NaI): m/z 246 ($C_9H_{17}DO_6$ + Na).

1-(2-Deoxy-α-D-glucopyranosyl)-2,3-(2*S*)-propanediol (14). The unlabeled tribenzyl diol **26** (14 mg, 0.028 mmol) was deprotected by the same procedure as the parent 2-benzyloxy compound to yield the polyol **14** as a clear colorless oil (6 mg). IR (neat): 3329 cm^{-1}, 2930, 1061. ^1H NMR (CD_3OD): δ 1.71 (1 H, ddd, J = 5.7, 10.8, 13.3 Hz); 1.71 (1 H, ddd, J = 5.1, 6.0, 14.2 Hz); 1.90 (1 H, ddd, J = 7.7, 8.7, 14.2 Hz); 1.91 (1 H, ddd, J = 2.5, 4.6, 13.3 Hz); 3.18 (1 H, dd, J = 8.5, 8.6 Hz); 3.51 (1 H, ddd, J = 2.7, 6.4, 8.5 Hz); 3.50–3.55 (2 H, m); 3.66 (1 H, dd, J = 6.4, 11.6 Hz); 3.70–3.76 (2 H); 3.79 (1 H, dd, J = 2.7, 11.6 Hz); 4.19 (1 H, dddd, J = 2.5, 5.7, 6.0, 8.7 Hz). ^{13}C NMR (CD_3OD): δ 35.77, 37.01, 63.16, 66.82, 70.14, 71.15, 71.43, 73.56, 75.87. MS (FAB, neg): m/z 221 (M − H). HRMS (FAB, neg): calcd for $C_9H_{18}O_6$ (M − H) 221.1025, found 221.1022. $[\alpha]_D$: +33.3° (c 0.55, CH_3OH).

1-(2-Deoxy-α-D-glucopyranosyl)-1(*R*)-deuteriopropane-2,3-(2*S*)-diol (15d_S). The monodeuterated tribenzyl diol **26**d_S (2.5 mg, 5.1 μmol) was deprotected by the same procedure as the parent 2-benzyloxy compound to yield the polyol **14**d_S as a clear colorless oil (1.2 mg). ^1H NMR (CD_3OD): δ 1.68 (1 H, dd, J = 4.8, 5.6 Hz); 1.70 (1 H, ddd, J = 5.6, 10.8, 13.2 Hz); 1.90 (1 H, ddd, J = 2.5, 4.8, 13.2 Hz); 3.18 (1 H, dd, J = 8.2, 8.7 Hz); 3.49 (1 H, ddd, J = 2.7, 6.4, 8.7 Hz); 3.50–3.55 (2 H, m); 3.66 (1 H, dd, J = 6.4, 11.6 Hz); 3.70–3.76 (2 H); 3.79 (1 H, dd, J = 2.7, 11.6 Hz); 4.19 (1 H, ddd, J = 2.5, 5.6, 5.6 Hz). MS (FAB, NaI): m/z 246 ($C_9H_{17}DO_6$ + Na).

1-(2-Deoxy-β-D-glucopyranosyl)-2,3-(2*R*)-propanediol (15). 1-(2-Deoxy-3,4,6-*O*-tribenzyl-β-D-glucopyranosyl)-2,3-(2*R*)-propanediol (9 mg, 0.018 mmol) was deprotected by the same procedure as the parent 2-benzyloxy compound to yield the polyol **15** as a clear colorless oil (4.1 mg). IR (neat): 3330 cm^{-1}, 2920, 2873, 1063. ^1H NMR (CD_3OD): δ 1.32 (1 H, ddd, J = 11.4, 11.4, 12.7 Hz); 1.65 (1 H, ddd, J = 5.0, 5.3, 14.1 Hz); 1.70 (1 H, ddd, J = 7.5, 7.7, 14.1 Hz); 2.01 (1 H, ddd, J = 1.8, 5.1, 12.7 Hz); 3.14 (1 H, dd, J = 8.4, 9.6 Hz); 3.18 (1 H, ddd, J = 2.4, 5.9, 9.6 Hz); 3.46 (1 H, dd, J = 5.8, 11.2 Hz); 3.49 (1 H, dd, J = 4.9, 11.2 Hz); 3.54 (1 H, ddd, J = 5.1, 8.4, 11.4 Hz); 3.62 (1 H, dd, J = 5.9, 11.8 Hz); 3.64 (1 H, dddd, J = 1.8, 5.0, 7.5, 11.4 Hz); 3.78 (1 H, dddd, J = 4.9, 5.3, 5.8, 7.7 Hz); 3.84 (1 H, dd, J = 2.4, 11.8 Hz). ^{13}C NMR (CD_3OD): δ 40.06, 40.65, 63.27, 67.07, 71.12, 73.55, 73.91, 74.89, 81.78. MS (FAB): m/z 223 (M + H). HRMS (FAB, neg): calcd for $C_9H_{18}O_6$ (M − H) 221.1025, found 221.1035. $[\alpha]_D$: +2.6° (c 0.43, CH_3OH).

1-(2-Deoxy-β-D-glucopyranosyl)-2,3-(2*S*)-propanediol (16). 1-(2-Deoxy-3,4,6-*O*-tribenzyl-β-D-glucopyranosyl)-2,3-(2*S*)-propanediol (8 mg, 0.016 mmol) was deprotected by the same procedure as the parent 2-benzyloxy compound to yield the polyol **16** as a clear colorless oil (3.6 mg). IR (neat): 3327 cm^{-1}, 2920, 2870, 1064. ^1H NMR (CD_3OD): δ 1.35 (1 H, ddd, J = 11.4, 11.4, 12.7 Hz); 1.46 (1 H, ddd, J = 2.8, 9.6, 14.3 Hz); 1.67 (1 H, ddd, J = 3.1, 9.6, 14.3 Hz); 1.93 (1 H, ddd, J = 1.9, 5.1, 12.7 Hz); 3.14 (1 H, dd, J = 8.3, 9.5 Hz); 3.18 (1 H, ddd, J = 2.3, 5.8, 9.5 Hz); 3.43 (1 H, dd, J = 6.1, 11.2 Hz); 3.49 (1 H, dd, J = 4.9, 11.2 Hz); 3.55 (1 H, ddd, J = 5.1, 8.3, 11.4 Hz); 3.63 (1 H, dd, J = 5.8, 11.7 Hz); 3.67 (1 H, dddd, J = 1.9, 2.8, 9.6, 11.4 Hz); 3.85 (1 H, dd, J = 2.3, 11.7 Hz); 3.86 (1 H, dddd, J = 3.1, 4.9, 6.1, 9.6 Hz). ^{13}C NMR (CD_3OD): δ 40.53, 41.25, 63.32, 67.63, 69.79, 73.31, 73.61, 74.05, 81.60. MS (FAB): m/z 223 (M + H). HRMS (FAB, neg): calcd for $C_9H_{18}O_6$ (M − H) 221.1025, found 221.1034. $[\alpha]_D$: −2.5° (c 0.39, CH_3OH).

Acknowledgment. Financial support from the National Institutes of Health (NS 12108) and the National Science Foundation (CHE 89-09762) is gratefully acknowledged.

Registry No. **1**, 110352-30-2; **1d$_R$**, 110316-51-3; **2**, 110352-31-3; **2d$_R$**, 110316-52-4; **3**, 110352-32-4; **3d$_S$**, 110352-33-5; **4**, 3736-73-0; **5**, 54548-38-8; **5d$_R$**, 110352-38-0; **6**, 54503-51-4; **6d$_S$**, 110352-36-8; **7**, 82659-52-7; **7d$_R$**, 136089-03-7; **β-7**, 81972-19-2; **8**, 136088-95-4; **8d$_R$**, 136089-04-8; **9**, 136172-66-2; **9d$_S$**, 136172-71-9; **10**, 136088-96-5; **11d$_S$**, 136089-05-9; **12d$_R$**, 136172-73-1; **13**, 110316-53-5; **13d$_R$**, 110316-54-6; **14**, 110352-34-6; **14d$_S$**, 110352-35-7; **15**, 110352-39-1; **15** 3,4,6-tri-*O*-benzyl derivative, 136172-72-0; **16**, 110352-37-9; **16** 3,4,6-tri-*O*-benzyl derivative, 136172-74-2; **17**, 136088-97-6; **18d$_R$**, 136089-06-0; **19**, 136088-98-7; **20**, 136172-67-3; **21**, 136172-68-4; **21d$_R$**, 136172-75-3; **22**, 136172-69-5; **22d$_S$**, 136172-76-4; **23**, 136088-99-8; **24**, 136089-00-4; **25**, 136089-01-5; **25d$_R$**, 136089-07-1; **26**, 136172-70-8; **26d$_S$**, 136172-77-5; (2,3,4,6-*O*-tetrabenzyl-α-D-glucopyranosyl)methanol, 79258-16-5; (2,3,4,6-*O*-tetrabenzyl-α-D-glucopyranosyl)carboxaldehyde, 113019-43-5; (2-deoxy-3,4,6-*O*-tribenzyl-α-D-glucopyranosyl)methanol, 136089-02-6; (2,3,4,6-*O*-tetrabenzyl-β-D-glucopyranosyl)methanol, 89064-71-1.

Supplementary Material Available: Complete spectroscopic data (IR, ^1H NMR, ^{13}C NMR, MS, HRMS/analysis, and copies of ^1H NMR spectra) for all compounds (58 pages). Ordering information is given on any current masthead page.

Preferred Conformation of *C*-Glycosides. 7. Preferred Conformation of Carbon Analogues of Isomaltose and Gentiobiose†,‡

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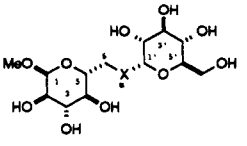
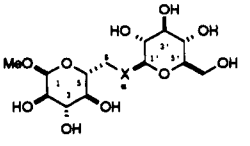
Received March 20, 1991

The preferred solution conformation of the 1,6-linked *C*-disaccharides **3** and **4**, carbon analogues of methyl isomaltoside and methyl gentiobioside, was shown to be **3-A** and **4-A**, respectively, by ^1H NMR spectroscopy.

We have shown that the preferred solution conformation of *C*-monoglycosides can be determined on the basis of vicinal coupling constants measured from the ^1H NMR and that the carbon analogues mirror the glycosidic conformation of the parent *O*-glycosides.[1] We sought to extend our analysis to the case of the 1,6-linked disaccharides, methyl isomaltoside (**1**) and methyl gentiobioside (**2**).[2]



1: X = O
3: X = CH_2



2: X = O
4: X = CH_2

The conformation of the 1,6-disaccharides can be analyzed in terms of two independent monoglycosidic systems.

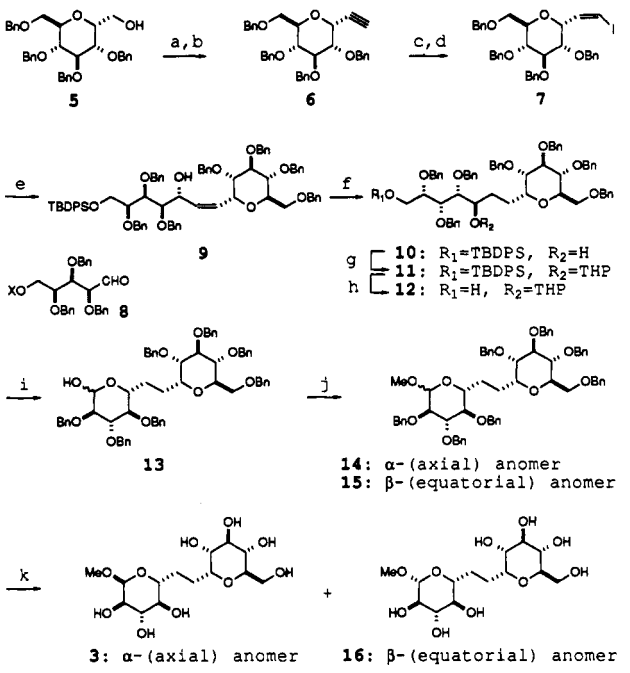
† Preliminary results of this work have been published: Goekjian, P. G.; Wu, T.-C.; Kang, H.-Y.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 4823. For part 6 of this series, see: Goekjian, P. G.; Wu, T.-C.; Kishi, Y. *J. Org. Chem.*, previous article in this issue.

‡ Taken in part from Goekjian, P. G. Ph.D. Dissertation, Harvard University, 1990.

(1) Wu, T.-C.; Goekjian, P. G.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 4819. Goekjian, P. G.; Wu, T.-C.; Kishi, Y. *J. Org. Chem.*, previous paper in this issue.

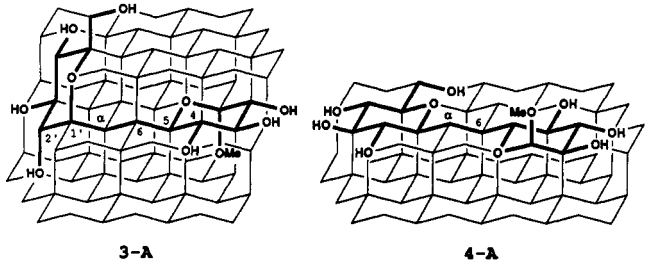
0022-3263/91/1956-6422$02.50/0

Scheme I[a]



[a] (a) i, DMSO, $(COCl)_2$, NEt_3, CH_2Cl_2; ii, CBr_4, PPh_3, CH_2Cl_2; (b) *n*-BuLi, THF, −100 °C; (c) I_2, morpholine, benzene; (d) KO_2CN=NCO_2K, AcOH, dioxane; (e) **8**, 0.1% $NiCl_2/CrCl_2$, DMSO; (f) H_2, Pt/Al_2O_3, EtOAc; (g) DHP, PPTS, CH_2Cl_2; (h) TBAF, THF. (i) i, DMSO, $(COCl)_2$, NEt_3, CH_2Cl_2; ii, *p*-TsOH, MeOH; (j) i, NaH, CH_3I, THF; ii, chromatographic separation; (k) H_2, $Pd(OH)_2/C$, $MeOH/CH_2Cl_2$.

In the case of the carbon analogues **3** and **4**, one notes that the functionalities at C.1′ and C.5 are identical; both C.1′–C.α and C.5–C.6 can be treated as C-glycosidic bonds. We predict that both will adopt the "exo-anomeric" conformation with the central bond antiperiplanar to the pyranose C–C bond. Thus, the C.α–C.6 bond will be antiperiplanar to both the C.1′–C.2′ and the C.5–C.4 bonds. Assuming that the ethylene bridge will favor an extended conformation around the central bond, we then expect the carbon analogues of isomaltose and gentiobiose to adopt preferentially the conformations **3-A** and **4-A**, respectively.



3-A
C-Isomaltoside

4-A
C-Gentiobioside

The synthesis of the methyl glycosides of *C*-isomaltose and *C*-gentiobiose was undertaken in order to confirm these predictions. The β(1,6)-linked analogue **4** has previously been synthesized by Sinaÿ.[3] No synthesis of the α(1,6)-linked analogue **3** was available.

Table I. ^{1}H NMR Data (500 MHz, Methanol-d_4) for Compound 3 at Room Temperature

proton	chemical shift (ppm), coupling pattern, (Hz)
H.1	4.61 (d, J = 3.8)
H.2	3.37 (dd, J = 3.8, 9.6)
H.3	3.55 (dd, J = 9.0, 9.6)
H.4	3.06 (dd, J = 9.0, 9.5)
H.5	3.50 (ddd, J = 2.2, 9.5, 9.5)
H.6	1.59 (dddd, J = 3.6, 9.5, 10.8, 13.3)
H.6	1.83 (dddd, J = 2.2, 5.2, 10.8, 13.3)
H.α	1.69 (dddd, J = 3.2, 5.2, 10.8, 13.5)
H.α	1.93 (dddd, J = 3.6, 10.8, 11.7, 13.5)
H.1′	3.90 (ddd, J = 3.2, 5.7, 11.7)
H.2′	3.59 (dd, J = 5.7, 9.5)
H.3′	3.53 (dd, J = 8.5, 9.5)
H.4′	3.25 (dd, J = 8.5, 9.5)
H.5′	3.41 (ddd, J = 2.5, 5.6, 9.5)
H.6′	3.63 (dd, J = 5.6, 11.7)
H.6′	3.77 (dd, J = 2.5, 11.7)

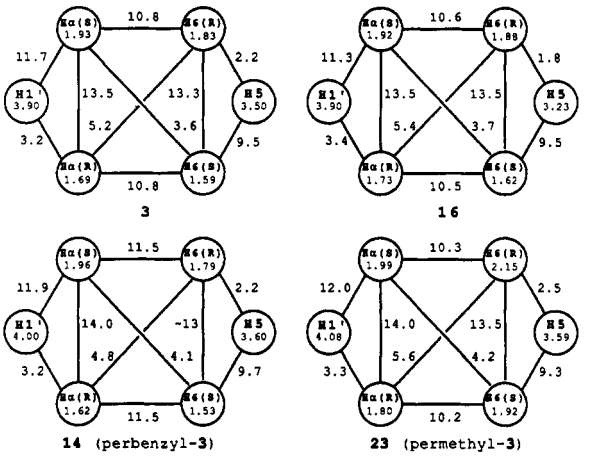


Figure 1. Coupling constant schemes for compounds **3**, **16**, **14**, and **23**.

Results and Discussion

***C*-Isomaltoside.** It was necessary to develop a synthesis of the α(1,6)-linked disaccharide, which should be applicable to the preparation of stereospecifically deuterated compounds on the ethylene bridge (Scheme I). It was anticipated that deuteration of the allylic alcohol **9** could be directed by the free hydroxyl group.[4]

The primary alcohol **5** was converted to the vinyl iodide **7** in five steps via the acetylene **6**. Ni(II)/Cr(II)-mediated coupling of the vinyl iodide with the protected lyxose **8** in DMSO yielded the allylic alcohol **9** in 15:1 *erythro*:*threo* selectivity. The relative stereochemistry of the allylic alcohol (C.5) and the neighboring benzyloxy group (C.4) in the major isomer was established unambiguously on the basis of the vicinal coupling constant ($J_{4,5}$ = 9.5 Hz) in the pyranoside **14**. Hydrogenation of the double bond gave **10**. Protecting-group manipulation yielded **12**, which was oxidized to the aldehyde and deprotected to yield the protected *C*-isomaltose **13**. Methylation provided a 1:1 mixture of methyl glycosides **14** and **15**. Chromatographic separation and deprotection led to the carbon analogues **3** and **16** of methyl isomaltoside.

