C-Glycosidation of Pyridyl Thioglycosides

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Abstract: Silver(I) activation of pyridyl thioglycosides in the presence of carbon nucleophiles yield *C*-glycosides under mild conditions with high stereoselectivity. Pyridyl thioglycosides of suitably protected carbohydrates represent stable precursors to structurally complex *C*-glycosides. Per-*O*-benzyl-(2′-thiopyridyl)-D-glucose (**1**), per-*O*-benzyl-(2′-thiopyridyl)-D-ribose (**2**), and 1-(2′-thiopyridyl)-2,3-*O*-isopropylidene-5-*O*-(*tert*-butyldiphenylsilyl)-D-ribofuranose (**3**) were prepared, and their reactions with a variety of both electron-rich aromatics and silyl enol ethers of carbonyl compounds are reported. The glucose substrate shows a general α selectivity. However, the ribosyl substrates exhibit high α,β selectivities which reveal a large dependence upon the specific nucleophile.

The formation of C–C bonds at the anomeric center of carbohydrates has become an increasingly important area in synthetic organic chemistry. In particular, a wide variety of medicinally important *C*-nucleosides[1] have been discovered as well as several *C*-glycosyl flavonoids[2] and other structurally diverse C-glycosides.[3] Efficient and stereocontrolled methods for C-glycosidation remain an important synthetic objective, not only for the preparation of naturally occurring *C*-glycosides and *C*-nucleosides but also for the homologation of carbohydrates to serve as chiral templates for other synthetic objectives.[4]

As part of an ongoing program in these and related areas, we wish to report a mild method for the C-glycosidation of pyridyl thioglycosides[5] by using silver(I) activation.[6] This methodology nicely complements the silyl-based systems of Kishi,[4a] Kozikowski,[4b] and Townsend[4c] as well as the trichloroacetimidate method of Schmidt.[4d] Our objectives in this area were to stereospecifically couple electronically neutral carbon nucleophiles bearing appropriate functionality and substitution with the pyridyl thioacetals to allow the rapid construction of the target *C*-nucleosides and *C*-glycosides.

Results and Discussion

We have prepared the three pyridyl thioglycosides **1**, **2**, and **3** (Schemes I, II, and III) from the corresponding hemiacetals by reaction with tri-*n*-butylphosphine and 2,2′-dipyridyl disulfide in CH₂Cl₂ or by acid-catalyzed thioacetalization. The glucopyranose derivative **1** is obtained as a single diastereomer (β); on the other hand, the ribose derivatives **2**[7] and **3**[8] are obtained as α/β mixtures (1:1 and 3:1, respectively). The stereochemical outcome of the coupling reactions, however, does not appear to be related to the stereochemistry of the starting thioglycoside indicative of oxonium ion or common ion pairs **4** and **5** as the reactive electrophilic species.
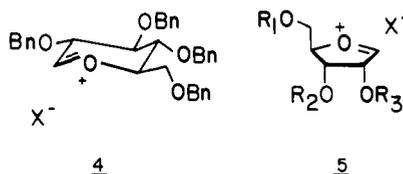
Thus reaction of **1**, **2**, or **3** with silver(I) triflate and several trimethylsilyl enol ethers or electron-rich aromatics at room temperature affords the *C*-glycosides **6–9** (Schemes IV and V), respectively (Table I provides the yields). The sterochemistry of the glucopyranose products at C-1 was determined by examination of the C₁–C₂ spin–spin coupling constants in the ¹H NMR spectrum of the derived per-*O*-acetylated derivatives **12** and **13** (see Scheme VI). In the ribofuranose products, the stereochemistry at C-1 was assigned either by conversion to the 2,3-acetonide derivatives **16** or by correlation to known compounds. Final stereochemical assignments were made by analysis of characteristic ¹³C NMR and ¹H NMR data.[9]

Scheme I

Bn = CH₂C₆H₅
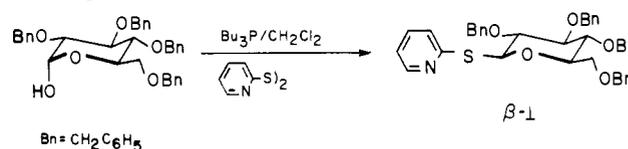
Scheme II

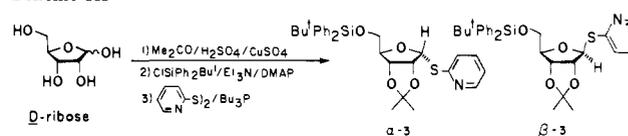**Scheme III**

D-ribose
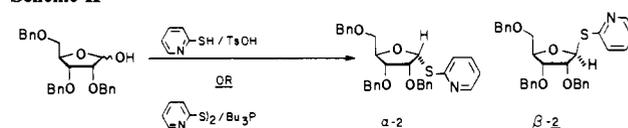
In the case of the glucopyranose substrate **1**, α mode of attack is the general trend with moderately nucleophilic species. The

(1) For reviews, see: (a) Suhadolnik, R. J. "Nucleoside Antibiotics"; Wiley-Interscience: New York, 1970. (b) Daves, G. D.; Cheng, C. C. *Prog. Med. Chem.* **1976**, *13*, 303. (c) Hanessian, S.; Pernet, A. G., *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111.

(2) For examples, see: (a) Eade, R. A.; McDonald, F. J.; Simes, J. J. H. *Aust. J. Chem.* **1975**, *28*, 2011. (b) Eade, R. A.; McDonald, F. J.; Pham, H.-P. *Ibid.* **1978**, *31*, 2699. (c) Eade, R. A.; Pham, H.-P. *Ibid.* **1979**, *32*, 2483.

(3) For examples, see: (a) Markham, K. R.; Woolhouse, A. D. *Phytochemistry* **1983**, *22*, 2827. (b) Hochlowski, J. E.; Faulkner, J. D.; Matsumoto, G. K.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 7413.

(4) (a) Lewis, M. D.; Cha, K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976. (b) Kozikowski, A. P.; Sorgi, K. L. *Tetrahedron Lett.* **1982**, *23*, 2281. (c) Cupps, T. L.; Wise, D. S.; Townsend, L. B. *J. Org. Chem.* **1982**, *47*, 5115. (d) Schmidt, R. R.; Hoffman, M. *Tetrahedron Lett.* **1982**, *23*, 409. (e) Danishefsky, S.; Kerwin, J. F. *J. Org. Chem.* **1982**, *47*, 3803.
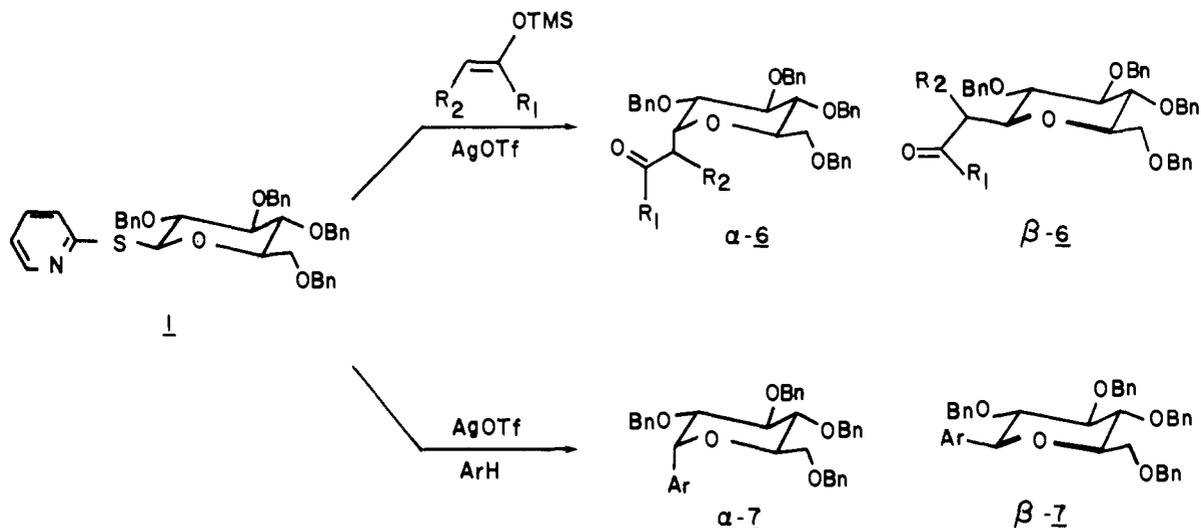
(5) (a) Williams, R. M.; Stewart, A. O. *Tetrahedron Lett.* **1983**, *24*, 2715. For related uses of thioglycosides for O-glycosidation, see: (b) Ferrier, R. J.; Hay, R. W.; Vethavlyasar, A. *Carbohydr. Res.* **1973**, *27*, 55. (c) Mukaiyama, T.; Nakatsuka, T.; Shoda, S. *Chem. Lett.* **1979**, 487. (d) Hannessian, S.; Bacquet, C.; Lehong, N. *Carbohydr. Res.* **1980**, *80*, C17. (e) Woodward, R. B.; Logusch, E.; Nambiar, K. P.; Sakan, K.; Ward, D. E.; Au-Yeung, B. W.; Balaram, P.; Browne, L. J.; Card, P. J.; Chen, C. H.; Chenevert, R. B.; Fliri, A.; Frobel, K.; Gais, H. J.; Garratt, D. G.; Hayakawa, K.; Heggie, W.; Hesson, D. P.; Hoppe, D.; Hoppe, I.; Hyatt, J. A.; Ikeda, D.; Jacobi, P. A.; Kim, K. S.; Kobuke, Y.; Kojima, K.; Krowicki, K.; Lee, V. J.; Leutert, T.; Malchenko, S.; Martens, J.; Matthews, R. S.; Ong, B. S.; Press, J. B.; Rajan Babu, T. V.; Rousseau, G.; Sauter, H. M.; Suzuki, M.; Tatsuta, K.; Tolbert, L. M.; Truesdale, E. A.; Uchida, I.; Ueda, Y.; Uyehara, T.; Vasella, A. T.; Vladuchick, W. C.; Wade, P. A.; Williams, R. M.; Wong, N. C. *J. Am. Chem. Soc.* **1981**, *103*, 3215.

(6) (a) Pyridylthio esters have been extensively used for C–C bond formation furnishing ketones; see: Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95*, 4763. (b) Macrolactonizations via pyridylthio esters have also been extensively utilized; see: Corey, E. J.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1974**, *96*, 5614. See also: Gerlach, H.; Thalman, A. *Helv. Chim. Acta* **1974**, *57*, 2661.

