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Ring Expansion of Oxyglycals. Synthesis and Conformational Analysis of Septanoside-Containing Trisaccharides

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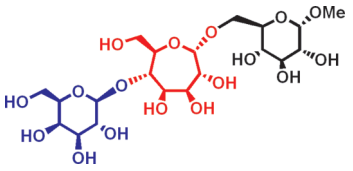

Oxyglycals, derived from lactose and maltose, were expanded to trisaccharides through a ring expansion method. Trisaccharides with *6*−*7*−*5* and *6*−*7*−*6* ring sizes were prepared through the ring expansion method, with high diastereoselectivities, in each step of their synthesis. The NOE and ROESY NMR spectroscopies were used to assess the dipolar couplings within the trisaccharide. A computational study was undertaken, from which low energy conformations, as well as, dihedral angles that define the glycosidic linkages were identified.

Seven-membered cyclic sugars, namely, septanoses are unnatural sugars. Although reports on identification of septanoses could be traced back to early work of Stevens in the 1970s,[1] elaborate synthetic methods and studies appeared much later. Notable advancements in the synthesis of septanoses in recent years are (i) the ring-expansion strategies of Hoberg[2] and Nagarajan[3] on 1,5-anhydrohex-1-enitols, namely, glycals and (ii) ring-closing metathesis reaction of suitably functionalized acyclic diene precursors of van Boom and co-workers[4] and Peczuh and co-workers.[5] Few methods that describe formation of seven-membered oxepane ring systems, wherein one or more deoxy carbon(s) constitute the ring system, are (i) the intramolecular nitrone cycloaddition involving appropriately nitrone and olefin-functionalized acyclic precursors[6] and (ii) metal-catalyzed cyclizations of γ-allenols[7] and alkynols.[8] Ring-closing metathesis reaction[9] and cyclic hemiacetal formation[10] are also found to be useful in the construction of oxepanes. Septanoside and oxepine formation through cyclization of acyclic precursors leads to *endo*-cyclic participation of C-6 and the attendant loss of *exo*-cyclic hydroxymethyl group in many occasions. On the other hand, ring-expansion strategies involving glycals lead to C-2 deoxy-septanoses, requiring additional synthetic manipulation of C-2. This limitation of C-2 deoxy septanose formation through pyranose ring expansion could be overcome in a facile manner through utilizing oxyglycals. The method involving oxyglycals, wherein an oxygen functionality resides at C-2 of glycals, formed the focus of our efforts to synthesize septanoses and septanosides.[11] The oxyglycals are subjected to a cyclopropanation, followed by a nucleophilic ring-opening, leading to C-2 and C-3 functionalized oxepines. The ring-opening of cyclopropanated oxyglycals is stereoselective generally, leading to α-substituted oxepines.[11a] However, a loss in stereoselectivity could be noticed when phenoxides were used.[11b] On the other hand, alkoxides derived from sugars formed oxepines, with concomitant formation of the glycoside bond at C-1. Following initial observation of the use of sugars, we undertook the synthesis trisaccharides incorporated with septanoside residues. Following synthesis, efforts to identify conformational features of the new trisaccharides, with the aid of NMR spectroscopy and computational methods, were undertaken. Synthesis and studies of septanoside containing trisaccharides are reported herein.

Synthesis. Syntheses of hepta-*O*-benzyl-protected oxylactal **2** and hepta-*O*-benzyl-protected oxymaltal **5** were initiated from D-lactose and D-maltose, respectively. The protected lactose derivative **1** was synthesized through procedures known previously.[12] Chlorination of **1**, using $SOCl_2$ and DMF, followed by a dehydrohalogenation, in the presence of DBU/Et_3N in CH_3CN, afforded

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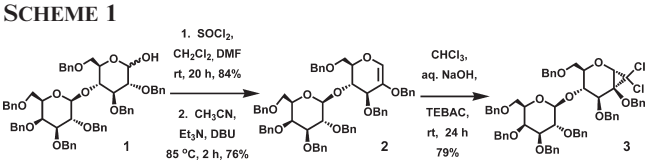
SCHEME 1