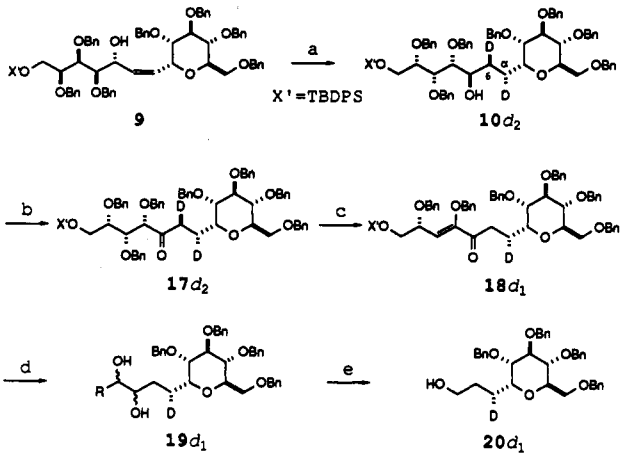
The ^{1}H NMR data for compound **3** are presented in Table I. All signals are well resolved and were assigned

(2) For the conformational analysis of 1,6-disaccharides in solution, see: (a) Ohrui, H.; Nishida, Y.; Itoh, H.; Meguro, H. *J. Org. Chem.* **1990**, *56*, 1726. Ohrui, H.; Nishida, Y.; Watanabe, M.; Hori, H.; Meguro, H. *Tetrahedron Lett.* **1985**, *26*, 3251. (b) Lemieux, R. U.; Wong, T. C.; Thøgersen, H. *Can. J. Chem.* **1982**, *60*, 81. (c) Bock, K.; Vignon, M. *Nouv. J. Chim.* **1982**, *6*, 301. (d) Melberg, S.; Rasmussen, K. *Carbohydr. Res.* **1980**, *78*, 215. (e) Gagnaire, D. Y.; Nardin, R.; Taravel, F. R.; Vignon, M. R. *Nouv. J. Chim.* **1977**, *1*, 423.

(3) Rouzaud, D.; Sinaÿ, P. *Chem. Comm.* **1983**, 1353.

(4) (a) Fujimoto, R.; Kishi, Y.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7154. (b) Evans, D. A.; Morrissey, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3866.

Scheme II[a]



[a] (a) D_2, Pt/Al_2O_3, EtOAc; (b) DMSO, $(COCl)_2$, NEt_3, CH_2Cl_2; (c) NaOMe, MeOH; (d) i, $NaBH_4$, MeOH; ii, 2 N H_2SO_4, THF; iii, $NaBH_4$, MeOH. (e) i, $NaIO_4$, THF/H_2O; ii, $NaBH_4$, MeOH.

by homonuclear decoupling. Coupling constants were determined by first-order analysis. The values around the pyranose rings show that they adopt the expected chair form. The coupling constants observed across the C.5–C.6–C.α–C.1′ bridge (Figure 1) indicate a preference for one dominant conformation.

In the absence of an assignment of the absolute stereochemistry of the C.α and C.6 protons, 2 of the 27 possible staggered conformers across the ethylene bridge are consistent with the observed coupling constants. The couplings around the C.1′–C.α bond (J = 11.7, 3.2 Hz) indicate that two rotamers are possible around this bond. The first rotamer places the C.α–C.6 bond antiperiplanar to the C.1′–C.2′ bond; the coupling constants around the C.α–C.6 and C.6–C.5 bonds then fully define the conformation around the remaining bonds, giving conformer **3-A**. The second rotamer places the C.α–C.6 bond antiperiplanar to the C.1′–O.5′ bond; the conformation around the C.α–C.6 and C.6–C.5 bonds is again defined by the remaining coupling constants. This case corresponds to the conformer with the C.α–C.6 bond antiperiplanar to both the C.1′–O.5′ and the C.5–O.5 bonds.

In conformer **3-A**, the *pro-S* proton is antiperiplanar to the C.1′ proton. In the alternative conformer, the *pro-R* proton is antiperiplanar to the C.1′ proton. The deuterium-labeled carbon analogues of methyl isoimaltoside were prepared according to Scheme II. Use of deuterium gas in place of hydrogen in the reduction of the cis olefin[5] **9** gave the C.α,C.6-dideuterated compound **10**d_2. As expected,[4a] the deuteration proceeded with high facial selectivity (ca. 10:1).

The absolute stereochemistry of the deuterium labels was assigned by chemical degradation. The secondary alcohol was oxidized to the ketone **17**d_2. Treatment with sodium methoxide in methanol resulted in elimination of the β-benzyloxy group and washing out of the C.6 label to yield the monodeuterated α-keto enol ether **18**d_1. Sodium borohydride reduction of the ketone, acid hydrolysis of the enol ether, and reduction of the resulting ketone yielded a mixture of vicinal diols **19**d_1. Sodium periodate cleavage and sodium borohydride reduction provided the degradation product **20**d_1. Comparison of the proton NMR of the degradation product with that of authentic C.α-(*R*)- and C.α-(*S*)-deuterated samples[6] unambiguously establishes the degradation product as **20**d_R. The deuteration product **10**d_2 therefore can be assigned as the C.αd_R,C.6d_S isomer. This compound was carried on to the carbon disaccharide by the same route as the parent compound.

Table II. Selected ^{1}H NMR Coupling Constants (Hz) for Compounds 14d_2 in $CDCl_3$ and 3d_2 in CD_3OD at Varying Temperatures

T (K)	3, H.α (*S*)	14, H.α (*S*)	3, H.6 (*R*)	14, H.6 (*R*)
308	11.7, 10.2	11.9, 11.3	2.4, 10.2	2.2, 11.3
298	12.0, 10.4	12.1, 11.3	2.3, 10.4	2.1, 11.3
283	12.2, 10.6	12.4, 11.9	2.2, 10.6	1.8, 11.9
273	12.2, 10.7	12.4, 12.0	2.1, 10.7	1.5, 12.0
263	12.3, 10.8	12.6, 12.1	1.9, 10.8	1.2, 12.1
247	12.5, 10.9	12.7, 12.1	1.7, 10.9	≈1, 12.1
237	12.5, 11.0	12.7, 12.2	1.6, 11.0	≈1, 12.2

Comparison of the ^{1}H NMR spectrum of the deuterated compound with that of the parent polyol shows loss of the signals at δ 1.69 and 1.59. This assigns these resonances to the C.α *pro-R* and C.6 *pro-S* protons, respectively. The remaining C.α methylene signal bearing the large coupling to the C.1′ proton belongs to the C.α *pro-S* proton. This establishes the conformation as **3-A**. This is the conformation predicted on the basis of our previous results. The magnitude of the observed coupling constants precludes a major contribution from other conformers.

It is interesting to note that the coupling constants observed for the equatorial methyl glycoside **16** do not differ significantly from the anomer **3** (Figure 1). The fact that the conformation around the 1,6-linkage of the carbon disaccharide does not depend significantly on the configuration at C.1 suggests that the conformation of *C*-oligosaccharides can be interpreted in terms of independent glycosidic systems.

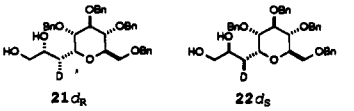
Furthermore, comparison of the coupling constants observed for the polyol **3** (D_2O/CD_3OD), the perbenzyl **14** ($CDCl_3$), and the permethyl disaccharide **23** (C_6D_6) shows that these three compounds are essentially conformationally identical. Temperature studies on perbenzyl disaccharide **14**d_2 and polyol **3**d_2 (Table II) further demonstrate their similarity. The fact that the same trends are observed in the temperature-dependent behavior of the protected and polyol forms suggests that the factors controlling their conformation are similar. These results exclude electrostatic interactions and hydrogen bonds as major factors in governing the overall conformation of these systems.

***C*-Gentiobioside.** Sinaÿ's synthesis of the carbon analogue **4** of methyl gentiobioside was well suited for our purpose, since the intermediacy of acetylene **24** allows for the introduction of deuterium labels. The β(1,6)-linked carbon disaccharide was synthesized according to the published procedure, and the ^{1}H NMR spectrum in 10% D_2O/CD_3OD is shown in Figure 2.

While the proton resonances in the downfield region are well resolved and can be analyzed by first-order analysis,

(5) Extensive purging of the catalyst with D_2 gas prior to addition of the substrate was necessary to avoid incorporation of hydrogen. See: Lee, R. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 369.

(6) Authentic samples with known deuterium stereochemistry were derived from the deuterated diols **23**d_R and **24**d_S[1b] by Corey–Winter olefination followed by hydroboration.



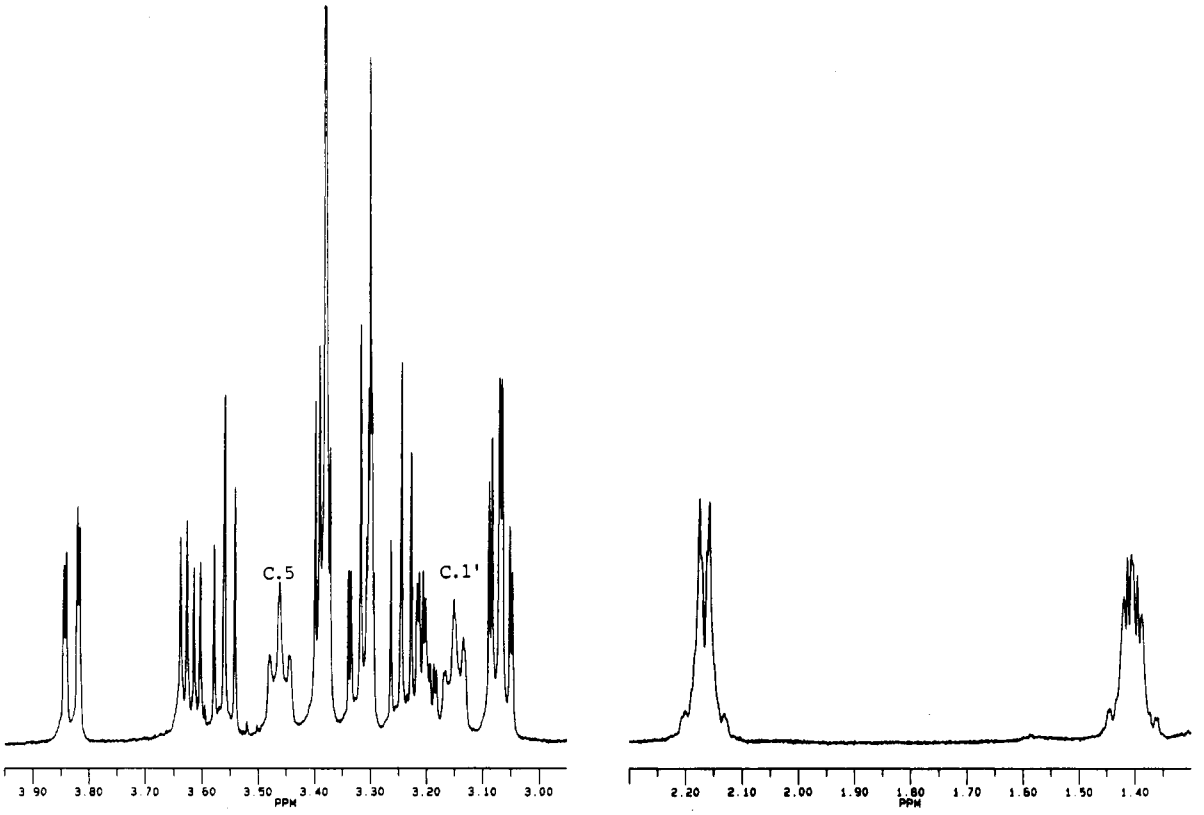


Figure 2. ^1H NMR spectrum (500 MHz) of **4** in 10% D_2O/CD_3OD at room temperature.

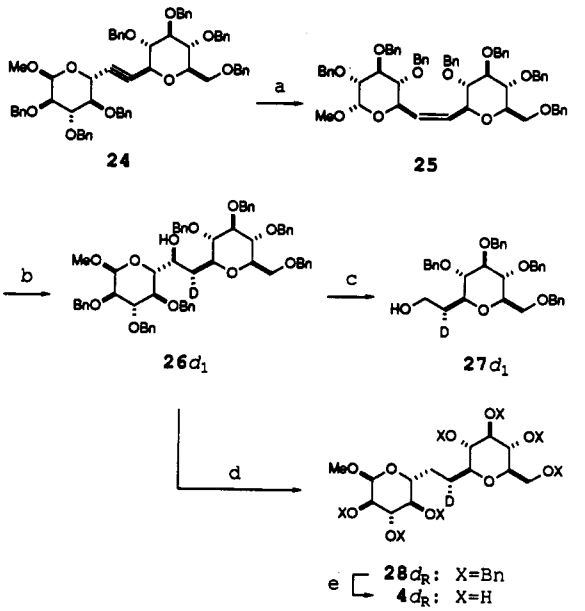
the resonances in the upfield region (δ 1.3–2.3) are clearly higher order. No reliable coupling constants can be derived from these patterns.[7]

This raises an interesting challenge. The possibility of higher order effects can represent a serious limitation to the general application of our approach. It is therefore important to demonstrate that the conformation of the carbon analogues of carbohydrates can be determined experimentally even in cases where a first-order analysis of the ^1H NMR spectrum cannot be applied to obtain vicinal coupling constants.

The gross conformation around the two C-glycosidic bonds, C.1′–C.α and C.5–C.6, can be determined on the basis of two selective deuteration experiments. There are nine possible staggered conformations around these bonds. In the ^1H NMR spectrum of the polyol **4**, the resonances corresponding to the C.1′ (δ 3.15) and C.5 (δ 3.46) protons (Figure 2) each bear two large (ca. 9 Hz) and one small (ca. 2 Hz) couplings. There is apparently some distortion due to higher order effects. Nonetheless, since both protons have a large and a small coupling to the neighboring methylene proton, one of the three conformations around each bond can be excluded. The conformer with the central C–C bond gauche to both the pyranose C–C and C–O bonds would have two small couplings. This narrows the possible conformations to four combinations around the C–glycosidic bonds.

The four possible conformers can be distinguished by assigning the absolute stereochemistry of the protons at C.α and C.6. Adopting the strategy used for the monoglycosides, acetylene **24** was converted to the cis olefin **25**, which was treated with deuterated borane–THF complex (Scheme III). The four isomers (ca. 5:3:1:0.6 ratio) were

Scheme III[a]

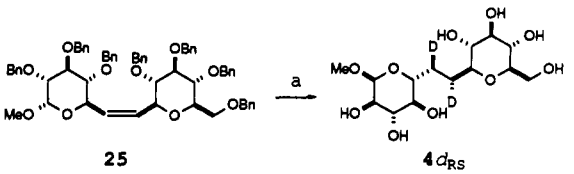


[a] (a) H_2, Lindlar cat., EtOAc; (b) i, BD_3·THF; ii, H_2O_2, NaOH; iii, chromatographic separation; (c) i, 1,2-ethanedithiol, BF_3·Et_2O; ii, $NaIO_4$, THF/water; iii, $NaBH_4$, MeOH; (d) i, NaH, CS_2, CH_3I, THF; ii, *n*-Bu_3SnH, AIBN, toluene; (e) H_2, $Pd(OH)_2/C$, MeOH/CH_2Cl_2.

separated and the major product was assigned the regiochemistry **26**d_1 by homonuclear decoupling. The stereochemistry was assigned by chemical degradation. Opening of the methyl glycoside, sodium periodate cleavage of the resulting vicinal diol dithioacetal, and borohydride reduction provided the degradation product **27**d_1. Comparison of the ^1H NMR spectra of the degradation product with that of authentic stereospecifically labeled samples[8]

(7) Although PANIC computer simulations can be used to extract coupling constants from higher order patterns, the complexity of the coupling system makes this approach impractical in the present case.

Scheme IV[a]



25 $4d_{RS}$

[a] (a) D_2, $Pd(OH)_2/C$, $MeOH/CH_2Cl_2$.

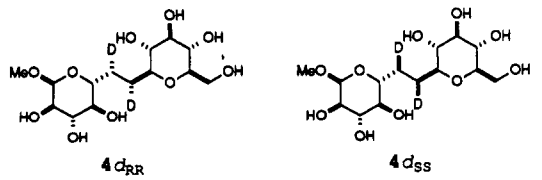
assigns the degradation product as $27d_R$ and therefore the secondary alcohol as $26d_S$.

The deuterated secondary alcohol $26d_S$ was converted to the monodeuterated disaccharide. Formation of the xanthate followed by treatment with tributyltin hydride yields the protected deuterated disaccharide $28d_R$. Deprotection yields the monodeuterated polyol $4d_R$. Comparison of the ^1H NMR spectra shows that one of the resonances at δ 1.4 and the large coupling to C.1′ are lost. The C.α proton antiperiplanar to C.1′ is therefore the *pro-R* proton.

Having established the absolute stereochemistry of $28d_R$, the absolute stereochemistry of the C.6 protons can be assigned by determining the relative stereochemistry of the C.α and C.6 protons. Deuteration of the cis olefin **25** over Pearlman's catalyst yielded a 3:1 mixture of *erythro* deuterated disaccharides (Scheme IV). Comparison of the ^1H NMR spectrum of the deuterated sample to that of the parent polyol shows that the major compound lacks both protons that resonate at δ 1.4 and the large couplings to both the C.1′ and C.5 protons. The C.6 proton antiperiplanar to the C.5 proton is therefore *erythro* to the C.α *pro-R* proton, i.e., *pro-S*.

The assignment of the C.α proton antiperiplanar to C.1 as *pro-R* and the C.6 antiperiplanar to C.5 as *pro-S* firmly establishes the conformation around the two C-glycosidic bonds as that shown in **4-A**. The experimental conformation around the C-glycosidic C.1′–C.α and C.5–C.6 bonds is therefore in accord with our prediction.

