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The *exo*-deoxoanomeric effect in the conformational preferences of *C*-glycosides

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Abstract—Rotational studies of a series of β-D-*C*-glycopyranosides were carried out by CD and NMR spectroscopy. The populations around the *C*-glycosidic bond were strongly dependent on the structure of the *C*-aglycon, the *exo–syn* rotamer population increasing with the degree of substitution on the *C*-aglycon. The hydroxymethyl group populations also showed dependence on the aglycon, although to a lesser degree; its *gt* rotamer smoothly increases with the substitution on the aglycon. These rotational preferences, together with the experimentally observed correlations between ^{1}H and ^{13}C NMR chemical shifts and the structural nature of the *C*-aglycon, point to a stereoelectronic σ_{CH}–σ^{*}_{CO} effect (hyperconjugation) directly involved in the rotation around the pseudo-glycosidic bond and indirectly around the C5–C6 bond (hydroxymethyl group).

1. Introduction

Carbohydrates play a central role in a variety of important physiological events, including inflammation, metastasis, immune response, and bacterial and viral infection.[1] This has recently stimulated the development of effective therapeutic strategies based upon the recognition of these carbohydrates. One approach lies in the replacement of the exocyclic oxygen with a carbon to provide *C*-glycosidic analogues, which have a high resistance to degradation by glycosidases. This has led to a wealth of synthetic approaches[2] and consequently biological data on *C*-glycosides have started to emerge.[3] To understand these events from a molecular point of view, not only their three-dimensional structure but also their conformational preferences in solution must be known. Numerous studies have therefore been performed on the conformational properties of *C*-glycosides. Kishi et al.[4] concluded from their NMR data that glycosides and their *C*-glycosyl analogues share the same conformational properties in solution as in the protein-bound state.[4d,e] Using NMR and molecular mechanics calculations, Jiménez-Barbero et al.[5] demonstrated that the glycosidic linkages of *C*-glycosyl analogues present a higher degree of flexibility than those of the natural *O*-glycosides,[5a,b,e] and that conformational differences between them do exist, both in solution and in the protein-bound state.[5b–g] However, both research groups agree that the predominant conformer adopts the '*exo*-anomeric' conformation around the *C*-glycosidic bond, the C1–C2 bond being antiperiplanar to the C1′–C2′ bond (*exo–syn* conformer) (Figs. 1 and 2).

The similar conformational properties observed by Kishi et al.[4] between *C*-glycosides and the corresponding *O*-glycosides led them to conclude that steric effects determine the preferences of these two types of compounds. In addition, after their conformational study with 2-deoxy

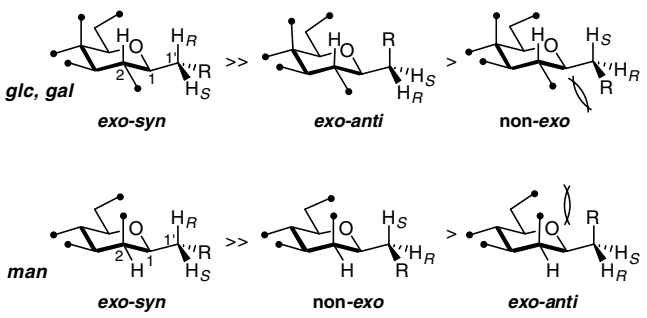

Figure 1. Conformational preferences around the β-*C*-glycosidic bond.

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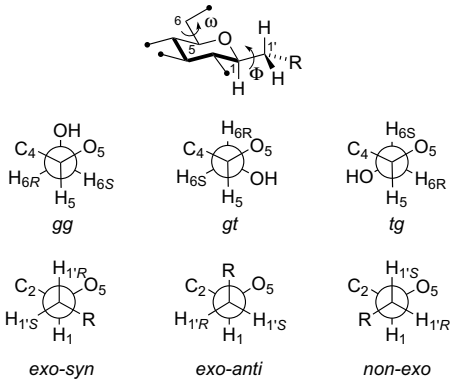


Figure 2. Torsion angle Φ, around the *C*-glucosidic C1′–C1 bond, and ω around the C5–C6 bond (top). Newman projections of the idealized staggered rotamers around the C5–C6 bond (central) and the C1′–C1 bond (bottom).

analogues, they exclude the 1,3-diaxial-like interaction from being the factor controlling this behavior and attribute the preference for the '*exo*-anomeric' conformation in *C*-glycosides to *gauche* interactions.[4a] These results even led them to question the existence of an electronic stabilization (the *exo*-anomeric effect) for *O*-glycosides.[4] The origin of the observation by Kishi et al. that *C*-glycosides have a *gauche* O–C1–C1′–C2′ torsional arrangement was investigated by Houk et al.[6] by ab initio quantum mechanic calculations with acyclic and cyclic models. This study concluded that this preference, which they call *exo*-deoxoanomeric effect, arises from static and induced electrostatic interactions, along with steric ones. The importance of 1,3-type interactions was shown in 2-ethyltetrahydropyran when a hydroxyl group was located at the 3-position, explaining the higher stability of the *exo–syn* versus non-*exo* conformers, by 0.7–2.2 kcal/mol. Recently, Jiménez-Barbero et al.[5d] have confirmed the existence of an important stereoelectronic stabilization for the *exo–syn* conformer of *O*-glycosides and conclude that the *exo*-anomeric effect[7] is indeed a key factor in determining the conformational behavior of Φ angles in *O*-glycosides (>2.3 kcal/mol). Moreover, the unique existence of the *exo*-anomeric conformation around the Φ angle in *O*-glycosides with an equatorial hydroxyl group at the 2-position (β-gluco and β-galacto series) is explained by adding the 1,3-type interactions (>3.3 kcal/mol) to the *exo*-anomeric effect.

In addition to the torsion angle Φ, the torsion angle ω around the C5–C6 bond (Fig. 2) needs to be considered in determining the structure of oligosaccharides, especially when the hydroxymethyl group is involved in a linkage. This angle is also used to describe the conformation of unsubstituted hydroxymethyl groups. The conformation of the hydroxymethyl group around the C5–C6 bond is generally described by means of the populations of the *gauche–gauche* (*gg*), *gauche–trans* (*gt*), and *trans–gauche* (*tg*) rotamers.[8] Since the torsion angle ω in *O*-glycosides has been proved to be conformationally dependent on the structure of the aglycon,[9] which fact is attributable to the *exo*-anomeric effect, this conformational study of the hydroxymethyl group in *C*-glycosides was undertaken to determine whether this group follows the same behavior as *O*-glycosides. The absence of the exocyclic oxygen with its non-bonding electron pairs in the *C*-glycosides suggests, a priori, that its hydroxymethyl group would behave differently than in *O*-glycosides, since the *exo*-anomeric effect cannot be involved.

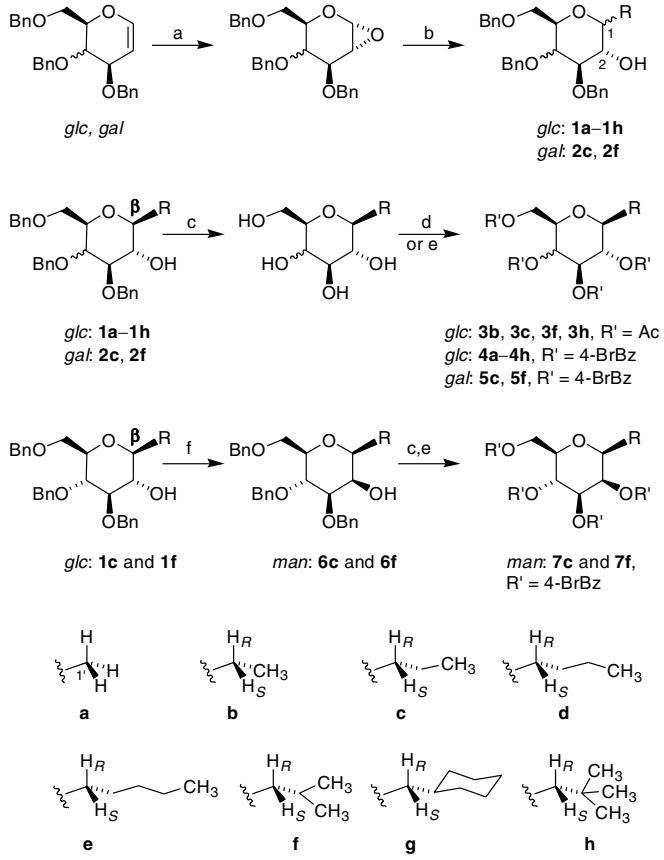
In this article, we report an experimental study of the rotational dependence of the *C*-glycosidic bond and the hydroxymethyl group on the structure of *C*-aglycon. While non-bonded interactions can explain the former dependence, these cannot account for the rotational behavior of the hydroxymethyl group. On the basis of the experimental data obtained, we propose that the *exo*-deoxoanomeric effect,[6] as a stereoelectronic σ_{CH}–σ^*_{CO} effect, is also involved in the rotation around the pseudo-glycosidic bond and indirectly around the C5–C6 bond (hydroxymethyl group).

2. Results and discussion

2.1. Synthesis

Among the different methodologies for the preparation of *C*-glycosides,[2] the addition of carbon nucleophiles to activated glycal epoxides has been widely used.[10] In accordance with this practice, the model *C*-gluco- and *C*-mannosides were prepared from tri-*O*-benzyl D-glucal, while the *C*-galactosides were prepared from tri-*O*-benzyl D-galactal. Thus, epoxidation of the glycal using dimethyldioxirane (DMDO) in acetone/CH_2Cl_2, according to Danishefsky's protocol,[11] and the addition of Grignard reagents to the resulting 1,2-anhydrosugar[12] led to a mixture of α- and β-*C*-glycoside derivatives. Although the α/β ratio was variable, under our solvent and temperature conditions the β-isomer was favored (Scheme 1), the β-D-*C*-glucosides **1a**–**1h** and β-D-*C*-galactosides **2c** and **2f** were obtained in moderate to good yields. Deprotection of the benzyl groups with hydrogen, and subsequent acetylation or 4-bromobenzoylation led to the tetra-*O*-acetyl *C*-glucosides **3b**, **3c**, **3f**, and **3h**, the tetra-*O*-(4-bromobenzoyl) *C*-glucosides **4a**–**4h**, or the tetra-*O*-(4-bromobenzoyl) *C*-galactosides **5c** and **5f**. The model β-D-*C*-mannosides **7c** and **7f** were synthesized from the β-D-*C*-glucosides **1c** and **1f**, as follows:[13] (i) oxidation with DMSO–Ac_2O, (ii) subsequent reduction with $NaBH_4$ in CH_2Cl_2/MeOH (1:1) to give *C*-mannosides **6c** and **6f**, (iii) hydrogenation and (iv) 4-bromobenzoylation in pyridine.

Vinyl *C*-glucopyranoside **8** (Scheme 2) was obtained by epoxidation of the tri-*O*-benzyl D-glucal, using dimethyldioxirane (DMDO) in acetone/CH_2Cl_2, and subsequent addition of divinylcuprate[14] to the resulting oxacyclopropane. Ozonolysis and then reduction with $NaBH_4$ in CH_2Cl_2/MeOH (1:1) led to diol **9**. This compound was acetylated with Ac_2O/Py to give **10**, which was treated with hydrogen in Pd–C to remove the benzyl groups and then again with Ac_2O/Py to obtain the penta-acetyl *C*-glucopyranoside **11**. Acetonide **12**, obtained by protecting diol **9** with 2,2-dimethoxypropane and *p*-toluenesulfonic acid, was treated first with hydrogen and then with Ac_2O/Py



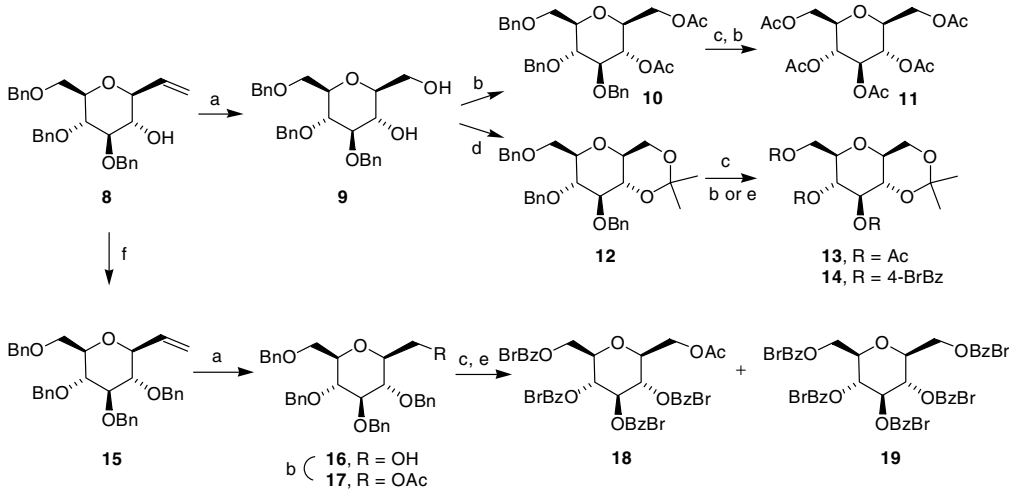
Scheme 1. Synthesis of model β-D-*C*-glycosides. Reagents and conditions: (a) DMDO, acetone/CH_2Cl_2, 0 °C; (b) RMgX, Et_2O, −40 °C; (c) H_2, 5% Pd–C, EtOH; (d) Ac_2O/Py, rt; (e) *p*-BrBzCl, DMAP, Py, 60 °C; (f) (1) DMSO, Ac_2O (2:1); (2) $NaBH_4$, CH_2Cl_2/MeOH (1:1).

to give acetonide **13** or with 4-bromobenzoyl chloride/Py to provide acetonide **14**. Alternatively, the hydroxyl group of vinyl *C*-glucoside **8** was protected with benzyl bromide to give the tetra-benzyl derivative **15**, which by ozonolysis and reductive workup led to mono-alcohol **16**. Acetylation of its primary hydroxyl group led to **17**, which was subjected to catalytic hydrogenolysis to remove the benzyl groups, and then via a per-4-bromobenzoylation to give mainly the expected compound **18**, as well as a small amount of the transesterified *meso* derivative **19**.