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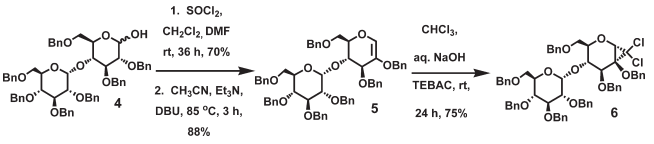

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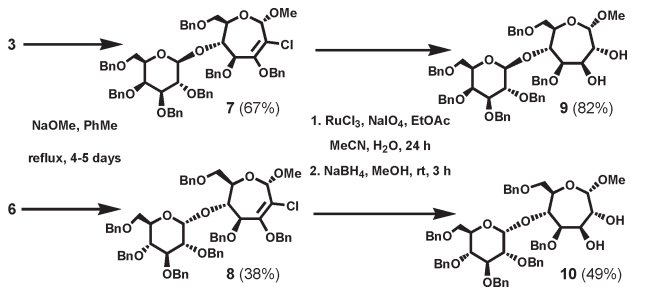

2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galacto-pyranosyl)-1,5-anhydro-D-*arabino*-hex-1-enitol (**2**) (Scheme 1), in a moderate yield. The ^{13}C NMR spectrum showed peaks at 127.8 ppm and 138.6 ppm, for C-1 and C-2 of oxyglycal moiety and 103.0 ppm for the anomeric carbon of β-galacto moiety, respectively. Cyclopropanation of oxylactal **2** was conducted using dichlorocarbene, prepared in situ by treatment of $CHCl_3$ with aq NaOH, under phase-transfer conditions. The carbene addition was effective and the cyclopropanated adduct **3** was obtained as a single diastereomer. The ^{13}C NMR spectrum of **3** showed a resonance at 63.6 ppm, corresponding to the newly introduced carbon with two chloro substituents.

Hepta-*O*-benzyl-protected oxymaltal **5** was synthesized similarly (Scheme 2) and the cyclopropanated disaccharide **6** formed in 75% yield. Dichloroadducts **3** and **6** were subjected to ring-opening reactions, conducted with methoxide initially. The solvolysis of **3** and **6** afforded chloro-oxepines **7** and **8** (Scheme 3). The reaction was sluggish with **6**, and only 38% yield of **8** was obtained after 5 days of reaction. It is likely that the cyclopropane moiety in **6** is more hindered due to an α-orientation of the nonreducing end sugar attached at C-4. Also the reaction was conducted for prolonged duration, a mixture of polar products was identified, in addition to the chloro-oxepine product. Efforts to isolate and identify the products were unsuccessful.

The chloro-oxepine product formed stereoselectively, and only the α-anomer was obtained. The C-1 nucleus in **7** was observed at 100.7 ppm, along with a resonance at 105.5 ppm for the anomeric carbon of the β-galacto moiety. The olefinic carbons were ascertained from resonances at 121.4 and 152.7 ppm in ^{13}C NMR spectrum of **7**. In the ^{1}H NMR spectrum of **8**, resonances of anomeric protons appeared as a doublet (J_{H1-H2} = 3.6 Hz) and as a singlet (5.22 ppm, J_{H1-H2}) corresponding to α-gluco- and chloro-oxepine units, respectively. Similarly, ^{13}C NMR spectra showed anomeric carbon signals at 95.3 and 99.9 ppm for α-gluco- and chloro-oxepine units, respectively. HR-MS analysis further confirmed the composition of **7** and **8**.

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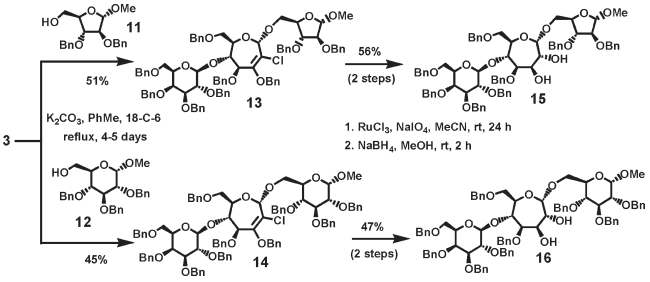

The chloro-vinyl ether moiety in **7** and **8** were converted to diols **9** and **10**, through an oxidation, followed by a reduction. The reduction of diketo intermediate occurred with high selectivity and a single diastereomer of partially protected septanosides **9** and **10** were obtained. The anomeric proton of the septanoside unit in **9** and **10** resonated as a doublet (~4.9 ppm, J = 4.8 Hz), and the corresponding carbon nucleus was observed at ~99.8 ppm.