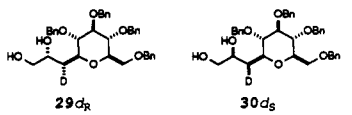
In order to determine the conformation around the central C.α–C.6 bond, it is necessary to measure first-order coupling constants between the methylene protons in the upfield (δ 1.4–2.1) region. In addition, although approximate values for the coupling constants around the C-glycosidic bonds were obtained from the parent spectrum, reliable quantitative values must be measured on a spectrum without substantial higher order effects. A first-order pattern can be obtained in this case only if there is one resonance at δ 1.4 and one resonance at δ 2.1. This requires the synthesis of the two *threo* dideuterated compounds $4d_{RR}$ and $4d_{SS}$.



$4d_{RR}$ $4d_{SS}$

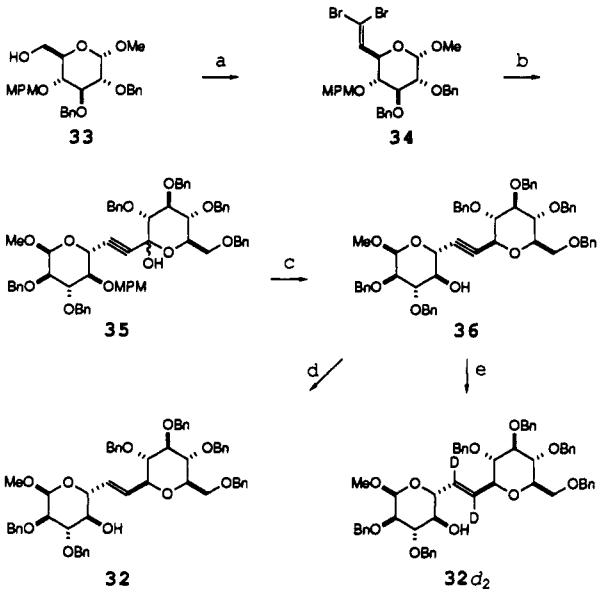
Synthesis of the *threo* deuterated disaccharides by stereoselective deuteration of a trans olefin was investigated. We were unable to achieve a satisfactory level of selectivity with **31** under a variety of deuteration conditions. This was not unexpected in view of the fairly symmetrical nature of the fully protected trans disaccharide. We therefore prepared the O.4-deprotected trans olefin **32** in the hope that the free hydroxyl group would provide an effective directing group for the deuteration.

(8) Authentic samples with known deuterium stereochemistry were derived from the deuterated diols $29d_R$ and $30d_S$[1b] by periodate cleavage followed by sodium borohydride reduction.



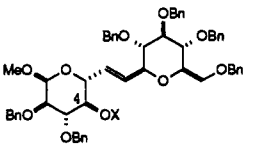
$29d_R$ $30d_S$

Scheme V[a]



33 **34** **35** **36** **32** $32d_2$

[a] (a) i, DMSO, $(COCl)_2$, NEt_3, CH_2Cl_2; ii, CBr_4, PPh_3, CH_2Cl_2; (b) *n*-BuLi, tetrabenzylgluconolactone, THF; (c) Et_3SiH, $BF_3{\cdot}Et_2O$, CH_3CN/CH_2Cl_2; (d) Red-Al, Et_2O; (e) $LiAlD_4$, 2-methoxyethanol, Et_2O.



31: X=Bn
32: X=H

The differentially protected compound was readily obtained by substituting *p*-methoxybenzyl (MPM) for the O.4 benzyl group in the synthesis of the disaccharide. Methyl 2,3-di-*O*-benzyl-4-*O*-MPM-α-D-glucopyranoside[9] was converted to the dibromo olefin **34** (Scheme V). Treatment with *n*-butyllithium followed by an excess of 2,3,4,6-*O*-tetrabenzylgluconolactone yielded the acetylenic hemiketal **35**. Lewis acid catalyzed silane reduction resulted in simultaneous reduction of the hemiketal and loss of the MPM protecting group to yield the acetylene **36**. Treatment of the homopropargylic alcohol **36** with Red-Al (Aldrich) led directly to the trans olefin **32**.[10] The dideuterated trans olefin $32d_2$ was accessible as well by a related procedure.

Hydrogenation of the deuterated trans olefin $32d_2$ was investigated under a variety of conditions. Although none of the conditions was completely stereospecific, the high-pressure hydrogenation conditions over $[Rh(nbd)(diphos\text{-}4)]BF_4$ developed by Evans[4b] gave satisfactory results. Despite some distortion due to the presence of the minor isomer, the ^1H NMR spectrum of the resulting deuterated

(9) Johansson, R.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. I* **1984**, 2371.

(10) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 4245.

Table III. ^{1}H NMR Data (500 MHz) for Compounds $4d_{RR}$, $4d_{SS}$, $37d_{RR}$, and $37d_{SS}$ at Room Temperature

proton	chemical shift (ppm), coupling pattern, (Hz)
$4d_{RR}$	
H.1	3.13 (dd, J = 2.6, 9.5)
H.α (S)	2.14 (dd, J = 2.6, 5.0)
H.6 (S)	1.38 (dd, J = 5.0, 9.2)
H.5	3.44 (dd, J = 9.2, 9.6)
$37d_{RR}$	
H.1	(unresolved)
H.α (S)	2.06 (dd, J = 2.0, 5.3)
H.6 (S)	1.46 (dd, J = 5.3, 8.4)
H.5	3.51 (dd, J = 8.4, 9.5)
$4d_{SS}$	
H.1	3.12 (dd, J = 8.6, 9.5)
H.α (R)	2.15 (dd, J = 2.4, 5.0)
H.6 (R)	1.37 (dd, J = 5.0, 8.6)
H.5	3.44 (dd, J = 2.4, 9.6)
$37d_{SS}$	
H.1	(unresolved)
H.α (R)	1.45 (dd, J = 5.5, 7.7)
H.6 (R)	2.03 (dd, J = 2.9, 5.5)
H.5	3.51 (dd, J = 2.9, 9.5)

disaccharide $37d_{RR}$ and its deprotected for $4d_{RR}$ could be interpreted by first-order analysis.

The other *threo* deuterated disaccharide $37d_{SS}$ could be obtained by inverting the sequence of deuterium and hydrogen incorporation into the molecule. Deuteration of the non-deuterated trans olefin **32** over Rh/Al_2O_3 thus yielded $37d_{SS}$. The ^{1}H NMR data from the deuterated disaccharides $4d_{RR}$ and $4d_{SS}$ and their protected forms $37d_{RR}$ and $37d_{SS}$ are listed in Table III. First-order vicinal coupling constants around both C-glycosidic bonds are available from these compounds: 2.4 Hz and 9.2 Hz for the C.5–C.6 bond and 2.6 and 8.6 Hz around the C.1′–C.α bond. In addition, two of the coupling constants across the central C–C bond are also available: C.α(S)–C.6(S) = 5.0 Hz, C.α(R)–C.6(R) = 5.0 Hz.

First-order constants have been determined for all vicinal couplings except those between the C.α *pro-S* and C.6 *pro-R* protons and between the C.α *pro-R* and C.6 *pro-S* protons. These are couplings between overlapping protons. In the anticipated extended conformation, the C.α *pro-S* and C.6 *pro-R* protons would be antiperiplanar, as would the C.α *pro-R* and C.6 *pro-S* protons. These vicinal coupling constants are therefore the most important in establishing the conformational behavior around the central bond.

Since the difference in chemical shift is less than the coupling constant, it is impossible to determine these coupling constants in the unperturbed system. The fortuitous observation that acetylation of the C.4 hydroxy resulted in a substantial shift of the C.α *pro-S* suggested a possible solution. We have shown in previous cases that the conformation of carbon glycosides is unaffected by the presence and nature of protecting groups.[1] It is therefore reasonable to expect that acetylation of the C.4-OH will represent only a minor perturbation to the conformational behavior of the carbon disaccharide.

Lindlar hydrogenation of **36** led to the cis olefin **38** (Scheme VI). Acetylation followed by deuteration over Pt/Al_2O_3 gave a 4:1 mixture of *erythro* dideuterated disaccharides $39d_{RS}$ and $39d_{SR}$. Deprotection provided the 4-*O*-acetyl polyol $40d_{RS}$. Acetylation of the *threo* dideuterated compounds $37d_{RR}$ and $37d_{SS}$ yielded $39d_{RR}$ and $39d_{SS}$, respectively, which were deprotected to the 4-*O*-acetyl polyols $40d_{RR}$ and $40d_{SS}$.

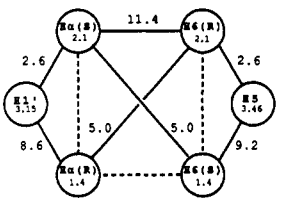
The relevant ^{1}H NMR data are summarized in Table IV. The coupling constant of 11.4 Hz observed between

Table IV. ^{1}H NMR Data (500 MHz) for Compound $40d_{RS}$, $40d_{RR}$, $40d_{SS}$, $39d_{RS}$, $39d_{RR}$, and $39d_{SS}$ at Room temperature

proton	chemical shift (ppm), coupling pattern (Hz)
$40d_{RS}$	
H.1	3.12 (dd, J = 2.6, 9.4)
H.α (S)	2.10 (dd, J = 2.6, 11.4)
H.6 (R)	1.79 (dd, J = 2.6, 11.4)
H.5	3.59 (dd, J = 2.6, 9.4)
$39d_{RS}$	
H.1	3.17 (dd, J = 2.5, 9.2)
H.α (S)	2.09 (dd, J = 2.5, 11.3)
H.6 (R)	1.75 (dd, J = 2.5, 11.3)
H.5	3.57 (dd, J = 2.5, 9.2)
$40d_{RR}$	
H.1	3.10 (dd, J = 2.5, 9.5)
H.α (S)	2.12 (dd, J = 2.5, 4.9)
H.6 (S)	1.36 (dd, J = 4.9, 9.3)
H.5	3.59 (dd, J = 9.3, 9.4)
$39d_{RR}$	
H.1	3.17 (dd, J = 2.5, 9.4)
H.α (S)	2.09 (dd, J = 2.5, 5.4)
H.6 (S)	1.37 (dd, J = 5.4, 9.4)
H.5	3.57 (dd, J = 9.4, 9.7)
$40d_{SS}$	
H.1	3.09 (dd, J = 8.5, 9.5)
H.α (R)	1.33 (dd, J = 4.9, 8.5)
H.6 (S)	1.80 (dd, J = 2.6, 4.9)
H.5	3.59 (dd, J = 2.6, 9.4)
$39d_{SS}$	
H.1	3.17 (dd, J = 8.8, 9.3)
H.α (R)	1.33 (dd, J = 4.9, 8.8)
H.6 (S)	1.75 (dd, J = 2.4, 4.9)
H.5	3.57 (dd, J = 2.4, 9.7)

Table V. Selected ^{1}H NMR Coupling Constants (Hz) for Compounds $37d_2$ in $CDCl_3$ and $4d_2$ in CD_3OD at Varying Temperatures

T (K)	4, H.α (S)	37, H.α (S)	4, H.6 (S)	37, H.6 (S)
317	2.6, 5.1		5.1, 9.1	
307	2.5, 4.9	2.1, 5.5	4.9, 9.2	5.5, 8.2
297	2.5, 4.9	2.1, 5.3	4.9, 9.3	5.3, 8.4
285	2.3, 4.8	2.3, 5.2	4.8, 9.7	5.2, 8.5
273	2.2, 4.8	2.6, 5.2	4.8, 9.7	5.2, 8.5
263	2.1, 4.7	2.6, 5.2	4.7, 9.9	5.2, 8.5



H.1: 4.62 (d, 3.8 Hz)
H.2: 3.39 (dd, 3.8, 9.5 Hz)
H.3: 3.56 (dd, 9.2, 9.5 Hz)
H.4: 3.07 (dd, 9.2, 9.5 Hz)
H.5: 3.39 (ddd, 2.6, 9.2, 9.5 Hz)
H.1′: 3.15 (ddd, 2.6, 8.6, 9.4 Hz)
H.2′: 3.06 (dd, 8.9, 9.4 Hz)
H.3′: 3.31 (dd, 8.5, 8.9 Hz)
H.4′: 3.25 (dd, 8.5, 9.6 Hz)
H.5′: 3.22 (ddd, 2.2, 5.7, 9.6 Hz)
H.6′: 3.63 (dd, 5.7, 11.9 Hz)
H.6′: 3.84 (dd, 2.2, 11.9 Hz)

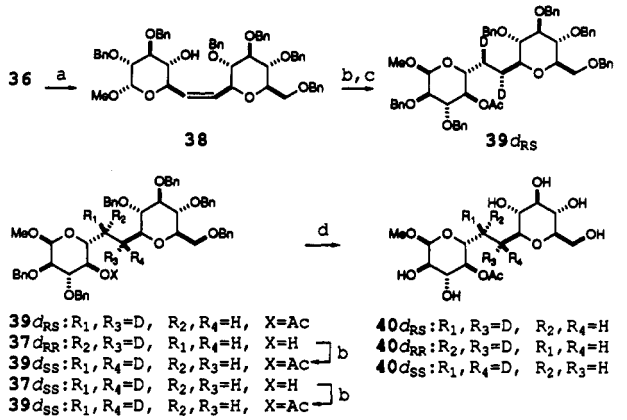
Figure 3. Coupling constant scheme and ^{1}H NMR data for compound **4**.

C.α(S) and C.6(R) in the *erythro* dideuterated 4-*O*-acetyl disaccharides clearly demonstrates that the conformation of the central C.α–C.6 bond is extended, with C.1–C.α antiperiplanar to C.6–C.5. The fact that all of the remaining coupling constants, obtained from the *threo* deuterated 4-*O*-acetyl disaccharides, are unchanged[11] when compared to the polyol case shows that no conformational change results from the presence of the 4-acetoxy group. The coupling constants observed for the acetoxy compound can therefore be extrapolated back to the parent polyol **4**.

Taking into consideration all measured coupling constants and the stereochemistry assignments (Figure 3), we

(11) **69** vs **34**: $J_{5,6}$ = 2.6, 9.3 vs 2.6, 9.2 Hz; $J_{6,\alpha}$ = 4.9, 4.9 vs 5.0, 5.0 Hz; $J_{1',\alpha}$ = 2.6, 8.5 vs 2.6, 8.6 Hz.

Scheme VI[a]



[a] (a) H_2, Lindlar cat., EtOAc; (b) Ac_2O, pyridine DMAP; (c) D_2, Pt/Al_2O_3, EtOAc; (d) H_2, $Pd(OH)_2/C$, MeOH.

can conclude that the carbon disaccharide exists predominantly in the C.2′–C.1′–C.α–C.6–C.5–C.4 extended form **4-A**. This conformation was the one predicted on the basis of our analysis.[12]

Temperature studies were performed on the hexabenzyl compound **37**d_2 and the polyol **4**d_2, and the results are summarized in Table V. As was the case with the carbon analogue **3** of methyl isomaltoside, the ^1H NMR spectra of the two compounds exhibit similar temperature dependence. The observed coupling constants correspond to a population of the major conformer ranging from ca. 80% at −24 °C to ca. 70% at 35 °C around the C.5–C.6 bond. This is further evidence that the net effect of electrostatic and hydrogen-bonding interactions can be disregarded in predicting the preferred solution conformation.

Conclusions

We have shown that our approach can be extended to disaccharides, including a case where the ^1H NMR spectrum shows substantial higher order effects. The conformation of the 1,6-linked carbon disaccharides methyl *C*-isomaltoside and methyl *C*-gentiobioside has been shown to be **3-A** and **4-A**, respectively. The temperature-dependent ^1H NMR behavior around the C-glycosidic bonds of **3** and **4** is parallel to that of the corresponding carbon monoglycosides.[1] This supports the contention that the conformation of the 1,6-linked disaccharides can be analyzed in terms of independent monoglycosidic systems. The similarity in the conformation and variable-temperature ^1H NMR behavior among the polyol, permethyl, and perbenzyl disaccharides indicates that electrostatic and hydrogen-bonding factors do not play a major role in the overall conformational behavior. These results are in accord with our initial predictions based solely on steric considerations.

Experimental Section

General Experimental Procedures. Only selected spectral data are presented in the Experimental Section. Aqueous workups were performed by diluting the reaction mixture with the indicated solvent and washing with saturated NH_4Cl, saturated $NaHCO_3$, and brine (other washes indicated with the solvent). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. For other general procedures, see ref 1b.

Dibromo Olefin 41. (2,3,4,6-*O*-Tetrabenzyl-α-D-glucopyranosyl)methanol (**5**) (981 mg, 1.77 mmol) was oxidized according to usual Swern procedure.[1b] The crude aldehyde was azeotroped with toluene and used without further purification. A vigorously stirred solution of carbon tetrabromide (1.25 g, 3.77 mmol) in CH_2Cl_2 (1 mL) at 0 °C under argon was treated with triphenylphosphine (2.00 g, 7.62 mmol) and stirred at room temperature for 20 min. The resulting bright orange slurry was cooled to 0 °C, and solution of the aldehyde (1.77 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise. The mixture was stirred for 5 min at 0 °C and 25 min at room temperature. The reaction was filtered through silica gel in CH_2Cl_2. Silica gel chromatography (flash silica, toluene, 10%, 15% ether/hexanes) yielded the dibromo olefin **41** as a cloudy, colorless oil (1.051 g, 1.483 mmol, 84% yield). IR (neat): 1605 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.58 (1 H, ddd, J = 2.2, 2.8, 9.3 Hz); 3.67 (1 H, dd, J = 2.0, 10.7 Hz); 3.70–3.77 (3 H, m); 3.81 (1 H, dd, J = 6.0, 9.1 Hz); 4.69 (1 H, dd, J = 6.0, 7.7 Hz); 6.89 (1 H, d, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$): δ 96.40, 132.80. MS (FAB, NaI): m/z 731 (M + Na). HRMS (FAB, NaI): calcd for $C_{36}H_{36}O_5Br_2$ (M + Na) 731.0811, found 731.0811. $[\alpha]_D$: +62.3° (c 1.46, $CHCl_3$).