2.2. Characterization and spectroscopic analysis

All these compounds[15] were characterized on the basis of their one- (^1H and ^{13}C) and two-dimensional (COSY-G, HMQC, and T-ROESY) NMR spectra. These model compounds contain acetates or *p*-bromobenzoate esters, to facilitate analyses by CD and, in addition, because these groups affect the proton and carbon resonances where they are located leading to less crowded NMR spectra, allowing the coupling constants under study to be measured accurately by means of a first order NMR analysis. The stereochemistry at C1 (β equatorial) of the synthesized *C*-glycosides **3**–**5** (Scheme 1) was established by analyzing the ^1H NMR $J_{1,2}$ value (around 9.5 Hz) and confirmed by means of the T-ROESY experiments, by observing the intense clear cross peaks involving the pseudo-anomeric proton H1, that is, between H1 and H3, H5, and H1′*S* as well as between H2 and H1′*R*. Since for *C*-mannopyranosides **7** the C1 (β equatorial) configuration was in their precursor glucopyranosides, there was no need to establish this; however it was confirmed by T-ROESY experiments.

The ^1H NMR signals of the prochiral protons at C6, H6*R*, and H6*S* were differentiated on the basis of their chemical shifts and coupling constants (accuracy ±0.2 Hz);[16] that is, in general, for the 4-bromobenzoyl series of gluco- and mannopyranosides, H6*R* proton signals appear at a higher field than H6*S* signals ($\delta_{H6S} > \delta_{H6R}$),[16a,b] the reverse behavior being observed for the galactopyranosides and the acetyl glucopyranosides ($\delta_{H6S} < \delta_{H6R}$).[16a,c] On the other hand, as a general rule, $J_{H5,H6R}$ coupling constants have higher values than $J_{H5,H6S}$.[16a,b]



Scheme 2. Synthesis of model β-D-*C*-glucosides. Reagents and conditions: (a) (1) O_3, CH_2Cl_2/MeOH (1:1), −78 °C; (2) $NaBH_4$, CH_2Cl_2/MeOH (1:1), from −78 °C to rt; (b) Ac_2O/Py, rt; (c) H_2, 5% Pd–C, EtOH; (d) 2,2-dimethoxypropane, *p*-TsOH, THF; (e) *p*-BrBzCl, DMAP, Py, 60 °C; (f) BnBr, NaH, DMF.

The assignment of H1′*R* and H1′*S* was in agreement with the values of the coupling constants $J_{H1,H1'R}$ and $J_{H1,H1'S}$, as determined by Kishi et al. using specifically deuterated *C*-glycosides,[4] and with the above mentioned ROE effects. For some compounds, such as **3c**, **4c**, **4d**, and **4e**, H1′*R* and H1′*S* exhibited identical chemical shifts, so their coupling constants with the pseudo-anomeric proton H1 were obtained by analyzing H1 signals.

Among the different types of Karplus equations, we have chosen those of Serianni et al.[17] to calculate the rotamer populations of the hydroxymethyl group, since they contain new limiting values for $J_{H5,H6R}$ and $J_{H5,H6S}$, based on *J*-couplings computed from density functional theory (DFT). This set of equations yields a more accurate representation of the rotameric populations in solution and positive values for the *tg* rotamer population in all cases. Although these equations were optimized for the analysis of the C5–C6 rotamer populations, as a good approximation they were similarly used to calculate the C1–C1′ rotamer populations of the *C*-glycosidic bond. Errors on the percent rotamer population smaller than 5% can be estimated from coupling constant values (accuracy ±0.2 Hz).

The IUPAC system of nomenclature (*R*–*S* system) was used to designate the prochiral protons at C1′ and C6. The *R*/*S* descriptors for the protons at C6 remain invariable throughout this paper, whereas they alter for those at C1′ as a consequence of the changes of priority, carbon versus oxygen.[18] Therefore, care must be taken in the assignation of these protons when applying coupling constants in the Karplus equations.

The CD exciton chirality method[19] offers a versatile sensitive approach for determining the absolute configuration and conformation of a variety of molecules in solution; as a result, we have applied it in this study. *C*-Glycosides **4a**–**4h**, **5c**, **5f**, **7c**, and **7f** were analyzed by CD, exhibiting the intramolecular charge-transfer band of the 4-bromobenzoate chromophore around 245 nm in UV, and exciton Cotton effects around 252 and 234 nm in the CD spectra.

2.3. Conformational analysis

In β-*C*-glycosides, rotation around the glycosidic bond (angle *Φ*, O5–C1–C1′–C2′) led to the *exo–syn*, *exo–anti*, and non-*exo* rotamers, while the rotation around the C5–C6 bond (angle *ω*, O5–C5–C6–O6) led to the *gg*, *gt*, and *tg* rotamers (Fig. 2). Thus, these rotations gave rise to nine ideal staggered conformers, as shown in Fig. 3. The glycosidic and hydroxymethyl populations were calculated from the experimental $J_{H1,H1'R}$ and $J_{H1,H1'S}$ and $J_{H5,H6R}$ and $J_{H5,H6S}$ coupling constants, respectively, by using the Karplus equations recently published by Serianni et al.[17]

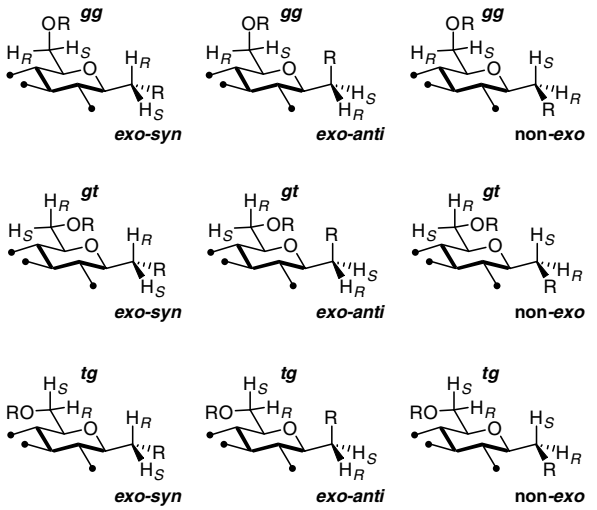


Figure 3. Different orientations around the *ϕ* and *ω* torsion angles of *C*-glycosyl compounds.

Analysis of the coupling constants of the prochiral protons at C1′ and C6, or their calculated rotamer populations, reveals a relationship with the structure of the *C*-aglycon. Thus, a strong dependence of the glycosidic populations (*exo–syn*, *exo–anti*, and non-*exo* rotamers) and a slight dependence of the hydroxymethyl populations (*gg*, *gt*, and *tg* rotamers) on the structure of the *C*-aglycon were observed. The rotational study around the C1–C1′ of the *C*-glucopyranosides showed the *exo–syn* rotamer to be the most stable for both the acetyl series **3b**–**3h** (Table 1) and the 4-bromobenzoyl series **4b**–**4h** (Table 2), as also observed in the T-ROESY experiments. Furthermore, its population increases with the degree of substitution on the *C*-aglycon, that is, in the benzoyl series, from around 60% in unbranched *C*-alkyls **4b**–**4e**, to 90% for secondaries **4f** and **4g**, and 100% for a tertiary branched *C*-aglycon **4h**.[20] This increase in the *exo–syn* population is at the expense of the other two rotamers, as seen in Graph 1 and Table 2. Further analysis of the populations around the pseudo-glucosidic bond (Tables 1 and 2) revealed a variable degree of flexibility, which was possible to correlate with the substitution of the *C*-aglycon. Thus, unbranched

Table 1. $J_{H1,H1'}$ and $J_{H5,H6}$ Coupling constants ($CDCl_3$) and calculated rotameric populations (%) for the model acetyl β-D-*C*-glucopyranosides **3b**–**3h**, **11**, and **13**

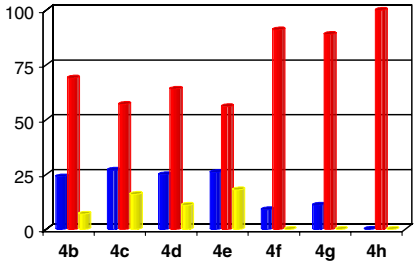
Compd.	$J_{H1,H1'S}$	$J_{H1,H1'R}$	*exo–syn*	*exo–anti*	non-*exo*	$J_{H5,H6S}$	$J_{H5,H6R}$	*gg*	*gt*	*tg*
3b	2.9	8.3	72	21	7	2.3	5.0	58	42	0
3c	4.3	7.0	53	25	22	2.3	5.1	57	43	0
3f	2.3	9.9	91	9	0	2.3	5.3	55	45	0
3h	ND	8.9	100	0	0	2.3	6.2	47	53	0
11	4.9	2.1	39	61	0	2.1	4.9	61	39	0
13	5.3	10.5	0	0	100	2.0	4.8	60	40	0

ND: Not detected.[20]

Table 2. $J_{H1,H1'}$ and $J_{H5,H6}$ coupling constants ($CDCl_3$) and calculated rotameric populations (%) for the model *p*-bromobenzoyl β-D-*C*-glucopyranosides **4a**–**4h**, **14**, **18**, and **19**

Compd.	$J_{H1,H1'S}$	$J_{H1,H1'R}$	*exo–syn*	*exo–anti*	non-*exo*	$J_{H5,H6S}$	$J_{H5,H6R}$	*gg*	*gt*	*tg*
4a	—	—	—	—	—	3.1	4.8	57	37	6
4b	3.0	8.0	69	24	7	3.1	5.1	54	40	6
4c	3.8	7.1	57	27	16	3.2	5.3	51	41	8
4d	3.3	7.7	64	25	11	3.1	5.4	50	43	7
4e	4.0	7.1	56	26	18	3.2	5.4	50	42	8
4f	2.2	9.9	91	9	0	3.1	5.7	47	46	7
4g	2.3	9.7	89	11	0	3.0	6.1	44	50	6
4h	ND	8.8	100	0	0	2.9	6.6	39	56	5
14	5.2	10.5	0	0	100	2.7	4.8	60	39	1
18	5.0	2.9	40	56	4	3.1	4.9	56	38	6
19	5.2	3.0	41	53	6	3.0	5.2	53	41	6

ND: Not detected.[20]



Graph 1. Rotational populations (%) around the C1–C1′ bond, calculated from the $J_{H1,H1'}$ coupling constants of compounds **4b**–**4h** ($CDCl_3$); *exo–syn*/*exo–anti*/non-*exo* rotamers (red/blue/yellow).

or secondary C2′ aglycons are highly flexible around the C1–C1′ bond, in agreement with Jiménez-Barbero's results, while branched tertiary C2′ or quaternary C2′ aglycons have slight or no flexibility at all, respectively, which supports Kishi's observations.

Analysis of the *C*-galacto- and *C*-mannopyranoside derivatives (Table 3) revealed the same conformational behavior as *C*-glucopyranosides.[21] Thus, compounds **5f** and **7f** with branched aglycons showed higher $J_{H1,H1'R}$ and smaller $J_{H1,H1'S}$ coupling constants than compounds **5c** and **7c** with an unbranched aglycon, and therefore the former pair possesses higher *exo–syn* populations. Additional features can be observed by comparing these mannopyranosides with their corresponding glucopyranosides (**4c** and **4f**) or galactopyranosides (**5c** and **5f**). The populations of the non-*exo* rotamers are higher in the *C*-mannopyranosides than in the *C*-gluco- or *C*-galactopyranosides. The β axial configuration at C-2 in mannopyranosides permits an increase in its non-*exo* populations, since the 1,3-type interaction for this rotamer in the glucose series disappeared in the mannose one. Thus, while a small increase in the non-*exo* population was observed by comparing either compound **4c** (16%) or **5c** (13%) with **7c** (23%), a greater change was observed for those stereoisomers having a more voluminous *C*-aglycon, **4f** (0%), **5f** (0%), and **7f** (20%).

Furthermore, there is an alternation in the *exo–syn* and non-*exo* populations as the length of the chain increases: compounds having an unbranched alkyl chain with an even number of carbon atoms showed higher *exo–syn* and lower non-*exo* populations than their homologs with an odd number of carbon atoms. This observation establishes a dependency of the glycosidic linkage on the structure of the *C*-aglycon, in both the degree of substitution and the length of the aglyconic chain. This last result is striking in solution, a different polarization along the even/odd chain may account for this behavior.

