular sieves (1.0 g) in ethanol (10 mL) gave **5c** as a yellow solid (0.621 g, 58%): mp 99−101 °C; R_f = 0.48 (hexane/EtOAc = 2/3); $[\alpha]_D$ = −19.65 (*c* 0.20, $CHCl_3$); IR (cm^{-1}) 1720, 1690, 1600; ^1H NMR (300 MHz) δ 1.39 (s, 3H), 1.67 (s, 3H), 3.90 (s, 3H), 4.28 (dd, *J* = 8.6, 4.2 Hz, 1H), 4.6 (d, *J* = 12.1 Hz, 1H), 4.65 (dd, *J* = 4.2, 3.5 Hz, 1H), 4.75 (d, *J* = 12.1 Hz, 1H), 5.50 (d, *J* = 8.6 Hz, 1H), 5.84 (d, *J* = 3.5 Hz, 1H), 6.81 (d, *J* = 1.9 Hz, 1H), 6.87−6.91 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.20−7.34 (m, 5H), 7.50 (d, *J* = 8.8 Hz, 1H), 8.24 (s, 1H); ^{13}C NMR (75 MHz) δ 26.9, 27.2, 56.1, 72.5, 78.6, 79.5, 81.9, 84.2, 100.4, 105.2, 111.9, 113.8, 120.9, 127.9, 128.0, 128.3, 131.2, 137.4, 147.8, 157.6, 158.5, 165.3, 195.5. Anal. Calcd for $C_{25}H_{24}O_8$: C, 66.36; H, 5.35. Found: C, 66.28; H, 5.29.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*xylo*-pentofuran-5-ulose)]-3,4-dihydro-2*H*-1-benzopyran-2-one (6). To a stirred solution of **4a** (1.0 g, 2.37 mmol) in methoxymethanol (20 mL) at −78 °C was added $NaBH_4$ (0.044 g, 1.18 mmol) in three portions. The reaction mixture was further stirred at −78 °C for 30 min, quenched with 2 N HCl (2 mL), and concentrated. The residue was extracted with Et_2O (5 × 20 mL), and the combined extract was washed with water and brine and dried (Na_2SO_4). Removal of the solvent afforded a yellow solid which was crystallized (pet. ether/EtOAc = 4/1) to give **6** as a pale yellow solid (0.804 g, 80%): mp 148−150 °C; R_f = 0.42 (hexane/EtOAc = 3/2); $[\alpha]_D$ = −31.3 (*c* 0.02, $CHCl_3$, after 48 h);[25] IR (cm^{-1}) 1755, 1720, 1450; ^1H NMR (300 MHz) δ 1.33 (s, 3H), 1.49 (s, 3H), 2.61 (dd, *J* = 16.1, 6.4 Hz, 1H), 3.31 (dd, *J* = 16.1, 12.5 Hz, 1H), 4.32 (d, *J* = 3.6 Hz, 1H), 4.39 (dd, *J* = 12.5, 6.4 Hz, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.58 (d, *J* = 11.2 Hz, 1H), 4.62 (d, *J* = 3.6 Hz, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 6.07 (d, *J* = 3.6 Hz, 1H), 6.88−7.42 (m, 9H). ^{13}C NMR (75 MHz) 25.2, 26.5, 27.1, 47.3, 72.7, 81.5, 84.5, 85.6, 106.3, 112.8, 116.7, 121.8, 124.5, 124.7, 128.1, 128.3, 128.4, 128.6, 136.6, 151.5, 165.8, 203.8. Anal. Calcd for $C_{24}H_{24}O_7$: C, 67.91; H, 5.70. Found: C, 67.73; H, 5.62. The ^1H and ^{13}C NMR spectra showed additional signals (<5%) corresponding to the enol form and/or other isomer.