Acetylene 6. A stirred solution of the dibromo olefin **41** (1.014 g, 1.431 mmol) in dry THF (2.5 mL) at −100 °C under argon was treated with *n*-BuLi (1.35 mL, 3.1 mmol) and stirred at −80 °C for 10 min. The reaction was warmed to 0 °C and quenched with water. Aqueous workup (CH_2Cl_2) and silica gel chromatography (flash silica, 10%, 15% ether/hexanes) yielded the acetylene **6** as a clear colorless oil (702.7 mg, 1.281 mmol, 89% yield). IR (neat): 3277 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.60 (1 H, d, J = 2.2 Hz); 3.61–3.69 (3 H, m); 3.75 (1 H, dd, J = 3.5, 10.8 Hz); 3.97 (1 H, dd, J = 9.2, 9.3 Hz); 3.99 (1 H, ddd, J = 2.1, 3.1, 10.0 Hz); 4.75 (1 H, dd, J = 2.2, 5.3 Hz). ^{13}C NMR ($CDCl_3$): δ 66.56, 78.49. MS (FAB, NaI): m/z 571 (M + Na). HRMS (FAB, NaI): calcd for $C_{36}H_{36}O_5$ (M + Na) 571.2460, found 571.2469. $[\alpha]_D$: +46.7° (c 1.7, $CHCl_3$).

Iodoacetylene 42. A stirred solution of morpholine (1.0 mL, 11.5 mmol) in dry benzene (10 mL) at 45 °C under argon was treated with iodine (450 mg, 1.77 mmol) and stirred at 45 °C for 45 min. A solution of the acetylene **6** (699.5 mg, 1.275 mmol) in benzene (5 mL) was added, and the reaction was stirred at 45 °C for 24 h. The reaction was cooled to room temperature, diluted with ether, and filtered through glass wool. Aqueous workup (ether; Na_2SO_3) and silica gel chromatography (flash silica, 10%, 15% ether/hexanes) yielded the iodoacetylene **42** as a clear colorless oil (838.1 mg, 1.242 mmol, 97% yield). IR (neat): 2179 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.59–3.66 (2 H); 3.67 (1 H, dd, J = 2.0, 10.8 Hz); 3.76 (1 H, dd, J = 3.5, 10.8 Hz); 3.93 (1 H, dd, J = 9.3, 9.3 Hz); 3.95 (1 H, ddd, J = 2.0, 3.5, 10.0 Hz); 4.89 (1 H, d, J = 5.7 Hz). ^{13}C NMR ($CDCl_3$): δ 5.97, 89.54. MS (FAB, NaI): m/z 697 (M + Na). HRMS (FAB, NaI): calcd for $C_{36}H_{35}O_5I$ (M + Na) 697.1427, found 697.1417. $[\alpha]_D$: +93.7° (c 1.75, $CHCl_3$).

Vinyl Iodide 7. A stirred solution of the iodoacetylene **42** (838.1 mg, 1.242 mmol) and potassium azodicarboxylate (1.25 g, 6.43 mmol) in dioxane (15 mL) at room temperature under argon was treated with acetic acid (3.8 M in dioxane, 3 mL, 11.4 mmol) via syringe pump over a period of 9 h. After the addition was complete, the reaction was stirred at room temperature for 5 h while being monitored carefully by TLC in 40% ether/hexanes. (Best results are obtained if the reaction is interrupted when the amount of starting material is comparable to the amount of overreduced material). Aqueous workup (ether) and silica gel chromatography (flash silica, 10%, 15% ether/hexanes) yielded the vinyl iodide **7** as a white solid (648 mg, 0.958 mmol, 77% yield). An analytical sample was obtained by recrystallization from MeOH/water; white needles, mp 83–86 °C. IR (neat): 1604 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.57 (1 H, ddd, J = 2.1, 3.0, 9.3 Hz); 3.68 (1 H, dd, J = 2.1, 10.7 Hz); 3.71 (1 H, dd, J = 3.0, 10.7 Hz); 3.72 (1 H, dd, J = 8.7, 9.3 Hz); 3.77 (1 H, dd, J = 8.7, 8.9 Hz); 3.83 (1 H, dd, J = 5.9, 8.9 Hz); 4.77 (1 H, br dd, J = 5.9, 7.4 Hz); 6.74 (1 H, dd, J = 7.4, 7.8 Hz); 6.81 (1 H, dd, J = 0.7, 7.8 Hz). ^{13}C NMR ($CDCl_3$): δ 89.36, 134.83. MS (FAB, NaI): m/z 699 (M + Na). Anal. Calcd for $C_{36}H_{37}O_5I$: C, 63.90; H, 5.51. Found: C, 63.95; H, 5.56. $[\alpha]_D$: +43.8° (c 1.6, $CHCl_3$).

(12) The crystal structure of methyl *C*-gentiobioside (**4**) was published recently: Neuman, A.; Longchambon, F.; Abbes, O.; Gillier-Pandraud, H.; Perez, S.; Rouzaud, D.; Sinaÿ, P. *Carbohydr. Res.* **1990**, *195*, 187. It is interesting to note that the solid-state structure cannot be reconciled with the solution ^1H NMR data.

Tribenzyllyxose Dithioacetal 43. A stirred solution of lyxose dithioacetal (1.3 g, 5.07 mmol) in pyridine (15 mL) at room temperature under argon was treated with *p*-anisylchlorodiphenylmethane (1.8 g, 5.83 mmol) and stirred at room temperature for 24 h. The reaction was concentrated in vacuo. Silica gel chromatography (flash silica, CH_2Cl_2, 10% MeOH/CH_2Cl_2) yielded the monomethoxytrityllyxose dithioacetal as a light yellow oil (2.6 g, 4.92 mmol, 97% yield). A solution of monomethoxytrityllyxose dithioacetal (2.6 g, 4.92 mmol) in DMF/THF (2:1, 12 mL) was added dropwise at 0 °C under argon to a stirred suspension of sodium hydride (1 g, hexane washed, 21 mmol) in THF (6 mL). The mixture was stirred at room temperature for 1 h, cooled to 0 °C, and treated with benzyl bromide (2.4 mL, 20 mmol). The reaction was warmed to room temperature and stirred for 24 h. The reaction was quenched with methanol (5 mL) and then NH_4Cl (15 mL). Aqueous workup (CH_2Cl_2) and silica gel chromatography (flash silica, 15% ethyl acetate/hexanes) yielded the tribenzylmonomethoxytrityllyxose dithioacetal as a light yellow oil (3.68 g, 4.61 mmol, 94% yield). A stirred solution of the monomethoxy trityl ether (2.45 g, 3.06 mmol) in THF (50 mL) at room temperature under nitrogen was treated with HCl (6 N, 15 mL, 90 mmol) and stirred at room temperature for 36 h. Aqueous workup (CH_2Cl_2) and silica gel chromatography (flash silica, 5%, 10%, 20% ether/hexanes) yielded the primary alcohol **43** as a clear colorless oil (1.26 g, 2.39 mmol, 78% yield). IR (neat): 3453 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (3 H, t, J = 7.4 Hz); 1.20 (3 H, t, J = 7.4 Hz); 2.53–2.65 (2 H, m); 2.69 (2 H, q, J = 7.4 Hz); 3.66 (1 H, ddd, J = 4.5, 4.6, 4.6 Hz); 3.69 (1 H, dd, J = 4.6, 11.4 Hz); 3.83 (1 H, dd, J = 4.5, 11.4 Hz); 3.99 (1 H, d, J = 4.2 Hz); 4.06 (1 H, dd, J = 4.2, 6.2 Hz); 4.18 (1 H, dd, J = 4.6, 6.2 Hz); 4.60 (1 H, d, J = 11.7 Hz); 4.66 (1 H, d, J = 11.7 Hz); 4.72 (1 H, d, J = 11.3 Hz); 4.81 (1 H, d, J = 11.1 Hz); 4.81 (1 H, d, J = 11.3 Hz); 4.91 (1 H, d, J = 11.1 Hz). ^{13}C NMR ($CDCl_3$): δ 137.93, 138.15, 138.39. MS (FAB, NaI): m/z 549 (M + Na). HRMS (FAB, NaI): calcd for $C_{30}H_{38}O_4S_2$ (M + Na) 549.2109, found 549.2122. $[\alpha]_D$: +6.3° (c 1.11, $CHCl_3$).

Tribenzyl *tert*-Butyldiphenylsilyl Dithioacetal 44. A stirred solution of the tribenzyl dithioacetal **43** (1.26 g, 2.39 mmol) and imidazole (0.5 g, 7.3 mmol) in DMF (2.5 mL) at room temperature under argon was treated with *tert*-butylchlorodiphenylsilane (0.75 mL, 0.29 mmol) and stirred at room temperature overnight. Aqueous workup (hexanes/ether) and silica gel chromatography (flash silica, hexanes, 2.5%, 5% ether/hexanes) yielded the silyl ether **44** as a clear colorless oil (1.77 g, 2.31 mmol, 97% yield). IR (neat): 1112 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.12 (9 H, s); 1.20 (3 H, t, J = 7.4 Hz); 1.25 (3 H, t, J = 7.4 Hz); 2.49–2.61 (2 H, m); 2.75 (2 H, q, J = 7.4 Hz); 3.72 (1 H, m); 3.74 (1 H, d, J = 3.7 Hz); 3.93 (1 H, dd, J = 5.6, 10.5 Hz); 4.00 (1 H, dd, J = 5.8, 10.5 Hz); 4.12 (1 H, dd, J = 3.7, 7.2 Hz); 4.31 (1 H, dd, J = 3.4, 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 19.10, 26.85. MS (FAB, NaI) m/z 787 (M + Na). HRMS (FAB, NaI): calcd for $C_{46}H_{56}O_4S_2Si$ (M + Na) 787.3287, found 787.3293 $[\alpha]_D$: +2.2° (c 7.0, $CHCl_3$).

Allylic Alcohol 9. A solution of *N*-bromosuccinimide (450 mg, 2.53 mmol) in acetone/water (9:1, 10 mL) and collidine (650 μL) at room temperature was treated with $AgNO_3$ (465 mg, 2.73 mmol). The solution was stirred at room temperature for 10 min and cooled to 0 °C. A solution of the dithioacetal **44** (321 mg, 0.419 mmol) in acetone (3 mL) was added, and the solution was stirred at 0 °C for 15 min. The reaction was treated with saturated Na_2SO_3 (4.5 mL) and brine (4.5 mL). The reaction was diluted with CH_2Cl_2/hexanes (1:1, 75 mL) and filtered through Celite. Aqueous workup and silica gel chromatography (non-flash silica, 15% ethyl acetate/hexanes) yielded the aldehyde **8** as a clear colorless oil (231.4 mg, 0.351 mmol, 84% yield). A solution of the vinyl iodide **7** (275.0 mg, 0.4064 mmol) and the aldehyde **8** (175.0 mg, 0.2656 mmol) in dry DMSO (4 mL) at room temperature in a glovebox was treated with an excess of $CrCl_2$ containing 0.11% $NiCl_2$ (added in ca. 30-mg portions). The solution was stirred at room temperature for 7 days. The reaction was treated with saturated NH_4Cl (2 mL) and CH_2Cl_2 (2 mL) and stirred for 3 h. The mixture was extracted with ethyl acetate, and the combined organic layers were washed with water and brine. The organic layer was dried over $MgSO_4$, filtered through Fluorosil, and concentrated in vacuo. The product was isolated by size exclusion chromatography (JAI-LC-908, chloroform) to yield the allylic alcohols as a 15:1 mixture of diasteriomers. Silica gel chromatography (flash silica, 10%, 15% ethyl acetate/hexanes) yielded the *erythro* allyl alcohol **9** as a clear colorless oil (215.2 mg, 0.1779 mmol, 67% yield).

Major Diasteriomer. IR (neat): 3451 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.05 (9 H, s); 3.42 (1 H, dd, J = 1.7, 10.6 Hz); 3.48 (1 H, dd, J = 3.1, 10.6 Hz); 3.57 (1 H, ddd, J = 1.7, 3.1, 9.8 Hz); 3.60 (1 H, d, J = 4.5 Hz); 3.69 (1 H, dd, J = 8.7, 9.7 Hz); 3.85–3.92 (2 H); 3.93 (1 H, dd, J = 4.1, 4.0 Hz); 3.99 (1 H, m); 4.78 (1 H, m); 4.91 (1 H, br dd, J = 5.9, 5.9 Hz); 5.90 (1 H, dd, J = 7.5, 11.5 Hz); 5.97 (1 H, dd, J = 6.8, 11.5 Hz). ^{13}C NMR ($CDCl_3$): δ 26.91, 125.96. MS (FAB, NaI): m/z 1231 (M + Na). HRMS (FAB, NaI): calcd for $C_{78}H_{84}O_{10}Si$ (M + Na) 1231.5730, found 1231.5670. $[\alpha]_D$: +39.9° (c 1.2, $CHCl_3$).

Minor Diasteriomer. ^1H NMR ($CDCl_3$): δ 1.05 (9 H, s); 3.08 (1 H, d, J = 4.9 Hz); 3.53–3.58 (2 H); 3.60–3.67 (2 H); 3.84–3.92 (2 H); 3.94 (1 H, dd, J = 4.2, 4.2 Hz); 4.36 (1 H, m); 5.99 (1 H, ddd, J = 2.0, 5.9, 15.9 Hz); 6.01 (1 H, br dd, J = 4.0, 15.9 Hz).

Secondary Alcohol 10. A stirred solution of the allylic alcohol **9** (98.2 mg, 0.0812 mmol) in ethyl acetate (10 mL) was hydrogenated over Pt on Al_2O_3 (10% Pt, 16 mg) for 3 h. The reaction was filtered through Celite and concentrated in vacuo. Silica gel chromatography (flash silica, 20%, 40% ether/hexanes) yielded the secondary alcohol **10** as a clear colorless oil (92.1 mg, 0.0760 mmol, 94% yield). IR (neat): 3491 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.05 (9 H, s); 1.50–1.66 (2 H); 1.70 (1 H, m); 1.98 (1 H, m); 3.06 (1 H, d, J = 4.5 Hz); 3.49 (1 H, dd, J = 4.4, 6.5 Hz); 3.70–3.79 (2 H); 3.91 (1 H, dd, J = 4.9, 9.8 Hz); 4.00 (1 H, dd, J = 3.8, 3.9 Hz); 4.07 (1 H, ddd, J = 3.2, 5.6, 12.0 Hz). ^{13}C NMR ($CDCl_3$): δ 20.90, 29.41. MS (FAB, NaI): m/z 1233 (M + Na). HRMS (FAB, NaI): calcd for $C_{78}H_{86}O_{10}Si$ (M + Na) 1233.5890, found 1233.5940. $[\alpha]_D$: +38.6° (c 1.1, $CHCl_3$).

Dideuterated Secondary Alcohol 10d_2. A stirred suspension of Pt on Al_2O_3 (10%, 5.0 mg) in ethyl acetate in a two-necked flask at room temperature was purged with argon (3 times, stirring for 5 min between purges) and then deuterium gas (3 times, stirring for 20 min between purges). A solution of the allyl alcohol **9** (24.5 mg, 0.0202 mmol) in ethyl acetate was added. The reaction mixture was stirred under deuterium for 2 h, with careful monitoring by TLC in 20% ethyl acetate/hexanes. The reaction was filtered through Celite and the filter pad was rinsed with ethyl acetate. Silica gel chromatography (flash silica, chloroform) yielded the dideuterated secondary alcohol **10d_2** as a clear colorless oil (20.5 mg, 0.0169 mmol, 84% yield). ^1H NMR ($CDCl_3$): δ 1.05 (9 H, s); 1.58 (1 H, dd, J = 1.8, 10.5 Hz); 1.95 (1 H, dd, J = 10.5, 11.8 Hz); 3.06 (1 H, d, J = 4.6 Hz); 3.49 (1 H, dd, J = 4.4, 6.5 Hz); 3.70–3.79 (2 H); 3.91 (1 H, dd, J = 4.9, 9.8 Hz); 4.00 (1 H, dd, J = 3.8, 3.9 Hz); 4.07 (1 H, dd, J = 5.6, 12.0 Hz). MS (FAB, NaI): m/z 1236 ($C_{78}H_{84}D_2O_{10}Si$ + Na).

THP Primary Alcohols 12a,b. A stirred solution of the secondary alcohol **10** (81.2 mg, 0.0670 mmol) and dihydropyran (200 μL, 2.19 mmol) in CH_2Cl_2 (5 mL) at room temperature under argon was treated with PPTS (catalytic amount). The reaction was stirred at room temperature overnight. Aqueous workup (CH_2Cl_2) and silica gel chromatography (flash silica, 7.5%, 10% ethyl acetate/hexanes) yielded an inseparable mixture of the THP ethers **11** as a clear colorless oil (76.8 mg, 0.0593 mmol, 88% yield). These were carried on as a mixture of diasteriomers. A stirred solution of the mixture of THP ethers **11** (70.0 mg, 0.0540 mmol) in THF (3.0 mL) at room temperature under argon was treated with TBAF (1 M, 135 μL, 0.135 mmol). The reaction was stirred at room temperature overnight. Aqueous workup (ethyl acetate) and silica gel chromatography (flash silica, 20% ethyl acetate/hexanes) yielded the primary alcohols **12a,b** as clear colorless oils. The alcohols were combined for preparative purposes (55.6 mg, 0.0526 mmol, 97% yield). **Mixture of silyl THP ethers 11**: see supplementary material. **THP Diasteriomer 12a.** IR (neat): 3451 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.45 (1 H, m); 1.54 (1 H, m); 1.63 (1 H, m); 1.74 (1 H, m); 2.36 (1 H, m); 3.17 (1 H, m); 3.52 (1 H, dd, J = 8.7, 9.3 Hz); 3.83 (1 H, dd, J = 8.6, 9.4 Hz); 4.03–4.08 (2 H); 4.30 (1 H, ddd, J = 5.0, 5.7, 10.2 Hz). ^{13}C NMR ($CDCl_3$): δ 98.07. MS (FAB, NaI): m/z 1079 (M + Na). HRMS (FAB, NaI): calcd for $C_{67}H_{76}O_{11}$ (M + Na) 1079.5290, found 1079.5320. $[\alpha]_D$: +58.5° (c 0.82, $CHCl_3$). **THP Diasteriomer 12b.** IR (neat): 3476 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.85 (1 H, m); 1.93 (1 H, m); 2.18 (1 H, dd, J = 5.1, 7.4 Hz); 3.38 (1 H, m); 3.50–3.55 (2 H); 3.87 (1 H, m); 3.91 (1 H, ddd, J = 3.1, 3.3, 8.5 Hz); 3.98 (1 H, ddd, J = 4.2,

4.9, 11.3 Hz); 4.06 (1 H, dd, J = 3.3, 6.5 Hz). ^{13}C NMR ($CDCl_3$): δ 100.51. MS (FAB, NaI): m/z 1079 (M + Na). HRMS (FAB, NaI): calcd for $C_{67}H_{76}O_{11}$ (M + Na) 1079.5290, found 1079.5240. $[\alpha]_D$: +23.3° (c 0.78, $CHCl_3$).