Synthesis of Septanosyl Trisaccharides. Appropriately protected sugar alcohols **11** and **12** were used for ring expansion of lactose derivative **3**. Reaction of **3** with **11**/**12** (2 molar equiv) was carried out under reflux conditions, in the presence of K_2CO_3 (15 molar equiv), in PhMe for 4−5 days (Scheme 4). The ring expansion occurred with both the sugars and the chloro-oxepine derived *6*−*7*−*5* trisaccharide **13** and *6*−*7*−*6* trisaccharide **14** were obtained, in 51% and 45% yields, respectively. The ring-opening occurred in a stereoselective manner and only the α-anomers formed. The ^{1}H NMR spectra of **13** and **14** showed a singlet at ~5.5 ppm for the anomeric proton of chloro-oxepine sugar unit. Mass spectral analysis further confirmed the composition. Subsequent oxidation and reduction reactions were performed on **13** and **14**. The $NaBH_4$ reduction of diketo derivatives observed to occur with high diastereoselectivities and a single diastereomer was obtained (Scheme 4). Trisaccharides **15** and **16** were obtained in moderate yields. In the ^{1}H NMR spectra, H-1 of the septanoside residue in **15** and **16** appeared as a doublet at ~5.03 ppm (J_{H1-H2} ~4.5 Hz), whereas ^{13}C NMR spectrum showed resonances at 107.1 ppm (α-arabino-), 105.4 ppm (β-galacto-) and 100.1 ppm (α-septano-) for the anomeric carbons of **15**. Similarly, resonances at 105.5 ppm (β-galacto), 99.0 ppm (α-septano-), and 97.8 ppm (α-gluco-) were observed for the anomeric carbons of **16**.

The *O*-benzyl groups in **9**, **10**, **15**, and **16** were deprotected (Pd/C, H_2) to afford the free septanoside-containing di- and trisaccharides **17**−**20**, respectively (Figure 1). Constitutions of the deprotected sugars **17**-**20** were confirmed by NMR spectroscopic and mass spectrometric techniques.

The ring-opening reaction of maltose-derived dichloro-adduct **6** was conducted using sugars **11** and **12**. Reactions were found to be less effective and < 10% conversion was observed with both **11** and **12**, even after several days under reflux conditions.

Conformational Analysis. Upon synthesis of septanosyl sugar-containing trisaccharides, an assessment of their conformational features, in terms of overall conformation and

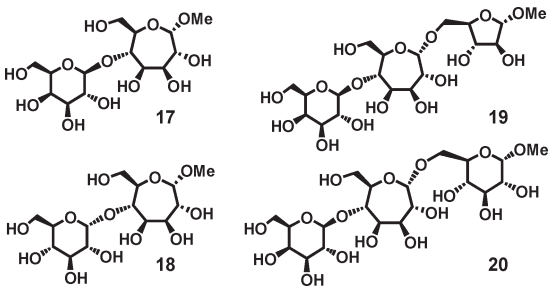

FIGURE 1. Molecular structures of **17**−**20**.

dihedral angles that define the glycosidic linkages, was undertaken. The ring conformations of the septanoses and oxepines were studied by Peczuh[9a,13] and others.[9c] With an objective to assess the lowest energy conformations of trisaccharides, the *6*−*7*−*6* trisaccharide **20** was undertaken for the study, which included solution-state and computational methods. The solution-state studies were utilized to identify dipolar couplings. The computational method was utilized further to derive minimum energy conformations. The solution-state conformational analysis was performed with nuclear Overhauser spectroscopy (NOE) and rotating-frame Overhauser spectroscopy (ROESY). Prior to these experiments, structural assignment of the proton signals was verified using double quantum filtered correlated spectroscopy (DQF-COSY), 2D heteronuclear single quantum coherence (2D-HSQC) and depolarization transfer (^{13}C-DEPT) NMR techniques. Unambiguous assignments were possible by following the connectivities initiated with nonoverlapping protons. From these, the rest of the protons could be assigned, which facilitated analysis of subsequent dipolar coupling patterns.