With respect to the populations around the C5–C6 bond (hydroxymethyl group), an increase in the $J_{H5,H6R}$ coupling constant around the C5–C6 bond (ω) in *C*-gluco-, *C*-galacto-, and *C*-mannopyranosides was also observed as the substitution in the aglycon increased. For the acetyl *C*-glucosides series, this coupling constant increased from 5.0 up to 6.2 Hz, passing from compounds **3b** to **3h**. Similarly, a gradual increase from 4.8 to 6.6 Hz was observed for the *p*-bromobenzoyl series from **4a** to **4h**. Namely, from **4a** (4.8) to compounds with an unbranched aglycon: **4b** (5.1), **4c** (5.3), **4d** (5.4), and **4e** (5.4 Hz), to compounds with a branched aglycon: **4f** (5.7), **4g** (6.1), and **4h** (6.6 Hz). Moreover, the unbranched alkyl chain of the *C*-galacto- and *C*-mannosides **5c** and **7c** exhibited a smaller $J_{H5,H6R}$ coupling constant than their respective compounds with a branched alkyl chain: compounds **5f** and **7f**. On the other hand, the $J_{H5,H6S}$ value remained more or less constant

Table 3. $J_{H1,H1'}$ and $J_{H5,H6}$ coupling constants ($CDCl_3$) and calculated rotameric populations (%) for the model *p*-bromobenzoyl β-D-*C*-galacto- (**5c** and **5f**) and mannopyranosides (**7c** and **7f**)

Compd.	$J_{H1,H1'S}$	$J_{H1,H1'R}$	*exo–syn*	*exo–anti*	non-*exo*	$J_{H5,H6S}$	$J_{H5,H6R}$	*gg*	*gt*	*tg*
5c	3.5[a]	8.0[a]	67	20	13	6.5	6.7	12	40	48
5f	2.2	9.9	91	9	0	6.1	7.0	12	45	43
7c	4.3	7.8	61	16	23	2.9	4.9	57	39	4
7f	4.0	8.7	71	9	20	2.8	5.1	55	41	4

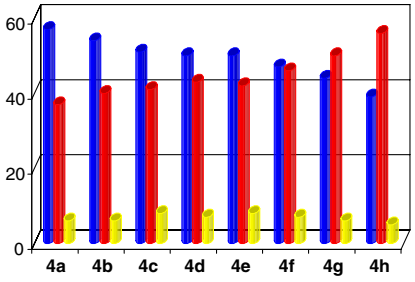
[a] Coupling constants obtained from the doublet of doublets observed for H-1 when H-2 was irradiated.

(around 2.3 Hz for the acetyl series and around 3.1 Hz for the benzoyl series). These experimental NMR data correlate with the increased *gt* population of the hydroxymethyl group at the expense of *gg*, with the *tg* population remaining constant, as seen in Graph 2 for the benzoyl *C*-glucosides series. Although the same rotamer behavior was observed for the two structural series analyzed, slightly higher *tg* populations were obtained for the series containing benzoates than for the tetra-acetyl series (Tables 1 and 2). These increases in the rotational population of the *tg* rotamer in the former series may be explained by favorable π–π interactions between the two aromatic rings in this array.

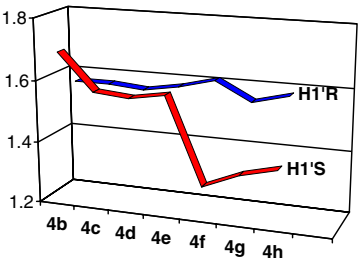
Analyses of the ^{1}H NMR coupling constants of compounds **4b**, **4f**, and **4h** in non-polar (benzene and chloroform) and polar aprotic (acetonitrile and dimethyl sulfoxide) solvents revealed that while rotation around the glycosidic bond is relatively independent of the solvent, that around the C5–C6 bond is somewhat solvent dependent. In general, ranging from non-polar to aprotic-polar solvents, the population of the *gt* rotamer decreased while that of the *gg* rotamer increased. In any case, the overall observed rotational trends are independent of the solvents.

The ^{1}H and ^{13}C NMR chemical shifts of the anomeric and prostereogenic carbons C1′ and C6 for both the acetyl and the 4-bromobenzoyl *C*-glucopyranosides series are shown in Table 4. It is striking that only the prochiral hydrogen H1′*S* shows a clear displacement toward higher fields throughout both series. For instance, for the 4-bromobenzoyl series, from compounds with an unbranched aglycon: **4b** (1.69), **4c** (1.57), **4d** (1.56), and **4e** (1.58 ppm), to compounds with a ramified aglycon: **4f** (1.30), **4g** (1.35), and **4h** (1.38 ppm); whereas H1′*R* remains almost constant (at approximately 1.57 ppm), as shown in Graph 3. In addition, the chemical shift of C1′ and C1 is deshielded and shielded, respectively, as the structure of the *C*-aglycon is enlarged or ramified. Figure 4 summarizes these results.

The interpretation of the chemical shifts for protons in alkyl groups larger than methyl is unfortunately not as simple as one would hope, since inductive and steric effects, hydrogen bonding, and shielding by magnetically aniso-



Graph 2. Rotational populations (%) around the C5–C6 bond (hydroxymethyl group) calculated from the $J_{H5,H6}$ coupling constants of compounds **4a**–**4h** ($CDCl_3$); *gg*/*gt*/*tg* rotamers (blue/red/yellow).



Graph 3. ^{1}H NMR chemical shifts of the H1′*R* (blue) and H1′*S* (red) protons of compounds **4b**–**4h** ($CDCl_3$).

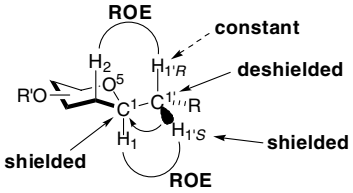


Figure 4. ^{1}H and ^{13}C NMR chemical shift characteristics of *C*-glycosides as the substituent R increases in size.

Table 4. ^{1}H and ^{13}C NMR chemical shifts ($CDCl_3$) for the model *C*-glycosides **3**–**5**, and **7**

R	H1	C1	C1′	H1′*S*	H1′*R*	C6	H6*S*	H6*R*
3b	3.34	78.8	24.3	1.60	1.45	62.4	4.10	4.25
3c	3.39	77.6	33.3	1.44	1.44	62.4	4.09	4.24
3f	3.45	76.3	40.1	1.18	1.46	62.4	4.07	4.24
3h	3.48	75.9	44.2	1.25	1.44	62.7	4.06	4.19
4a	3.87	74.7	17.7	—	—	63.5	4.56	4.43
4b	3.66	79.2	24.5	1.69	1.57	63.5	4.57	4.44
4c	3.72	78.0	33.3	1.57	1.57	63.5	4.56	4.43
4d	3.70	78.2	31.0	1.56	1.56	63.6	4.55	4.43
4e	3.70	78.1	31.4	1.58	1.58	63.6	4.55	4.44
4f	3.77	76.7	40.1	1.30	1.61	63.7	4.54	4.43
4g	3.80	76.2	38.8	1.35	1.55	63.7	4.53	4.43
4h	3.81	76.3	44.3	1.38	1.58	63.9	4.52	4.40
5c	3.72	78.3	33.6	1.64	1.64	62.5	4.32	4.59
5f	3.78	77.0	40.4	1.37	1.71	62.6	4.34	4.58
7c	3.87	77.1	32.6	1.47	1.70	63.5	4.68	4.44
7f	3.94	75.7	39.4	1.28	1.63	63.6	4.67	4.44

tropic groups may be involved. The same behavior in both series (acetate and 4-bromobenzoate) rules out the possibility of an anisotropic effect toward H1′*S* from the 4-bromobenzoyl group at C2. Furthermore, since similar *C*-glycosidic populations were obtained in both series, no significant steric differences should exist to account for the observed rotational behavior. Among the different possible explanations for the observed proton chemical shifts, the anisotropic shielding by carbon–carbon (and possibly carbon–hydrogen) single bonds is the most plausible. The observed shielding for H1′*S* and C1 can be attributed to greater electron densities around such nuclei.

2.4. Circular dichroism analysis

The high sensitivity and simple spectral interpretation of the circular dichroic exciton chirality method[19] provides further conformational data. The exciton-coupled chromophores in our molecules, namely *p*-bromobenzoates, permit analysis by this method, applying the additivity principle in multichromophoric systems,[22,23] the interchromophoric distance, and the dihedral angle of the chromophores involved in each pairwise interaction.[19] According to this method, the CD spectrum of a 2,3,4,6-tetra chromophorically substituted glycopyranosyl system is composed of six pairwise interactions.[22,23] Three have constant intensity and sign: the 2/3, 3/4, and 2/4 interactions; and the other three have variable intensity and sign: the 2/6, 3/6, and 4/6, which involve the chromophore at the 6-position. Furthermore, the amplitude of the split Cotton effects (*A* value)[24] depends on the interchromophoric distance and the dihedral angle;[19] therefore, the sign and intensity of the pairwise interactions depend on the glycopyranosyl system configurations under study: glucose,[9a] galactose,[9b] or mannose[9c] type. Since no ring distortion has been observed for our model compounds, the 2/3, 3/4, and 2/4 interactions are constant and therefore the CD spectral differences between the model compounds arise from the pairwise interactions involving the chromophore at the 6-position.

The tetrachromophoric compounds **4a**–**4h** exhibited exciton Cotton effects around 252 and 234 nm in the CD spectra in CH_3CN. The amplitude of the split CD curve (*A* value) gradually decreased from compounds **4a** (28.9), **4b** (27.0), **4c** (25.1), **4d** (23.5), **4e** (23.4), **4f** (21.9), and **4g** (15.9) to **4h** (14.2). Figure 5 shows the CD spectra of some representative compounds: with an unbranched aglycon or a secondary C2′ (**4c**), with a tertiary C2′ (**4f**), and with a quaternary C2′ (**4h**). These intensities are only consistent with reduced positive contributions from the pairwise interactions between the chromophore at the 6-position (*gg* rotamer) and those at positions 3 and 4 (Fig. 6)[9a] and therefore to a reduction in the population of this *gg* rotamer throughout the series from compounds **4a** to **4h**, which is in agreement with the above NMR results.

As for the *C*-galactopyranosides, the amplitude of the split CD curve (*A* value) of compound **5c** ($A = 90.4$) was less than that of **5f** ($A = 96.1$), as expected from the CD analysis of their pairwise interactions,[9b] especially 4/6 (Fig. 7). This is in accordance with a greater negative contribution

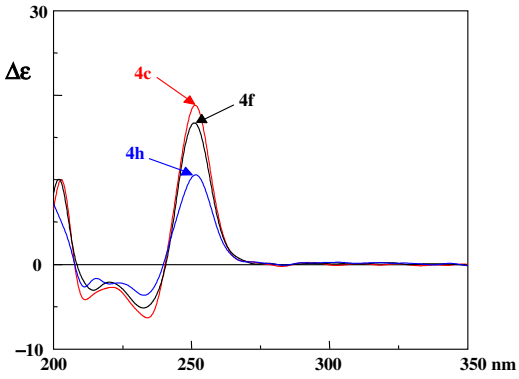


Figure 5. CD spectra comparison of compounds **4c**, **4f**, and **4h** (CH_3CN).

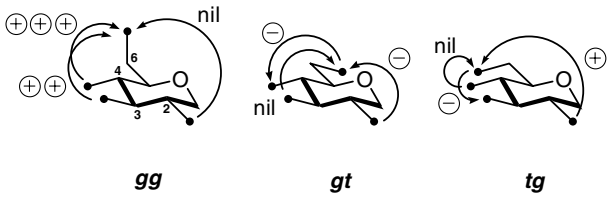


Figure 6. 2/6, 3/6, and 4/6 pairwise interactions involving the chromophore at the 6-position in each of the three stable rotamers (*gg*, *gt*, and *tg*) for the glucopyranosyl system.

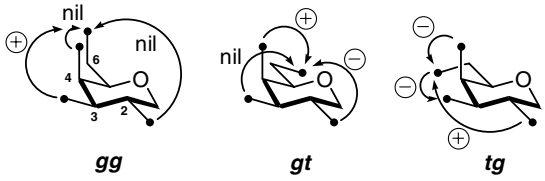


Figure 7. 2/6, 3/6, and 4/6 pairwise interactions involving the chromophore at the 6-position in each of the three stable rotamers (*gg*, *gt*, and *tg*) for the galactopyranosyl system.

of the 4/6 pairwise interaction in the *tg* rotamer and/or a lesser positive contribution from this pairwise interaction in the *gt*. Therefore, these CD spectra are totally in agreement with their corresponding NMR results.

Data comparison of *C*-mannopyranosides **7c** and **7f** (Table 3) shows that as in the *C*-glucopyranosides, the *exo–syn* population is higher for the compound with the ramified *C*-aglycon **7f**, the increase of which also correlates with a slightly higher *gt* population. These NMR results correlate very well with those by CD. The amplitude of the split CD curve (*A* value) for compound **7c** ($A = -90.2$) was smaller than that of **7f** ($A = -94.1$), as expected from the CD analysis of their pairwise interactions,[9c] especially 4/6 (Fig. 8).

2.5. The *exo*-deoxoanomeric effect

For the most stable conformer around the C1–C1′ bond, the *exo–syn* or '*exo*-anomeric' conformer, the H1′*S* is in an *anti* disposition to the endocyclic oxygen (O5) (Fig. 9). Therefore, a stereoelectronic interaction between

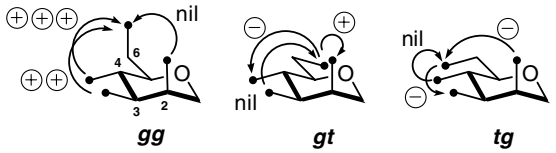


Figure 8. 2/6, 3/6, and 4/6 pairwise interactions involving the chromophore at the 6-position in each of the three stable rotamers (*gg*, *gt*, and *tg*) for the mannopyranosyl system.

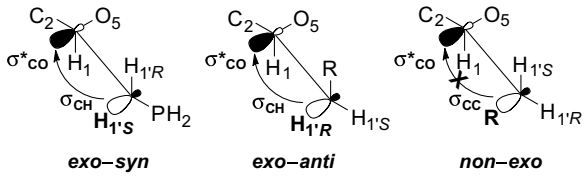
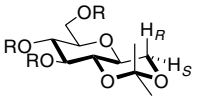


Figure 9. Molecular orbitals involved in the *exo*-deoxoanomeric effect.