Dideuterated THP Ether Primary Alcohols 12d_2. The dideuterated secondary alcohol **12d_2** (15.2 mg, 0.0125 mmol) was converted to the primary alcohol by the same procedure as used for the parent compound. Preparative TLC (0.5 mm, 25% ethyl acetate/hexanes) yielded the primary alcohols as clear colorless oils (**12d_2a**: 5.6 mg, 5.3 mmol, 42% yield; **12d_2b**: 5.3 mg, 5.0 mmol, 40% yield). **THP Diasteriomer 12d_2a.** ^{1}H NMR ($CDCl_3$): δ 1.45 (1 H, m); 1.51 (1 H, dd, J = 2.1, 7.1 Hz); 1.63 (1 H, m); 1.74 (1 H, m); 1.91 (1 H, dd, J = 7.1, 12.3 Hz); 2.36 (1 H, dd, J = 4.7, 6.4 Hz); 3.17 (1 H, m); 3.52 (1 H, dd, J = 8.7, 9.3 Hz); 3.83 (1 H, dd, J = 8.6, 9.4 Hz); 4.03–4.08 (2 H); 4.30 (1 H, dd, J = 5.8, 12.3 Hz). MS (FAB, NaI): m/z 1081 ($C_{67}H_{74}D_2O_{11}$ + Na). **THP Diasteriomer 12d_2b.** ^{1}H NMR ($CDCl_3$): δ 1.56 (1 H, dd, J = 3.0, 10.3 Hz); 1.65–1.79 (2 H); 1.82 (1 H, dd, J = 10.3, 11.9 Hz); 2.18 (1 H, dd, J = 5.1, 7.4 Hz); 3.38 (1 H, m); 3.50–3.55 (2 H); 3.87 (1 H, m); 3.98 (1 H, dd, J = 3.1, 3.3 Hz); 3.98 (1 H, dd, J = 5.3, 11.9 Hz); 4.05 (1 H, dd, J = 3.3, 6.4 Hz). MS (FAB, NaI): m/z 1081 ($C_{67}H_{74}D_2O_{11}$ + Na).

Perbenzyl Methyl Glycosides 14 and 15. A stirred solution of a mixture of the primary alcohols **12a,b** (39.6 mg, 0.0375 mmol) in dry CH_2Cl_2 (3 mL) at room temperature under argon was treated with Dess–Martin reagent (53 mg, 0.125 mmol). The suspension was stirred at room temperature for 30 min. The reaction was concentrated in vacuo, taken up in ether, and filtered through Celite. Aqueous workup (ether; Na_2SO_3) yielded the aldehyde as a white solid, which was used without further purification. A stirred solution of the aldehyde in THF/water (10:1, 2.2 mL) at room temperature under nitrogen was treated with p-TsOH·H_2O (30 mg). The solution was stirred at room temperature for 3 days. THF (0.5 mL) and p-TsOH·H_2O (15 mg) were added, and the mixture was stirred overnight. Aqueous workup (CH_2Cl_2) and preparative TLC (0.5 mm, 25% ethyl acetate/hexanes) followed by silica gel chromatography (flash silica, 70% $CHCl_3$/hexanes, $CHCl_3$) yielded the hemiacetal **13** as a white solid (26.7 mg, 0.0275 mmol, 73%). A stirred solution of the hemiacetal **13** (16.3 mg, 0.0168 mmol) in dry THF (2 mL) at 0 °C under argon was treated with NaH (hexane washed, 20 mg, 0.9 mmol). The mixture was stirred at 0 °C for 10 min and room temperature for 5 min. The reaction was cooled to 0 °C and treated with methyl iodide (300 μL, 4.8 mmol). The mixture was stirred at room temperature for 1 h and quenched with methanol. Aqueous workup (ether) and preparative TLC (0.5 mm) in 25% ethyl acetate/hexanes yielded the methyl glycosides **14** and **15** as white solids (**14** (axial): 7.3 mg, 7.4 μmol, 44% yield; **15** (equatorial): 7.8 mg, 7.9 μmol, 47% yield). An analytical sample of **14** was obtained by recrystallization from MeOH/water; white needles, mp 134–137 °C. ***C*-Isomaltose hemiacetal 13**: see supplementary material. **Axial Methyl Glycoside 14.** IR (neat): 1091 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.53 (1 H, dddd, J = 4.1, 9.7, 11.5, 13.0 Hz); 1.62 (1 H, dddd, J = 3.2, 4.8, 11.5, 14.0 Hz); 1.79 (1 H, dddd, J = 2.2, 4.8, 11.5, 13.0 Hz); 1.96 (1 H, dddd, J = 4.1, 11.5, 11.9, 14.0 Hz); 3.15 (1 H, dd, J = 9.2, 9.3 Hz); 3.35 (3 H, s); 3.49 (1 H, dd, J = 3.5, 9.6 Hz); 3.55 (1 H, ddd, J = 2.0, 3.7, 9.9 Hz); 3.60 (1 H, dd, J = 2.0, 10.5 Hz); 3.57–3.66 (2 H); 3.68 (1 H, dd, J = 3.7, 10.5 Hz); 3.74 (1 H, dd, J = 5.6, 9.5 Hz); 3.78 (1 H, dd, J = 8.2, 9.5 Hz); 3.97 (1 H, dd, J = 9.2, 9.3 Hz); 4.00 (1 H, ddd, J = 3.2, 5.6, 11.9 Hz); 4.53 (1 H, d, J = 3.5 Hz). ^{13}C NMR ($CDCl_3$): δ 20.73, 27.76, 55.17, 68.94, 69.92, 70.65, 73.10, 73.24, 73.41, 74.12, 75.15, 75.27, 75.43, 75.65, 78.22, 80.18, 80.25, 81.97, 82.43, 82.56, 97.66. MS (FAB, NaI): m/z 1007 (M + Na). Anal. Calcd for $C_{63}H_{68}O_{10}$: C, 76.80; H, 6.95. Found: C, 76.72; H, 6.95. $[\alpha]_D$: +32.4° (c 0.73, $CHCl_3$). **Equatorial Methyl Glycoside 15.** IR (neat): 1072 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.64 (1 H, dddd, J = 4.0, 9.4, 11.0, 13.5 Hz); 1.74 (1 H, dddd, J = 3.3, 5.2, 11.0, 14.0 Hz); 1.84 (1 H, dddd, J = 2.2, 5.2, 11.0, 13.5 Hz); 2.00 (1 H, dddd, J = 4.0, 11.0, 11.7, 14.0 Hz); 3.24 (1 H, dd, J = 9.0, 9.3 Hz); 3.32 (1 H, ddd, J = 2.2, 9.4, 9.4 Hz); 3.40 (1 H, dd, J = 7.9, 9.1 Hz); 3.53 (3 H, s); 3.56–3.68 (4 H); 3.69 (1 H, dd, J = 3.5, 10.6 Hz); 3.73–3.80 (2 H); 4.05 (1 H, ddd, J = 3.3, 5.1, 11.7 Hz); 4.27 (1 H, d, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$): δ 20.72, 27.59, 57.06, 68.91, 70.77, 73.17, 73.42, 73.84, 74.39, 74.72, 74.93, 75.26, 75.46, 75.60, 78.16, 80.21, 82.10, 82.61, 84.60, 104.58. MS (FAB, NaI): m/z 1107 (M + Na). HRMS (FAB, NaI): calcd for $C_{63}H_{68}O_{10}$ (M + Na) 1007.4710, found 1007.4760. $[\alpha]_D$: +24.5° (c 0.78, $CHCl_3$).

Dideuterated Methyl Glycosides 14d_2 and 15d_2. The dideuterated primary alcohols **12d_2** (10.9 mg, 0.0103 mmol) were oxidized to the mixture of THP aldehydes by the usual Swern procedure. The crude mixture of dideuterated THP aldehydes was taken up in dilute methanolic p-TsOH (1.6 mM, 6 mL), and the solution was stirred under nitrogen for 12 h. Aqueous workup (CH_2Cl_2) yielded the crude deuterated hemiacetal **13d_2**, which was filtered through silica gel in chloroform, azeotroped with toluene, and used without further purification. The crude hemiacetal was converted to the mixture of methyl glycosides by the same procedure as the parent compound. Preparative TLC (0.5 mm) in 25% ethyl acetate/hexanes yielded the methyl glycosides as white solids (**14d_2** (axial): 4.0 mg, 4.1 μmol, 40% yield; **15d_2** (equatorial): 3.4 mg, 3.5 μmol, 34% yield). **Axial Methyl Glycoside 14d_2.** ^{1}H NMR ($CDCl_3$): δ 1.76 (1 H, dd, J = 2.1, 11.4 Hz); 1.94 (1 H, dd, J = 11.4, 11.8 Hz); 3.15 (1 H, dd, J = 9.2, 9.3 Hz); 3.35 (3 H, s); 3.49 (1 H, dd, J = 3.5, 9.6 Hz); 3.55 (1 H, ddd, J = 2.0, 3.7, 9.9 Hz); 3.60 (1 H, dd, J = 2.0, 10.5 Hz); 3.57–3.66 (2 H); 3.68 (1 H, dd, J = 3.7, 10.5 Hz); 3.74 (1 H, dd, J = 5.6, 9.5 Hz); 3.78 (1 H, dd, J = 8.2, 9.5 Hz); 3.97 (1 H, dd, J = 9.2, 9.3 Hz); 4.00 (1 H, dd, J = 5.4, 11.8 Hz); 4.53 (1 H, d, J = 3.5 Hz). MS (FAB, NaI): m/z 1009 ($C_{63}H_{66}D_2O_{10}$ + Na). **Equatorial Methyl Glycoside 15d_2.** ^{1}H NMR ($CDCl_3$): δ 1.84 (1 H, dd, J = 2.3, 11.0 Hz); 2.00 (1 H, dd, J = 11.0, 11.9 Hz); 3.24 (1 H, dd, J = 9.0, 9.3 Hz); 3.32 (1 H, dd, J = 2.3, 9.5 Hz); 3.39 (1 H, dd, J = 7.9, 9.1 Hz); 3.53 (3 H, s); 3.56–3.68 (4 H); 3.69 (1 H, dd, J = 3.5, 10.6 Hz); 3.73–3.80 (2 H); 4.03 (1 H, dd, J = 5.1, 11.9 Hz); 4.27 (1 H, d, J = 7.9 Hz). MS (FAB, NaI): m/z 1009 ($C_{63}H_{66}D_2O_{10}$ + Na).

Axial Methyl Glycoside Polyol 3. A stirred solution of the perbenzylated methyl glycoside **14** (7.3 mg, 7.41 μmol) in MeOH/CH_2Cl_2 (4:1, 6 mL) was hydrogenated over Pearlman's catalyst for 18 h. The reaction was filtered through Celite and the pad was rinsed with methanol. The organic filtrate was concentrated in vacuo to yield the polyol **3** as a clear colorless oil (0.27 mg). IR (neat): 3342 cm^{-1}, 2921, 1047. ^{1}H NMR (10% D_2O/CD_3OD): δ 1.59 (1 H, dddd, J = 3.6, 9.5, 10.8, 13.3 Hz); 1.69 (1 H, dddd, J = 3.2, 5.2, 10.8, 13.5 Hz); 1.83 (1 H, dddd, J = 2.2, 5.2, 10.8, 13.3 Hz); 1.93 (1 H, dddd, J = 3.6, 10.8, 11.7, 13.5 Hz); 3.06 (1 H, dd, J = 9.0, 9.5 Hz); 3.25 (1 H, dd, J = 8.5, 9.5 Hz); 3.36 (3 H, s); 3.37 (1 H, dd, J = 3.8, 9.6 Hz); 3.41 (1 H, ddd, J = 2.5, 5.6, 9.5 Hz); 3.50 (1 H, ddd, J = 2.2, 9.5, 9.5 Hz); 3.53 (1 H, dd, J = 8.5, 9.5 Hz); 3.55 (1 H, dd, J = 9.0, 9.6 Hz); 3.59 (1 H, dd, J = 5.7, 9.5 Hz); 3.63 (1 H, dd, J = 5.6, 11.7 Hz); 3.77 (1 H, dd, J = 2.5, 11.7 Hz); 3.90 (1 H, ddd, J = 3.2, 5.7, 11.7 Hz); 4.61 (1 H, d, J = 3.8 Hz). ^{13}C NMR (10% D_2O/CD_3OD): δ 21.28, 28.27, 55.68, 63.03, 71.75, 72.26, 73.00, 73.55, 74.11, 75.01, 75.20, 75.53, 76.84, 101.02. MS (FAB, neg): m/z 353 (M − H). HRMS (FAB, neg): calcd for $C_{14}H_{26}O_{10}$ (M − H) 353.1448, found 353.1461. $[\alpha]_D$: +134° (c 0.27, CH_3OH).

Dideuterated Axial Methyl Glycoside Polyol 3d_2. The perbenzylated methyl glycoside **14d_2** (3.0 mg, 3.1 μmol) was deprotected by the same procedure as the unlabeled compound, to yield the polyol **3d_2** as a clear colorless oil (2.9 mg). ^{1}H NMR (10% D_2O/CD_3OD): δ 1.83 (1 H, dd, J = 2.2, 10.8 Hz); 1.93 (1 H, dd, J = 10.8, 11.7 Hz); 3.06 (1 H, dd, J = 9.0, 9.5 Hz); 3.25 (1 H, dd, J = 8.5, 9.5 Hz); 3.36 (3 H, s); 3.37 (1 H, dd, J = 3.8, 9.6 Hz); 3.41 (1 H, ddd, J = 2.5, 5.6, 9.5 Hz); 3.50 (1 H, dd, J = 2.2, 9.5 Hz); 3.53 (1 H, dd, J = 8.5, 9.5 Hz); 3.55 (1 H, dd, J = 9.0, 9.6 Hz); 3.59 (1 H, dd, J = 5.7, 9.5 Hz); 3.63 (1 H, dd, J = 5.6, 11.7 Hz); 3.77 (1 H, dd, J = 2.5, 11.7 Hz); 3.90 (1 H, dd, J = 5.7, 11.7 Hz); 4.61 (1 H, d, J = 3.8 Hz). MS (FAB, neg): m/z 355 (M − H).

Equatorial Methyl Glycoside Polyol 16. The perbenzylated methyl glycoside **15** (7.8 mg, 7.92 μmol) was deprotected by the same procedure as the axial methyl glycoside, to yield the polyol **16** as a clear colorless oil (3.2 mg). IR (neat): 3305 cm^{-1}, 2920, 1047. ^{1}H NMR (10% D_2O/CD_3OD): δ 1.62 (1 H, dddd, J = 3.7, 9.5, 10.5, 13.5 Hz); 1.73 (1 H, dddd, J = 3.4, 5.4, 10.5, 13.5 Hz); 1.88 (1 H, dddd, J = 1.8, 5.4, 10.6, 13.5 Hz); 1.92 (1 H, dddd, J = 3.7, 10.6, 11.3, 13.5 Hz); 3.08 (1 H, dd, J = 9.0, 9.5 Hz); 3.14 (1 H, dd, J = 7.8, 9.2 Hz); 3.23 (1 H, ddd, J = 1.8, 9.5, 9.5 Hz); 3.27 (1 H, dd, J = 8.5, 9.5 Hz); 3.32 (1 H, dd, J = 9.0, 9.2 Hz); 3.42 (1 H, ddd, J = 2.5, 5.6, 9.5 Hz); 3.50 (3 H, s); 3.53 (1 H, dd,

J = 8.5, 9.5 Hz); 3.59 (1 H, dd, J = 5.7, 9.5 Hz); 3.63 (1 H, dd, J = 5.6, 11.8 Hz); 3.78 (1 H, dd, J = 2.5, 11.8 Hz); 3.90 (1 H, ddd, J = 3.4, 5.7, 11.3 Hz); 4.13 (1 H, d, J = 7.8 Hz). ^{13}C NMR (10% D_2O/CD_3OD): δ 21.10, 28.31, 57.42, 63.03, 72.26, 73.00, 74.15, 75.17, 75.40, 76.17, 76.63, 77.89, 105.17. MS (FAB, neg): m/z 353 (M − H). HRMS (FAB, neg): calcd for $C_{14}H_{28}O_{10}$ (M − H) 353.1448, found 353.1452. $[\alpha]_D$: +38.2° (c 0.32, CH_3OH).

Dideuterated Equatorial Methyl Glycoside Polyol 16d_2. The perbenzylated methyl glycoside **15**d_2 (2.9 mg, 3 μmol) was deprotected by the same procedure as the axial methyl glycoside, to yield the polyol **16**d_2 as a clear colorless oil (1.8 mg). ^{1}H NMR (10% D_2O/CD_3OD): δ 1.88 (1 H, dd, J = 1.8, 10.6 Hz); 1.91 (1 H, dd, J = 10.6, 11.3 Hz); 3.08 (1 H, dd, J = 9.0, 9.5 Hz); 3.14 (1 H, dd, J = 7.8, 9.2 Hz); 3.23 (1 H, dd, J = 1.8, 9.5 Hz); 3.27 (1 H, dd, J = 8.5, 9.5 Hz); 3.32 (1 H, dd, J = 9.0, 9.2 Hz); 3.42 (1 H, ddd, J = 2.5, 5.6, 9.5 Hz); 3.50 (3 H, s); 3.53 (1 H, dd, J = 8.5, 9.5 Hz); 3.59 (1 H, dd, J = 5.7, 9.5 Hz); 3.63 (1 H, dd, J = 5.6, 11.8 Hz); 3.78 (1 H, dd, J = 2.5, 11.8 Hz); 3.90 (1 H, dd, J = 5.7, 11.3 Hz); 4.13 (1 H, d, J = 7.8 Hz). MS (FAB, neg): m/z 355 (M − H).