The NOE studies were conducted on **20** in D_2O at ambient temperature. Well-resolved signals of the ^{1}H NMR spectrum were subjected to NOE irradiations. Key NOE enhancements were observed upon saturation of Sep-H-1 and Gal-H-1. Similar enhancements were observed upon irradiation of other protons. Further analysis of the dipolar couplings was performed with the aid of ROESY experiments. An examination of the ROESY spectrum revealed the following significant correlations. The Sep-H-1 nucleus showed strong cross peaks with H-6a of the methyl pyranoside residues Sep-H-2 and Sep-H-7a. Similarly, Gal-H-1 showed cross peaks with Gal-H-5, Sep-H-4, and Sep-H-6 of the adjacent septanoside ring. A weak cross peak between Gal-H-1 and Sep-H-7a was also observed. Figure 2 summarizes distinct cross-peaks between different protons in **20**, as observed in NOE and ROESY experiments.

Molecular modeling study was undertaken subsequently in order to identify energy-minimized conformations of **20**. Monte Carlo multiple search protocol, as implemented in Macromodel (version 8.5),[14] was used to generate a large pool of conformers of **20**. Spatial distances from NMR experiments were incorporated before molecular dynamics were performed

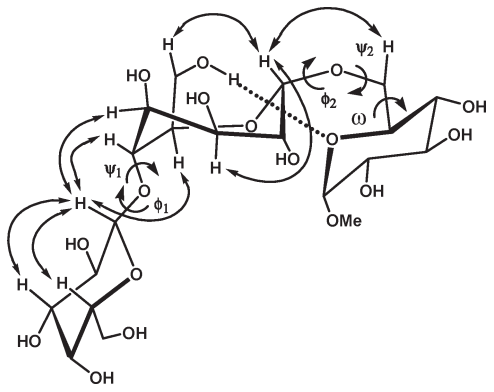

FIGURE 2. Significant dipolar couplings observed in **20**. Dihedral angles (ϕ, Ψ, and ω) are given in Table 1. The observed hydrogen bonding is shown as a dotted line.

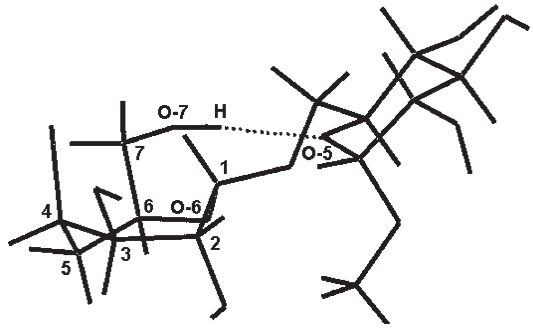

FIGURE 3. Septanoside conformation of an optimized structure of **20**, with labeling. The galactopyranoside portion is removed for clarity. This structure represents conformation 3 of computational studies (cf. the Supporting Information). The observed hydrogen-bonding interaction is shown as a dotted line. Atoms involved in hydrogen bonding are labeled.

with the AMBER* force field. This process led to identifying 114 unique conformers with <1 kcal mol^{-1} of global minimum. Conformers with good convergence and with relative energies <0.3 kcal mol^{-1} were taken for further optimizations using B3LYP/6-31+G* level, at gas phase. Figure 3 shows the septanoside conformation from an optimized structure of **20**, calculated with the above basis set. The septanoside adopted a twist-chair conformation, in the $^{O,1}TC_{5,6}$ form, derived on the basis that a coplanarity in the septanoside ring could be observed only with C2−C3−C4 atoms. A contiguous positive sign and remaining alternate positive and negative signs of dihedral angles represented a twist-chair conformation. The contiguous positive signs for C2−C3 and C3−C4 dihedral angles within the ring denoted further the $^{O,1}TC_{5,6}$ conformation.[15] The geometry of C6−C7 rotamers of septanoside was found to be "gauche-trans". A hydrogen-bonding interaction between exocyclic hydroxymethyl group of septanoside and endocyclic oxygen of glucopyranoside as well as sterically unencumbered spatial disposition of the galactopyranoside about the septanoside were observed. The conformation of the trisaccharide herein differs from tthe $^{3,4}TC_{5,6}$ conformation identified for methyl α/β-D-septanosides studied by Peczuh and co-workers.[9a] Substituent effects on septanoside and the