(7) 2,3,5-Tri-*O*-benzyl-D-ribofuranose was prepared according to: Barker, R.; Fletcher, H. G. *J. Org. Chem.* **1961**, *26*, 4605.
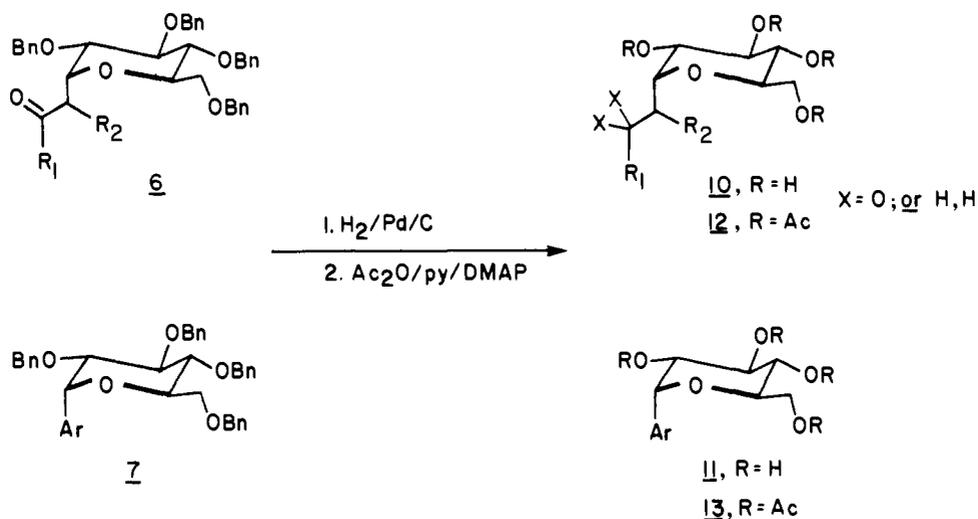
Scheme IV

Scheme V

$$\underline{2}, R_1 = R_2 = R_3 = CH_2Ph$$

$$\underline{3}, R_1 = SiPh_2Bu^+$$
$$R_2 \not{=} R_3 = C(Me)_2$$
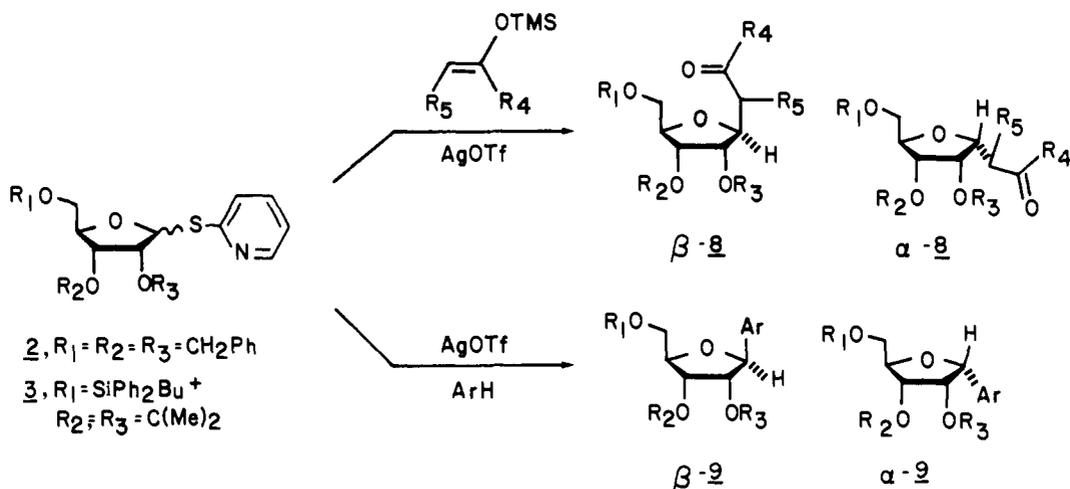
Scheme VI

reactions presumably involve rapid formation of oxonium ion **4** since the anomalous behavior of 1,3,5-trimethoxybenzene which gives exclusive β attack in CH_2Cl_2 precludes simple SN_2-type displacement. In a nonpolar, nonparticipating solvent such as methylene chloride, the oxonium ion **4** should exist as either the solvent-separated triflate ion pair of the α/β-triflates A and B.
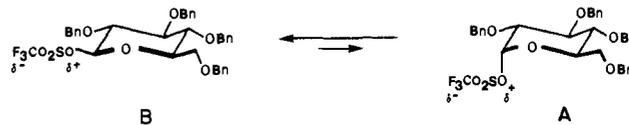
(8) 2,3-*O*-Isopropylidene-D-ribofuranose was prepared according to: Levene, P. A.; Stiller, E. T. *J. Biol. Chem.* **1933**, *102*, 187.

(9) Ohrui, H.; Jones, G. H.; Moffat, J. G.; Maddox, M. L.; Christensen, A. T.; Byram, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 4602.

Table I. C-Glycosidation of Thioacetals

entry	nucleophile	substrate	stereochem and reaction solv	isolated yield %
1	MeO⟨⟩OMe, OMe	1	β (CH$_2$Cl$_2$) α/β, 5:1 (Et$_2$O)	63[a]
2	MeO⟨⟩OMe, OMe	2	β (CH$_2$Cl$_2$)	49
3	MeO⟨⟩OMe, OMe	3	β (CH$_2$Cl$_2$)	61
4	MeO⟨⟩OMe	1	α (CH$_2$Cl$_2$)	48[a]
5	OSiMe$_3$ ⟨⟩Ph	1	α (CH$_2$Cl$_2$)	81[a]
6	OSiMe$_3$ (furanone)	1	α/β, 4:1 (CH$_2$Cl$_2$)	60[a]
7	OSiMe$_3$ (furanone)	2	α (CH$_2$Cl$_2$)	70
8	OSiMe$_3$ (furanone)	3	α (CH$_2$Cl$_2$)	56
9	MeO—O—OSiMe$_3$—OMe	1	α (CH$_2$Cl$_2$)	43
10	MeO—O—OSiMe$_3$—OMe	2	β (CH$_2$Cl$_2$)	72
11	OSiMe$_3$	1	α (CH$_2$Cl$_2$)	35[a]
12	(furan)	3	α/β, 5:1 furan, (CH$_2$Cl$_2$)	63

[a] See ref 5a.

Based on earlier work of Schuerch,[10] it is reasonable to expect that the β-triflate B should be the predominant reactive species due to a "reverse anomeric effect" and consequently give rise to α selectivity upon coupling. In the case of 1,3,5-trimethoxybenzene, the anomalous β selectivity in CH$_2$Cl$_2$ can be rationalized on the presumption that this highly reactive nucleophile intercepts the oxonium ion **4** from the less hindered[11] β face before the equilibrium[12] between the triflates can be established as in the case of the less nucleophilic species.[5a] In more polar solvents such as ether, α selectivity is observed exclusively. Again, a β-solvent-stabilized oxonium ion can be invoked as the reactive intermediate. Highly polar solvents such as acetonitrile or tetrahydrofuran were found to be unsuccessful for these C-glycosidations.

In our preliminary communication,[5a] we reported an α/β ratio of 3:2 for the reaction of **1** and the ketene silyl acetal of γ-butyrolactone. Closer inspection of this system revealed, however, that the reaction produces all four diastereomers in an α/β ratio of ca. 4:1. Our initial assignment[5a] was obtained from the per-O-acetylated derivatives **10**; subsequent trials revealed that the configurational stability of these compounds are very sensitive to

(10) West, A. C.; Schuerch, C. *J. Am. Chem. Soc.* **1973**, *95*, 1333. It should be noted that the formation of the putative β-triflate (**B**) presumably arises by a distinct mechanism than that observed in the double S$_N$2 displacements reported by Scheurch.
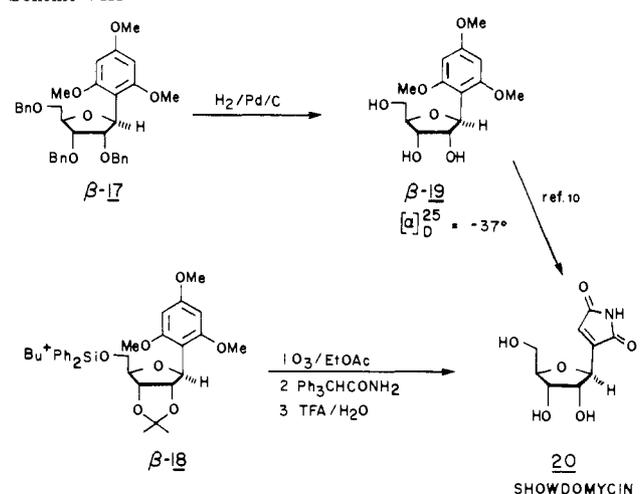(11) Kronzer, F. J.; Schuerch, C. *Carbohydrate Res.* **1973**, *27*, 379.
(12) It proved impractical to study this putative equilibrium in the absence of the nucleophile; i.e., incubation of the substrates (**1**) with silver(I) triflate led to rapid formation of internal C-glycosides resulting from a Friedle-Crafts-type reaction with the benzyl groups.

Scheme VII
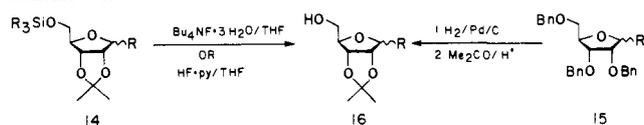
Scheme VIII

a particular set of acetylation reaction conditions. One of the two α diastereomers turned out to be a thermodynamic minimum; epimerization of the other α isomer to this stable compound was readily realized in NaOMe/MeOH at 25 °C (100% conversion). A configurational assignment at the lactone α carbons was not possible by using spectroscopic methods. Molecular models unfortunately do not give a clear indication why either diastereomer should be so favored.

In general, the β-thioacetal **1** is a reasonably consistent substrate for α-C-glycosidation; little dependence on the nucleophile, the solvent, or the temperature was exhibited in the cases examined. These results are consistent with the complementary examples reported by Kishi.[4a]

Stereochemical assignments for the ribosyl products, however, turned out to be more difficult since the spin–spin coupling constants between H$_1$ and H$_2$ are not consistently diagnostic. We therefore turned to the empirical ^{13}C NMR chemical shift correlation developed by Moffat[9] for the acetonide carbon in derivatives **16** (Scheme VII); the acetonide carbon of the α and β isomers absorb at 112–113 and 113–114 ppm, respectively. In addition, the α isomers (**16**) generally display a $J_{H_{3,4}} = 0$ in the ^{1}H NMR spectrum.

The C-glycosidation of both substrates **2** and **3** with 1,3,5-trimethoxybenzene gave the corresponding β-C-glycosides **17** and **18** (Scheme VIII; Table I, entries 2 and 3). The stereochemistry of **17** was readily assigned by hydrogenolytic removal of the benzyl groups to afford the known[13] β-triol **19** that has previously been converted into showdomycin (**20**) by Kalvoda.[13a] The stereochemical assignment for **18**, however, was more difficult since all attempts to produce triol **19** from **18** under acidic conditions resulted in anomerization at C-1. We therefore converted **18** into showdomycin by a modification of several literature procedures[13-15] and, thus, established the stereochemistry of **18** as β.

Ozonolysis of **18** followed by olefination of the labile α-keto ester and hydrolysis of the protecting groups in aqueous trifluoroacetic acid[15] furnished synthetic (+)-showdomycin (**20**).

We were quite surprised to discover that reaction of **2** or **3** with γ-butyrolactone–trimethylsilyl enol ether furnished exclusively the corresponding α-lactones **21a,b** and **22a,b** (Scheme IX).
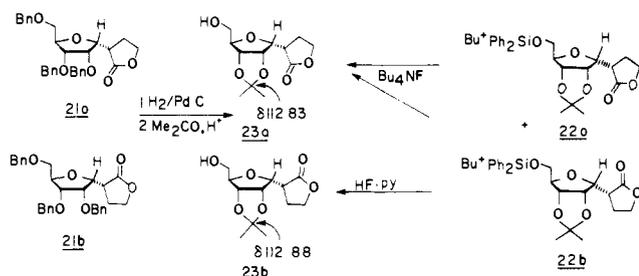
(13) (a) Kalvoda, L.; Farkas, J.; Sorm, F. *Tetrahedron Lett.* **1970**, 2297.
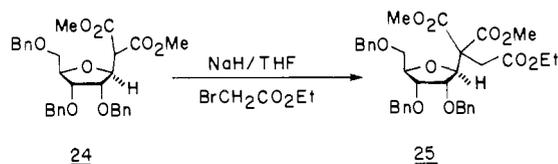(b) Ohrui, H.; Kuzuhara, H.; Emoto, S. *Agr. Biol. Chem.* **1972**, *36*, 1651.
(14) Trummlitz, G.; Moffatt, J. G. *J. Org. Chem.* **1973**, *38*, 1841.
(15) Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1981**, *103*, 3923.