Dideuterated Ketone 17d_2. The deuterated secondary alcohol **10**d_2 (20.5 mg, 0.0169 mmol) was oxidized to the dideuterated ketone **17**d_2 (clear colorless oil, 20.0 mg, 0.0165 mmol, 97% yield) by the usual Swern procedure. ^{1}H NMR ($CDCl_3$): δ 1.05 (9 H, s); 1.76 (1 H, dd, J = 8.4, 12.2 Hz); 2.43 (1 H, d, J = 8.4 Hz); 3.36–3.43 (12 H); 3.54–3.59 (2 H); 3.64 (1 H, dd, J = 5.3, 10.9 Hz); 3.65–3.73 (2 H); 3.76 (1 H, q, J = 4.9 Hz); 3.86 (1 H, dd, J = 4.3, 10.9 Hz); 3.93 (1 H, dd, J = 5.2, 11.2 Hz); 4.03 (1 H, d, J = 4.1 Hz); 4.08 (1 H, dd, J = 4.1, 4.9 Hz). MS (FAB, NaI): m/z 1233 (M + Na). HRMS (FAB, NaI): calcd for $C_{78}H_{82}D_2O_{10}Si$ (M + Na) 1233.5860, found 1233.5890.

Monodeuterated α-Keto Enol Ether 18d_1. A sample of the dideuterated ketone **17**d_2 (8.0 mg, 6.6 μmol) was dissolved in a solution of sodium methoxide in methanol (5 mL, freshly prepared by dissolving a washed sodium sphere in 10 mL of methanol) at room temperature under argon. The reaction mixture was stirred at room temperature overnight. Aqueous workup (CH_2Cl_2) and silica gel chromatography (flash silica, 10% ethyl acetate/hexanes) yielded the keto enol ether **18**d_1 as a clear colorless oil (6.7 mg, 6.1 μmol, 92% yield). ^{1}H NMR ($CDCl_3$): δ 1.05 (9 H, s); 1.97 (1 H, ddd, J = 3.6, 7.3, 11.9 Hz); 2.65 (2 H, m); 3.71 (1 H, dd, J = 6.4, 10.7 Hz); 3.74 (1 H, dd, J = 5.7, 9.5 Hz); 3.80 (1 H, dd, J = 8.5, 9.5 Hz); 4.02 (1 H, dd, J = 5.7, 11.9 Hz); 4.52 (1 H, ddd, J = 4.2, 6.3, 8.8 Hz); 6.05 (1 H, d, J = 8.8 Hz). MS (FAB, NaI): m/z 1124 ($C_{71}H_{75}DO_9Si$ + Na).

Degradation Product 20d_1. A stirred solution of the keto enol ether **18**d_1 (6.7 mg, 6.1 mmol) in methanol (5 mL) at 0 °C was treated with sodium borohydride (45 mg). The reaction mixture was stirred at 0 °C for 10 min, followed by aqueous workup (CH_2Cl_2). The resulting 1:1 mixture of hydroxy enol ethers was taken up in THF (2 mL) and treated with H_2SO_4 (1.8 N, 0.25 mL). The mixture was stirred at room temperature overnight, followed by aqueous workup (CH_2Cl_2). The crude product was reduced with sodium borohydride by the same procedure as the keto enol ether. A solution of the resulting mixture of diols **19**d_1 in THF/water (4 mL) was treated with sodium periodate (52.5 mg, excess), and the mixture was stirred at room temperature for 10 h. The reaction was quenched with ethylene glycol (5 drops) and stirred for 5 min at room temperature. Aqueous workup (CH_2Cl_2) gave the crude aldehyde, which was reduced with sodium borohydride by the same procedure as the keto enol ether. Preparative TLC (0.5 mm, 30% ethyl acetate/hexanes) yielded the degradation product **20**d_1 as a white solid (3.1 mg, 5.3 μmol, 87% yield). ^{1}H NMR ($CDCl_3$): δ 1.65 (2 H, m); 1.78 (2 H, m); 3.56 (1 H, m); 3.73 (1 H, dd, J = 5.7, 9.5 Hz); 3.79 (1 H, dd, J = 8.4, 9.5 Hz); 4.04 (1 H, dd, J = 5.6, 11.6 Hz). MS (FAB, NaI): m/z 606 ($C_{37}H_{41}DO_6$ + Na).

Unlabeled Authentic Sample 20. A stirred solution of 1-(2,3,4,6-O-tetrabenzyl-α-D-glucopyranosyl)-2-propene[1b] (26.2 mg, 0.0464 mmol) in dry THF (1.5 mL) at 0 °C under argon was treated with BH_3·THF (0.9 M in THF, 250 μL, 0.225 mmol). The reaction mixture was stirred at room temperature for 3 h. The reaction was quenched with NaOH (10% w/w, 35 drops) and H_2O_2 (30%, 25 drops) and stirred at room temperature overnight. Aqueous workup (CH_2Cl_2) and preparative TLC (0.5 mm, 30% ethyl acetate/hexanes) yielded the primary alcohol **20** as a white crystalline solid (19.9 mg, 0.342 mmol, 74% yield). An analytical sample was obtained by recrystallization from ethyl acetate/hexanes; white needles, mp 92–93 °C. IR (neat): 3273 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.65 (2 H, m); 1.80 (3 H, m); 3.56 (1 H, ddd, J = 2.1, 8.4, 11.8 Hz); 3.73 (1 H, dd, J = 5.7, 9.5 Hz); 3.79 (1 H, dd, J = 8.4, 9.5 Hz); 4.04 (1 H, ddd, J = 5.7, 5.8, 8.7 Hz). ^{13}C NMR ($CDCl_3$): δ 20.91, 29.24, 62.38, 69.12, 71.14, 73.14, 73.50, 74.37, 75.03, 75.45, 78.21, 80.19, 82.39. MS (FAB, NaI): m/z 605 (M + Na). Anal. Calcd for $C_{37}H_{42}O_6 \cdot {}^1/_3H_2O$: C, 75.48; H, 7.30. Found: C, 75.53; H, 7.24. $[\alpha]_D$: +24.4° (c 1.28, $CHCl_3$).

Authentic Deuterated Degradation Products 20d_R and 20d_S. A stirred solution of the monodeuterated diol **21**d_R (7.5 mg, 0.0125 mmol) and DMAP (20 mg, 0.164 mmol) in dry CH_2Cl_2 (0.5 mL) at 0 °C under argon was treated with a solution of thiophosgene (2.0 μL, 0.026 mmol) in CH_2Cl_2 (18 μL). The reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched with water, stirred for 1 h, diluted with a mixture of saturated NH_4Cl/1 N HCl (1:1), and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered through Celite and K_2CO_3, and concentrated in vacuo. The resulting white solid was azeotroped from benzene and used without further purification. A solution of the crude thiocarbonate in trimethyl phosphite (4 mL) was stirred at 100 °C under nitrogen for 24 h. The mixture was concentrated in vacuo and purified by preparative TLC (0.25 mm, 6% acetone/toluene). A solution of the resulting monodeuterated allyl glucose in THF (1.5 mL) at 0 °C under argon was treated with BH_3·THF (1.0 M, 0.5 mL, 0.5 mmol), and the solution was stirred at room temperature overnight. The reaction was quenched with NaOH (10% w/w, 15 drops) and H_2O_2 (30%, 12 drops) and stirred at room temperature. Aqueous workup (CH_2Cl_2) and preparative TLC (0.25 mm, 30% ethyl acetate/hexanes) yielded the α-labeled authentic sample **20**d_R as a white solid (3.2 mg, 5.5 mmol, 44% yield).

The monodeuterated diol **22**d_S (6.7 mg, 0.0112 mmol) was converted to the labeled authentic sample **20**d_S (white solid, 1.2 mg, 2.05 mmol, 18% yield) by the same procedure. **α-Labeled Authentic Sample 20d_R.** ^{1}H NMR ($CDCl_3$): δ 1.65 (2 H, m); 1.80 (2 H, m); 3.56 (1 H, m); 3.73 (1 H, dd, J = 5.6, 9.5 Hz); 3.79 (1 H, dd, J = 8.4, 9.5 Hz); 4.04 (1 H, dd, J = 5.6, 11.6 Hz). MS (FAB, NaI): m/z 606 ($C_{37}H_{41}DO_6$ + Na). **β-Labeled Authentic Sample 20d_S.** ^{1}H NMR ($CDCl_3$): δ 1.65 (2 H, m); 1.78 (2 H, m); 3.56 (1 H, m); 3.73 (1 H, dd, J = 5.7, 9.5 Hz); 3.79 (1 H, dd, J = 8.4, 9.5 Hz); 4.04 (1 H, dd, J = 2.8, 5.2 Hz). MS (FAB, NaI): m/z 606 ($C_{37}H_{41}DO_6$ + Na).

***C*-Gentiobioside Polyol 4.** Methyl *C*-gentiobioside (**4**) was prepared according to the procedure of Rouzaud and Sinaÿ (*J. Chem. Soc., Chem. Commun.* **1983**, 1353). IR (neat): 3358 cm^{-1}, 2917, 1047. ^{1}H NMR (10% D_2O/CD_3OH): δ 1.36–1.44 (2 H, m); 2.12–2.21 (2 H, m); 3.06 (1 H, dd, J = 8.8, 9.4 Hz); 3.07 (1 H, dd, J = 9.1, 9.5 Hz); 3.14 (1 H, br dd, J = 9.0, 9.0 Hz); 3.21 (1 H, ddd, J = 2.1, 5.6. 9.6 Hz); 3.24 (1 H, dd, J = 8.6, 9.6 Hz); 3.32 (1 H, dd, J = 8.6, 8.8 Hz); 3.38 (3 H, s); 3.39 (1 H, dd, J = 3.8, 9.6 Hz); 3.46 (1 H, br dd, J = 9.0, 9.0 Hz); 3.56 (1 H, dd, J = 9.1, 9.6 Hz); 3.63 (1 H, dd, J = 5.6, 11.9 Hz); 3.84 (1 H, dd, J = 2.1, 11.9 Hz); 4.62 (1 H, d, J = 3.8 Hz). ^{13}C NMR ($CDCl_3$): δ 28.69, 29.17, 55.54, 63.23, 72.11, 72.76, 73.74, 75.09, 75.55, 75.74, 79.84, 81.13, 81.56, 101.09. MS (FAB, neg): m/z 353 (M − H). HRMS (FAB, NaI): calcd for $C_{14}H_{26}O_{10}$ (M − H) 353.1448, found 353.1435. $[\alpha]_D$: +82.7° (c 0.49, CH_3OH).

Heptabenzyl Cis Olefin 25. A stirred solution of the heptabenzyl acetylene **24**[3] (250.0 mg, 0.255 mmol) and quinoline (15 μL) in ethyl acetate (15 mL) was hydrogenated over Lindlar catalyst (52 mg) at room temperature. The reaction was carefully monitored by TLC in 20% ethyl acetate/hexanes and interrupted after 20 min. The reaction was filtered through Celite and the pad was rinsed with ether and $CHCl_3$/MeOH (1:1). The organic layer was concentrated in vacuo. Silica gel chromatography (flash silica, chloroform) yielded the cis olefin **25** as a white solid (250.1 mg, 0.254 mmol, 100% yield). IR (neat): 1066 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.32 (3 H, s); 3.32 (1 H, dd, J = 9.3, 9.4 Hz); 3.40 (1 H, dd, J = 9.0, 9.1 Hz); 3.43 (1 H, ddd, J = 2.0, 3.4, 9.4 Hz); 3.51 (1 H, dd, J = 3.6, 9.7 Hz); 3.64 (1 H, dd, J = 9.0, 8.6 Hz); 3.95 (1 H, dd, J = 9.3, 9.3 Hz); 4.29 (1 H, dd, J = 6.6, 9.5 Hz); 4.53 (1 H, d, J = 3.6 Hz); 4.59 (1 H, dd, J = 6.5, 9.7 Hz); 5.67 (1 H, dd, J = 6.5, 11.4 Hz); 5.71 (1 H, dd, J = 6.6, 11.4 Hz). ^{13}C NMR ($CDCl_3$): δ 132.37, 132.60. MS (FAB, NaI): m/z 1005 (M + Na).

HRMS (FAB, NaI): calcd for $C_{63}H_{66}O_{10}$ (M + Na) 1005.4550, found 1005.4600. $[\alpha]_D$: +4.5° (*c* 1.03, $CHCl_3$).

Heptabenzyl Disaccharide 28. A stirred solution of the cis olefin **25** (10.2 mg, 0.0104 mmol) and potassium azodicarboxylate (13.4 mg, 0.069 mmol) in dioxane (1 mL) at room temperature under argon was treated with acetic acid (7.5 μL, 0.13 mmol). The reaction mixture was stirred for 24 h. Aqueous workup (CH_2Cl_2) and preparative TLC (0.5 mm, 5% acetone/toluene) yielded the perbenzyl disaccharide **28** as a white solid (9.8 mg, 9.9 μmol, 96% yield). IR (neat): 1059 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.43 (2 H, m); 2.11 (2 H, m); 3.16 (1 H, dd, *J* = 9.2, 9.4 Hz); 3.21 (1 H, ddd, *J* = 2.4, 7.7, 9.5 Hz); 3.24 (1 H, dd, *J* = 8.0, 9.5 Hz); 3.29 (3 H, s); 3.37 (1 H, ddd, *J* = 2.8, 3.1, 9.2 Hz); 3.50 (1 H, dd, *J* = 3.6, 9.6 Hz); 3.57 (1 H, dd, *J* = 2.3, 9.3, 9.3 Hz); 3.62 (1 H, dd, *J* = 9.1, 9.2 Hz); 3.66 (1 H, dd, *J* = 8.0, 9.1 Hz); 3.70 (2 H, m); 3.94 (1 H, dd, *J* = 9.1, 9.3 Hz); 4.53 (1 H, d, *J* = 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ 27.71, 27.97, 54.90, 69.22, 70.44, 73.25, 73.50, 74.93, 75.22, 75.50, 75.73, 78.65, 78.98, 79.47, 80.18, 82.09, 82.21, 82.52, 87.30, 97.74. MS (FAB, NaI): *m/z* 1007 (M + Na). HRMS (FAB, NaI): calcd for $C_{63}H_{68}O_{10}$ (M + Na) 1007.4710, found 1007.4750. $[\alpha]_D$: +8.0° (*c* 0.81, $CHCl_3$).

Heptabenzyl Monodeuterated Secondary Alcohol 26d_1. A stirred solution of the heptabenzyl cis olefin **25** (137.1 mg, 0.139 mmol) in THF (3 mL) at 0 °C under argon was treated with BD_3·THF (1.0 M in THF, 1 mL, 1 mmol). The reaction was stirred at room temperature overnight. The mixture was treated with NaOH (10% w/w, 2 mL) and H_2O_2 (30%, 1.5 mL), diluted with THF (2 mL), and stirred at room temperature for 2 h. Aqueous workup (CH_2Cl_2) yielded a crude mixture of secondary alcohols. The isomers were separated as the acetates by HPLC (20% ethyl acetate/hexanes), which on hydrolysis yielded the secondary alcohol **26d_1** as a white solid (35.0 mg, 0.0350 mmol, 25% yield). ^1H NMR ($CDCl_3$): δ 2.17 (1 H, dd, *J* = 2.7, 10.4 Hz); 2.21 (1 H, d, *J* = 7.4 Hz); 3.27 (3 H, s); 3.28 (1 H, m); 3.34 (1 H, br d, *J* = 10.0 Hz); 3.41 (1 H, m); 3.50 (1 H, dd, *J* = 3.6, 9.7 Hz); 3.56 (1 H, dd, *J* = 2.9, 10.6 Hz); 3.72 (1 H, dd, *J* = 3.7, 10.7 Hz); 3.95 (1 H, dd, *J* = 9.3, 9.4 Hz); 4.17 (1 H, br dd, *J* = 8.2, 9.4 Hz). MS (FAB, NaI): *m/z* 1024 (M + Na). HRMS (FAB, NaI): calcd for $C_{63}H_{67}DO_{11}$ (M + Na) 1024.4720, found 1024.4750.

Heptabenzyl Monodeuterated Disaccharide 28d_R. A stirred solution of the monodeuterated secondary alcohol **28d_S** (7.5 mg, 7.5 μmol) in dry THF (2 mL) at room temperature under argon was treated with NaH (50% oil dispersion, 43 mg, 0.9 mmol). The reaction mixture was stirred for 15 min. Carbon disulfide (45 μL, 0.75 mmol) was added, and the mixture was stirred for an additional 1.25 h. The reaction was treated with methyl iodide (100 mL, 1.61 mmol), stirred for 1 h, and quenched with saturated NH_4Cl. Aqueous workup (ether) yielded the crude xanthate, which was azeotroped with toluene and used without further purification. A solution of the xanthate (7.5 μmol), tributyltin hydride (250 μL, 0.93 mmol), and AIBN (catalytic amount) in toluene (2 mL) under argon was submerged in a bath that had been preheated to 120 °C. The solution was stirred for 10 min and cooled to room temperature. The mixture was applied to a flash silica gel column and eluted with toluene followed by 15% ethyl acetate/hexanes to yield a white solid. Preparative TLC (0.5 mm, 1:10 acetone/toluene) yielded the monodeuterated disaccharide **33d_R** as a white solid (6.6 mg, 6.7 μmol, 89% yield). ^1H NMR ($CDCl_3$): δ 1.41 (1 H, dd, *J* = 4.1, 9.2, 13.0 Hz); 2.07 (1 H, ddd, *J* = 2.5, 3.9, 11.3 Hz); 2.13 (1 H, ddd, *J* = 2.3, 11.3, 13.0 Hz); 3.16 (1 H, dd, *J* = 9.2, 9.4 Hz); 3.21 (1 H, dd, *J* = 2.5, 9.4 Hz); 3.25 (1 H, dd, *J* = 8.1, 9.4 Hz); 3.30 (3 H, s); 3.38 (1 H, ddd, *J* = 2.8, 3.2, 9.3 Hz); 3.50 (1 H, dd, *J* = 3.6, 9.6 Hz); 3.58 (1 H, ddd, *J* = 2.3, 9.2, 9.5 Hz); 3.62 (1 H, dd, *J* = 9.1, 9.2 Hz); 3.67 (1 H, dd, *J* = 8.0, 9.1 Hz); 3.70 (2 H, m); 3.95 (1 H, dd, *J* = 9.2, 9.3 Hz); 4.53 (1 H, d, *J* = 3.6 Hz). MS (FAB, NaI): *m/z* 1008 ($C_{63}H_{67}DO_{10}$ + Na).