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TABLE 1. Glycosidic Linkage Dihedral Angles and Calculated Relative Energies for Three Lowest Energy Conformations of 20[a]

		1→5 glycosidic linkage of Gal-Sep		1→6 glycosidic linkage of Sep-Glc		
conformer	B3LYP/6-31+G* E_{rel} (kcal/mol)	ϕ_1	Ψ_1	ϕ_2	Ψ_2	ω
1	0.245	−80.7	−155.3	83.8	−111.6	80.1
3	0.00	−79.9	−148.9	83.0	−109.7	80.4
5	1.73	−73.7	−147.2	82.1	−109.5	81.0

[a] ϕ_1 = O5−C1−O1−C5′; Ψ_1 = C1−O1−C5′−C6′; ϕ_2 = O6′−C1′−O1′−C6″, Ψ_2 = C1′−O1′−C6″−C5″; ω = O1′−C6″−C5″−O5″. 1, 5; 1′, 5′, 6′; and 1″, 5″, 6″ refer to carbons of Gal-; Sep-; and Glc-residues, respectively.

attendant intramolecular interactions appear to be the reasons for the observed differences at present. The torsion angles about the glycosidic linkages identified for a few conformers after global minimizations are given in Table 1. Synclinal and anticlinal arrangements are observed for the glycosidic bonds involved with the septanoside sugar.

Oxyglycals as useful synthons for cyclopropanation and ring expansion are exemplified herein with the synthesis of trisaccharides, relating to *galacto-septano-arabinofurano-* and *galacto-septano-glucopyrano* configurations. The synthesis leads not only to a ring expansion but also a concomitant glycoside formation in a stereoselective manner. Following synthesis, distant constraints were assessed by NOE and ROESY NMR spectroscopies. Conformational analysis using computational methods showed $^{O,1}TC_{5,6}$ conformations for the septanoside.