3-[5-(1,2-*O*-Isopropylidene-3-*O*-benzyl-α-D-*gluco*-pentofuranose)]-2*H*-1-benzopyran-2-one (7a). To a stirred solution of **4a** (1.0 g, 2.37 mmol) and anhydrous cerous chloride (1.17 g, 4.74 mmol) in methanol (30 mL) at −78 °C was added $NaBH_4$ (0.143 g, 3.79 mmol) in three portions. After being stirred for 30 min at −78 °C, the solution was quenched with 2 N HCl (2 mL) and concentrated. The residue was extracted with ether (5 × 20 mL), and the combined extract was washed with water and brine and dried (Na_2SO_4). Removal of the solvent and chromatography (elution with pet. ether/EtOAc = 9/1) gave **7a** as a pale yellow solid (0.804 g, 80%): mp 75−76 °C; R_f = 0.64 (hexane/EtOAc = 1/1); $[\alpha]_D$ = +5.92 (*c* 0.51, $CHCl_3$); IR (cm^{-1})

(25) Compound **6** in chloroform solution showed keto−enol tautomerism that resulted in a change in the optical rotation value. The ^1H and ^{13}C NMR spectra showed <5% signals corresponding to enol tautomer.

3440−3425, 1730, 1607; ^{1}H NMR (300 MHz) δ 1.30 (s, 3H), 1.48 (s, 3H), 4.03 (d, J = 8.4 Hz, 1H, disappears on D_2O exchange), 4.17 (d, J = 2.9 Hz, 1H), 4.57−4.66 (m, 3H), 4.73 (d, J = 11.5 Hz, 1H), 4.98 (dd, J = 8.4, 8.1 Hz, after D_2O exchange appears as a doublet with J = 8.1 Hz), 5.95 (d, J = 3.6 Hz, 1H), 7.26−7.56 (m, 9H), 7.72 (s, 1H); ^{13}C NMR (75 MHz) δ 26.3, 26.8, 69.5, 72.7, 79.8, 82.3, 82.5, 105.2, 112.1, 116.5, 119.1, 124.6, 127.1, 127.9, 128.1, 128.6, 131.6, 137.2, 140.8, 153.2, 161.5. Anal. Calcd for $C_{24}H_{24}O_7$: C, 67.91; H, 5.70. Found: C, 68.02; H, 5.88.

3-[5-(3-*O*-Benzyl-α,*β*-D-*gluco*-hexopyranose)]-2*H*-1-benzopyran-2-one (8). A solution of **7a** (1.82 g, 4.74 mmol) in THF/3 N HCl (1/1, 20 mL) was heated at 70 °C for 2 h. After being cooled, the reaction mixture was neutralized with saturated Na_2CO_3 solution to pH 7 and concentrated. The residue was extracted with EtOAc (5 × 20 mL), and the combined extract was dried (Na_2SO_4) and evaporated to give an oil that on chromatography (first elution with chloroform and then with $CHCl_3$/MeOH = 99/1) afforded a pale brown solid (1.44 g, 80%): mp 72−74 °C; R_f = 0.34 ($CHCl_3$/MeOH = 9/1); $[\alpha]_D$ = +10.97 (*c* 1.01 g, $CHCl_3$, after 16 h); IR (cm^{-1}) 3600, 2300, 1710, 1607; ^{1}H NMR (300 MHz) δ 1.40−1.80 (broad, 2H, exchanges with D_2O, α- and *β*-anomer), 2.35−2.45 (broad, exchanges with D_2O, α- and *β*-anomer), 3.51−4.90 (m, α- and *β*-anomer), 4.62 (d, J = 9.7 Hz, α-anomer), 4.80 (d, J = 7.8 Hz, *β*-anomer), 4.92 (AB quartet, J = 11.4 Hz, α- and *β*-anomer), 5.11 (d, J = 9.1, *β*-anomer), 5.36 (d, J = 3.1 Hz, α-anomer), 7.20−7.82 (m, α- and *β*-anomer), 7.88 (s, α-anomer), 7.92 (s, *β*-anomer). The ^{1}H NMR showed an anomeric ratio of α/*β* = 3:2. Anal. Calcd for $C_{21}H_{20}O_7 \cdot 2H_2O$: C, 59.99; H, 5.75. Found: C, 59.30; H, 5.60.