Scheme IX

Scheme X

Although the *relative* configuration between C-1 and the lactone α carbon was not established, the anomeric configuration was assigned by conversion of **21a,b** and **22a,b** into the corresponding 2,3-acetonides **23a,b**. Both the ^{13}C NMR chemical shift of the isopropylidene carbons and the $J_{3,4}$ value (=0) is consistent with the empirical correlation for α stereochemistry reported by Moffat.[9] As with the glucopyranose lactone example discussed above, we found that deprotection of the silyl ether of **22a** and **22b** under basic conditions (Bu$_4$NF) led to the *same* lactone **23a**. Under neutral conditions (HF·pyridine), **22b** was converted into **23b**. The putative enolate anion generated from **22a,b** with Bu$_4$NF apparently has a marked preference for protonation from one face; inspection of molecular models does not suggest an obvious preference however.[16] Thus for substrate **3** a highly stereocontrolled access to one of four possible stereoisomeric C-glycosyl lactones is realized.

To examine whether the disparity of the stereochemical outcome from these ribosyl substrates was related to the general type of nucleophile (i.e., aromatic or silyl enol ether), we examined the coupling of **2**[17] with carbomethoxy ketene methyl trimethylsilyl acetal. In marked contrast to the butyrolactone case, a single β-C-glycosyl malonate[18] **24** was obtained (Scheme X, Table I, entry 10). Compound **24** could be further functionalized to the triester[18] **25** without loss of stereochemical integrity at C-1. Substrate **25** should prove to be a useful compound for preparation of other C-nucleoside antibiotics.

On the other hand, Friedel–Crafts-type coupling of **3** with furan gave rise to a 5:1 α/β ratio[19] of C-glycosyl furans **9** (Ar = 2-furanyl). The sterochemical assignments were based on ^{1}H and ^{13}C NMR spectral behavior as well as correlation (Bu$_4$NF·3H$_2$O, THF) to the recently reported[20] acetonides **9** (Ar = 2-furanyl, R$_1$ = H; R$_2$, R$_3$ = C(Me)$_2$).

In summary, the C-glycosidation of the pyridyl thioglycosides of glucose and ribose give rapid entry to C-glycosides that are useful for the preparation of C-nucleosides. The ease of preparation, handling, and storage of these thioacetal compounds make them a useful, complimentary addition to the existing methods for C-glycosidation. The glucose substrate **1** is uniformly useful for the preparation of α-C-glycosides. The ribose substrates **2**

and **3** exhibit high degrees of α/β stereocontrol but show an interesting and, at present, not clearly understood dependence on the specific nucleophile. The ostensible lack of neighboring group participation on substrates **1–3** in exerting an influence on the stereochemical course of the C–C bond formation makes these substrates well suited for further in-depth examination of the subtle effects that solvent, metal salt, steric, and stereoelectronic interactions might play.

Experimental Section

^{1}H NMR spectra were recorded on JEOL FX-100 (100 MHz), IBM WP-270 (270 MHz), or Nicolet (360 MHz) spectrometers and are reported in δ values. Melting points were recorded on a Mel-Temp instrument in open capillaries and are uncorrected. Microanalyses were performed by MHW Laboratories and are within ±0.3% of the calculated values.

Thin-layer chromatography (TLC) was carried out on 0.25-mm E. Merck precoated silica gel glass plates (60F-254) by using 5% phosphomolybdic acid in ethanol heat and/or UV light as developing agent. Preparative-layer chromatography (PTLC) was carried out on glass-backed TLC plates with a fluorescent indicator on a Harrison Res. chromatotron by using 1.0, 2.0, or 4.0 mm layer thickness silica gel adsorbents. Flash column chromatography was performed by using Woelm silica gel 32-63.

Solvents and reagents were all purified and dried by using standard protocol. Silver(I) triflate was freshly prepared according to the method of Whitesides (ref 21). 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose was obtained commercially.

The following abbreviations are used throughout this section: Et$_2$O = diethyl ether; EtOAc = ethyl acetate; Ac$_2$O = acetic anhydride; THF = tetrahydrofuran; DMAP = *N*,*N*-(dimethylamino)pyridine; MeOH = methanol; EtOH = ethanol.

β-2,3,4,6-Tetra-*O*-benzyl-1-(2′-thiopyridyl)-D-glucopyranose (1). To a stirred solution of 2,3,4,6-tetra-*O*-benzylglucopyranose (0.504 g, 0.93 mmol, 1.0 equiv) and 2,2′-dipyridyl disulfide (0.226 g, 1.03 mmol, 1.1 equiv) in CH$_2$Cl$_2$ (25 mL) at 0 °C was added tri-*n*-butylphosphine (0.208 g, 1.03 mmol, 1.1 equiv) dropwise. After stirring for 0.5 h at 0 °C, 3.0 g of silica gel was added and the mixture evaporated to dryness. The silica gel powder containing the adsorbed reaction mixture was loaded on top of a silica gel flash column (eluted with 25% Et$_2$O in hexanes) to afford 0.406 g (69%) of **1**[5a] as a waxy solid: [α]^{25}$_D$ +8.8° (CH$_2$Cl$_2$, c 2.0); mp 74–76 °C (recryst Et$_2$O/hexanes); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 3.40–3.86 (6 H, m), 4.24–5.07 (8 H, m), 5.43 (1 H, d, J = 9.6 Hz), 6.50–7.60 (23 H, m), 8.41 (1 H, m). Anal (C$_{39}$H$_{39}$NO$_5$S) C, H, N, S.

2,3,5-Tri-*O*-benzyl-1-(2′-thiopyridyl)-D-ribose (2). Method A. To a stirred solution of 2,3,5-tri-*O*-benzylribofuranose[7] (98 mg, 0.23 mmol, 1.0 equiv) and 2,2′-dipyridyl disulfide (77 mg, 0.35 mmol, 1.1 equiv) in CH$_2$Cl$_2$ (7 mL) at 0 °C was added tri-*n*-butylphosphine (69 mg, 0.31 mmol, 1.2 equiv) dropwise. After stirring for 1 h at 0 °C, the solution was concentrated and separated on PTLC silica gel (eluted with 10% Et$_2$O in toluene) to afford the two diastereomeric thioglycosides **2** (47% combined): α anomer 25.3 mg (21%); β-anomer 30.5 mg (26%).

β **Anomer:** ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 3.40–3.80 (2 H, m), 4.15–4.85 (9 H, m), 6.21 (1 H, d, J = 2.69 Hz), 6.9–7.70 (18 H, m), 8.40–8.50 (1 H, m); [α]^{25}$_D$ +16.7° (CH$_2$Cl$_2$, c 1.1); IR (NaCl, neat) 3065, 3030, 2830, 1580, 1452 cm^{-1}; mp 87–89 °C (recryst Et$_2$O/hexanes). Anal (C$_{31}$H$_{31}$NO$_4$S) C, H, N, S.

α **anomer:** (oil) ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 3.40–3.60 (2 H, m), 3.90–4.85 (9 H, m), 6.72 (1 H, d, J = 5.62 Hz), 6.90–7.60 (18 H, m), 8.42–8.48 (1 H, m); [α]^{25}$_D$ +147.3° (CH$_2$Cl$_2$, c 1.6); IR (NaCl, neat) 3060, 3025, 2855, 1575, 1452 cm^{-1}.

Method B. For this particular substrate, this method was found to be preferred due to the difficult separation problems inherent in method A and was found to be applicable to a large scale.

A solution of 2,3,5-tri-*O*-benzylribofuranose[7] (7.0 g, 16.67 mmol, 1.0 equiv), 2-mercaptopyridine (7.20 g, 64.7 mmol, 3.8 equiv), and *p*-toluenesulfonic acid (350 mg, 1.85 mmol, 0.1 equiv) in dry benzene (300 mL) was refluxed (Dean-Stark azeotrope) for 15 h. The mixture was cooled to room temperature, washed twice with 75-mL portions of saturated NaHCO$_3$, concentrated, and separated on a silica gel flash column (eluted with 20% EtOAc in hexanes) to afford 2.76 g of the α anomer and 3.83 g of the β anomer (77% combined or 92% based on unreacted starting material 1.04 g (15%)).

1-(2′-Thiopyridyl-2,3-*O*-isopropylidene-5-*O*-(*tert*-butyldiphenylsilyl)-D-ribofuranose (3). To a stirred solution of ribofuranose 2,3-acetonide[8] (4.67 g, 24.5 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (100 mL) was added

(16) Compounds **21a,b**, **22a,b**, and **23a,b** are each a corresponding set of α diastereomers; the relative configurations at the lactone α carbons were not assigned.

(17) The corresponding coupling reaction with **3** provided approximately the same stereochemical outcome (β/α, 3:1) but the yields were not synthetically useful (15–20%).

(18) For related cases of C-ribosyl malonates, see: (a) Hanessian, S.; Pernet, A. G. *Can. J. Chem.* **1974**, *52*, 1266; (b) **1974**, *52*, 1280.

(19) The same ratio was obtained in furan as the solvent or in CH$_2$Cl$_2$ with addition of 2 equiv of furan.

(20) Maeba, I.; Iwata, K.; Usami, F.; Furukawa, H. *J. Org. Chem.* **1983**, *48*, 2998.

(21) Whitesides, G. M.; Gutowski, F. D. *J. Org. Chem.* **1976**, *41*, 2882.

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Et$_3$N (2.73 gm, 27 mmol, 1.1 equiv), *tert*-butyldiphenylsilyl chloride (7.43 g, 27 mmol, 1.1 equiv), and DMAP (300 mg, 2.45 mmol, 0.1 equiv) at 0 °C. The cooling bath was removed, and the mixture was allowed to stir for 5 h at ambient temperature. The solvent was removed under reduced pressure, and the residue was triturated with THF and filtered to remove Et$_3$N·HCl. The filtrate was concentrated, absorbed onto 15 g of silica gel, dried, loaded onto a flash column (silica gel, 150 g, prepared in hexanes), and eluted with 20% Et$_2$O in hexane to afford 8.36 g (79%) of the C-5 silyloxy derivative (α,β mixture) which was directly used for the following transformation.

To a stirred solution of the hemiacetal obtained above (1.35 g, 3.15 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (30 mL) was added 2,2'-dipyridyl disulfide (830 mg, 3.77 mmol, 1.2 equiv) and tri-*n*-butylphosphine (762 mg, 3.77 mmol, 1.2 equiv) at 0 °C. The reaction was allowed to stir for 30 min at 0 °C, poured onto the silica gel (5 gm) containing 10 mL of CH$_2$Cl$_2$, evaporated to dryness, loaded onto a flash column (silica gel, 50 g, prepared in hexanes) and eluted with 10% Et$_2$O in CCl$_4$ (500 mL) to afford 1.3 g (79%) of thioacetal **3** which was a mixture of anomers (α/β = 3:1) (oil). Analytical samples of each were obtained by PTLC (silica gel, 10% Et$_2$O in CCl$_4$). The mixture as obtained above was directly used for C-glycosidations.

α anomer: (oil) $[\alpha]^{25}_D$ +90.4° (*c* 1.3, CH$_2$Cl$_2$); ^{1}H NMR (270 MHz) (CDCl$_3$) δ (TMS) 1.07 (9 H, s), 1.41 (3 H, s), 1.60 (3 H, s), 3.73–3.90 (2 H, m), 4.28 (1 H, br s), 4.94 (1 H, d, *J* = 6.4 Hz), 5.08 (1 H, m), 6.68 (1 H, d, *J* = 4.44 Hz), 7.09 (1 H, m) 7.26–7.75 (12 H, m), 8.38 (1 H, m); IR (NaCl, neat) 2930, 1580, 1420, 1110, 700 cm^{-1}; mass spectrum, *m/z* 522 (M$^+$ + 1, 9.8), 464 (5.2), 59 (100).