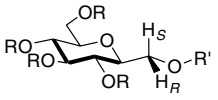
the C1′–H1′*S* bonding orbital and the C1–O5 antibonding orbital can be established,[25] since σ_{CH} is a moderate donor and σ^*_{CO} a good acceptor. This interaction can also occur in the *exo–anti* conformation, by means of the molecular bonding orbital C1′–H1′*R*; although as the *C*-aglycon becomes bulkier, the population of this rotamer decreases due to the steric effects. In addition, it is known that σ_{CC} bonds are worse donors than σ_{CH};[26] therefore the σ_{CC}–σ^*_{CO} interaction (non-*exo* conformer) must be much weaker than the former or nil.

As the series **3b** to **3h**, or **4b** to **4h** progresses (the degree of substitution at C2′ increasing from Me to R = ^{t}Bu), the population of the *exo–syn* rotamer increases (Tables 1 and 2) along with the electron density on the pseudo-anomeric carbon C1 (Table 4). Therefore, the donor capacity of the C1′–H1′*S* bonding orbital toward the C1–O5 antibonding orbital increases as the substitution at C2′ increases along with the population of the *exo–syn* rotamer. This hyperconjugation phenomenon could involve the contraction of the C1–C1′ bond and the consequent enlargement of the C1–O5 bond, as observed in *O*-glycosides,[9] altering the surroundings of the hydroxymethyl group, and therefore its populations (Graph 2). When comparing Graphs 1 and 2, the rise in the *gt* rotamer population of the hydroxymethyl group (Graph 2) correlates with that in the *exo–syn* population (Graph 1).

To test this theory further, acetonides **13** and **14**, acetyls **11** and **18**, and 4-bromobenzoyl **19** were synthesized, since a nil or low *exo*-deoxoanomeric effect would be expected for them. For acetonides **13** and **14**, the conformation is totally restricted to the non-*exo* rotamer, so the interaction σ_{CH}–σ^*_{CO} is not possible. These compounds exhibited high $J_{H1,H1'R}$ (10.5 Hz) and low $J_{H1,H1'S}$ (5.3 Hz) values (Tables 1 and 2) in agreement with the spatial disposition of the H1′ protons and also confirming the correct NMR assignment for these protons. Besides this, their $J_{H5,H6}$ values gave high *gg* and low *gt* hydroxymethyl populations. This result confirms the correlation between the rotamer population around the pseudo-glycosidic bond and that around the C5–C6 bond (hydroxymethyl group). It also confirms that the non-*exo* rotamer (interaction σ_{CH}–σ^*_{CO}) does not favor the *gt* rotamer of the hydroxymethyl group.



13, R = Ac
14, R = 4-BrBz



11, R = R' = Ac
18, R = 4-BrBz, R' = Ac
19, R = R' = 4-BrBz

For **18** and the *meso* compounds **11** and **19**, the presence of an electron-withdrawing group at C1′, acetyloxys **11** and **18** or 4-bromobenzoyloxy **19**, would debilitate or even annul this stereoelectronic effect. Analysis of the $J_{H1,H1'}$ coupling constants of compound **18** led to the highest *exo–anti* and lowest *exo–syn* populations (Table 2) of the alkyl *C*-glucopyranosides, in both the acetyl **3b**–**3h** and 4-bromobenzoyl **4b**–**4h** series. This result supports the existence of hyperconjugation in alkyl *C*-glycosides. In *meso* compounds **11** and **19**, the populations around C1–C1′ and C5–C6 bonds at either side of the molecule were the same, because $J_{H1,H1'S} = J_{H5,H6R}$ and $J_{H1,H1'R} = J_{H5,H6S}$. Thus, for compound **19**, the *exo–anti* = *gg* = 53; *exo–syn* = *gt* = 41; and non-*exo* = *tg* = 6. While these are obviously normal values for a hydroxymethyl group, when considering one of the two as if it was a *C*-aglycon, high *exo–anti* and low *exo–syn* populations were obtained, since an electron-withdrawing group at C1′ weakens or annuls the hyperconjugation.

3. Conclusions

On the basis of the ^{1}H NMR coupling constant values and CD spectral differences, the present conformational analysis of *C*-glycoside shows that the rotamer populations around the pseudo-glycosidic linkage (torsion angle Φ) and those of the hydroxymethyl group (torsion angle ω) depend on the structural nature of the *C*-aglycon, the population of the *exo–syn* rotamer ('*exo*-anomeric' conformation), and that of the *gt* rotamer, increasing with the degree of substitution of the *C*-aglycon. When an electron-withdrawing group is located at C1′ in the *C*-aglycon, the *exo–anti* rotamer becomes the most stable and the *gt* rotamer population decreases. All these observations, together with the correlations between ^{1}H and ^{13}C NMR chemical shifts and the size or degree of substitution of the *C*-aglycon, point to hyperconjugation as another factor involved in the conformational preferences around the glycosidic bond of *C*-glycosides, in addition to the 1,3-type interactions. We can explain this hyperconjugation as a stereoelectronic effect of type σ_{CH}–σ^*_{CO}, which influences the conformation around the *C*-glycosidic bond; the term *exo*-deoxoanomeric effect being proposed for this hyperconjugation by analogy with the *exo*-anomeric effect in *O*-glycosides. The stability of the *exo–syn* rotamer can be explained in terms of steric and stereoelectronic interactions, which occurs in *O*-glycosides. The observed rotational dependence of the hydroxymethyl group on the structure of the *C*-aglycon, increasing as it does the population of the *gt* rotamer as that of the *exo–syn* rotamer in-

creases, could be explained by the *exo*-deoxoanomeric effect. The similar but not identical conformational behavior of *C*- and *O*-glycosides in solution is probably due to stereoelectronic effects caused by the σ–σ^* and n–σ^* interactions, respectively, along their 1,3-type steric interactions.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded at 400 or 500 MHz, and ^{13}C NMR at 100 MHz, VTU 300.0 K. Chemical shifts are reported in parts per million. The residual solvent peak ($CDCl_3$) was used as an internal reference, 7.26 for proton and 77.0 ppm for the central peak for carbon NMR. Optical rotations were measured on a digital polarimeter in a 1 dm cell. UV and CD spectra were recorded in the range 400–200 nm using 10 mm cells. The concentrations of the CD samples were ascertained from the UV spectra, using the experimentally determined ε values at 245 nm: tetra-(4-bromobenzoate) ε 76,400. For analytical thin-layer chromatography, silica gel ready-foils were used, developed with 254 nm UV light and/or spraying with AcOH/H_2O/H_2SO_4 (80:16:4) and heating at 150 °C. Flash column chromatography was performed using silica gel (60 Å). All reagents were from commercial sources, and used without further purification; and solvents were dried and distilled before use. All reactions were performed under a dry nitrogen atmosphere. The compounds prepared were characterized on the basis of their one- (^{1}H and ^{13}C) and two-dimensional (COSY, HMQC, and TROESY) NMR spectra, as well as by elemental analysis, HRMS, UV, and CD spectroscopy.

4.2. General procedure for the preparation of β-*C*-glucosides or β-*C*-galactosides

A solution of dimethyldioxirane in acetone (2 equiv, ca. 0.075 M) was added to a stirred solution of the corresponding tri-*O*-benzyl-D-glycal (glucal or galactal) in dry CH_2Cl_2 (5 mL/mmol) at 0 °C under a nitrogen atmosphere, and the reaction stirred at 0 °C for 30 min. The 1,2-anhydrosugar thus obtained was concentrated under reduced pressure and left under vacuum for 2 h. It was then dissolved in dry Et_2O (10 mL/mmol) under dry nitrogen, cooled to −40 °C and the corresponding Grignard reagent was added. When the reaction was completed, it was diluted with Et_2O, quenched with NH_4Cl saturated solution, and extracted with Et_2O three times. The combined organic layers were washed with $NaHCO_3$ saturated solution and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated in a vacuum. The product was purified by silica gel column chromatography.

4.3. General procedure for the preparation of β-*C*-mannosides

The sugar was treated with 1:2 acetic anhydride/dimethyl sulfoxide (8 mL/mmol) mixture. The reaction was left for 24 h at room temperature under a nitrogen atmosphere, after which it was concentrated to dryness, dissolved in CH_2Cl_2, and washed with water and brine. The organic extract was dried over anhydrous $MgSO_4$, filtered, and evaporated in a vacuum. Then, 2 equiv of sodium borohydride was added to a solution of the crude reaction mixture in dry 1:1 CH_2Cl_2/MeOH (10 mL/mmol) at 0 °C in a nitrogen atmosphere and then the ice bath removed. When the reaction was complete, it was diluted with CH_2Cl_2 and washed with water, 1% citric acid solution, $NaHCO_3$ saturated solution, and brine. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated in a vacuum. The product was purified by silica gel column chromatography.

4.4. General procedure for debenzylation and acetylation or *p*-bromobenzoylation

To a solution of the substrate in dry ethanol (10 mL/mmol) was added 100 mg/mmol of palladium at 5% on activated carbon with sufficient hydrogen. After the reaction was complete, the mixture was diluted in ethanol, filtered through a bed of Celite, and evaporated under reduced pressure. (a) *Acetylation*: The crude reaction mixture was dissolved in 20 mL/mmol of a 1:1 solution of dry pyridine/acetic anhydride at room temperature and stirred overnight. The solvent was removed under reduced pressure in the presence of toluene and the residue chromatographed. (b) *p-Bromobenzoylation*: The crude reaction mixture was dissolved in dry pyridine (10 mL/mmol), and then treated with 6 equiv of *p*-bromobenzoyl chloride and DMAP as catalyst. The solution was heated at 60 °C and stirred overnight. The solvent was removed under reduced pressure in the presence of toluene and the residue chromatographed.

4.5. General procedure for reductive ozonolysis and acetylation or ketal formation

A solution of sugar in dry 1:1 CH_2Cl_2/MeOH (65 mL/mmol) under a nitrogen atmosphere was cooled to −78 °C, and ozone was bubbled in until it became blue (approx. 5 min). Then nitrogen was bubbled through to expel excess ozone, and the mixture allowed to warm to 0 °C. $NaBH_4$ (8 equiv) was added and the solution stirred for 1 h at room temperature, then poured into an aqueous solution of 10% HCl, and extracted with CH_2Cl_2. The organic layer was washed with a saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4 anhydrous, and concentrated under reduced pressure. (a) *Acetylation*: The mixture was dissolved in 20 mL/mmol of a 1:1 solution of dry pyridine/acetic anhydride at room temperature and stirred overnight. The solvent was removed under reduced pressure in the presence of toluene and the residue chromatographed. (b) *Ketal formation*: The mixture was dissolved in 5 mL/mmol of dry THF at room temperature, and then treated with 20 equiv of 2,2-dimethoxypropane and 0.25 equiv of *p*-toluenesulfonic acid, and stirred overnight. The reaction was quenched with the addition of 0.5 mL of Et_3N. The solvent was removed under reduced pressure and the residue chromatographed.

4.6. 2,6-Anhydro-4,5,7-tri-*O*-benzyl-1-deoxy-D-*glycero*-D-*gulo*-heptitol 1a

Following the general procedure for the preparation of β-*C*-glucosides, 35 mL (2.63 mmol) of a solution of DMDO in acetone was added to a solution of glucal (550 mg, 1.32 mmol) in 6.5 mL of dry CH_2Cl_2 at 0 °C. Later, the product was directly dissolved in Et_2O (13 mL) and methylmagnesium iodide (4.0 mL, 4.00 mmol) was added. Flash column chromatography (*n*-hexane/EtOAc, 7:3) of the residue yielded **1a** (356 mg, 0.79 mmol, 60%) as an epimer mixture β/α = 12: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = +42.9$ (*c* 1.1, $CHCl_3$); HRMS (FAB) Calcd for $C_{28}H_{31}O_5$ $(M-1)^+$: 447.2171. Found: 447.2171; IR $\tilde{\nu} = 3308\ cm^{-1}$ (OH); ^1H NMR ($CDCl_3$): δ 7.42–7.18 (m, 15H), 4.96 (d, $J = 11.6$ Hz, 1H), 4.81 (d, $J = 10.8$ Hz, 1H), 4.77 (d, $J = 11.6$ Hz, 1H), 4.66 (d, $J = 12.2$ Hz, 1H), 4.57 (d, $J = 10.8$ Hz, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 3.76–3.68 (m, 2H), 3.62 (t, $J = 9.2$ Hz, 1H), 3.51–3.45 (m, 2H), 3.32 (dddd, $J = 5.6$, 5.6, 5.6, and 9.0 Hz, 1H), 3.26 (t, $J = 8.9$ Hz, 1H), 2.44 (br s, 1H), 1.33 (d, $J = 5.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.5, 137.9 (×2), 128.5–127.5, 86.6, 78.7, 78.4, 75.5, 75.4, 74.9, 74.6, 73.3, 68.9, 17.9. Anal. Calcd for $C_{28}H_{32}O_5$: C, 74.97; H, 7.19. Found: C, 74.98; H, 7.07.