Monodeuterated Disaccharide Polyol 4d_R. A stirred solution of monodeuterated heptabenzyl disaccharide **28d_R** (5 mg, 5 μmol) in $MeOH/CH_2Cl_2$ (5:1, 4 mL) was deuterated over Pearlman's catalyst overnight. The reaction was filtered through Celite and concentrated in vacuo to yield the C.α monodeuterated polyol **4d_R** as a white solid. ^1H NMR (10% D_2O/CD_3OH): δ 1.40 (1 H, m); 2.12–2.21 (2 H, m); 3.06 (1 H, dd, *J* = 8.8, 9.4 Hz); 3.07 (1 H, dd, *J* = 9.1, 9.5 Hz); 3.14 (1 H, dd, *J* = 2.0, 9.6 Hz); 3.21 (1 H, dd, *J* = 2.1, 5.6, 9.6 Hz); 3.24 (1 H, dd, *J* = 8.6, 9.6 Hz); 3.32 (1 H, dd, *J* = 8.6, 8.8 Hz); 3.38 (3 H, s); 3.39 (1 H, dd, *J* = 3.8, 9.6 Hz); 3.46 (1 H, br ddd, *J* = 2.0, 9.0, 9.0 Hz); 3.56 (1 H, dd, *J* = 9.1, 9.6 Hz); 3.63 (1 H, dd, *J* = 5.6, 11.9 Hz); 3.84 (1 H, dd, *J* = 2.1, 11.9 Hz); 4.62 (1 H, d, *J* = 3.8 Hz). MS (FAB, neg): *m/z* 354 ($C_{14}H_{25}DO_{10}$ - H).

***erythro* Dideuterated Polyol 4d_{RR}.** A stirred solution of hexabenzyl cis olefin **25** (8.0 mg, 8.1 μmol) in $MeOH/CH_2Cl_2$ (5:1, 4 mL) was deuterated over Pearlman's catalyst for 29 h. The reaction was filtered through Celite and concentrated in vacuo to yield the *threo* dideuterated polyol **4d_{RR}** as a white solid. ^1H NMR (10% D_2O/CD_3OH): δ 1.36–1.44 (<0.5 H, m); 2.12–2.21 (2 H, m); 3.06 (1 H, dd, *J* = 8.8, 9.4 Hz); 3.07 (1 H, dd, *J* = 9.1, 9.5 Hz); 3.14 (1 H, dd, *J* = 2.0, 9.5 Hz); 3.21 (1 H, ddd, *J* = 2.1, 5.6, 9.6 Hz); 3.24 (1 H, dd, *J* = 8.6, 9.6 Hz); 3.32 (1 H, dd, *J* = 8.6, 8.8 Hz); 3.37 (3 H, s); 3.39 (1 H, dd, *J* = 3.8, 9.6 Hz); 3.46 (1 H, dd, *J* = 1.7, 9.6 Hz); 3.56 (1 H, dd, *J* = 9.1, 9.6 Hz); 3.63 (1 H, dd, *J* = 5.6, 11.9 Hz); 3.84 (1 H, dd, *J* = 2.1, 11.9 Hz); 4.62 (1 H, d, *J* = 3.8 Hz). MS (FAB, neg): *m/z* 355 ($C_{14}H_{24}D_2O_{10}$ - H).

Degradation Product 27d_1. A stirred solution of the monodeuterated secondary alcohol **26d_1** (5.5 mg, 5.5 μmol) in propanedithiol (1 mL) was divided into five (200 μL) portions. Each portion was cooled to 0 °C under argon and treated with BF_3·Et_2O (250 μL, 2.03 mmol). The reaction mixtures were stirred at 0 °C for 10 min. Aqueous workup (CH_2Cl_2) and preparative TLC (30% ethyl acetate/hexanes) yielded the dithioacetal and recovered starting material. The recovered starting material was resubmitted to the reaction. The products were combined and repurified by preparative TLC (12% acetone/toluene) to yield the dithioacetal **29d_1** as a white solid. A stirred solution of the dithioacetal in THF/water (1:1, 2 mL) at room temperature was treated with a large excess of sodium periodate, and the mixture was stirred at room temperature for 1 h. Aqueous workup (CH_2Cl_2) gave the crude aldehyde, which was taken up in $MeOH/CH_2Cl_2$ (4.1, 2.5 mL) and treated with an excess of sodium borohydride. Aqueous workup (CH_2Cl_2) followed by three successive preparative TLC purifications (a: 30% ethyl acetate/hexanes; b: 10% acetone/toluene; c: 30% ethyl acetate/hexanes) yielded the degradation product **27d_1** as a white solid (ca. 0.2 mg). ^1H NMR ($CDCl_3$): δ 2.03 (1 H, m); 3.34 (1 H, dd, *J* = 9.2, 9.2 Hz); 3.48 (1 H, ddd, *J* = 2.0, 5.2, 9.7 Hz); 3.49 (1 H, dd, *J* = 2.7, 9.5 Hz); 3.57 (1 H, dd, *J* = 9.1, 9.1 Hz); 3.59 (1 H, dd, *J* = 5.2, 10.6 Hz); 3.66 (1 H, dd, *J* = 2.0, 10.6 Hz); 3.69 (1 H, dd, *J* = 8.9, 9.0 Hz); 3.78 (2 H, m).

Unlabeled Authentic Degradation Product 27. A stirred solution of 1-(2,3,4,6-*O*-tetrabenzyl-β-D-glucopyranosyl)-2,3-propanediol[1b] (18.2 mg, 0.0304 mmol) in THF/water (1:1, 2 mL) at room temperature was treated with $NaIO_4$ (100 mg, 0.47 mmol). The reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with ethylene glycol (10 drops) and THF (1 mL), followed by aqueous workup (CH_2Cl_2). The crude aldehyde was taken up in methanol (7.5 mL), cooled to 0 °C, and treated with sodium borohydride (100 mg, 2.64 mmol). The mixture was stirred at 0 °C for 15 min. Aqueous workup (CH_2Cl_2) and preparative TLC (0.5 mm, 40% ethyl acetate/hexanes) yielded the primary alcohol **27** as a white crystalline solid (16.5 mg, 0.290 mmol, 95% yield). IR (neat): 3454 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.75 (1 H, dddd, *J* = 5.9, 6.1, 9.2, 14.5 Hz); 2.06 (1 H, dddd, *J* = 2.8, 4.9, 4.9, 14.5 Hz); 2.64 (1 H, t, *J* = 5.8 Hz); 3.34 (1 H, dd, *J* = 9.2, 9.2 Hz); 3.48 (1 H, ddd, *J* = 2.0, 5.2, 9.7 Hz); 3.49 (1 H, ddd, *J* = 2.8, 9.2, 9.5 Hz); 3.57 (1 H, dd, *J* = 9.2, 9.6 Hz); 3.59 (1, H, dd, *J* = 5.2, 10.6 Hz); 3.67 (1 H, dd, *J* = 2.0, 10.6 Hz); 3.69 (1 H, dd, *J* = 8.9, 9.0 Hz); 3.78 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 33.78, 61.47, 69.14, 73.50, 75.04, 75.30, 75.58, 78.54, 78.68, 79.79, 81.79, 87.04. MS (FAB, NaI): *m/z* 591 (M + Na). HRMS (FAB, NaI): calcd for $C_{36}H_{40}O_6$ (M + Na) 591.2722, found 591.2733. $[\alpha]_D$: +1.9° (*c* 0.91, $CHCl_3$).

Authentic Deuterated Degradation Products 27d_R and 27d_S. The monodeuterated diols **29d_R** (2.8 mg, 4.7 μmol) and **30d_S** (2.7 mg, 4.5 μmol) were converted to the alcohols **27d_R** (white solid, 2.0 mg, 3.5 μmol, 75% yield) and **27d_S** (white solid, 1.4 mg, 2.5 μmol, 55% yield), respectively, by the same procedure as the parent unlabeled compound. **α-Labeled Authentic Sample 27d_R.** ^1H NMR ($CDCl_3$): δ 2.03 (1 H, m); 3.34 (1 H, dd, *J* = 9.2, 9.2 Hz); 3.48 (1 H, ddd, *J* = 2.0, 5.2, 9.7 Hz); 3.49 (1 H, dd, *J* = 2.7, 9.5 Hz); 3.57 (1 H, dd, *J* = 9.1, 9.1 Hz); 3.59 (1 H, dd, *J* = 5.2, 10.6 Hz); 3.66 (1 H, dd, *J* = 2.0, 10.6 Hz); 3.69 (1 H, dd, *J*

= 8.9, 9.0 Hz); 3.78 (2 H, m). MS (FAB, NaI): m/z 592 ($C_{36}H_{39}DO_6$ + Na). **β-Labeled Authentic Sample 27d_S.** ^{1}H NMR ($CDCl_3$): δ 1.72 (1 H, ddd, 5.7, 6.0, 9.1 Hz); 3.34 (1 H, dd, J = 9.2, 9.3 Hz); 3.48 (1 H, ddd, J = 2.0, 5.2, 9.7 Hz); 3.49 (1 H, dd, J = 9.2, 9.5 Hz); 3.57 (1 H, dd, J = 9.1, 9.1 Hz); 3.59 (1 H, dd, J = 5.2, 10.6 Hz); 3.66 (1 H, dd, J = 2.0, 10.6 Hz); 3.69 (1 H, dd, J = 8.9, 9.0 Hz); 3.78 (2 H, m). MS (FAB, NaI): m/z 592 ($C_{36}H_{39}DO_6$ + Na).

2,3-*O*-Dibenzyl-4-*O*-*p*-methoxybenzyl Dibromo Olefin 34. Methyl 2,3-*O*-dibenzyl-4-*O*-(*p*-methoxybenzyl)-α-D-glucopyranoside (**33**) (1.12 g, 2.43 mmol) was converted to the dibromo olefin **34** (white crystalline solid, 1.03 g, 1.59 mmol, 65% yield) by the same procedure as compound **41**. An analytical sample was obtained by recrystallization from ethyl acetate/hexanes; white needles, mp 95–97 °C. IR (neat): 1612 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.31 (1 H, dd, J = 9.2, 9.4 Hz); 3.42 (3 H, s); 3.47 (1 H, dd, J = 3.5, 9.7 Hz); 3.80 (3 H, s); 3.99 (1 H, dd, J = 9.2, 9.3 Hz); 4.36 (1 H, dd, J = 9.2, 9.4 Hz); 4.51 (1 H, d, J = 3.5 Hz); 6.20 (1 H, d, J = 8.9 Hz). ^{13}C NMR ($CDCl_3$): δ 95.69, 135.76. MS (FAB, NaI): m/z (rel intensity) 671 (M + Na, 18), 673 (9), 669 (9), 462 (1), 121 (100), 91 (96). Anal. Calcd for $C_{30}H_{32}O_6Br_2$: C, 55.57; H, 4.97. Found: C, 55.63; H, 4.98. $[\alpha]_D$: 0° (c 1.2, $CHCl_3$).

Hexabenzyl Acetylene 36. A stirred solution of the dibromo olefin **34** (820 mg, 1.265 mmol) in dry THF (7.5 mL) at −50 °C under argon was treated with *n*-BuLi (2.3 M, 1.2 mL, 2.76 mmol). The reaction mixture was warmed to 0 °C for 1 min and cooled back to −50 °C. A solution of 2,3,4,6-*O*-tetrabenzylgluconolactone (900 mg, 1.67 mmol) in THF (5 mL) was added, and the solution was stirred at −50 °C for 30 min. The reaction was warmed to room temperature and quenched with saturated NH_4Cl. Aqueous workup (ether) and silica gel chromatography (flash silica, 15% to 35% ethyl acetate/hexanes) yielded the hemiketal **35** as a slightly yellow foam (1.176 g, 1.146 mmol, 91% yield). A stirred solution of the 4-*O*-*p*-methoxybenzyl hemiketal **35** (1.176 g, 1.146 mmol) and triethylsilane (1.1 mL, 6.9 mmol) in dry CH_3CN/CH_2Cl_2 (17:3, 60 mL) at 0 °C under argon was treated with boron trifluoride etherate (1.6 mL, 13 mmol; added dropwise in 400-μL portions, while monitoring by TLC). Aqueous workup (ether) and silica gel chromatography (Chromatotron, 15% to 45% ethyl acetate/hexanes) yielded the 4-hydroxy acetylene **36** as a white solid (0.72 g, 0.81 mmol, 69% yield). An analytical sample was obtained by recrystallization from ethyl acetate/hexanes; white needles, mp 127–129 °C. IR (neat): 3451 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.31 (1 H, d, J = 3.2 Hz); 3.39 (3 H, s); 3.41 (1 H, m); 3.48 (1 H, dd, J = 3.5, 9.5 Hz); 3.55 (1 H, ddd, J = 3.2, 9.0, 9.7 Hz); 3.67 (1 H, dd, J = 4.2, 10.9 Hz); 3.72 (1 H, dd, J = 1.9, 10.9 Hz); 3.75 (1 H, dd, J = 9.0, 9.5 Hz); 4.09 (1 H, m); 4.34 (1 H, br d, J = 9.7 Hz); 4.57 (1 H, d, J = 3.5 Hz). ^{13}C NMR ($CDCl_3$): δ 62.85, 98.48. MS (FAB, NaI): m/z 913 (M + Na). Anal. Calcd for $C_{56}H_{58}O_{10}$: C, 75.48; H, 6.56. Found: C, 75.48; H, 6.58. $[\alpha]_D$: +3.5° (c 2.2, $CHCl_3$).

Hexabenzyl Trans Olefin 32. A stirred solution of the hexabenzyl acetylene **36** (31.1 mg 0.0349 mmol) in dry ether (5 mL) at room temperature under argon was treated with Red-Al (3.6 M in toluene, 250 μL, 0.90 mmol). The mixture was stirred at room temperature for 45 min. The reaction was quenched with methanol followed by Na_2SO_4·$10H_2O$ and stirred overnight. The mixture was filtered through silica gel and concentrated in vacuo. Preparative TLC (0.5 mm, 25% ethyl acetate/hexanes) yielded the trans olefin **32** as a white solid (23.9 mg, 0.0268 mmol, 77% yield). An analytical sample was obtained by recrystallization from ethyl acetate/hexanes; white needles, mp 116–118.5 °C. IR (neat): 3450 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.03 (1 H, d, J = 2.8 Hz); 3.26 (1 H, ddd, J = 2.8, 9.1, 9.4 Hz); 3.32 (1 H, dd, J = 9.0, 9.2 Hz); 3.36 (3 H, s); 3.46 (1 H, ddd, J = 2.7, 3.2, 9.5 Hz); 3.53 (1 H, dd, J = 3.6, 9.6 Hz); 3.64 (1 H, dd, J = 9.1, 9.3 Hz); 3.69 (1 H, dd, J = 8.8, 9.0 Hz); 3.68–3.75 (2 H); 3.79 (1 H, dd, J = 9.2, 9.4 Hz); 3.81 (1 H, br dd, J = 1.9, 9.6 Hz); 4.04 (1 H, br dd, J = 2.7, 9.8 Hz); 5.99 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 130.13, 130.35. MS (FAB, NaI): m/z 915 (M + Na). Anal. Calcd for $C_{56}H_{60}O_{10}$: C, 75.31; H, 6.77. Found: C, 75.02; H, 6.79. $[\alpha]_D$: +4.7° (c 1.03, $CHCl_3$).

Hexabenzyl Dideuterated Trans Olefin 32d_2. A stirred suspension of $LiAlD_4$ (23.8 mg, 0.567 mmol) in dry ether (4 mL) at 0 °C in a two-necked flask equipped with a septum and a nitrogen bubbler was treated with 2-methoxyethanol (90 μL, 1.14 mmol). The reaction mixture was stirred at room temperature for 5 min and cannulated into a stirred solution of the hexabenzyl acetylene **36** (25.6 mg, 0.0287 mmol). The reaction mixture was stirred at room temperature for 45 min and quenched with CD_3OD followed by Na_2SO_4·$10H_2O$. The mixture was stirred overnight, filtered through silica gel, and concentrated in vacuo. Preparative TLC (0.5 mm, 25% ethyl acetate/hexanes) yielded the dideuterated trans olefin **32d_2** as a white solid (23.0 mg, 0.0257 mmol, 89% yield). ^{1}H NMR ($CDCl_3$): δ 1.99 (1 H, d, J = 2.8 Hz); 3.26 (1 H, ddd, J = 2.8, 9.0, 9.6 Hz); 3.32 (1 H, dd, J = 9.1, 9.1 Hz); 3.37 (3 H, s); 3.46 (1 H, ddd, J = 2.7, 3.2, 9.4 Hz); 3.53 (1 H, dd, J = 3.6, 9.6 Hz); 3.65 (1 H, dd, J = 9.1, 9.3 Hz); 3.70 (1 H, dd, J = 8.8, 9.2 Hz); 3.72 (2 H, m); 3.79 (1 H, dd, J = 9.2, 9.4 Hz); 3.81 (1 H, d, J = 9.6 Hz); 4.04 (1 H, d, J = 9.8 Hz). MS (FAB, NaI): m/z 917 ($C_{56}H_{58}D_2O_{10}$ + Na).