β anomer: (oil) $[\alpha]^{25}_D$ −115.8° (*c* 1.3, CH$_2$Cl$_2$); ^{1}H NMR (270 MHz) (CDCl$_3$) δ (TMS) 1.06 (9 H, s), 1.26 (3 H, s), 1.56 (3 H, s), 3.76–3.83 (2 H, m), 4.37 (1 H, m), 4.82 (2 H, m), 6.19 (1 H, d, *J* = 1.4 Hz), 7.0 (1 H, m), 7.19–7.70 (12 H, m), 8.46 (1 H, m); IR (NaCl, neat) 2930, 1580, 1415, 1105, 1085, 700 cm^{-1}; mass spectrum, *m/z* 522 (M$^+$ + 1, 46.1), 464 (17.6), 59 (100).

General Procedure for C-Glycosidation of 1. To a stirred solution of **1** (1.0 equiv) in distilled, dry CH$_2$Cl$_2$ (0.16 M) was added the aromatic or TMS enol ether substrate (3.5 equiv) in one portion, followed by addiiton of silver(I) triflate (2.2 equiv). The mixture was stirred at room temperature for 2 h (or until TLC analysis indicates disappearance of starting material), diluted with CH$_2$Cl$_2$, filtered, and washed with 0.1 N NaOH. The organic layer was separated, dried over anhydrous sodium sulfate, filtered, evaporated, and separated by silica gel chromatography. Solvent systems for separations are given with the reaction scale and spectral data for each compound. All reactions were carried out in CH$_2$Cl$_2$ unless otherwise stated under a nitrogen atmosphere.

General Procedure for C-Glycosidation of 2 and 3. To a stirred solution of **2** (1.0 equiv) in distilled, dry CH$_2$Cl$_2$ (0.05 M) was added the aromatic or TMS enol ether substrate (1.5–2.0 equiv) followed by addition of silver(I) triflate (1.25–2.0 equiv). The mixture was stirred at room temperature for 0.5 h (or until TLC analysis indicated disappearance of starting material), diluted with CH$_2$Cl$_2$, and washed with 0.1 N NaOH. The combined organic extracts were dried over anhydrous sodium sulfate, filtered. evaporated, and separated by silica gel chromatography. Solvent systems for separations are given with the reaction scale and spectra data for each compound.

General Procedures for Hydrogenolysis of Benzyl Protecting Groups. To a stirred solution of the per-*O*-benzyl *C*-glycoside (1.0 equiv) in THF (0.01 M) at 25 °C was added 10% Pd on charcoal (0.1 mol equiv). The reaction vessel was evacuated by using standard aspirator suction and the pressure relieved by introduction of H$_2$ gas. The evacuation/H$_2$ flushing sequence is repeated 4 times, and the mixture was allowed to stir vigorously for 12 h. The suspension was filtered through a small plug of Celite and separated by silica gel chromatography. The solvent systems for separation are given with the reaction scale and spectral data for each polyol product. In some cases, the polyol was directly used for the subsequent acetylation or acetonization reaction without chromatographic isolation and spectroscopic characterization.

General Procedure for Per-O-acetylation of C-Glycosides. To a stirred, room-temperature solution of the polyol substrate (1.0 equiv) in CH$_2$Cl$_2$ (0.02 M), pyridine (50 equiv), and acetic anhydride (6.0 equiv) was added DMAP (0.1 equiv). The mixture was stirred at room temperature for 1 h, diluted with CH$_2$Cl$_2$, and washed twice with 0.1 N HCl. The organic layer was dried over anhydrous sodium sulfate, filtered, evaporated, and separated by PTLC silica gel. The solvent systems for separation are given with the reaction scale and spectral data for each product.

1-Deoxy-1-(C-2',4',6'-trimethoxyphenyl)-2,3,4,6-tetra-O-benzyl-D-glucopyranose (7, Ar = 2,4,6-Trimethoxyphenyl). From 25 mg (0.04 mmol) of **1**, 17 mg (0.1 mmol) of 1,3,5-trimethoxybenzene, and 26 mg (0.1 mmol) of silver(I) triflate in CH$_2$Cl$_2$ (1.5 mL), 17.2 mg (63%) of pure β-**7** was obtained[5a] (isolated on PTLC silica gel, eluted with 50%

Et$_2$O in hexanes) (oil): $[\alpha]^{25}_D$ +5.4° (*c* 0.4, CHCl$_3$) [lit.[4d] +5.4°]; ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 3.40–5.12 (15 H, m), 3.66 (3 H, s), 3.73 (3 H, s), 3.76 (3 H, s), 6.10 (2 H, m), 6.62–7.40 (20 H, m); IR (NaCl, neat) 1605, 1585, 1450, 1200, 1150, 1115, 1090, 1060, 690 cm^{-1}; mass spectrum, *m/z* 690 (M$^+$, 1.0), 599 (13.0), 287 (68.2), 97 (100). Under identical conditions, except in Et$_2$O (1.5 mL) as reaction solvent, a 5:1 α/β ratio of product 7 was obtained. α-**7**: (oil) $[\alpha]^{25}_D$ +40.0° (*c* 0.2, CHCl$_3$); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 3.30–4.96 (14 H, m), 3.72 (6 H, s), 3.81 (3 H, s), 5.88 (1 H, d, *J* = 7.5 Hz), 6.14 (2 H, s), 6.80–7.40 (20 H, m); IR (NaCl, neat) 3050, 2920, 1610, 1455 cm^{-1}; mass spectrum, *m/z* 690 (M$^+$, 0.4), 599 (18.4), 287 (98.3), 91 (100).

β-1-Deoxy-1-(2',4',6'-trimethoxyphenyl)-2,3,4,6-tetra-O-acetyl-D-glucopyranose (11, R = COCH$_3$, Ar = 2,4,6-Trimethoxyphenyl). From 70.3 mg (0.1 mmol) of β-**7**, 15 mg of 10% Pd/C in THF (10 mL), 26.7 mg (79%) of the tetraol **10** was obtained by filtration of the catalyst and evaporation of the solvent. This material was directly acetylated without further purification. Acetylation using 0.8 mg DMAP, 43 mg Ac$_2$O, and 276 mg pyridine in CH$_2$Cl$_2$ (3 mL) afforded 19.8 mg (40%) of the tetraacetate **11**[5a] (chromatographed on PTLC silica gel, eluted with 50% EtOAc in hexanes) (oil): $[\alpha]^{25}_D$ −14.4° (*c* 1.2, CH$_2$Cl$_2$); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 1.73 (3 H, s), 2.01 (3 H, s), 2.05 (6 H, s), 3.80–4.28 (3 H, m), 3.78 (6 H, s), 3.83 (3 H, s), 4.80–5.40 (3 H, m), 5.70–6.20 (3 H, m); ^{1}H NMR (360 MHz) (CDCl$_3$) δ (TMS) 5.02 (1 H, d, $J_{1,2}$ = 10.5 Hz); IR (NaCl, neat) 2940, 1750, 1612, 1225 cm^{-1}.

α-1-Deoxy-1-(C-2',4',6'-trimethoxyphenyl)-2,3,4,6-tetra-O-acetyl-D-glucopyranose (11, R = COCH$_3$, Ar = 2,4,6-Trimethoxyphenyl). From 48 mg (0.07 mmol) of α-**7**, 10 mg of 10% Pd/C in THF (8 mL), 16.2 mg (70%) of the tetrol **10** was obtained by filtration of the catalyst and evaporation of the solvent. Direct acetylation of this material (10.6 mg, 0.03 mmol) using 20 mg of Ac$_2$O, 0.4 mg of DMAP, and 126 mg of pyridine in CH$_2$Cl$_2$ (1.5 mL) afforded 10.2 mg (64%) of tetraacetate **11**[5a] (oil): $[\alpha]^{25}_D$ +67.6° (*c* 0.8, CH$_2$Cl$_2$); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 1.78 (3 H, s), 2.04 (9 H, s), 3.84 (3 H, s), 3.90 (6 H, s), 3.80–4.36 (3 H, m), 4.92–5.60 (2 H, m), 5.80–6.16 (2 H, m), 6.17 (2 H, s); ^{1}H NMR (360 MHz) (CDCl$_3$) δ (TMS) 6.03 (1 H, d, *J* = 7.6 Hz).

α-1-Deoxy-1-(C-2',4'-dimethoxyphenyl)-2,3,4,6-tetra-O-benzyl-D-glucopyranose (7, Ar = 2,4-Dimethoxyphenyl). From 700 mg (1.11 mmol) of **1**, 534 mg (3.87 mmol) of *m*-dimethoxybenzene, and 625 mg (2.43 mmol) of silver(I) triflate in CH$_2$Cl$_2$ (7 mL), 351 mg (48%) of C-glycosylated product 7[5a] was obtained (chromatographed on a silica gel column with 40% Et$_2$O in hexanes) (oil): $[\alpha]^{25}_D$ +22.7° (CHCl$_3$); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 3.60–4.12 (6 H, m), 3.67 (3 H, s), 3.80 (3 H, s), 4.20–5.00 (8 H, m), 5.42 (1 H, d, *J* = 3.4 Hz), 6.29–6.57 (2 H, m), 6.83–7.43 (20 H, m), 7.62 (1 H, d, *J* = 7.8 Hz); IR (NaCl, neat) 1610, 1580, 1500, 1460, 1450, 1205, 1085, 1065, 730, 690 cm^{-1}; mass spectrum, *m/z* 660 (M$^+$, 0.3), 569 (1.6), 257 (51.6), 91 (100).

α-1-Deoxy-1-(C-2',4'-dimethoxyphenyl)-2,3,4,6-tetra-O-acetyl-D-glucopyranose (11, R = COCH$_3$; Ar = 2,4-Dimethoxyphenyl). From 170 mg (0.26 mmol) of 7, 20 mg of 10% Pd/C in THF (15 mL), the tetraol **10** (66.5 mg, 85%) was obtained by silica gel PTLC chromatography (10% MeOH in CH$_2$Cl$_2$) and was used directly for the acetylation reaction.

From 35.0 mg (0.12 mmol) of the tetraol, DMAP (2 mg, 0.011 mmol), 71.7 mg of Ac$_2$O, and 462 mg of pyridine in CH$_2$Cl$_2$ (2 mL) was obtained 37.0 mg (66%) of tetraacetate **11**[5a] (oil): $[\alpha]^{25}_D$ +26.1° (*c* 3.7, CH$_2$Cl$_2$); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 1.84 (3 H, s), 2.06 (3 H, s), 2.06 (3 H, s,), 2.12 (3 H, s), 3.80 (3 H, s), 3.80 (3 H, s), 3.90–4.50 (3 H, m), 5.00–5.60 (4 H, m), 6.45 (2 H, m), 7.42 (1 H, d, *J* = 7.8 Hz); ^{1}H NMR (360 MHz) (CDCl$_3$) δ (TMS) 5.51 (1 H, d, $J_{1,2}$ = 4.14 Hz).

α-1-Deoxy-1-(C-phenacyl)-2,3,4,6-tetra-O-benzyl-D-glucopyranose (6, R^1 = Ph, R^2 = H). From 78 mg (0.12 mmol) of **1** (118 mg, 0.61 mmol) of the TMS enol ether of acetophenone and 63 mg (0.24 mmol) of silver(I) triflate in CH$_2$Cl$_2$ (2.5 mL), 64.3 mg (81%) of the ketone **6**[5a] (R^1 = Ph, R^2 = H) was obtained (chromatographed on PTLC silica gel, eluted with 33% Et$_2$O in hexanes): mp 74.5–75 °C (recryst Et$_2$O/hexanes); $[\alpha]^{25}_D$ +48.2° (CHCl$_3$); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 3.30 (2 H, m), 3.50–3.90 (6 H, m), 4.30–5.00 (9 H, m), 7.00–7.90 (25 H, m); IR (NaCl, neat) 3015, 2860, 1680, 1080 cm^{-1}. Anal (C$_{42}$H$_{42}$O$_6$) C, H.