3-[5-(1,2,4-Tri-*O*-acetyl-3-*O*-benzyl-α-D-*gluco*-hexopyranoside)]-2*H*-1-benzopyran-2-one (9α) and 3-[5-(1,2,4-Tri-*O*-acetyl-3-*O*-benzyl-*β*-D-*gluco*-hexopyranoside)]-2*H*-1-benzopyran-2-one (9*β*). To a solution of **8** (1.48 g, 3.85 mmol) in pyridine (6.91 mL, 73.22 mmol) cooled to 0 °C were added acetic anhydride (10 mL, 123.33 mmol) dropwise for a period of 30 min and DMAP (5.0 mg, 0.041 mmol). The reaction mixture was allowed to warm to room temperature, stirred for 15 h, and concentrated. Chromatographic purification by eluting first with pet. ether/Et_2O = 2/3 gave **9**α as a pale yellow solid (1.317 g, 67%): mp 220−221 °C; R_f = 0.46 (hexane/EtOAc = 1/1); $[\alpha]_D$ = +45.05 (*c* 0.2, $CHCl_3$); IR (cm^{-1}) 1743, 1713, 1631, 1608; ^{1}H NMR (500 MHz) δ 1.92 (s, 3H), 2.02 (s, 3H), 2.20 (s, 3H), 4.16 (dd, J = 9.8, 9.4 Hz, 1H), 4.69−4.73 (AB quartet, J = 11.8 Hz, 2H), 5.10−5.17 (m, 3H), 6.41 (d, J = 3.7 Hz, 1H), 7.23−7.53 (m, 9H), 7.94 (s, 1H); ^{13}C NMR (125 MHz) δ 20.8, 21.0, 21.2, 67.5, 68.2, 72.1, 74.1, 75.0, 89.5, 89.8, 116.4, 119.0, 125.2, 127.3, 128.1, 128.3, 129.0, 129.4, 133.0, 138.2, 141.9, 153.6, 160.9, 169.2, 170.0. The ^{1}H and ^{13}C NMR spectra showed additional signals (<5%) corresponding to the *β*-anomer. Anal. Calcd for $C_{27}H_{26}O_{10}$; C, 63.52; H, 5.13. Found: C, 63.28, H, 5.03.

Further elution with dichloromethane afforded **9***β* as a white solid (0.45 g, 23%): mp 244−246 °C; R_f = 0.43 (hexane/EtOAc = 1:1); $[\alpha]_D$ = +25.00 (*c* 0.22, $CHCl_3$); IR (cm^{-1}) 1737, 1712, 1632, 1607; ^{1}H NMR (500 MHz) δ 1.91 (s, 3H), 1.99 (s, 3H), 2.10 (s, 3H), 3.93 (dd, J = 9.1, 8.8 Hz, 1H), 4.64 (d, J = 11.8 Hz, 1H), 4.67 (d, J = 11.8 Hz, 1H), 4.89 (d, J = 9.7 Hz, 1H), 5.17 (dd, J = 9.7, 9.1 Hz, 1H), 5.26 (dd, J = 8.8, 8.3 Hz, 1H), 5.78 (d, J = 8.3 Hz, 1H), 7.21−7.34 (m, 7H), 7.49−7.54 (m, 2H), 7.91 (s, 1H); ^{13}C NMR (125 MHz) δ 21.0, 21.0, 21.1, 70.3, 71.1, 72.6, 74.3, 74.9, 80.2, 92.6, 117.2, 119.0, 124.8, 127.6, 128.4, 129.1, 129.4, 131.9, 137.9, 153.7, 160.6, 169.2, 169.5, 170.0. Anal. Calcd for $C_{27}H_{26}O_{10}$: C, 63.52; H, 5.13. Found: C, 63.45, H, 4.80.