4.7. 3,7-Anhydro-5,6,8-tri-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*gulo*-octitol 1b

Following the general procedure for the preparation of β-*C*-glucosides, 40 mL (3.00 mmol) of a solution of DMDO in acetone was added to a solution of glucal (620 mg, 1.49 mmol) in 7.5 mL of dry CH_2Cl_2 at 0 °C. Later, the product was directly dissolved in Et_2O (15 mL) and ethylmagnesium bromide (4.5 mL, 4.50 mmol) was added. Flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5) of the residue yielded **1b** (549 mg, 1.19 mmol, 80%) as an epimer mixture β/α = 10: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = +35.8$ (*c* 1.1, $CHCl_3$); HRMS (FAB) Calcd for $C_{29}H_{33}O_5$ $(M-1)^+$: 461.2328. Found: 461.2308; IR $\tilde{\nu} = 3311\ cm^{-1}$ (OH); ^1H NMR ($CDCl_3$): δ 7.38–7.21 (m, 15H), 4.97 (d, $J = 11.6$ Hz, 1H), 4.80 (d, $J = 10.8$ Hz, 1H), 4.73 (d, $J = 11.6$ Hz, 1H), 4.65 (d, $J = 12.2$ Hz, 1H), 4.61 (d, $J = 10.8$ Hz, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 3.76–3.72 (m, 2H), 3.62 (t, $J = 9.3$ Hz, 1H), 3.47 (t, $J = 8.9$ Hz, 1H), 3.42 (m, 1H), 3.32 (t, $J = 9.0$ Hz, 1H), 3.10 (ddd, $J = 2.6$, 8.5, and 8.5 Hz, 1H), 2.03 (br s, 1H), 1.86 (m, 1H), 1.51 (m, 1H), 1.19 (d, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.2, 138.0, 128.7–127.5, 86.9, 80.4, 79.0, 78.6, 75.1, 74.7, 73.5, 73.5, 69.0, 24.7, 9.6. Anal. Calcd for $C_{29}H_{34}O_5$: C, 75.30; H, 7.41. Found: C, 75.29; H, 7.66.

4.8. 4,8-Anhydro-6,7,9-tri-*O*-benzyl-1,2,3-trideoxy-D-*glycero*-D-*gulo*-nonitol 1c

Following the general procedure for the preparation of β-*C*-glucosides, 45 mL (3.38 mmol) of a solution of DMDO in acetone was added to a solution of glucal (697 mg, 1.67 mmol) in 8.5 mL of dry CH_2Cl_2 at 0 °C. Later, the product was directly dissolved in Et_2O (17 mL) before adding *n*-propylmagnesium chloride (5.0 mL, 5.00 mmol). Flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5) of the residue yielded **1c** (608 mg, 1.28 mmol, 76%) as an epimer mixture β/α = 1.5: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +30.2$ (*c* 1.1, $CHCl_3$); HRMS (FAB) Calcd for $C_{30}H_{35}O_5$ $(M-1)^+$: 475.2484. Found: 475.2474; IR $\tilde{\nu} = 3336\ cm^{-1}$ (OH); ^1H NMR ($CDCl_3$): δ 7.37–7.20 (m, 15H), 4.96 (d, $J = 11.6$ Hz, 1H), 4.80 (d, $J = 10.8$ Hz, 1H), 4.75 (d, $J = 11.6$ Hz, 1H), 4.65 (d, $J = 12.2$ Hz, 1H), 4.60 (d, $J = 10.8$ Hz, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 3.75–3.69 (m, 2H), 3.62 (t, $J = 9.3$ Hz, 1H), 3.47 (t, $J = 8.9$ Hz, 1H), 3.42 (m, 1H), 3.31 (t, $J = 9.0$ Hz, 1H), 3.16 (ddd, $J = 2.3$, 8.6, and 9.0 Hz, 1H), 2.37 (br s, 1H), 1.77 (m, 1H), 1.59 (m, 1H), 1.53 (m, 2H), 1.03 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.5, 138.1, 138.0, 128.5–127.4, 86.9, 79.1, 78.9, 78.4, 75.0, 74.6, 73.9, 73.3, 68.9, 33.8, 18.5, 14.0. Anal. Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.57; H, 7.58.

4.9. 5,9-Anhydro-7,8,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-D-*glycero*-D-*gulo*-decitol 1d

Following the general procedure for the preparation of β-*C*-glucosides, 13 mL (0.98 mmol) of a solution of DMDO in acetone was added to a solution of glucal (199 mg, 0.48 mmol) in 2.4 mL of dry CH_2Cl_2 at 0 °C. Later, the product was directly dissolved in Et_2O (5.0 mL) before adding *n*-butylmagnesium bromide (1.5 mL, 1.50 mmol). Flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5) of the residue yielded **1d** (148 mg, 0.30 mmol, 63%) as an epimer mixture β/α = 2: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +29.0$ (*c* 1.0, $CHCl_3$); HRMS (FAB) Calcd for $C_{31}H_{38}O_5$ $(M)^+$: 490.2719. Found: 490.2742; IR $\tilde{\nu} = 3440\ cm^{-1}$ (OH); ^1H NMR ($CDCl_3$): δ 7.37–7.22 (m, 15H), 4.97 (d, $J = 11.6$ Hz, 1H), 4.83 (d, $J = 11.0$ Hz, 1H), 4.79 (d, $J = 11.6$ Hz, 1H), 4.66 (d, $J = 12.3$ Hz, 1H), 4.62 (d, $J = 11.0$ Hz, 1H), 4.56 (d, $J = 12.3$ Hz, 1H), 3.75 (m, 2H), 3.64 (t, $J = 9.2$ Hz, 1H), 3.50 (t, $J = 8.7$ Hz, 1H), 3.45 (m, 1H), 3.33 (t, $J = 8.9$ Hz, 1H), 3.17 (br t, $J = 8.2$ Hz, 1H), 2.53 (br s, 1H), 1.85 (m, 1H), 1.70–1.47 (m, 5H), 1.05 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.5, 138.1, 138.0, 128.4–127.3, 86.9, 79.1, 78.9, 78.4, 74.9, 74.5, 73.9, 73.2, 68.9, 33.3, 27.4, 22.6, 14.0. Anal. Calcd for $C_{31}H_{38}O_5$: C, 75.89; H, 7.81. Found: C, 75.91; H, 7.77.

4.10. 6,10-Anhydro-8,9,11-tri-*O*-benzyl-1,2,3,4,5-pentadeoxy-D-*glycero*-D-*gulo*-undecitol 1e

Following the general procedure for the preparation of β-*C*-glucosides, 32 mL (2.40 mmol) of a solution of DMDO in acetone was added to a solution of glucal (500 mg, 1.20 mmol) in 6.0 mL of dry CH_2Cl_2 at 0 °C. Then, the product was directly dissolved in Et_2O (12 mL) before adding a 1.0 M solution of *n*-pentylmagnesium bromide in Et_2O (3.6 mL, 3.60 mmol). Flash column chromatography (*n*-hexane/EtOAc, 9:1) of the residue yielded **1e** (438 mg, 0.87 mmol, 72%) as an epimer mixture β/α = 2: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +24.8$ (*c* 1.0, $CHCl_3$); HRMS (FAB) Calcd for $C_{32}H_{40}O_5$ $(M)^+$: 504.2876. Found: 504.2862; IR $\tilde{\nu} = 3354\ cm^{-1}$ (OH); ^1H NMR ($CDCl_3$): δ 7.40–7.24 (m, 15H), 4.97 (d, $J = 11.6$ Hz, 1H), 4.80 (d, $J = 10.8$ Hz, 1H), 4.72 (d,

$J = 11.6$ Hz, 1H), 4.65 (d, $J = 12.3$ Hz, 1H), 4.60 (d, $J = 10.8$ Hz, 1H), 4.57 (d, $J = 12.3$ Hz, 1H), 3.74 (dd, $J = 2.2$ and 10.9 Hz, 1H), 3.69 (dd, $J = 4.1$ and 10.9 Hz, 1H), 3.61 (t, $J = 9.3$ Hz, 1H), 3.46 (t, $J = 8.9$ Hz, 1H), 3.41 (ddd, $J = 2.2$, 4.1, and 9.7 Hz, 1H), 3.31 (t, $J = 9.0$ Hz, 1H), 3.15 (ddd, $J = 2.5$, 8.9, and 8.9 Hz, 1H), 2.06 (br s, 1H,), 1.78 (m, 1H), 1.55 (m, 2H), 1.45 (m, 1H), 1.34–1.24 (m, 4H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.3, 138.1, 128.7–127.5, 87.0, 79.4, 79.1, 78.6, 75.1, 74.7, 73.9, 73.4, 69.0, 31.9, 31.7, 25.0, 22.6, 14.0. Anal. Calcd for $C_{32}H_{40}O_5$: C, 76.16; H, 7.99. Found: C, 76.41; H, 7.89.

4.11. 4,8-Anhydro-6,7,9-tri-*O*-benzyl-1,2,3-trideoxy-2-methyl-D-*glycero*-D-*gulo*-nonitol 1f

Following the general procedure for the preparation of β-*C*-glucosides, 32 mL (2.40 mmol) of a solution of DMDO in acetone was added to a solution of glucal (505 mg, 1.21 mmol) in 6.0 mL of dry CH_2Cl_2 at 0 °C. Then, the product was directly dissolved in Et_2O (12 mL) before adding *iso*-butylmagnesium bromide (3.6 mL, 3.60 mmol). Flash column chromatography (*n*-hexane/EtOAc, 9:1) of the residue yielded **1f** (525 mg, 1.07 mmol, 88%) as an epimer mixture $\alpha/\beta = 2$: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +18.2$ (*c* 1.1, $CHCl_3$); HRMS (FAB) Calcd for $C_{31}H_{39}O_5$ $(M+1)^+$: 491.2797. Found: 491.2799; IR $\tilde{\nu} = 3511$ cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 7.36–7.22 (m, 15H), 4.97 (d, $J = 11.6$ Hz, 1H), 4.82 (d, $J = 10.9$ Hz, 1H), 4.77 (d, $J = 11.6$ Hz, 1H), 4.65 (d, $J = 12.2$ Hz, 1H), 4.62 (d, $J = 10.9$ Hz, 1H), 4.57 (d, $J = 12.2$ Hz, 1H), 3.76–3.69 (m, 2H), 3.64 (t, $J = 9.3$ Hz, 1H), 3.49 (t, $J = 8.7$ Hz, 1H), 3.42 (m, 1H), 3.29 (t, $J = 9.2$ Hz, 1H), 3.23 (br t, $J = 9.2$ Hz, 1H), 2.36 (br s, 1H), 1.93 (m, 1H), 1.60 (m, 1H), 1.45 (m, 1H), 1.00 (d, $J = 6.7$ Hz, 3H), 0.92 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.2, 138.1, 128.5–127.4, 86.7, 79.0, 78.4, 77.7, 75.0, 74.6, 74.4, 73.3, 68.9, 40.7, 24.3, 23.7, 21.7. Anal. Calcd for $C_{31}H_{38}O_5$: C, 75.89; H, 7.81. Found: C, 75.81; H, 7.85.

4.12. 2,6-Anhydro-4,5,7-tri-*O*-benzyl-1-cyclohexyl-1-deoxy-D-*glycero*-D-*gulo*-heptitol 1g

Following the general procedure for the preparation of β-*C*-glucosides, 15 mL (1.13 mmol) of a solution of DMDO in acetone was added to a solution of glucal (230 mg, 0.55 mmol) in 2.8 mL of dry CH_2Cl_2 at 0 °C. The product was then directly dissolved in Et_2O (5.5 mL) before adding bromomagnesium methylcyclohexane (1.7 mL, 1.70 mmol). Flash column chromatography (*n*-hexane/EtOAc, 9:1) of the residue yielded **1g** (140 mg, 0.26 mmol, 48%) as an epimer mixture $\beta/\alpha = 2$: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 8.5:1.5); $[\alpha]_D = +22.3$ (*c* 1.1, $CHCl_3$); HRMS (FAB) Calcd for $C_{34}H_{42}O_5$ $(M+1)^+$: 530.3032. Found: 530.3060; IR $\tilde{\nu} = 3516$ cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 7.35–7.22 (m, 15H), 4.97 (d, $J = 11.6$ Hz, 1H), 4.81 (d, $J = 10.8$ Hz, 1H), 4.73 (d, $J = 11.6$ Hz, 1H), 4.65 (d, $J = 12.1$ Hz, 1H), 4.61 (d, $J = 10.8$ Hz, 1H), 4.58 (d, $J = 12.1$ Hz, 1H), 3.75 (dd, $J = 2.1$ and 11.0 Hz, 1H), 3.69 (dd, $J = 4.2$ and 11.0 Hz, 1H), 3.62 (t, $J = 9.3$ Hz, 1H), 3.47 (t, $J = 8.6$ Hz, 1H), 3.40 (m, 1H), 3.32–3.22 (m, 2H), 2.03 (br s, 1 H), 1.79–1.56 (m, 7H), 1.41 (m, 1H), 1.29–1.16 (m, 3H), 0.99–0.85 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 138.5, 138.2, 138.0, 128.5–127.4, 86.9, 78.9, 78.4, 77.2, 75.0, 74.5, 74.4, 73.2, 68.9, 39.3, 34.3, 33.8, 32.4, 26.5, 26.3, 26.1. Anal. Calcd for $C_{34}H_{42}O_5$: C, 76.95; H, 7.98. Found: C, 76.94; H, 7.90.