Hexabenzyl Cis Olefin 38. The hexabenzyl acetylene **36** (30.0 mg, 0.0337 mmol) was converted to the olefin **38** (white solid, 25.0 mg, 0.0280 mmol, 83% yield) by the same procedure as the heptabenzyl compound. IR (neat): 3433 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.24 (1 H, ddd, J = 3.5, 8.9, 9.0 Hz); 3.37 (1 H, d, J = 3.5 Hz); 3.39 (3 H, s); 3.42 (1 H, dd, J = 9.1, 9.2 Hz); 3.46 (1 H, dd, J = 3.5, 11.7 Hz); 3.50 (1 H, ddd, J = 2.7, 3.0, 9.7 Hz); 3.76–3.82 (2 H); 4.17 (1 H, br dd, J = 8.4, 8.7 Hz); 4.38 (1 H, br dd, J = 6.6, 9.5 Hz); 4.56 (1 H, d, J = 3.5 Hz); 5.58 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 130.33, 133.12. MS (FAB, NaI): m/z 915 (rel intensity) (M + Na, 27), 825 (6), 329 (3), 91 (100). HRMS (FAB, NaI): calcd for $C_{56}H_{60}O_{10}$ (M + Na) 915.4084, found 915.4132. $[\alpha]_D$: +23.1° (c 1.3, $CHCl_3$).

Hexabenzyl Disaccharide 37. The hexabenzyl acetylene **36** (14.2 mg, 0.0159 mmol) was converted to the hexabenzyl disaccharide **37** (white solid, 12.7 mg, 0.0142 mmol, 89% yield) by the same procedure as the heptabenzyl compound. IR (neat): 3486 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.44–1.52 (2 H, m); 2.03–2.13 (2 H, m); 2.36 (1 H, d, J = 3.0 Hz); 3.31 (3 H, s); 3.38 (1 H, ddd, J = 1.9, 4.1, 9.5 Hz); 3.49 (1 H, dd, J = 3.5, 9.6 Hz); 3.51 (1 H, br dd, J = 8.0, 9.0); 3.60 (1 H, dd, J = 9.2, 9.3 Hz); 3.73 (1 H, dd, J = 9.2, 9.3 Hz); 4.56 (1 H, d, J = 3.5 Hz). ^{13}C NMR ($CDCl_3$): δ 27.14, 27.25. MS (FAB, NaI): m/z 917 (M + Na). HRMS (FAB, NaI): calcd for $C_{56}H_{62}O_{10}$ (M + Na) 917.4241, found 917.4277. $[\alpha]_D$: +7.4° (c 1.09, $CHCl_3$).

Hexabenzyl *threo* Dideuterated Disaccharide 37d_{RR}. A solution of the dideuterated trans olefin **32d_2** (18.0 mg, 0.0201 mmol) in CH_2Cl_2 (2 mL) was added to [Rh(nbd)(diphos-4)]BF_4 (2.5 mg, 3.5 μmol) under argon. The solution was hydrogenated at 900 psi for 4 h. The reaction mixture was applied to a short silica gel column and eluted with chloroform. Preparative TLC in 25% ethyl acetate/hexanes yielded the threo dideuterated disaccharide **37d_{RR}** as a white solid (14.7 mg, 0.0164 mmol, 82% yield). ^{1}H NMR ($CDCl_3$): δ 1.46 (1 H, dd, J = 5.3, 8.4 Hz); 2.06 (1 H, dd, J = 2.0, 5.3 Hz); 2.33 (1 H, d, J = 3.0 Hz); 3.31 (3 H, s); 3.37 (1 H, ddd, J = 1.9, 4.1, 9.5 Hz); 3.49 (1 H, dd, J = 3.5, 9.6 Hz); 3.51 (1 H, dd, J = 8.4, 9.5); 3.60 (1 H, dd, J = 9.2, 9.3 Hz); 3.73 (1 H, dd, J = 9.2, 9.3 Hz); 4.56 (1 H, d, J = 3.5 Hz). MS (FAB, NaI): m/z 920 ($C_{56}H_{60}D_2O_{10}$ + Na).

Hexabenzyl *threo* Dideuterated Disaccharide 37d_{SS}. The trans olefin **35** (21.6 mg, 0.0242 mmol) was deuterated over Rh on Al_2O_3 by the same procedure as the isomaltose intermediate **39**, to yield the threo dideuterated disaccharide **37d_{SS}** (white solid, 7.5 mg, 8.4 μmol, 35% yield). ^{1}H NMR ($CDCl_3$): δ 1.45 (1 H, dd, J = 5.5, 7.7 Hz); 2.03 (1 H, dd, J = 2.9, 5.5 Hz); 2.32 (1 H, d, J = 2.9 Hz); 3.31 (3 H, s); 3.37 (1 H, ddd, J = 1.9, 4.1, 9.5 Hz); 3.49 (1 H, dd, J = 3.5, 9.6 Hz); 3.51 (1 H, dd, J = 2.9, 9.5 Hz); 3.60 (1 H, dd, J = 9.2, 9.3 Hz); 3.73 (1 H, dd, J = 9.2, 9.3 Hz); 4.56 (1 H, d, J = 3.5 Hz). MS (FAB, NaI): m/z 919 ($C_{56}H_{60}D_2O_{10}$ + Na).

***threo* Dideuterated Disaccharide Polyol 4d_{RR}.** The threo dideuterated hexabenzyl disaccharide **37d_{RR}** (4.3 mg, 4.8 μmol) was deprotected by the same procedure as the monodeuterated compound **33d_R**, to yield the threo dideuterated polyol **4d_{RR}** as a white solid (3.1 mg). ^{1}H NMR (CD_3OD): δ 1.38 (1 H, dd, J = 5.0, 9.2 Hz); 2.14 (1 H, dd, J = 2.6, 5.0 Hz); 3.04 (1 H, dd, J = 8.8, 9.4 Hz); 3.05 (1 H, dd, J = 9.1, 9.5 Hz); 3.13 (1 H, dd, J = 2.6, 9.5 Hz); 3.18 (1 H, ddd, J = 2.1, 5.6, 9.6 Hz); 3.23 (1 H, dd, J = 8.6, 9.6 Hz); 3.29 (1 H, dd, J = 8.6, 8.8 Hz); 3.37 (1 H, dd, J = 3.8, 9.6 Hz); 3.38 (3 H, s); 3.44 (1 H, dd, J = 9.2, 9.6 Hz); 3.55 (1 H, dd, J = 9.1, 9.6 Hz); 3.61 (1 H, dd, J = 5.6, 11.9 Hz); 3.83

(1 H, dd, J = 2.1, 11.9 Hz); 4.62 (1 H, dd, J = 3.8 Hz). MS (FAB, neg): m/z 355 ($C_{14}H_{24}D_2O_{10}$ - H).

***threo* Dideuterated Disaccharide Polyol 4d_{SS}.** The threo dideuterated hexabenzyl disaccharide 37d_{SS} (3.0 mg, 3.3 μmol) was deprotected by the same procedure as the monodeuterated compound 33d_R, to yield the threo dideuterated polyol 4d_{SS} as a white solid (3.0 mg). ^{1}H NMR (CD_3OD): δ 1.37 (1 H, dd, J = 5.0, 8.6 Hz); 2.15 (1 H, dd, J = 2.4, 5.0 Hz); 3.04 (1 H, dd, J = 8.8, 9.4 Hz); 3.05 (1 H, dd, J = 9.1, 9.5 Hz); 3.12 (1 H, dd, J = 8.6, 9.5 Hz); 3.18 (1 H, ddd, J = 2.1, 5.6, 9.6 Hz); 3.23 (1 H, dd, J = 8.6, 9.6 Hz); 3.29 (1 H, dd, J = 8.6, 8.8 Hz); 3.37 (1 H, dd, J = 3.8, 9.6 Hz); 3.38 (3 H, s); 3.44 (1 H, dd, J = 2.4, 9.6 Hz); 3.55 (1 H, dd, J = 9.1, 9.6 Hz); 3.62 (1 H, dd, J = 5.6, 11.9 Hz); 3.83 (1 H, dd, J = 2.1, 11.9 Hz); 4.62 (1 H, d, J = 3.8 Hz). MS (FAB, neg): m/z 355 ($C_{14}H_{24}D_2O_{10}$ - H).

Hexabenzyl 4-*O*-Acetyl Disaccharide 39. A stirred solution of the hexabenzyl disaccharide 37 (10.9 mg, 0.0122 mmol) and DMAP (catalytic amount) in pyridine (1 mL) at room temperature under argon was treated with acetic anhydride (1 mL). The reaction mixture was stirred at room temperature overnight. The reaction was concentrated in vacuo and filtered through silica gel in ether. Silica gel chromatography (flash silica, 15% ethyl acetate/hexanes) yielded the acetate 39 as a white solid (10.2 mg, 0.0109 mmol, 89% yield). IR (neat): 1740 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.32–1.44 (2 H, m); 1.77 (1 H, m); 1.85 (3 H, s); 2.12 (1 H, m); 3.18 (1 H, br ddd, J = 2.0, 8.0, 9.4 Hz); 3.22 (1 H, dd, J = 8.4, 9.2 Hz); 3.30 (3 H, s); 3.35 (1 H, ddd, J = 2.7, 3.3, 9.3 Hz); 3.54 (1 H, dd, J = 3.6, 9.5 Hz); 3.57 (1 H, m); 3.61 (1 H, dd, J = 9.3, 9.4 Hz); 3.86 (1 H, dd, J = 9.4, 9.4 Hz). ^{13}C NMR ($CDCl_3$): δ 20.85, 169.88. MS (FAB, NaI): m/z 959 (M + Na). HRMS (FAB, NaI): calcd for $C_{58}H_{64}O_{11}$ (M + Na) 959.4346, found 959.4387. $[\alpha]_D$: +2.3° (c 0.91, $CHCl_3$).

Hexabenzyl 4-*O*-Acetyl *erythro* Dideuterated Disaccharide 39d_{RS}. The hexabenzyl cis olefin 38 (6.0 mg, 6.7 μmol) was acetylated by the same procedure was the acetate 39. The acetate was deuterated over Pt on Al_2O_3 by the same procedure as the isomaltose intermediate 9, to yield the erythro dideuterated hexabenzyl 4-O-acetyl disaccharide as a white solid (5.8 mg, 6.1 μmol, 91% yield). ^{1}H NMR ($CDCl_3$): δ 1.33 (0.1 H, dd, J = 8.9, 10.7 Hz); 1.37 (0.1 H, dd, J = 9.1, 10.7 Hz); 1.75 (1 H, dd, J = 2.5, 11.3 Hz); 1.85 (3 H, s); 2.09 (1 H, dd, J = 2.5, 11.3 Hz); 3.17 (1 H, dd, J = 2.5, 9.2 Hz); 3.22 (1 H, dd, J = 8.4, 9.2 Hz); 3.30 (3 H, s); 3.35 (1 H, ddd, J = 2.7, 3.3, 9.3 Hz); 3.54 (1 H, dd, J = 3.6, 9.5 Hz); 3.57 (1 H, dd, J = 2.5, 9.2 Hz); 3.61 (1 H, dd, J = 9.3, 9.4 Hz); 3.86 (1 H, dd, J = 9.4, 9.4 Hz). MS (FAB, NaI): m/z 961 ($C_{58}H_{62}D_2O_{11}$ + Na).

Hexabenzyl 4-*O*-Acetyl *threo* Dideuterated Disaccharides 39d_{RR} and 39d_{SS}. The threo dideuterated hexabenzyl disaccharide 37d_{RR} (7.8 mg, 8.7 μmol) and 37d_{SS} (7.5 mg, 8.4 μmol) were acetylated to 39d_{RR} (white solid, 6.0 mg, 6.4 mmol, 73% yield) and 39d_{SS} (white solid, 7.2 mg, 7.7 μmol, 92% yield), respectively, by the same procedure as the unlabeled compound 39. 39d_{RR}: ^{1}H NMR ($CDCl_3$): δ 1.37 (1 H, dd, J = 5.4, 9.4 Hz); 1.85 (3 H, s); 2.09 (1 H, dd, J = 2.5, 5.4 Hz); 3.17 (1 H, dd, J = 2.5, 9.4 Hz); 3.22 (1 H, dd, J = 8.4, 9.2 Hz); 3.30 (3 H, s); 3.35 (1 H, ddd, J = 2.7, 3.3, 9.3 Hz); 3.54 (1 H, dd, J = 3.6, 9.5 Hz); 3.57 (1 H, dd, J = 9.4, 9.7 Hz); 3.61 (1 H, dd, J = 9.3, 9.4 Hz); 3.86 (1 H, dd, J = 9.4, 9.4 Hz). MS (FAB, NaI): m/z 961 ($C_{58}H_{62}D_2O_{11}$ + Na). 39d_{SS}: ^{1}H NMR ($CDCl_3$): δ 1.33 (1 H, dd, J = 4.9, 8.8 Hz); 1.75 (1 H, dd, J = 2.4, 4.9 Hz); 1.85 (3 H, s); 3.17 (1 H, dd, J = 8.8, 9.3 Hz); 3.22 (1 H, dd, J = 8.4, 9.2 Hz); 3.30 (3 H, s); 3.35 (1 H, ddd, J = 2.7, 3.3, 9.3 Hz); 3.54 (1 H, dd, J = 3.6, 9.5 Hz); 3.57 (1 H, dd, J = 2.4, 9.7 Hz); 3.61 (1 H, dd, J = 9.3, 9.4 Hz); 3.86 (1 H, dd, J = 9.4, 9.4 Hz). MS (FAB, NaI): m/z 961 ($C_{58}H_{62}D_2O_{11}$ + Na).

4-*O*-Acetyl *erythro* Dideuterated Disaccharide Polyol 40d_{RS}. A stirred solution of the erythro dideuterated hexabenzyl 4-O-acetyl disaccharide 39d_{RS} (4 mg, 4 μmol) in methanol (2 mL) was hydrogenated over Pearlman's catalyst (5.5 mg) for 1 h. The reaction was filtered through Celite and concentrated in vacuo to yield the erythro dideuterated 4-O-acetyl polyol 40d_{RS} as a white solid. ^{1}H NMR (CD_3OD): δ 1.79 (1 H, dd, J = 2.6, 11.4 Hz); 2.08 (3 H, s); 2.10 (1 H, dd, J = 2.6, 11.4 Hz); 3.04 (1 H, dd, J = 8.8, 9.4 Hz); 3.12 (1 H, dd, J = 2.6, 9.4 Hz); 3.19 (1 H, ddd, J = 2.3, 5.7, 9.5 Hz); 3.25 (1 H, dd, J = 8.8, 9.5 Hz); 3.31 (1 H, dd, J = 8.7, 9.3 Hz); 3.39 (3 H, s); 3.48 (1 H, dd, J = 3.8, 9.7 Hz); 3.59 (1 H, dd, J = 2.6, 9.4 Hz); 3.61 (1 H, dd, J = 5.7, 11.9 Hz); 3.69 (1 H, dd, J = 9.5, 9.5 Hz); 3.81 (1 H, dd, J = 2.3, 11.9 Hz); 4.60 (1 H, dd, J = 9.4, 9.8 Hz); 4.65 (1 H, d, J = 3.8 Hz). MS (FAB, neg): m/z 397 ($C_{16}H_{26}D_2O_{11}$ - H).

4-*O*-Acetyl *threo* Dideuterated Disaccharide Polyol 40d_{RR}. The threo dideuterated hexabenzyl 4-O-acetyl disaccharide 39d_{RR} (4.4 mg, 4.7 μmol) was deprotected by the same procedure as the *erythro* deuterated compound 40d_{RS}, to yield the threo dideuterated 4-O-acetyl polyol 40d_{RR} as a white solid (3.0 mg). ^{1}H NMR (CD_3OD): δ 1.36 (1 H, dd, J = 4.9, 9.3 Hz); 2.08 (3 H, s); 2.12 (1 H, dd, J = 2.5, 4.9 Hz); 3.02 (1 H, dd, J = 8.8, 9.4 Hz); 3.10 (1 H, dd, J = 2.5, 9.5 Hz); 3.17 (1 H, ddd, J = 2.3, 5.7, 9.5 Hz); 3.24 (1 H, dd, J = 8.8, 9.5 Hz); 3.29 (1 H, dd, J = 8.7, 9.3 Hz); 3.39 (3 H, s); 3.46 (1 H, dd, J = 3.8, 9.7 Hz); 3.59 (1 H, dd, J = 9.3, 9.4 Hz); 3.60 (1 H, dd, J = 5.7, 11.9 Hz); 3.69 (1 H, dd, J = 9.5, 9.5 Hz); 3.81 (1 H, dd, J = 2.3, 11.9 Hz); 4.61 (1 H, dd, J = 9.4, 9.8 Hz); 4.65 (1 H, d, J = 3.8 Hz). MS (FAB, neg): m/z 397 ($C_{16}H_{26}D_2O_{11}$ - H).

4-*O*-Acetyl *threo* Dideuterated Disaccharide Polyol 40d_{SS}. The threo dideuterated hexabenzyl 4-O-acetyl disaccharide 39d_{SS} (5.3 mg, 5.6 μmol) was deprotected by the same procedure as the *erythro* deuterated compound 39d_{RS}, to yield the threo dideuterated 4-O-acetyl polyol 40d_{SS} as a white solid (4.8 mg). ^{1}H NMR (CD_3OD): δ 1.33 (1 H, dd, J = 4.9, 8.5 Hz); 1.80 (1 H, dd, J = 2.6, 4.9 Hz); 2.08 (3 H, s); 3.02 (1 H, dd, J = 8.8, 9.4 Hz); 3.10 (1 H, dd, J = 8.5, 9.5 Hz); 3.17 (1 H, ddd, J = 2.3, 5.7, 9.5 Hz); 3.24 (1 H, dd, J = 8.8, 9.5 Hz); 3.29 (1 H, dd, J = 8.7, 9.3 Hz); 3.39 (3 H, s); 3.46 (1 H, dd, J = 3.8, 9.7 Hz); 3.59 (1 H, dd, J = 2.6, 9.4 Hz); 3.61 (1 H, dd, J = 5.7, 11.9 Hz); 3.69 (1 H, dd, J = 9.5, 9.5 Hz); 3.81 (1 H, dd, J = 2.3, 11.9 Hz); 4.61 (1 H, dd, J = 9.4, 9.8 Hz); 4.65 (1 H, d, J = 3.8 Hz). MS (FAB, neg): m/z 397 ($C_{16}H_{26}D_2O_{11}$ - H).

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Supplementary Material Available: Complete spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS, HRMS/analysis) for all compounds (54 pages). Ordering information is given on any current masthead page.