α-1-Deoxy-1-(C-1'-phenethyl)-2,3,4,6-tetra-O-acetyl-D-glucopyranose (10, R = COCH$_3$, R$_1$ = Ph, R$_2$ = H, X = H, H). From 40.3 mg (0.063 mmol) of **6** and 10 mg of 10% Pd/C in THF (8 mL), the tetrol **10** (R = H, R$_1$ = Ph, R$_2$ = H, X = H, H) (16.6 mg) (94%) was obtained (chromatographed on PTLC silica gel, eluted with 10% MeOH in CH$_2$Cl$_2$) as an amorphous solid: mass spectrum, *m/z* 268 (M$^+$, 1.0), 177 (2.2), 91 (100).

From 11.5 mg (0.04 mmol) of the tetrol, 1.0 mg of DMAP, 25 mg of Ac$_2$O, and 161 mg of pyridine in CH$_2$Cl$_2$ (2 mL) was obtained 9.6 mg

(52%) of the tetraacetate 10[5a] (chromatographed by PTLC silica gel, eluted with 50% EtOAc in hexanes) (oil): $[\alpha]^{25}_D$ +56.5° (*c* 0.9, CH_2Cl_2); ^1H NMR (100 MHz) ($CDCl_3$) δ (TMS) 1.60–2.38 (2 H, m), 2.01 (3 H, s), 2.03 (3 H, s), 2.04 (3 H, s), 2.10 (3 H, s), 2.40–3.00 (2 H, m), 3.70–4.00 (1 H, m), 4.00–4.36 (3 H, m), 4.75–5.40 (3 H, m), 7.18–7.40 (5 H, m); ^1H NMR (360 MHz) ($CDCl_3$) δ (TMS) 5.10 (1 H, dd, $J_{1,2}$ = 5.5 Hz); IR (NaCl, neat) 3020, 2950, 1745, 1365, 1220 cm^{-1}; mass spectrum, m/z 436 (M$^+$, 5.1), 376 (8.7), 316 (3.7), 91 (100).

1-Deoxy-1-(C-2′-butyrolactonyl)-2,3,4,6-tetra-O-benzyl-D-gluco-pyranose (6, R_1 = O, R_2 = CH_2CH_2).[5a] From 320 mg (0.5 mmol) of 1, 194 mg (1.0 mmol) of the TMS enol ether of γ-butyrolactone and 260 mg (1.0 mmol) of silver(I) triflate in CH_2Cl_2 (5 mL) was obtained 85 mg (28%) of one α-lactone and 96 mg (32%) of a faster three compound mixture which was rechromatographed (PTLC 12% Et_2O/toluene) (1:1.1(α):3.2(β) ratio) (overall α/β ratio = 4:1).

β isomer: $[\alpha]^{25}_D$ +3° (*c* 0.79, CH_2Cl_2); R_f = 0.34 (12% Et_2O/toluene); ^1H NMR 270 MHz) ($CDCl_3$) δ (TMS) 2.27 (1 H, m), 2.44 (1 H, m), 3.01 (1 H, m), 3.40–3.75 (6 H, m), 4.09–4.40 (3 H, m), 4.45–5.05 (8 H, m), 7.10–7.55 (20 H, m); IR (NaCl, neat) 3030, 2860, 1765, 1455, 1100 cm^{-1}; mass spectrum, m/z 637 (M$^+$ + 29, CI, CH_4, 3.7), 609 (M$^+$ + 1, 0.3), 517 (7.5), 91 (100).

β isomer: $[\alpha]^{25}_D$ −43° (*c* 0.415, CH_2Cl_2); R_f = 0.29 12% Et_2O/toluene); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.39 (1 H, m), 2.11 (1 H, m), 2.81 (1 H, m), 3.28 (1 H, m), 3.45 (1 H, m), 3.60–3.83 (5 H, m), 3.98 (1 H, m), 4.20 (1 H, m), 4.41–4.68 (4 H, m), 4.77–5.02 (4 H, m), 7.10–7.45 (20 H, m); IR (NaCl, neat) 3030, 2900, 1775, 1090 cm^{-1}; mass spectrum, m/z 637 (M$^+$ + 29, CI, CH_4, 0.7), 517 (0.7), 91 (100).

α isomer: $[\alpha]^{25}_D$ +28.6° (*c* 1.32, CH_2Cl_2); R_f = 0.25 12% Et_2O/toluene); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 2.39 (2 H, m), 3.04 (1 H, m), 3.54–3.80 (4 H, m), 3.95–4.20 (4 H, m), 4.30 (1 H, m), 4.38–4.73 (8 H, m), 7.12–7.60 (20 H, m); IR (NaCl, neat) 3030, 2860, 1770, 1455, 1090 cm^{-1}; mass spectrum m/z 517 (M$^+$ −91, 5.1), 425 (0.7), 411 (5.1), 91 (100).

α isomer: $[\alpha]^{25}_D$ +44.4° (*c* 0.63, CH_2Cl_2); R_f 0.18 12% Et_2O/toluene); mp 94–96 °C (recryst Et_2O/hexanes); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 2.44 (2 H, m), 3.01 (1 H, m), 3.60–3.95 (6 H, m), 4.07–4.28 (2 H, m), 4.36–4.90 (9 H, m), 7.08–7.45 (20 H, m); IR (NaCl, neat) 3015, 2860, 1770, 1455, 1090 cm^{-1}; mass spectrum, m/z (M$^+$ + 29, CI, CH_4, 0.2), 517 (0.7), 91 (100). Anal. ($C_{38}H_{40}O_7$) C, H.

α-1-Deoxy-1-(C-2′-butyrolactonyl)-2,3,4,6-tetra-O-acetyl-D-gluco-pyranose (10, R = $COCH_3$, R_1 = O, R_2 = CH_2CH_2, X = O). From 125 mg (0.206 mmol) of α-lactone 6 and 22 mg of 10% Pd/C in THF (15 mL), 63.2 mg of crude tetrol 10 (R = H, R_1 = O, R_2 = CH_2CH_2, X = 0) was obtained by filtration of the catalyst and evaporation of the solvent. Direct acetylation of this material (33 mg, 0.133 mmol) using 81 mg of Ac_2O, 1.6 mg of DMAP, and 157 mg of pyridine in CH_2Cl_2 (5 mL) afforded 12 mg (22%) of tetraacetate 10[5a] (chromatographed on PTLC silica gel, eluted with 2% acetone in Et_2O) (oil): $[\alpha]^{25}_D$ +35.2° (*c* 0.92, CH_2Cl_2); ^1H NMR (100 MHz) ($CDCl_3$) δ (TMS) 1.86–2.36 (2 H, m), 2.06 (3 H, s), 2.09 (3 H, s), 2.11 (3 H, s), 2.13 (3 H, s), 2.57–2.93 (1 H, m), 3.89–4.77 (7 H, m), 4.83–5.00 (1 H, m), 5.20–5.46 (1 H, m); ^1H NMR (360 MHz) ($CDCl_3$) δ (TMS) 4.43 (1 H, dd, $J_{1,2}$ = 5.13 Hz), IR (NaCl, neat) 2950, 1780–1740, 1370, 1220 cm^{-1}.

α-1-Deoxy-1-(C-2′-butyrolactonyl)-2,3,4,6-tetra-O-acetyl-D-gluco-pyranose (10, R = $COCH_3$, R_1 = O, R_2 = CH_2CH_2, X = O). From 60 mg (0.09 mmol) of β-lactone 6 and 11 mg of 10% Pd/C in THF (10 mL), 32.8 mg of crude tetrol 10 (R = H, R_1 = O, R_2 = CH_2CH_2, X = 0) was obtained by filtration of the catalyst and evaporation of the solvent. Direct acetylation of this material (20 mg, 0.08 mmol) using 49.4 mg of Ac_2O, 1 mg of DMAP, and 96 mg of pyridine in CH_2Cl_2 (4 mL) afforded 4.0 mg (12%) of tetraacetate 10[5a] (chromatographed on PTLC silica gel, eluted with Et_2O) (oil), $[\alpha]^{25}_D$ +79.2° (*c* 0.4, CH_2Cl_2); ^1H NMR (100 MHz) ($CDCl_3$) δ (TMS) 1.70–2.10 (2 H, m), 2.05 (3 H, s), 2.08 (3 H, s), 2.10 (6 H, s), 2.76–3.10 (1 H, m), 3.72–4.70 (6 H, m), 4.80–5.48 (3 H, m); ^1H NMR (360 MHz) ($CDCl_3$) δ (TMS) 4.61 (1 H, dd, $J_{1,2}$ = 7.6 Hz); IR (NaCl, neat) 2955, 1790–1740, 1370, 1220 cm^{-1}; mass spectrum, m/z 417 (M$^+$ + 1, 11.6), 357 (80).

1-Deoxy-1-(C-2′-hydroxyethyl)-2,3,4,6-tetra-O-benzyl-D-gluco-pyranose. From 80 mg (0.12 mmol) of 1, 22 mg (0.19 mmol) of the TMS enol ether of acetaldehyde, and 49 mg (0.19 mmol) of silver(I) triflate in CH_2Cl_2 (2 mL), the labile aldehyde product 6 (R_1 = R_2 = H) (obtained crude from extractive workup with 0.1 N $NaOH/CH_2Cl_2$) was directly subjected to LiAlH$_4$ (5 mg, 0.12 mmol) reduction in Et_2O (2 mL) at 0 °C. The reaction was quenched with Na_2SO_4·10H_2O, filtered, and separated on PTLC silica gel (eluted with 33% EtOAc in hexanes) to afford 25.2 mg (36% overall) of the corresponding primary alcohol[5a] (oil): $[\alpha]^{25}_D$ +29.7° (*c* 0.6, CH_2Cl_2); ^1H NMR (100 MHz) ($CDCl_3$) δ (TMS) 1.74–2.14 (2 H, m), 2.14–2.53 (1 H, br s, D_2O exch.), 3.14–3.93 (8 H, m), 4.00–4.28 (1 H, m), 4.28–4.97 (8 H, m), 6.95–7.54 (20 H, m); ^1H NMR (360 MHz) ($CDCl_3$) δ (TMS) 4.22 (1 H, dd, $J_{1,2}$ = 5.6 Hz);

IR (NaCl, neat) 3470, 3015, 2865, 1500, 1455 cm^{-1}; mass spectrum, m/z 569 (M$^+$ + 1, 0.5), 477 (0.5), 91 (100).

1-Deoxy-1-(C-dimethylmalonyl)-2,3,4,6-tetra-O-benzyl-D-gluco-pyranose (6, R_1 = OCH_3; R_2 = CO_2CH_3). From 193 mg (0.3 mmol) of 1, 122 mg (0.6 mmol) of carbomethoxy ketene methyl trimethylsilyl acetal and 117 mg (0.46 mmol) of silver(I) triflate in CH_2Cl_2 (5 mL), 94 mg (48%) of pure α-6 was obtained (isolated by PTLC silica gel, eluted with 50% Et_2O in hexanes): mp 100–101 °C (Et_2O/hexane) $[\alpha]^{25}_D$ +58.74 (*c* 0.825, CH_2Cl_2); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 3.36 (3 H, s), 3.50–3.90 (6 H, m), 3.68 (3 H, s), 4.05 (1 H, d, J = 11 Hz), 4.30–4.90 (8 H, m), 5.00 (1 H, dd, J = 4.7 Hz, J = 11.1 Hz), 7.15–7.31 (20 H, m); IR (NaCl, neat) 3025, 2860, 1765, 1735, 1500, 1445, 1085, 690. Anal. ($C_{39}H_{42}O_9$) C, H.