4.13. 4,8-Anhydro-6,7,9-tri-*O*-benzyl-1,2,3-trideoxy-2,2-dimethyl-D-*glycero*-D-*gulo*-nonitol 1h

Following the general procedure for the preparation of β-*C*-glucosides, 31 mL (2.33 mmol) of a solution of DMDO in acetone was added to a solution of glucal (478 mg, 1.15 mmol) in 5.8 mL of dry CH_2Cl_2 at 0 °C. Then, the product was directly dissolved in Et_2O (11.5 mL) before adding 2,2-dimethylpropylmagnesium bromide (3.5 mL, 3.50 mmol). Flash column chromatography (*n*-hexane/EtOAc, 9:1) of the residue yielded **1h** (397 mg, 0.79 mmol, 69%) as an epimer mixture $\alpha/\beta = 5$: TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +18.1$ (*c* 1.1, $CHCl_3$); HRMS (FAB) Calcd for $C_{32}H_{39}O_5$ $(M-1)^+$: 503.2797. Found: 503.2782; IR $\tilde{\nu} = 3512$ cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 7.38–7.25 (m, 15H), 5.00 (d, $J = 11.6$ Hz, 1H), 4.84 (d, $J = 10.9$ Hz, 1H), 4.77 (d, $J = 11.6$ Hz, 1H), 4.68- 4.64 (m, 2H), 4.58 (d, $J = 12.3$ Hz, 1H), 3.72 (m, 2H), 3.67 (t, $J = 9.3$ Hz, 1H), 3.51 (t, $J = 8.5$ Hz, 1H), 3.42 (m, 1H), 3.30–3.27 (m, 2H), 2.16 (br s, 1H), 1.74 (br d, $J = 14.5$ Hz, 1H), 1.42 (dd, $J = 8.5$ and 14.5 Hz, 1H), 1.00 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.3, 138.2, 128.6–127.5, 86.9, 78.9, 78.4, 77.2, 75.2, 74.6, 74.4, 73.4, 68.9, 44.5, 30.2 (×3), 30.1. Anal. Calcd for $C_{32}H_{40}O_5$: C, 76.16; H, 7.99. Found: C, 76.17; H, 8.30.

4.14. 4,8-Anhydro-6,7,9-tri-*O*-benzyl-1,2,3-trideoxy-D-*glycero*-L-*manno*-nonitol 2c

Following the general procedure for the preparation of β-*C*-galactosides, 14 mL (1.12 mmol) of a solution of DMDO in acetone was added to a solution of galactal (210 mg, 0.50 mmol) in 2.5 mL of dry CH_2Cl_2 at 0 °C. Then, the product was directly dissolved in Et_2O (5.0 mL) before adding a 2.0 M solution of *n*-propylmagnesium chloride in Et_2O (750 μL, 1.50 mmol). Flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5) of the residue yielded **2c** (175 mg, 0.37 mmol, 73%) as an epimer mixture $\beta/\alpha = 1$: TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 7:3); $[\alpha]_D = +152.7$ (*c* 1.1, $CHCl_3$); HRMS (EI) Calcd for $C_{23}H_{29}O_5$ $(M-C_7H_7)^+$: 385.2015. Found: 385.1998; ^{1}H NMR ($CDCl_3$): δ 7.39–7.33 (m, 15H), 4.88 (d, $J = 11.6$ Hz, 1H), 4.75 (d, $J = 11.7$ Hz, 1H), 4.66 (d, $J = 11.6$ Hz, 1H), 4.55 (d, $J = 11.7$ Hz, 1H), 4.51 (d, $J = 11.7$ Hz, 1H), 4.49 (d, $J = 11.7$ Hz, 1H), 3.69–3.59 (m, 3H), 4.06 (d, $J = 2.4$ Hz, 1H), 3.80 (t, $J = 9.3$ Hz, 1H), 3.67–3.59 (m, 3H), 3.40 (dd, $J = 2.8$ and 9.4 Hz, 1H), 3.21 (ddd, $J = 2.4$, 9.1, and 9.1 Hz, 1H), 2.44 (br s, 1H), 1.85 (m, 1H), 1.63–1.46 (m, 2H), 1.41 (m, 1H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.5, 137.9, 137.8, 128.5–127.5, 84.3, 79.7, 77.1, 74.3, 73.5, 72.6, 71.5, 70.7, 68.9, 33.9, 18.7, 14.0. Anal. Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.58; H, 7.45.

4.15. 4,8-Anhydro-6,7,9-tri-*O*-benzyl-1,2,3-trideoxy-2-methyl-D-*glycero*-L-*manno*-nonitol 2f

Following the general procedure for the preparation of β-*C*-glucosides, 13 mL (0.98 mmol) of a solution of DMDO in acetone was added to a solution of galactal (203 mg, 0.49 mmol) in 2.4 mL of dry CH_2Cl_2 at 0 °C. Then, the product was directly dissolved in Et_2O (4.9 mL) before adding a 2.0 M solution of *iso*-butylmagnesium bromide in Et_2O (730 μL, 1.46 mmol). Flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5) of the residue yielded **2f** (115 mg, 0.23 mmol, 48%) as an epimer mixture α/β = 3: TLC $R_f = 0.7$ (*n*-hexane/EtOAc, 7:3); $[\alpha]_D = +155.1$ (*c* 1.0, $CHCl_3$); HRMS (EI) Calcd for $C_{24}H_{31}O_5$ $(M-C_7H_7)^+$: 399.2171. Found: 399.2162; ^{1}H NMR ($CDCl_3$): δ 7.37–7.28 (m, 15H), 4.85 (d, $J = 11.7$ Hz, 1H), 4.72 (d, $J = 11.7$ Hz, 1H), 4.64 (d, $J = 11.7$ Hz, 1H), 4.52 (d, $J = 11.7$ Hz, 1H), 4.48 (d, $J = 11.7$ Hz, 1H), 4.46 (d, $J = 11.7$ Hz, 1H), 4.03 (d, $J = 2.6$ Hz, 1H), 3.74 (t, $J = 9.2$ Hz, 1H), 3.65–3.55 (m, 3H), 3.38 (dd, $J = 2.7$ and 9.3 Hz, 1H), 3.24 (ddd, $J = 2.3$, 9.5, and 9.5 Hz, 1H), 2.30 (br s, 1H), 1.89 (m, 1H), 1.62 (ddd, $J = 2.3$, 9.6, and 14.2 Hz, 1H), 1.50 (ddd, $J = 4.5$, 9.9, and 14.2 Hz, 1H), 0.92 (d, $J = 6.7$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.0, 137.8, 128.6–127.6, 84.4, 78.2, 77.2, 74.3, 73.5, 72.5, 71.6, 71.0, 69.0, 40.7, 24.2, 23.7, 21.6. Anal. Calcd for $C_{31}H_{38}O_5$: C, 75.89; H, 7.81. Found: C, 75.88; H, 7.99.

4.16. 4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-D-*glycero*-D-*gulo*-octitol 3b

Compound **3b** (15 mg, 0.042 mmol, 77%) was obtained from compound **1b** (50 mg, 0.054 mmol), following the procedure for debenzylation and acetylation, after column chromatography (*n*-hexane/EtOAc, 7.5:2.5): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = -8.7$ (*c* 0.5, $CHCl_3$); HRMS (FAB) Calcd for $C_{16}H_{25}O_9$ $(M+1)^+$: 361.1499. Found: 361.1505; ^{1}H NMR ($CDCl_3$): δ 5.17 (t, $J = 9.4$ Hz, 1H), 5.05 (t, $J = 9.7$ Hz, 1H), 4.90 (t, $J = 9.6$ Hz, 1H), 4.25 (dd, $J = 5.0$ and 12.2 Hz, 1H), 4.10 (dd, $J = 2.3$ and 12.2 Hz, 1H), 3.62 (ddd, $J = 2.3$, 5.0, and 9.9 Hz, 1H), 3.34 (ddd, $J = 2.9$, 8.3, and 9.9 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.60 (ddddd, $J = 2.9$, 7.4, 7.4, 7.4, and 14.8 Hz, 1H), 1.45 (ddddd, $J = 7.4$, 7.4, 7.4, 8.3, and 14.8 Hz, 1H), 0.96 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.4, 169.7, 169.5, 78.8, 75.6, 74.5, 71.7, 68.8, 62.4, 24.3, 20.7 (×2), 20.6 (×2), 9.3. Anal. Calcd for $C_{16}H_{24}O_9$: C, 53.33; H, 6.71. Found: C, 53.32; H, 6.54.

4.17. 5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-D-*glycero*-D-*gulo*-nonitol 3c

Compound **3c** (15 mg, 0.040 mmol, 80%) was obtained from compound **1c** (48 mg, 0.051 mmol), as for **3b**: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = -13.0$ (*c* 0.7, $CHCl_3$); HRMS (FAB) Calcd for $C_{17}H_{27}O_9$ $(M+1)^+$: 375.1655. Found: 375.1651; ^{1}H NMR ($CDCl_3$): δ 5.16 (t, $J = 9.4$ Hz, 1H), 5.04 (t, $J = 9.7$ Hz, 1H), 4.87 (t, $J = 9.6$ Hz, 1H), 4.24 (dd, $J = 5.1$ and 12.2 Hz, 1H), 4.09 (dd, $J = 2.3$ and 12.2 Hz, 1H), 3.61 (ddd, $J = 2.3$, 5.1, and 9.9 Hz, 1H), 3.39 (ddd, $J = 4.3$, 7.0, and 9.9 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.55 (m, 1H), 1.49–1.41 (m, 2H), 1.32 (m, 1H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.4, 169.7, 169.5, 77.6, 75.6, 74.5, 72.0, 68.8, 62.4, 33.3, 20.7 (×2), 20.6 (×2), 18.3, 13.8. Anal. Calcd for $C_{17}H_{26}O_9$: C, 54.54; H, 7.00. Found: C, 54.62; H, 7.12.

4.18. 5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-2-methyl-D-*glycero*-D-*gulo*-nonitol 3f

Compound **3f** (16 mg, 0.041 mmol, 80%) was obtained from compound **1f** (50 mg, 0.053 mmol), as for **3b**: TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = -14.5$ (*c* 0.5, $CHCl_3$); HRMS (FAB) Calcd for $C_{18}H_{29}O_9$ $(M+1)^+$: 389.1812. Found: 389.1799; ^{1}H NMR ($CDCl_3$): δ 5.17 (t, $J = 9.4$ Hz, 1H), 5.03 (t, $J = 9.7$ Hz, 1H), 4.84 (t, $J = 9.5$ Hz, 1H), 4.24 (dd, $J = 5.3$ and 12.2 Hz, 1H), 4.07 (dd, $J = 2.3$ and 12.2 Hz, 1H), 3.61 (ddd, $J = 2.3$, 5.3, and 9.9 Hz, 1H), 3.45 (ddd, $J = 2.3$, 9.9, and 9.9 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.81 (m, 1H), 1.46 (ddd, $J = 4.5$, 9.9, and 14.2 Hz, 1H), 1.18 (ddd, $J = 2.3$, 9.5, and 14.2 Hz, 1H), 0.91 (d, $J = 6.7$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.4, 170.0, 169.5, 76.3, 75.7, 74.5, 72.4, 68.8, 62.4, 40.1, 24.3, 23.4, 21.5, 20.7 (×2), 20.6 (×2). Anal. Calcd for $C_{18}H_{28}O_9$: C, 55.66; H, 7.27. Found: C, 55.49; H, 7.37.

4.19. 5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-2,2-dimethyl-D-*glycero*-D-*gulo*-nonitol 3h

Compound **3h** (10 mg, 0.025 mmol, 69%) was obtained from compound **1h** (35 mg, 0.036 mmol), following the procedure for debenzylation and acetylation, after column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = -7.8$ (*c* 0.4, $CHCl_3$); HRMS (FAB) Calcd for $C_{19}H_{31}O_9$ $(M+1)^+$: 403.1968. Found: 403.1962; ^{1}H NMR ($CDCl_3$): δ 5.17 (t, $J = 9.3$ Hz, 1H), 4.99 (t, $J = 9.7$ Hz, 1H), 4.82 (t, $J = 9.5$ Hz, 1H), 4.19 (dd, $J = 6.2$ and 12.1 Hz, 1H), 4.06 (dd, $J = 2.3$ and 12.1 Hz, 1H), 3.62 (ddd, $J = 2.3$, 6.2, and 9.9 Hz, 1H), 3.48 (t, $J = 8.9$ Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.44 (dd, $J = 8.9$ and 14.7 Hz, 1H), 1.25 (d, $J = 14.7$ Hz, 1H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.4, 169.8, 169.6, 75.9, 75.4, 74.5, 72.2, 69.0, 62.7, 44.2, 30.0, 29.8 (×3), 20.7 (×2), 20.6 (×2). Anal. Calcd for $C_{19}H_{30}O_9$: C, 56.71; H, 7.51. Found: C, 56.84; H, 7.57.

4.20. 2,6-Anhydro-3,4,5,7-tetra-*O*-(*p*-bromobenzoyl)-1-deoxy-D-*glycero*-D-*gulo*-heptitol 4a

Debenzylation of compound **1a** (208 mg, 0.46 mmol) and then *p*-bromobenzoylation were performed as in the general procedure, giving compound **4a** (384 mg, 0.42 mmol, 91%) after column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = +50.0$ (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.6$ Hz, 2H), 7.72 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.48 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 8.6$ Hz, 2H), 5.77 (t,

$J = 9.6$ Hz, 1H), 5.60 (t, $J = 9.7$ Hz, 1H), 5.30 (t, $J = 9.6$ Hz, 1H), 4.56 (dd, $J = 3.1$ and 12.2 Hz, 1H), 4.43 (dd, $J = 4.8$ and 12.2 Hz, 1H), 4.07 (ddd, $J = 3.1$, 4.8, and 9.7 Hz, 1H), 3.87 (dddd, $J = 6.1$, 6.1, 6.1, and 9.6 Hz, 1H), 1.34 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.4, 165.2, 164.7, 164.5, 131.8–131.2, 128.8 (×2), 128.7, 128.4, 128.3, 127.7, 127.5 (×2), 75.6, 74.7, 74.6, 74.0, 70.0, 63.5, 17.7; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (22.4), 234 nm (−6.5). Anal. Calcd for $C_{35}H_{26}Br_4O_9$: C, 46.19; H, 2.88. Found: C, 46.12; H, 2.92.