3-[5-(α,*β*-D-*gluco*-Hexopyranose)]-2*H*-1-benzopyran-2-one (10). A solution of **8** (0.20 g, 0.521 mmol) and 10% Pd/C (100 mg) in ethanol/AcOH (15 mL, 14.5/0.5) was hydrogenated at 1 atm for 24 h. The solution was filtered on Celite, washed with ethanol, and concentrated to afford a viscous liquid. Chromatographic purification (elution first with $CHCl_3$/MeOH = 9/0.1 and then with $CHCl_3$/MeOH = 9/1) afforded an anomeric mixture of **10** as a pale yellow solid (0.124 g, 79%): mp 148−151 °C; R_f = 0.34 ($CHCl_3$/MeOH = 8/2); $[\alpha]_D$ = +9.5 (*c* 1.22 g, $CHCl_3$, after 18 h); IR (cm^{-1}) 3665−2700, 1715; ^{1}H NMR (300 MHz, CD_3OD) δ 3.41−3.85 (m, 3H, α- and *β*-anomer), 4.49 (d, J = 9.7 Hz, α-anomer), 4.64 (d, J = 7.8 Hz, *β*-anomer), 4.70−4.95 (broad, −OH), 5.01 (d, J = 9.8, *β*-anomer), 5.20 (d, J = 3.6 Hz, α-anomer), 7.30−7.40 (m, α- and *β*-anomer), 7.55−7.75 (m, α- and *β*-anomer), 8.03 and 8.04 (s, α- and *β*-anomer). The ^{1}H NMR showed an anomeric ratio of α/*β* = 3:2. Anal. Calcd for $C_{14}H_{14}O_7 \cdot 2H_2O$: C, 50.90; H, 5.45. Found: C, 51.40; H, 5.58.

3-[5-(1,2,3,4-Tetra-*O*-acetyi-α,*β*-D-*gluco*-hexopyranoside]-2*H*-1-benzopyran-2-one (11). To a solution of **10** (1.48 g, 3.85 mmol) in pyridine (6.91 mL, 73.22 mmol) cooled to 0 °C was added acetic anhydride (10 mL, 123.33 mmol) for a period of 30 min followed by DMAP (5.0 mg, 0.041 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 15 h. The solution was poured into ice−water (10 mL), and the aqueous mixture was extracted with $CHCl_3$ (5 mL). The organic extracts were combined and successively washed with water (10 mL), cold hydrochloric acid 3% (6 × 5 mL), and saturated $NaHCO_3$ (5 mL). The removal of solvent gave a residue. Purification by chromatography (first elution with pet. ether/EtOAc = 4/1) gave **11** as an inseparable anomeric mixture as a white foamy solid (1.31 g, 56%): mp 50−53 °C; R_f = 0.75 (hexane/EtOAc = 1/1); IR (cm^{-1}) 1743, 1713, 1631, 1608; ^{1}H NMR δ 1.95, 1.97, 2.02, 2.03, 2.05, 2.06, 2.12, 2.23 (s), 4.97 (d, J = 9.8 Hz), 5.15−5.34 (m), 5.43 (dd, J = 9.5, 9.3 Hz), 5.63−5.72 (m), 5.87 (d, J = 8.2 Hz, *β*-anomer), 6.42 (d, J = 3.7 Hz, α-anomer), 7.00−7.60 (m), 7.89, 7.91 (s, 1H). The ^{1}H NMR showed an anomeric ratio of α:*β* = 3/2. Anal. Calcd for $C_{22}H_{22}O_{11}$: C, 57.14; H, 4.76. Found: C, 56.32, H, 5.53.

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Supporting Information Available: ^{1}H NMR (300 MHz/500 MHz) spectra of **4a**−**e**, **5a**−**c**, **6**, **7a**, and **8**−**11** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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