1-Deoxy-1-(C-2′,4′,6′-trimethoxyphenyl)-2,3,5-tri-O-benzyl-D-ribo-furanose (9, R_1 = R_2 = R_3 = CH_2Ph; Ar = 2,4,6-Trimethoxyphenyl). From 540 mg (1.05 mmol) of α-2 (the same result was obtained from the β isomer of 2), 194 mg (1.16 mmol) of 1,3,5-trimethoxybenzene, and 405 mg (1.58 mmol) of silver(I) triflate in CH_2Cl_2 (10 mL), 293 mg (49%) of pure β-9 was obtained (isolated on PTLC silica gel, eluted with 25% EtOAc/hexanes): $[\alpha]^{25}_D$ +18.0° (*c* 1.2, CH_2Cl_2), mp 93–95 °C (recryst Et_2O/hexanes); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 3.61 (6 H, s), 3.80 (3 H, s), 4.10–4.80 (11H, m), 5.55 (1 H, d, J = 4.4 Hz), 6.06 (2 H, s), 7.15–7.45 (15 H, m); mass spectrum, m/z 479 (M$^+$ − 91, 5.1), 463 (4.0), 391 (2.0), 107 (100). Anal. ($C_{35}H_{38}O_7$) C, H.

β-1-Deoxy-(C-2′,4′,6′-trimethoxyphenyl)-2,3,0-isopropylidene-5-O-(*tert*-butyldiphenylsilyl)-D-ribofuranose (9, R_1 = SiPh$_2$-*t*-Bu; R_2, R_3 = C(CH_3)$_2$; Ar = 2,4,6-Trimethoxyphenyl). From 330 mg (0.63 mmol) of 3 (α/β mixture) 160 mg (0.95 mmol) of 1,3,5-trimethoxybenzene, and 244 mg (0.95 mmol) of silver(I) triflate in CH_2Cl_2 (15 mL), 227 mg (61%) of pure β-9 was obtained (isolated on PTLC silica gel, eluted with 25% Et_2O in hexanes) (oil): $[\alpha]^{25}_D$ +13.84° (*c* 1.3, CH_2Cl_2); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.05 (9 H, s), 1.34 (3 H, s), 1.59 (3 H, s), 3.64 (6 H, s), 3.6–3.85 (2 H, m), 3.79 (3 H, s), 4.08 (1 H, m), 4.73 (1 H, m), 4.99 (1 H, m), 5.53 (1 H, d, J = 2.93 Hz), 6.06 (2 H, s), 7.24–7.75 (10 H, m); ^{13}C NMR (67.933 MHz) ($CDCl_3$) δ ($CDCl_3$) 19.33, 25.84, 26.94, 27.89, 55.32, 55.59, 64.89, 77.65, 83.13, 84.78, 85.03, 91.15, 108.33, 113.57, 127.53, 129.43, 133.71, 134.08, 135.75, 159.71, 161.51; IR (NaCl, neat) 1615, 1595, 1470, 1430, 1220, 1210, 1155, 1135, 1110, 1065, 700 cm^{-1}; mass spectrum, m/z 579 (M$^+$ + 1, 2.6), 563 (0.9), 549 (1.1), 521 (9.0), 503 (5.4), 463 (15), 443 (17.1), 181 (100).

β-1-Deoxy-1-(C-2′,4′,6′-trimethoxyphenyl)-D-ribofuranose (9, R_1 = R_2 = R_3 = H; Ar = 2,4,6-Trimethoxyphenyl). From 205 mg (0.36 mmol) of 9 (R_1 = R_2 = R_3 = CH_2Ph) and 160 mg of 10% Pd/C in THF (50 mL), the triol 9 (23 mg, 21%) was obtained.

The same triol was obtained from the substrate 9 (R_1 = SiPh$_2$-*t*-Bu; R_2, R_3 = C(CH_3)$_2$) by the following two-step procedure: To a stirred solution of C-glycoside 9 (300 mg, 0.519 mmol, 1.0 equiv) in THF (10 mL) at 25 °C was added Bu$_4$NF·3H_2O (196 mg, 0.62 mmol, 1.2 equiv). The mixture was allowed to stir 7 h at ambient temperature, poured into H_2O, and thoroughly extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, evaporated, and separated on PTLC silica gel (eluted with 50% EtOAc in hexanes) to afford 149 mg (85%) of the desilylated alchol 9 R_1 = H; R_2, R_3 = C(CH_3)$_2$; Ar = 2,4,6-trimethoxyphenyl) (oil): $[\alpha]^{25}_D$ −13.85° (*c* 1.3, CH_2Cl_2); ^1H NMR (270 MHz) ($CDCl_3$) δ ($CHCl_3$) 1.32 (3 H, s), 1.58 (3 H, s), 2.65 (1 H, br s, D_2O exch.), 3.72–3.88 (2 H, m), 3.78 (9 H, s), 4.06 (1 H, m), 4.86–4.97 (2 H, m), 5.54 (1 H, d, J = 4.23 Hz), 6.10 (2 H, s); ^{13}C NMR (67.933 MHz) ($CDCl_3$) δ ($CDCl_3$) 25.67, 27.79, 55.33, 55.69, 62.41, 78.00, 81.59, 84.29, 85.03, 91.37, 107.49, 113.95, 159.61, 161.73, IR (NaCl, neat) 3450, 1610, 1590, 1465, 1455, 1420, 1380, 1225, 1205, 1150, 1065 cm^{-1}; mass spectrum, m/z 340 (M$^+$, 15.3), 323 (10.1), 283 (45.8), 181 (100).

Treatment of the acetonide alcohol obtained above with camphor-sulfonic acid (cat.) in MeOH afforded a mixture. The β-triol identical with that obtained from hydrogenolysis of the corresponding tri-O-benzyl derivative was separated by PTLC silica gel.

β anomer: $[\alpha]^{25}_D$ −32.7° (*c* 0.4, H_2O) [lit.[10] −34°]; mp 96–98 °C [lit. 98–99 °C]; ^1H NMR (100 MHz) ($CDCl_3$) δ (TMS) 2.60 (1 H, m), 2.84 (2 H, m), 3.65–3.85 (3 H, m), 3.77 (6 H, s), 3.80 (3 H, s), 4.25 (1 H, m), 4.50 (1 H, m), 5.36 (1 H, d, J = 6.2 Hz), 6.13 (2 H, s).

α anomer: $[\alpha]^{25}_D$ −15° (*c* 0.45, H_2O) [lit.[10] −18°]; ^1H NMR (100 MHz) ($CDCl_3$) δ (TMS) 2.10 (1 H, m), 2.50 (1 H, m), 2.84 (1 H, m), 3.5–4.0 (3 H, m), 3.8 (9 H, s), 4.36 (2 H, m), 5.03 (1 H, d, J = 9.7 Hz), 6.13 (2 H, s).

1-Deoxy-1-(C-2′-butyrolactonyl)-2,3,5-tri-O-benzyl-D-ribofuranose (8, R_1 = R_2 = R_3 = CH_2Ph; R_4 = O; R_5 = CH_2CH_2). From 375 mg (0.73 mmol) of β-2, 230 mg (1.2 mmol) of the TMS enol ether of γ-butyro-lactone, and 308 mg (1.2 mmol) of silver(I) triflate in CH_2Cl_2 (10 mL), 249 mg (70% combined) of the α anomers 8 was obtained (isolated by chromatography on silica gel, eluted with 25% EtOAc in hexanes).

α anomer a: (oil) $[\alpha]^{25}_D$ +45.5° (*c* 1.3; CH_2Cl_2); R_f = 0.53 (50% EtOAc/hexanes); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 2.30–2.44 (2 H, m), 2.95–3.14 (1 H, m), 3.44–3.69 (2 H, m), 4.05–4.95 (12 H, m), 7.33 (15 H, m); IR (NaCl, neat) 1770, 1500, 1460, 1025, 740, 690 cm^{-1}; mass spectrum, *m/z* 489 (M$^+$ + 1, 3.7), 398 (3.0), 381 (18), 91(100).

α anomer b: (oil) $[\alpha]^{25}_D$ +40.5° (*c* 1.1; CH_2Cl_2); R_f = 0.41 (50% EtOAc/hexanes); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 2.07–2.26 (1 H, m), 2.46–2.64 (1 H, m), 3.06–3.24 (1 H, m), 3.45–3.72 (2 H, m), 3.90–4.86 (12 H, m), 7.31 (15 H, m); IR (NaCl, neat) 1770, 1500, 1460, 1025, 735, 695 cm^{-1}; mass spectrum, *m/z* 489 (M$^+$ + 1, 9.4), 397 (19.5), 381 (1.9), 91 (100).

α-1-Deoxy-1-(*C*-2′-butyrolactonyl)-2,3-*O*-isopropylidene-D-ribofuranose (8, R_1 = H; R_2, R_3 = C(CH$_3$)$_2$; R_4 = O; R_5 = CH$_2$CH$_2$). From 130 mg (0.27 mmol) of the α-tri-*O*-benzyl butyrolactone derivative (α anomer a) obtained above and 32 mg 10% Pd/C in THF (8 mL) was obtained 18 mg (31%) of the triol (isolated by PTLC silica gel, eluted with 10% MeOH in CH_2Cl_2) which was directly subjected to acetonide formation without further characterization. Treatment of the triol with dimethoxypropane (4 mL) and camphorsulfonic acid (3 mg) at room temperature for 12 h followed by evaporation and PTLC isolation (silica gel, eluted with 10% hexanes/EtOAc) afforded 8.2 mg (38%) of the α-acetonide 8 which was identical with that obtained from fluoride deprotection of the corresponding *tert*-butyldiphenylsilyl acetonide derivative prepared from 3 (R_f = 0.47, 10% hexane/EtOAc).

α-1-Deoxy-1-(*C*-2′-butyrolactonyl)-2,3-*O*-isopropylidene-D-ribofuranose (8, R_1 = H; R_2, R_3 = C(CH$_3$)$_2$; R_4 = O; R_5 = CH$_2$CH$_2$). From 108 mg (0.22 mmol) of the α-tri-*O*-benzyl butyrolactone derivative (α anomer b) obtained above and 26 mg 10% Pd/C in THF (10 mL) was obtained 20 mg (41%) of the triol (isolated by PTLC silica gel, eluted with 15% MeOH in CH_2Cl_2) which was directly subjected to acetonide formation without further characterization.

Treatment of the triol with acetone (2 mL), CuSO$_4$ (60 mg), and H$_2$SO$_4$ (0.2%, 0.04 mL) at room temperature for 5 h followed by addition of solid Ca(OH)$_2$, filtration, evaporation, and isolation by PTLC (silica gel, 10% hexanes/EtOAc) afforded 16 mg (28%) of the α-acetonide 8, which was identical with that obtained from HF·py deprotection of the corresponding *tert*-butyldiphenylsilyl acetonide derivative prepared from 3 (R_f = 0.24, 10% hexanes/EtOAc).

1-Deoxy-1-(*C*-2′-butyrolactonyl)-2,3-*O*-isopropylidene-5-*O*-(*tert*-butyldiphenyl)-D-ribofuranose (8, R_1 = SiPh$_2$-*t*-Bu; R_2, R_3 = C(CH$_3$)$_2$; R_4 = O; R_5 = CH$_2$CH$_2$). From 220 mg (0.42 mmol) of 3 (α/β, 3:1), 100 mg (0.65 mmol) of the TMS enol ether of γ-butyrolactone, and 130 mg (0.5 mmol) of silver(I) triflate in CH_2Cl_2 (7 mL) at 25 °C for 30 min afforded, after aqueous isolation and separation on PTLC silica gel (eluted with 25% EtOAc in hexanes), 117 mg (56% combined) of the α-configured lactones 8 (1:1 ratio).

Data for faster component on TLC (R_f = 0.5 in 50% Et$_2$O/hexanes) (oil): $[\alpha]^{25}_D$ +7.3° (*c* 1.1, CH_2Cl_2); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.05 (9 H, s), 1.36 (3 H, s), 1.5 (3 H, s), 2.35–2.5 (2 H, m), 2.05 (1 H, m), 3.63–3.81 (2 H, m), 4.14 (1 H, t, *J* = 3.8 Hz), 4.23 (1 H, q, *J* = 8.3 Hz), 4.40 (1 H, m), 4.53 (1 H, dd, *J* = 5.23, 2.7 Hz), 4.9 (2 H, m), 7.42 (6 H, m), 7.66 (4 H, m); IR (NaCl, neat) 2910, 1775, 1425, 1380, 1110 cm^{-1}; mass spectrum, *m/z* (methane CI) 525 (M$^+$ + 29, 8.2), 481 (4.5), 419 (100).