4.21. 3,7-Anhydro-4,5,6,8-tetra-*O*-(*p*-bromobenzoyl)-1,2-dideoxy-D-*glycero*-D-*gulo*-octitol 4b

Debenzylation of compound **1b** (409 mg, 0.88 mmol) and then *p*-bromobenzoylation were performed as in the general procedure, giving compound **4b** (796 mg, 0.86 mmol, 97%) after column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +42.8$ (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.55 (d, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 8.7$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 5.78 (t, $J = 9.5$ Hz, 1H), 5.57 (t, $J = 9.7$ Hz, 1H), 5.36 (t, $J = 9.6$ Hz, 1H), 4.57 (dd, $J = 3.1$ and 12.1 Hz, 1H), 4.44 (dd, $J = 5.1$ and 12.1 Hz, 1H), 4.05 (ddd, $J = 3.1$, 5.1, and 9.7 Hz, 1H), 3.66 (ddd, $J = 3.0$, 8.0, and 9.6 Hz, 1H), 1.69 (m, 1H), 1.57 (m, 1H), 1.01 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.4, 165.2, 164.7, 164.5, 131.8–131.1, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.6 (×2), 79.2, 75.6, 74.8, 72.4, 70.2, 63.5, 24.5, 9.3; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (21.0), 234 nm (−6.0). Anal. Calcd for $C_{36}H_{28}Br_4O_9$: C, 46.78; H, 3.05. Found: C, 46.87; H, 3.00.

4.22. 4,8-Anhydro-5,6,7,9-tetra-*O*-(*p*-bromobenzoyl)-1,2,3-trideoxy-D-*glycero*-D-*gulo*-nonitol 4c

Debenzylation of compound **1c** (171 mg, 0.36 mmol) and then *p*-bromobenzoylation were performed as in the general procedure, to give compound **4c** (300 mg, 0.32 mmol, 89%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +37.7$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.85 (d, $J = 8.6$ Hz, 2H), 7.78 (d, $J = 8.6$ Hz, 2H), 7.72 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.48 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 8.6$ Hz, 2H), 5.78 (t, $J = 9.5$ Hz, 1H), 5.56 (t, $J = 9.7$ Hz, 1H), 5.34 (t, $J = 9.6$ Hz, 1H), 4.56 (dd, $J = 3.2$ and 12.1 Hz, 1H), 4.43 (dd, $J = 5.3$ and 12.1 Hz, 1H), 4.04 (ddd, $J = 3.2$, 5.3, and 9.7 Hz, 1H), 3.72 (ddd, $J = 3.8$, 7.1, and 9.6 Hz, 1H), 1.61–1.54 (m, 3H), 1.40 (m, 1H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.3, 165.1, 164.6, 164.4, 131.8–131.1, 128.8, 128.7, 128.6, 128.4, 128.3, 127.7, 127.5 (×2), 78.0, 75.6, 74.8, 72.7, 70.1, 63.5, 33.3, 18.2, 13.8; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (18.8), 234 nm (−6.3). Anal. Calcd for $C_{37}H_{30}Br_4O_9$: C, 47.36; H, 3.22. Found: C, 47.56; H, 3.18.

4.23. 5,9-Anhydro-6,7,8,10-tetra-*O*-(*p*-bromobenzoyl)-1,2,3,4-tetradeoxy-D-*glycero*-D-*gulo*-decitol 4d

Debenzylation of compound **1d** (340 mg, 0.69 mmol) and then *p*-bromobenzoylation were performed as in the general procedure, to give compound **4d** (630 mg, 0.66 mmol, 95%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 9:1); $[\alpha]_D = +33.2$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.56–7.52 (m, 4H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 5.77 (t, $J = 9.5$ Hz, 1H), 5.55 (t, $J = 9.7$ Hz, 1H), 5.34 (t, $J = 9.6$ Hz, 1H), 4.55 (dd, $J = 3.1$ and 12.1 Hz, 1H), 4.43 (dd, $J = 5.4$ and 12.1 Hz, 1H), 4.04 (ddd, $J = 3.1$, 5.4, and 9.7 Hz, 1H), 3.70 (ddd, $J = 3.3$, 7.7, and 9.6 Hz, 1H), 1.60–1.53 (m, 3H), 1.35–1.25 (m, 3H), 0.84 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.4, 165.2, 164.7, 164.5, 131.8–131.1, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.6 (×2), 78.2, 75.7, 74.8, 72.7, 70.2, 63.6, 31.0, 27.2, 22.4, 13.9; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (17.6), 234 nm (−5.9). Anal. Calcd for $C_{38}H_{32}Br_4O_9$: C, 47.93; H, 3.39. Found: C, 47.77; H, 3.51.

4.24. 6,10-Anhydro-7,8,9,11-tetra-*O*-(*p*-bromobenzoyl)-1,2,3,4,5-pentadeoxy-D-*glycero*-D-*gulo*-undecitol 4e

Debenzylation of compound **1e** (148 mg, 0.29 mmol) and then *p*-bromobenzoylation were performed as in the general procedure, to give compound **4e** (276 mg, 0.29 mmol, 98%) after column chromatography (*n*-hexane /EtOAc, 8.5:1.5); $[\alpha]_D = +34.2$ (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.55–7.53 (m, 4H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 5.77 (t, $J = 9.5$ Hz, 1H), 5.55 (t, $J = 9.7$ Hz, 1H), 5.34 (t, $J = 9.6$ Hz, 1H), 4.55 (dd, $J = 3.2$ and 12.1 Hz, 1H), 4.44 (dd, $J = 5.4$ and 12.1 Hz, 1H), 4.04 (ddd, $J = 3.2$, 5.4, and 9.7 Hz, 1H), 3.70 (ddd, $J = 4.0$, 7.1, and 9.6 Hz, 1H), 1.58 (m, 3H), 1.35 (m, 1H), 1.24 (m, 4H), 0.83 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.2, 165.1, 164.6, 164.4, 131.7–131.1, 128.7 (×2), 128.6, 128.4, 128.2, 127.7, 127.5 (×2), 78.1, 75.7, 74.8, 72.7, 70.2, 63.6, 31.4, 31.3, 24.6, 22.4, 13.8; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (17.4), 234 nm (−6.0). Anal. Calcd for $C_{39}H_{34}Br_4O_9$: C, 48.48; H, 3.55. Found: C, 48.46; H, 3.42.

4.25. 4,8-Anhydro-5,6,7,9-tetra-*O*-(*p*-bromobenzoyl)-2-methyl-D-*glycero*-D-*gulo*-nonitol 4f

Debenzylation of compound **1f** (235 mg, 0.48 mmol) and then *p*-bromobenzoylation as in the general procedure gave compound **4f** (331 mg, 0.35 mmol, 73%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 9:1); $[\alpha]_D = +28.9$ (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.56–7.52 (m, 4H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 5.78 (t, $J = 9.5$ Hz, 1H), 5.54 (t, $J = 9.7$ Hz, 1H), 5.32 (t, $J = 9.6$ Hz, 1H), 4.54 (dd,

$J = 3.1$ and 12.1 Hz, 1H), 4.43 (dd, $J = 5.7$ and 12.1 Hz, 1H), 4.05 (ddd, $J = 3.1$, 5.7, and 9.7 Hz, 1H), 3.77 (ddd, $J = 2.2$, 9.6, and 9.9 Hz, 1H), 1.87 (m, 1H), 1.61 (ddd, $J = 4.4$, 9.9, and 14.2 Hz, 1H), 1.30 (ddd, $J = 2.2$, 9.5, and 14.2 Hz, 1H), 0.90 (d, $J = 6.7$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.4, 165.2, 164.7, 164.5, 131.9–131.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.8, 127.6 (×2), 76.7, 75.8, 74.8, 73.1, 70.2, 63.7, 40.1, 24.4, 23.4, 21.5; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (16.7), 234 nm (−5.2). Anal. Calcd for $C_{38}H_{32}Br_4O_9$: C, 47.93; H, 3.39. Found: C, 48.03; H, 3.63.

4.26. 2,6-Anhydro-3,4,5,7-tetra-*O*-(*p*-bromobenzoyl)-1-cyclohexyl-1-deoxy-D-*glycero*-D-*gulo*-heptitol 4g

Debenzylation of compound **1g** (205 mg, 0.39 mmol) and then *p*-bromobenzoylation as in the general procedure gave **4g** (353 mg, 0.36 mmol, 92%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 9:1); $[\alpha]_D = +22.1$ (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 8.6$ Hz, 2H), 5.77 (t, $J = 9.5$ Hz, 1H), 5.52 (t, $J = 9.7$ Hz, 1H), 5.30 (t, $J = 9.6$ Hz, 1H), 4.53 (dd, $J = 3.0$ and 12.0 Hz, 1H), 4.43 (dd, $J = 6.1$ and 12.0 Hz, 1H), 4.04 (ddd, $J = 3.0$, 6.1, and 9.7 Hz, 1H), 3.80 (ddd, $J = 2.3$, 9.7, and 9.7 Hz, 1H), 1.76–1.50 (m, 7H), 1.38–1.02 (m, 4H), 0.96–0.78 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 165.3, 165.2, 164.7, 164.5, 131.8–131.1, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.5 (×2), 76.2, 75.8, 74.8, 73.1, 70.3, 63.7, 38.8, 34.0, 33.9, 32.3, 26.3, 26.2, 26.0; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (12.2), 234 nm (−3.8). Anal. Calcd for $C_{41}H_{26}Br_4O_9$: C, 49.62; H, 3.66. Found: C, 49.46; H, 3.90.

4.27. 4,8-Anhydro-5,6,7,9-tetra-*O*-(*p*-bromobenzoyl)-1,2,3-trideoxy-2,2-dimethyl-D-*glycero*-D-*gulo*-nonitol 4h

Debenzylation of compound **1h** (66 mg, 0.13 mmol) and then *p*-bromobenzoylation as in the general procedure gave compound **4h** (96 mg, 0.099 mmol, 76%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 9:1); $[\alpha]_D = +14.7$ (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.74 (d, $J = 8.6$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.56–7.52 (m, 4H), 7.50 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 5.78 (t, $J = 9.5$ Hz, 1H), 5.49 (t, $J = 9.7$ Hz, 1H), 5.30 (t, $J = 9.6$ Hz, 1H), 4.52 (dd, $J = 2.9$ and 12.0 Hz, 1H), 4.40 (dd, $J = 6.6$ and 12.0 Hz, 1H), 4.07 (ddd, $J = 2.9$, 6.6, and 9.7 Hz, 1H), 3.81 (dd, $J = 8.8$ and 9.6 Hz, 1H), 1.58 (dd, $J = 8.8$ and 14.7 Hz, 1H), 1.38 (d, $J = 14.7$ Hz, 1H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 165.3, 165.2, 164.7, 164.6, 131.8–131.1, 128.9, 128.8, 128.6, 128.4, 128.3, 127.8, 127.5 (×2), 76.3, 75.6, 74.9, 72.7, 70.3, 63.9, 44.3, 30.1, 29.8 (×3); UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (10.6), 234 nm (−3.7). Anal. Calcd for $C_{39}H_{34}Br_4O_9$: C, 48.48; H, 3.55. Found: C, 48.49; H, 3.67.

4.28. 4,8-Anhydro-5,6,7,9-tetra-*O*-(*p*-bromobenzoyl)-1,2,3-trideoxy-D-*glycero*-L-*manno*-nonitol 5c

Debenzylation of compound **2c** (69 mg, 0.14 mmol) and then *p*-bromobenzoylation as in the general procedure led to **5c** (125 mg, 0.13 mmol, 92%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = +152.7$ (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.90 (d, $J = 8.5$ Hz, 2H), 7.86 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 5.93 (d, $J = 2.8$ Hz, 1H), 5.60 (t, $J = 9.7$ Hz, 1H), 5.53 (dd, $J = 3.3$ and 10.1 Hz, 1H), 4.59 (dd, $J = 6.7$ and 11.2 Hz, 1H), 4.32 (dd, $J = 6.5$ and 11.2 Hz, 1H), 4.23 (t, $J = 6.5$ Hz, 1H), 3.72 (ddd, $J = 3.5$, 8.0, and 9.7 Hz, 1H), 1.69–1.58 (m, 3H), 1.42 (m, 1H), 0.93 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.3, 164.9 (×3), 132.1–131.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.2, 128.0, 127.7, 78.3, 74.1, 73.3, 70.6, 69.1, 62.5, 33.6, 18.3, 13.9; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (66.9), 234 nm (−23.5). Anal. Calcd for $C_{37}H_{30}Br_4O_9$: C, 47.36; H, 3.22. Found: C, 47.36; H, 3.30.

4.29. 4,8-Anhydro-5,6,7,9-tetra-*O*-(*p*-bromobenzoyl)-2-methyl-D-*glycero*-L-*manno*-nonitol 5f

Debenzylation of compound **2f** (50 mg, 0.10 mmol) and then *p*-bromobenzoylation as in the general procedure led to **5f** (62 mg, 0.065 mmol, 64%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = +155.1$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.91 (d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 5.94 (d, $J = 2.7$ Hz, 1H), 5.57 (t, $J = 10.0$ Hz, 1H), 5.53 (dd, $J = 3.2$ and 10.0 Hz, 1H), 4.58 (dd, $J = 7.0$ and 11.3 Hz, 1H), 4.34 (dd, $J = 6.1$ and 11.3 Hz, 1H), 4.23 (t, $J = 6.6$ Hz, 1H), 3.78 (ddd, $J = 2.2$, 9.9, and 9.9 Hz, 1H), 1.92 (m, 1H), 1.71 (ddd, $J = 4.6$, 9.9, and 14.1 Hz, 1H), 1.37 (ddd, $J = 2.2$, 9.5, and 14.1 Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.3, 165.0 (×2), 164.9, 132.1–131.1, 129.0, 128.8, 128.7, 128.5, 128.4, 127.9 (×2), 127.7, 77.0, 74.6, 73.2, 70.9, 69.1, 62.6, 40.4, 24.4, 23.5, 21.5; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (70.4), 234 nm (−25.7). Anal. Calcd for $C_{38}H_{32}Br_4O_9$: C, 47.93; H, 3.39. Found: C, 47.93; H, 3.49.