Experimental Section

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-*β*-D-galactopyranosyl)-(1→5)-(2-chloro-2-deoxy-3,4,7-tri-*O*-benzyl-α-D-*arabino*-hept-2-enoseptanosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (14). A solution of alcohol **12** (0.54 g, 1.15 mmol) in PhMe (1 mL) was added to a stirring mixture of **3** (0.6 g, 0.58 mmol), K_2CO_3 (1.2 g, 8.6 mmol), and 18-C-6 (0.046 g, 0.17 mmol) in PhMe (4 mL) and the mixture refluxed for 5 days. The reaction mixture was filtered over Celite, and solvents were removed in vacuo. The residue was purified (hexane/EtOAc = 8:2) to afford **14** (0.381 g, 45%) as a colorless oil: R_f 0.30 (hexane/EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.19 (m, 50H), 5.55 (s, 1H), 4.96−4.86 (m, 2H), 4.83−4.73 (m, 8H), 4.69−4.56 (m, 10H), 4.48 (d, J = 12 Hz, 1H), 4.42 (d, J = 12.1 Hz, 2H), 4.33−4.22 (m, 5H), 3.99−3.81 (m, 5H), 3.74−3.65 (m, 2H), 3.61−3.55 (m, 2H), 3.50−3.32 (m, 2H), 3.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 138.9, 138.8, 138.5, 138.3, 138.2, 137.8, 137.2, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.3, 121.8, 105.6, 99.6, 97.8, 82.7, 82.1, 81.9, 80.2, 78.9, 78.7, 78.0, 75.6, 75.2, 74.9, 74.6, 73.4, 73.3, 73.0, 72.9, 72.7, 71.8, 71.5, 71.0, 70.9, 67.9, 66.1, 55.1; HRMS m/z $C_{90}H_{93}ClO_{16}NH_4$ calcd 1482.6496, found 1482.6548.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-*β*-D-galactopyranosyl)-(1→5)-(4,7-di-*O*-benzyl-α-D-*glycero*-D-*galacto*-septanosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (16). A solution of $RuCl_3 \cdot 3H_2O$ (0.002 g, 0.007 mmol) and $NaIO_4$ (0.028 g, 0.13 mmol) in water (0.8 mL) was added dropwise to a solution of chloro-oxepine **14** (0.15 g, 0.102 mmol) in MeCN/EtOAc (5 mL, 1:1), at 0 °C. After 24 h of stirring at room temperature, the reaction mixture was diluted with EtOAc (20 mL) and CH_2Cl_2 (20 mL), filtered through silica gel, and washed with EtOAc (2 × 20 mL), and the solvents were removed in vacuo. The crude 2,3-diketo derivative in MeOH (3 mL) was added with $NaBH_4$ (0.008 g, 0.205 mmol) at 0 °C, the mixture was stirred for 2 h, and solvents were removed in vacuo. The residue was dissolved in EtOAc (30 mL), washed with brine (20 mL), dried (Na_2SO_4), and concentrated in vacuo, and the crude product was purified (hexane/EtOAc = 3:2), to afford diol **16** (0.065 g, 47%) as a colorless oil: R_f 0.65 (hexane/EtOAc = 1:1); $[\alpha]^{24}_D$ +29.3 (c 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.18 (m, 45H), 5.04 (d, J = 4.2 Hz, 1H), 4.92 (dd, J = 11.1, 8.1 Hz, 2H), 4.77−4.64 (m, 8H), 4.60−4.47 (m, 5H), 4.43−4.23 (m, 5H), 4.14−4.01 (m, 4H), 3.96−3.91(m, 2H), 3.86 (app.s, 1H), 3.76−3.65 (m, 4H), 3.61−3.47 (m, 3H), 3.44−3.30 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 138.8, 138.5, 138.4, 138.2, 138.1, 137.9, 137.8, 128.4, 128.2, 128.1, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 105.5, 99.0, 97.8, 82.7, 82.3, 81.9, 80.3, 79.7, 79.3, 77.9, 75.6, 75.2, 74.9, 74.7, 73.6, 73.5, 73.4, 73.3, 73.2, 73.0, 72.9, 71.5, 71.3, 69.8, 69.6, 68.6, 67.8, 55.2; HRMS m/z $C_{83}H_{90}O_{17}Na$ calcd 1381.6076, found 1381.6137.

Methyl *O*-(*β*-D-Galactopyranosyl)-(1→5)-(α-D-*glycero*-D-*galacto*-septanosyl)-(1→6)-α-D-glucopyranoside (20). A solution of diol **16** (0.037 g, 0.027 mmol) in MeOH (3 mL) was added with Pd/C (10%, 0.015 g), and the mixture was stirred under a positive pressure of H_2 gas for 48 h. The reaction mixture was filtered over Celite and washed with MeOH (2 × 20 mL), and solvents were removed in vacuo to afford **20** (0.013 g, 88%) as a white foam: R_f 0.24 ($CHCl_3$/CH_3OH = 3:2); $[\alpha]^{24}_D$ +87.0 (c 1.00, MeOH); ^{1}H NMR (700 MHz, D_2O) δ 5.0 (d, J = 4.0 Hz, 1H), 4.82 (d, J = 4.0 Hz, 1H), 4.50 (d, J = 7.7 Hz, 1H), 4.22 (d, J = 6.3 Hz, 1H), 4.15 (dd, J = 7.7, 2.1 Hz, 1H), 4.12−4.05 (m, 2H), 3.93 (d, J = 2.8 Hz, 1H), 3.90−3.79 (m, 6H), 3.77−3.73 (m, 2H), 3.68−3.64 (m, 2H), 3.61−3.54 (m, 4H), 3.43 (s, 3H); ^{13}C NMR (75 MHz, D_2O) δ 104.7, 100.3, 98.1, 81.2, 76.2, 74.0, 73.5, 72.0, 71.8, 71.3, 71.0, 70.5, 70.4, 69.5, 62.9, 62.0, 56.0; HRMS m/z $C_{20}H_{36}O_{17}Na$ calcd 571.1850, found 571.1862.

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Supporting Information Available: General experimental procedure, ^{1}H and ^{13}C NMR spectral data of all new compounds, methods, and results of NMR and computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.