Data for slower components on TLC (R_f = 0.42 in 50% Et$_2$O/hexanes) (oil): $[\alpha]^{25}_D$ −3.5° (*c* 0.9, CH_2Cl_2); ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.05 (9 H, s), 1.34 (3 H, s), 1.50 (3 H, s), 2.13–2.32 (1 H, m), 2.35–2.55 (1 H, m), 3.05 (1 H, q, *J* = 9.2 Hz), 3.65–3.90 (2 H, m), 4.15–4.35 (3 H, m), 4.45 (1 H, dd, *J* = 3.95, 9.2 Hz), 4.77 (1 H, dd, *J* = 6.14, 3.95 Hz), 4.91 (1 H, d, *J* = 6.14 Hz), 7.416 (6 H, m), 7.63 (4 H, m); IR (NaCl, neat) 2915, 1775, 1430, 1370, 1110 cm^{-1}; mass spectrum, *m/z* (methane CI) 525 (M$^+$ + 29, 5.7), 481 (3.9), 419 (100).

α-1-Deoxy-1-(*C*-2′-butyrolactonyl)-2,3-*O*-isopropylidene-D-ribofuranose (8, R_1 = H; R_2, R_3 = C(CH$_3$)$_2$; R_4 = O; R_5 = CH$_2$CH$_2$). From 62 mg (0.125 mmol) of the *tert*-butyldiphenylsilyl lactone (8, R_1 = SiPh$_2$-*t*-Bu; R_2, R_3 = C(CH$_3$)$_2$; R_4 = O; R_5 = CH$_2$CH$_2$; faster component on TLC obtained above from 3) and 47 mg (0.15 mmol) of tetra-*n*-butylammonium fluoride·3H$_2$O in THF (10 mL), stirred at room temperature for 2 h, evaporated, and separated on PTLC silica gel (eluted with 10% hexanes in EtOAc), was obtained 16.5 mg (51%) of a single hydroxymethyl lactone derivative 8 (oil) (R_f = 0.47, 10% hexanes in EtOAc): ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.35 (3 H, s), 1.50 (3 H, s), 2.05 (1 H, br s, D$_2$O exch.), 3.02 (1 H, m), 3.65 (1 H, m), 4.10–4.30 (2 H, m), 4.30–4.48 (2 H, m), 4.70 (1 H, m), 4.87 (1 H, m); ^{13}C NMR (67.933 MHz) ($CDCl_3$) δ ($CDCl_3$) 24.620, 24.772, 27.478, 40.101, 62.354, 67.388, 79.219, 81.838, 82.537, 84.712, 112.83; IR (NaCl, neat) 3470, 2940, 1765, 1380, 1210, 1020 cm^{-1}; mass spectrum, *m/z* 259 (M$^+$ + 1, 44.8), 243 (38), 201 (100); $[\alpha]^{25}_D$ +14.0° (*c* 0.4, CH_2Cl_2).

Treatment of the epimeric lactone (slower component on TLC obtained above from 3) under identical conditions (Bu$_4$NF·3H$_2$O/THF, 25 °C) afforded, exclusively, the same hydroxymethyl lactone obtained above from the faster component. Stereochemical integrity of this material could be maintained by desilylation with the milder HF·pyridine complex as described below.

HF·pyridine complex was added to 83.0 mg (0.167 mmol) of the *tert*-butyldiphenylsilyl lactone (8, R_1 = SiPh$_2$-*t*-Bu; R_2, R_3 = C(CH$_3$)$_2$; R_4 = O; R_5 = CH$_2$CH$_2$; slower component on TLC obtained above from 3) in THF (7 mL) at room temperature and allowed to stir for 2.5 h. The mixture was diluted with CH_2Cl_2, poured into H$_2$O, and extracted with CH_2Cl_2. The combined extracts were dried over anhydrous sodium sulfate, filtered, concentrated, and separated on PTLC silica gel (eluted with 10% hexanes in EtOAc) to afford 21 mg (49%) of a single hydroxymethyl lactone 8 which was distinct from that obtained from the faster component above (R_f = 0.24, 10% EtOAc in hexanes): ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.32 (3 H, s), 1.50 (3 H, s), 2.19–2.55 (2 H, m), 3.0 (1 H, br s, D$_2$O exch.), 3.08 (1 H, q, *J* = 9.4 Hz), 3.65 (2 H, m), 4.14–4.47 (4 H, m), 4.66–4.78 (2 H, m); ^{13}C NMR (67.933 MHz) ($CDCl_3$) δ ($CDCl_3$) 24.758, 25.196, 26.145, 40.208, 62.403, 66.858, 79.163, 81.9125, 82.277, 85.241, 112.882; IR (NaCl, neat) 3470, 2940, 1765, 1380, 1210, 1020 cm^{-1}; mass spectrum, *m/z* 259 (M$^+$ + 1, 55.3), 243 (17.6), 59 (100).

β-1-Deoxy-1-(*C*-dimethylmalonyl)-2,3,5-tri-*O*-benzyl-D-ribofuranose (8, R_1 = R_2 = R_3 = CH$_2$Ph; R_4 = OCH$_3$; R_5 = CO$_2$CH$_3$). From 90 mg (0.175 mmol) of 2, 186 mg (1.06 mmol) of carbomethoxy ketene methyl trimethylsilyl acetal, and 163 mg (0.63 mmol) of silver(I) triflate in CH_2Cl_2 (4 mL), 67.2 mg (71%) of pure β-8 was obtained (isolated on flash column silica gel, eluted with 15% EtOAc in hexanes) (oil): $[\alpha]^{25}_D$ +16.5° (*c* 2.0, CH_2Cl_2); ^1H NMR (360 MHz) ($CDCl_3$) δ (TMS) 3.45–3.65 (2 H, m), 3.52 (3 H, s), 3.74 (3 H, s), 4.06–4.13 (2 H, m), 4.17–4.23 (1 H, m), 4.25–4.31 (1 H, m), 4.38–4.81 (7 H, m), 7.20–7.38 (15 H, m) (J_{12} from decoupling = 5.6 Hz); IR (NaCl, neat) 3024, 2947, 1750, 1735, 1459, cm^{-1}; mass spectrum, *m/z* 443 (M$^+$ − 91, 0.7), 351 (1.9), 122 (1.4), 91 (100).

1,1-Dimethyl-2-ethyl-1-(2,3,5-tri-*O*-benzyl-β-D-ribofuranosyl) 1,1,2-Ethanetricarboxylate (25). To a stirred solution of 8 (R_1 = R_2 = R_3 = CH$_2$Ph; R_4 = OCH$_3$; R_5 = CO$_2$CH$_3$) (840 mg, 1.57 mmol, 1.0 equiv) in THF (3 mL) was added a suspension of NaH (126 mg, 3.16 mmol, 2.0 equiv) in THF (20 mL). The mixture was allowed to stir for 2 h at room temperature and then 792 mg, 4.75 mmol, 3.0 equiv) was added dropwise. After stirring for 12 h at room temperature, the solvent was evaported under reduced pressure, diluted with CH_2Cl_2, poured into H$_2$O and thoroughly extracted with CH_2Cl_2. The cominbed organic extracts were dried over anhydrous sodium sulfate, filtered, concentrated, and separated by flash column silica gel (50 g, loaded in hexanes) (eluted with 25% Et$_2$O in CCl$_4$) to afford 770 mg (79%) of the β-triester (oil): $[\alpha]^{25}_D$ +16.1° (*c* 1.1, CH_2Cl_2): ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.19 (3 H, t, *J* = 7.2 Hz), 3.04 (1 H, $^1/_2$ABq, *J* = 17 Hz), 3.10 (1 H, $^1/_2$ABq, *J* = 17 Hz), 3.35–3.84 (3 H, m), 3.51 (3 H, s), 3.69 (3 H, s), 4.05 (2 H, q, *J* = 7.2 Hz), 4.16 (1 H, m), 4.26 (1 H, m), 4.37–4.84 (7 H, m), 7.12–7.44 (15 H, m); IR (NaCl, neat) 3030, 2950, 1745, 1450, 1200 cm^{-1}; mass spectrum, *m/z* 529 (M$^+$ − 91, 1.1), 423 (25.4), 106 (100).

1,1-Dimethyl-2-ethyl-1-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl) 1,1,2-Ethanetricarboxylate. Hydrogenation of 25 (65 mg, 0.105 mmol) with 18% Pd/C (10 mg) in absolute ethanol under a H$_2$ atmosphere for 12 h at room temperature afforded 25 mg (68%) of the corresponding triol (isolated by PTLC silica gel, eluted with 16% MeOH in CHCl$_3$) (oil): IR (NaCl, film) 3460, 2950, 1735, 1435 cm^{-1}; mass spectrum, *m/z* 319 (M$^+$ − 31, 0.9), 305 (1.5)8 145 (100); exact mass calcd (M + 1) 351.1291, found 351.1297.

Acetylation of this triol (20 mg, 0.057 mmol) with acetic anhydride (1 mL), pyridine (2 mL), sodium acetate (5 mg), and DMAP (0.5 mg) afforded 18.8 mg (69%) of the 2,3,5-triacetate (oil): $[\alpha]^{25}_D$ +17.0° (*c* 0.6, CH_2Cl_2): ^1H NMR (270 MHz) ($CDCl_3$) δ (TMS) 1.25 (3 H, t, *J* = 7.3 Hz), 2.046 (3 H, s), 2.08 (3 H, s), 2.11 (3 H, s), 3.09 (2 H, s), 3.76 (3 H, s), 3.78 (3 H, s), 4.0–4.35 (5 H, m), 4.63 (1 H, d, *J* = 4.8 Hz), 5.10 (1 H, t, *J* = 6 Hz), 5.15 (1 H, t, *J* = 5 Hz); IR (NaCl, neat) 2950, 1745, 1370, 1220 cm^{-1}.

2-[2,3-*O*-Isopropylidene-5-*O*-(*tert*-butyldiphenylsilyl)-β- and -α-D-ribofuranosyl]furan (9, R_1 = SiPh$_2$-*t*-Bu; R_2, R_3 = C(Me)$_2$; Ar = 2-furanyl). From 125 mg (0.24 mmol) of 3 (α/β, 3:1) and 92 mg (0.36 mmol) of silver (I) triflate in furan (5 mL) at room temperature for 15 min was obtained 12.5 mg (11%) of the β anomer and 60.1 mg (53%) of the α anomer (isolated by PTLC silica gel, eluted with 10% EtOAc/hexanes).

β-9: (oil): $[\alpha]^{25}_D$ −7.15° (*c* 1.1, CH_2Cl_2); ^1H NMR (100 MHz) ($CDCl_3$) δ (TMS) 1.07 (9 H, s), 1.40 (3 H, s), 1.60 (3 H, s), 3.75 (2 H, m), 4.20 (1 H, m), 4.80–4.95 (3 H, m), 6.31 (2 H, br s), 7.30–7.75 (11

H, m); IR (NaCl, neat) 3070, 2930, 1455, 1430, 700 cm^{-1}; mass spectrum, m/z 463 (M$^+$ − 15, 2.1), 421 (3.5), 151 (100).

α-9 (oil): [α]^{25}$_D$ −27.0° (c 0.75, CH$_2$Cl$_2$); ^{1}H NMR (100 MHz) (CDCl$_3$) δ (TMS) 1.08 (9 H, s), 1.35 (3 H, s), 1.50 (3 H, s), 3.80 (2 H, m), 4.21 (1 H, m), 4.95 (2 H, m), 5.33 (1 H, d, J = 4 Hz), 6.37 (1 H, m), 6.46 (1 H, m), 7.30–7.75 (11 H, m); IR (NaCl, neat) 3070, 2930, 1430, 1110, 700 cm^{-1}; mass spectrum, m/z 463 (M$^+$ − 15, 2,2), 421 (4.0), 129 (100).

2-(2,3-O-Isopropylidene-β- and -α-D-ribofuranosyl (9, R$_1$ = H; R$_2$, R$_3$ = C(Me)$_2$; Ar = 2-furanyl). To a stirred solution of the β-9 (14.9 mg, 0.031 mmol) in THF (5 mL) was added Bu$_4$NF·3H$_2$O (20 mg, 0.0625 mmol, 2.0 equiv) in one portion. The mixture was allowed to stir for 3 h at ambient temperature, concentrated, and separated by PTLC silica gel (eluted with 20% Et$_2$O in CHCl$_3$) to afford 3.8 mg (50%) of the β-alcohol (oil): [α]^{25}$_D$ −58.4° (c = 0.19, CH$_2$Cl$_2$); ^{1}H NMR (270 MHz) (CDCl$_3$) δ (TMS) 1.37 (3 H, s), 1.59 (3 H, s), 2.15 (1 H, br s), 3.75 (2 H, m), 4.21 (1 H, m), 4.81 (1 H, m), 4.91 (2 H, m), 6.36 (2 H, m), 7.42 (1 H, m); ^{13}C NMR (77 MHz) (CDCl$_3$) δ (CDCl$_3$) 114.48, 27.47, 25.53 [lit. 114.49, 27.37, 25.39].

In the same manner, 15 mg of α-9 was converted into 4.7 mg (62%) of the corresponding α-alcohol: mp 57–59 °C (recryst Et$_2$O/hexanes); [α]^{25}$_D$ −52.8° (c 0.24, CH$_2$Cl$_2$); ^{1}H NMR (270 MHz) (CDCl$_3$) δ (TMS) 1.34 (3 H, s), 1.52 (3 H, s), 1.80 (1 H, br s), 3.77 (2 H, m), 4.28 (1 H, m), 4.75 (1 H, m), 4.86 (1 H, m), 5.11 (1 H, d, J = 4.1 Hz), 6.39 (1 H, m), 6.50 (1 H, m), 7.42 (1 H, m); ^{13}C NMR (77 MHz) (CDCl$_3$) δ (CDCl$_3$) 113.48, 26.42, 25.27 [lit. 113.08, 26.20, 25.03]; IR (NaCl, neat) 3440, 2930, 1380, 745 cm^{-1}.

Showdomycin. A stirred solution of 9 (R$_1$ = SiPh$_2$-t-Bu; R$_2$, R$_3$ = C(CH$_3$)$_2$; Ar = 2,4,6-trimethoxyphenyl) (90 mg, 0.15 mmol) in EtOAc (5 mL) at −78 °C, was treated with ozone gas for 20 min. The resulting blue solution was stirred 1 h at −78 °C, and dimethyl sulfide (0.28 mL, 30 equiv) was added. The mixture gradually warmed to room temperature over a 90-min period and evaporated to dryness. The crude, labile α-keto methyl ester is then dissolved in CHCl$_3$ (10 mL) and treated with carbamoylmethylenetriphenylphosphorane (140 mg, 0.44 mmol, 3.0 equiv). The mixture was stirred for 45 min at ambient temperature, concentrated, and separated by PTLC silica gel (eluted with 50% Et$_2$O/hexanes) to afford 15.4 mg (20%, two steps) of the fully protected 2,3-O-isopropylidene-5-O-(*tert*-butyldiphenylsilyl)showdomyin derivative (oil): [α]^{25}$_D$ +8.5° (c 0.86, CH$_2$Cl$_2$); ^{1}H NMR (270 MHz) (CDCl$_3$) δ (TMS) 1.05 (9 H, s), 1.36 (3 H, s), 1.60 (3 H, s), 3.70–3.85 (2 H, m), 4.22 (1 H, m), 4.61–4.80 (2 H, m), 4.85 (1 H, m), 6.49 (1 H, d, J = 1.9 Hz), 7.30–7.75 (10 H, m); IR (NaCl, neat) 2900, 1720, 1100 cm^{-1}.

The material obtained above (18.5 mg, 0.036 mmol) was converted into showdomycin by treatment with aqueous trifluoroacetic acid[15] (4:1, TFA/H$_2$O, 5 mL) for 1.25 h at 25 °C. The mixture was evaporated to dryness and chromatographed by PTLC silica gel (eluted with 30% THF in EtOAc) to afford 6.5 mg (78%) of a white solid: mp 146–147 °C (recryst acetone/benzene) [lit. 153 °C]; [α]^{25}$_D$ +48.0° (c 0.05, H$_2$O) [lit. +47.1–49.9 °C). The spectral properties (TLC, ^{1}H NMR, IR, MS, and ^{13}C NMR) of the natural and synthetic materials were identical.

The melting point of the natural material obtained from syntex was 146–147 °C.

Registry No. 1, 74352-41-3; ε-2, 96689-78-0; α-2, 96689-79-1; α-3, 96689-80-4; ε-3, 96689-81-5; 6 (R^1 = R^2 = H), 96689-97-3; α-6 (R^1 = Ph; R^2 = H), 85422-87-3; ε-6 (R^1 = O; R^2 = CH$_2$CH$_2$) (isomer 1), 96689-82-6; β-6 (R^1 = O; R^2 = CH$_2$CH$_2$) (isomer 2), 96745-15-2; α-6 (R^1 = O; R^2 = CH$_2$CH$_2$) (isomer 1), 96745-16-3; α-6 (R^1 = O; R^2 = CH$_2$CH$_2$) (isomer 2), 96745-17-4; α-6 (R^1 = OCH$_3$; R^2 = CO$_2$CH$_3$), 96689-83-7; β-7 (Ar = 2,4,6-trimethoxyphenyl), 82300-67-2; α-7 (Ar = 2,4,6-trimethoxyphenyl), 93414-74-5; α-7 (Ar = 2,4-dimethoxyphenyl), 96689-84-8; α-8 (R^1 = R^2 = R^3 = CH$_2$Ph; R^4 =O; R^5 = CH$_2$CH$_2$) (anomer a), 96689-85-9; α-8 (R^1 = R^2 = R^3 = CH$_2$Ph; R^4 = O; R^5 = CH$_2$CH$_2$) (anomer 6), 96745-18-5; α-8 (R^1 = H; R^2, R^3 = C(CH$_3$)$_2$; R^4 = O, R^5 = CH$_2$CH$_2$) (anomer a), 96689-86-0; α-8 (R^1 = H; R^2, R^3 = C(CH$_3$)$_2$; R^4 = O; R^5 = CH$_2$CH$_2$) (anomer 6), 96745-19-6; α-8 (R^1 = SiPh$_2$-t-Bu; R^2, R^3 = C(CH$_3$)$_2$; R^4 = O; R^5 = CH$_2$CH$_2$) (isomer 1), 96689-87-1; α-8 (R^1 = SiPh$_2$-t-Bu; R^2, R^3 = C(CH$_3$)$_2$; R^4 = O; R^5 = CH$_2$CH$_2$) (isomer 2), 96745-20-9; β-8 (R^1 = R^2 = R^3 = CH$_2$Ph; R^4 = OCH$_3$; R^5 = CO$_2$CH$_3$), 96689-88-2; β-9 (R^1 = R^2 = R^3 = CH$_2$Ph; Ar = 2,4,6-trimethoxyphenyl), 96689-89-3; β-9 (R^1 = SiPh$_2$-t-Bu; R^2, R^3 = C(CH$_3$)$_2$; Ar = 2,4,6-trimethoxyphenyl), 96689-90-6; β-9 (R^1 = R^2 = R^3 = H; Ar = 2,4,6-trimethoxyphenyl), 29161-71-5; α-9 (R^1 = R^2 = R^3 = H; Ar = 2,4,6-trimethoxyphenyl), 39706-36-0; β-9 (R^1 = SiPh$_2$-t-Bu; R^2, R^3 = C(CH$_3$)$_2$; Ar = 2-furanyl), 96689-91-7; α-9 (R^1 = SiPh$_2$-t-Bu; R^2, R^3 = C(CH$_3$)$_2$; Ar = 2-furanyl), 96745-21-0; β-9 (R^1 = H; R^2, R^3 = C(CH$_3$)$_2$; Ar = 2-furanyl), 86528-52-1; α-9 (R^1 = H; R^2, R^3 = C(CH$_3$)$_2$; Ar = 2-furanyl), 86528-53-2; β-9 (R^1 = H; R^2, R^3 = C(CH$_3$)$_2$; Ar = 2,4,6-trimethoxyphenyl), 96689-98-4; α-10 (R = H; R^1 = Ph; R^2 = H; X = H, H), 96689-92-8; α-10 (R = COCH$_3$; R^1 = Ph; R^2 = H; X = H, H), 85422-91-9; α-10 (R = H; R^1 = 0; R^2 = CH$_2$CH$_2$; X = 0), 96689-93-9; α-10 (R = COCH$_3$; R^1 = O; R^2 == CH$_2$CH$_2$; X = 0), 96689-94-0; β-10 (R = H; R^1 = O; R^2 = CH$_2$CH$_2$; X = 0), 96745-22-1; β-10 (R = COCH$_3$; R^1 = 0; R^2 = CH$_2$CH$_2$; X = 0), 96745-23-2; β-11 (R = H; Ar = 2,4,6-trimethoxyphenyl), 89648-16-8; β-11 (R = COCH$_3$; Ar = 2,4,6-trimethoxyphenyl), 86762-94-9; α-11 (R = H; Ar = 2,4,6-trimethoxyphenyl), 73244-62-9; α-11 (R = COCH$_3$; Ar = 2,4,6-trimethoxyphenyl), 73244-61-8; α-11 (R = H; Ar = 2,4-dimethoxyphenyl), 96689-95-1; α-11 (R = COCH$_3$; Ar = 2,4-dimethoxyphenyl), 96689-96-2; **20**, 16755-07-0; **25**, 96689-99-5; 2,3,4,6-tetra-O-benzylglucopyranose, 6564-72-3; 2,2-dipyridyl disulfide, 2127-03-9; 2,3,5-tri-O-benzylribofuranose, 16838-89-4; 2-mercaptopyridine, 2637-34-5; ribofuranose 2,3-acetonide, 4099-88-1; *tert*-butyldiphenylsilyl chloride, 58479-61-1; 1,3,5-trimethoxybenzene, 621-23-8; *m*-dimethoxybenzene, 151-10-0; acetophenone trimethylsilylenol ether, 13735-81-4; γ-butyrolactone trimethylsilylenol ether, 51425-66-2; acetaldehyde trimethylsilylenol ether, 6213-94-1; 1-deoxy-1-(C-2-hydroxyethyl)-2,3,4,6-tetra-O-benzyl-D-glucopyranose, 81972-20-5; carbomethoxyketene methyl trimethylsilyl acetal, 40333-11-7; α-bromoethyl acetate, 105-36-2; 1,1-dimethyl-2-ethyl 1-(β-D-ribofuranosyl)-1,1,2-ethanetricarboxylate, 96690-00-5; 1,1-dimethyl-2-ethyl 1-(2′,3′,5′-tri-O-β-D-ribofuranosyl)-1,1,2-ethanetricarboxylate, 96690-01-6; furan, 110-00-9; carbamoylmethylenetriphenylphosphorane, 38821-11-3; 2,3-O-isopropylidene-5-O-(*tert*-butyldiphenylsilyl)showdomycin, 78442-67-8; 2,3-O-isopropylidene-5-o-(*tert*-butyldiphenylsilyl)-D-ribofuranose, 96690-02-7.