4.30. 4,8-Anhydro-6,7,9-tri-*O*-benzyl-1,2,3-trideoxy-D-*glycero*-D-*galacto*-nonitol 6c

Following the general procedure for the preparation of β-*C*-mannosides, 370 mg (0.78 mmol) of β-*C*-glucoside **1c** led to **6c** (200 mg, 0.42 mmol, 54%), after flash column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = -165.3$ (*c* 1.0, $CHCl_3$); HRMS (EI) Calcd for $C_{23}H_{29}O_5$ $(M-C_7H_7)^+$: 385.2015. Found: 385.1990; ^{1}H NMR ($CDCl_3$): δ 7.37–7.20 (m, 15H), 4.86 (d, $J = 10.8$ Hz, 1H), 4.76 (d, $J = 11.6$ Hz, 1H), 4.68 (d, $J = 11.6$ Hz, 1H), 4.62 (d, $J = 12.2$ Hz, 1H),

4.57 (d, $J = 12.2$ Hz, 1H), 4.53 (d, $J = 10.8$ Hz, 1H), 3.91 (d, $J = 2.6$ Hz, 1H), 3.79–3.73 (m, 2H), 3.68 (dd, $J = 5.1$ and 10.8 Hz, 1H), 3.59 (dd, $J = 3.3$ and 9.1 Hz, 1H), 3.40 (ddd, $J = 1.9$, 5.1, and 9.8 Hz, 1H), 3.32 (t, $J = 6.8$ Hz, 1H), 2.18 (br s, 1H), 1.80 (m, 1H), 1.59 (m, 1H), 1.48–1.39 (m, 2H), 0.95 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.5, 138.2, 128.6–126.2, 83.8, 79.4, 78.0, 75.2, 75.0, 73.8, 71.6, 69.7, 68.5, 33.0, 19.3, 14.3. Anal. Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.58; H, 7.64.

4.31. 4,8-Anhydro-6,7,9-tri-*O*-benzyl-1,2,3-trideoxy-2-methyl-D-*glycero*-D-*galacto*-nonitol 6f

Following the general procedure for the preparation of β-*C*-mannosides, 135 mg (0.28 mmol) of β-*C*-glucoside **1f** gave compound **6f** (74 mg, 0.15 mmol, 55%), after flash column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = -170.6$ (*c* 1.1, $CHCl_3$); HRMS (EI) Calcd for $C_{24}H_{31}O_5$ $(M-C_7H_7)^+$: 399.2171. Found: 399.2155; ^{1}H NMR ($CDCl_3$): δ 7.36–7.20 (m, 15H), 4.86 (d, $J = 10.8$ Hz, 1H), 4.75 (d, $J = 11.5$ Hz, 1H), 4.68 (d, $J = 11.5$ Hz, 1H), 4.62 (d, $J = 12.2$ Hz, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 4.54 (d, $J = 10.8$ Hz, 1H), 3.87 (d, $J = 3.0$ Hz, 1H), 3.78–3.72 (m, 2H), 3.68 (dd, $J = 5.1$ and 10.9 Hz, 1H), 3.60 (dd, $J = 3.2$ and 9.1 Hz, 1H), 3.41–3.37 (m, 2H), 1.95 (br s, 1H), 1.82–1.77 (m, 2H), 1.38 (m, 1H), 0.93 (d, $J = 6.4$ Hz, 3H), 0.91 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 138.3, 138.3, 137.8, 128.6–127.4, 83.7, 79.3, 76.2, 75.0, 74.8, 73.4, 71.5, 69.5, 68.7, 39.6, 24.6, 23.0, 22.4. Anal. Calcd for $C_{31}H_{38}O_5$: C, 75.89; H, 7.81. Found: C, 75.87; H, 7.86.

4.32. 4,8-Anhydro-5,6,7,9-tetra-*O*-(*p*-bromobenzoyl)-1,2,3-trideoxy-D-*glycero*-D-*galacto*-nonitol 7c

Debenzylation of compound **6c** (165 mg, 0.35 mmol) and then *p*-bromobenzoylation as in the general procedure led to **7c** (310 mg, 0.33 mmol, 95%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = -165.3$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.91 (d, $J = 8.6$ Hz, 2H), 7.85 (d, $J = 8.6$ Hz, 2H), 7.74 (d, $J = 8.6$ Hz, 2H), 7.61 (d, $J = 8.6$ Hz, 2H), 7.57 (d, $J = 8.5$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.6$ Hz, 2H), 5.86 (t, $J = 10.0$ Hz, 1H), 5.74 (d, $J = 3.1$ Hz, 1H), 5.55 (dd, $J = 3.2$ and 10.1 Hz, 1H), 4.68 (dd, $J = 2.9$ and 12.1 Hz, 1H), 4.44 (dd, $J = 4.9$ and 12.1 Hz, 1H), 4.05 (ddd, $J = 2.9$, 4.9, and 9.9 Hz, 1H), 3.87 (dd, $J = 4.3$ and 7.8 Hz, 1H), 1.70–1.47 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.2, 165.0, 164.9, 164.7, 132.0–131.0, 128.8 (×2), 128.6 (×2), 128.3, 128.0, 127.6 (×2), 77.1, 75.9, 73.5, 70.8, 67.9, 63.5, 32.6, 18.7, 13.8; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (−70.2), 234 nm (20.0). Anal. Calcd for $C_{37}H_{30}Br_4O_9$: C, 47.36; H, 3.22. Found: C, 47.34; H, 3.48.

4.33. 4,8-Anhydro-5,6,7,9-tetra-*O*-(*p*-bromobenzoyl)-2-methyl-D-*glycero*-D-*galalcto*-nonitol 7f

Debenzylation of compound **6f** (41 mg, 0.084 mmol) and then *p*-bromobenzoylation as in the general procedure led to compound **7f** (75 mg, 0.078 mmol, 95%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = -170.6$ (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.90 (d, $J = 8.5$ Hz, 2H), 7.86 (d, $J = 8.5$ Hz, 2H), 7.74 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 5.84 (t, $J = 10.0$ Hz, 1H), 5.71 (d, $J = 3.1$ Hz, 1H), 5.57 (dd, $J = 3.2$ and 10.1 Hz, 1H), 4.67 (dd, $J = 2.9$ and 12.0 Hz, 1H), 4.44 (dd, $J = 5.1$ and 12.0 Hz, 1H), 4.06 (ddd, $J = 2.8$, 5.1, and 9.8 Hz, 1H), 3.94 (dd, $J = 4.0$ and 8.7 Hz, 1H), 1.78 (m, 1H), 1.63 (ddd, $J = 6.2$, 8.7, and 14.3 Hz, 1H), 1.28 (ddd, $J = 4.0$, 7.9, and 14.3 Hz, 1H), 0.92 (d, $J = 6.7$ Hz, 3H), 0.89 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.3, 165.0, 164.9, 164.7, 132.0–131.1, 128.9, 128.8 (×2), 128.7, 128.3, 128.1, 127.7, 127.6, 76.0, 75.7, 73.5, 71.3, 67.5, 63.6, 39.4, 24.5, 22.9, 22.1; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (−71.3), 234 nm (22.9). Anal. Calcd for $C_{38}H_{32}Br_4O_9$: C, 47.93; H, 3.39. Found: C, 47.77; H, 3.43.

4.34. 3,7-Anhydro-5,6,8-tri-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*gulo*-oct-1-enitol 8

Following the general procedure for the preparation of β-*C*-glucosides, 39 mL (2.93 mmol) of a solution of DMDO in acetone was added to a solution of glucal (610 mg, 1.47 mmol) in 7.5 mL of dry CH_2Cl_2 at 0 °C. Then, the product was directly dissolved in Et_2O (30 mL, 20 mL/mmol) and 2.5 equiv of a solution of bromomagnesium divinylcuprate in diethyl ether (42.5 mL, 3.67 mmol) was added. Flash column chromatography (*n*-hexane/EtOAc, 7.5:2.5) of the residue yielded **8** (407 mg, 0.88 mmol, 60%) as an epimer mixture $\beta/\alpha = 4$.

4.35. 1,3-Di-*O*-acetyl-2,6-anhydro-4,5,7-tri-*O*-benzyl-D-*glycero*-D-*gulo*-heptitol 10

Compound **10** (33 mg, 0.059 mmol, 91%) was obtained from compound **8** (30 mg, 0.061 mmol), following the procedure for reductive ozonolysis and acetylation, after column chromatography (*n*-hexane/EtOAc, 7.5:2.5): TLC $R_f = 0.4$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = +19.9$ (*c* 1.1, $CHCl_3$); HRMS (FAB) Calcd for $C_{32}H_{37}O_8$ $(M+1)^+$: 549.2488. Found: 549.2502; ^{1}H NMR ($CDCl_3$): δ 7.35–7.26 (m, 13H), 7.17 (m, 2H), 5.06 (ddd, $J = 2.5$, 6.8, and 9.6 Hz, 1H), 4.83 (d, $J = 11.4$ Hz, 1H), 4.79 (d, $J = 10.8$ Hz, 1H), 4.67 (d, $J = 11.4$ Hz, 1H), 4.62 (d, $J = 12.1$ Hz, 1H), 4.59 (d, $J = 12.1$ Hz, 1H), 4.56 (d, $J = 10.8$ Hz, 1H), 4.21 (dd, $J = 5.2$ and 12.2 Hz, 1H), 4.11 (dd, $J = 2.3$ and 12.2 Hz, 1H), 3.76 (dd, $J = 1.6$ and 11.1 Hz, 1H), 3.72–3.65 (m, 3H), 3.56–3.49 (m, 2H), 2.07 (s, 3H), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.8, 169.6, 138.2, 138.1, 137.8, 128.4-127.6, 84.4, 79.3, 78.1, 76.0, 75.2, 75.0, 73.4, 70.3, 68.8, 62.8, 20.8 (×2). Anal. Calcd for $C_{32}H_{36}O_8$: C, 70.06; H, 6.61. Found: C, 70.01; H, 7.00.

4.36. 1,3,4,5,7-Penta-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptitol 11

Debenzylation of compound **10** (22 mg, 40.1 μmol) and then acetylation were performed as in the general

procedure leading to **11** (15 mg, 36.8 μmol, 92%) after column chromatography (*n*-hexane/EtOAc, 5:5): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 5:5); HRMS (FAB) Calcd for $C_{17}H_{25}O_{11}$ $(M+1)^+$: 405.1397. Found: 405.1389; ^{1}H NMR ($CDCl_3$): δ 5.21 (t, $J = 9.3$ Hz, 1H), 5.10 (t, $J = 9.7$ Hz, 2H), 4.26 (dd, $J = 4.9$ and 12.4 Hz, 2H), 4.12 (dd, $J = 2.1$ and 12.4 Hz, 2H), 3.69 (ddd, $J = 2.1$, 4.9, and 9.7 Hz, 2H), 2.09 (s, 6H), 2.03 (s, 6H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.6 (×2), 170.3, 169.4 (×2), 75.9 (×2), 74.2, 68.2 (×2), 62.1 (×2), 20.7 (×2), 20.6 (×3). Anal. Calcd for $C_{17}H_{24}O_{11}$: C, 50.49; H, 5.98. Found: C, 50.45; H, 6.20.

4.37. 2,6-Anhydro-4,5,7-tri-*O*-benzyl-1,3-*O*-*iso*-propylidene-D-*glycero*-D-*gulo*-heptitol 12

Compound **12** (338 mg, 0.67 mmol, 93%) was obtained from compound **8** (333 mg, 0.72 mmol), following the procedure for reductive ozonolysis and ketal formation, after column chromatography (*n*-hexane/EtOAc, 7.5:2.5): TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = +18.7$ (*c* 1.4, $CHCl_3$); HRMS (FAB) Calcd for $C_{31}H_{37}O_6$ $(M+1)^+$: 505.2590. Found: 505.2589; ^{1}H NMR ($CDCl_3$): δ 7.39–7.28 (m, 13H), 7.16 (m, 2H), 4.93 (d, $J = 11.3$ Hz, 1H), 4.88 (d, $J = 10.8$ Hz, 1H), 4.77 (d, $J = 11.3$ Hz, 1H), 4.61 (d, $J = 12.3$ Hz, 1H), 4.53 (d, $J = 12.3$ Hz, 1H), 4.50 (d, $J = 10.8$ Hz, 1H), 3.97 (dd, $J = 5.3$ and 10.8 Hz, 1H), 3.79 (t, $J = 10.5$ Hz, 1H), 3.74–3.66 (m, 4H), 3.62 (t, $J = 9.4$ Hz, 1H), 3.54 (ddd, $J = 1.7$, 3.7, and 9.3 Hz, 1H), 3.29 (ddd, $J = 5.3$, 9.6, and 9.6 Hz, 1H), 1.52 (s, 3H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 138.9, 138.2, 137.9, 128.6-127.5, 99.1, 83.6, 79.5, 77.5, 75.2, 74.9, 74.6, 73.5, 71.4, 69.0, 62.4, 29.2, 19.2. Anal. Calcd for $C_{31}H_{36}O_6$: C, 73.79; H, 7.19. Found: C, 73.64; H, 7.11.

4.38. 4,5,7-Tri-*O*-acetyl-2,6-anhydro-1,3-*O*-*iso*-propylidene-D-*glycero*-D-*gulo*-heptitol 13

Debenzylation of compound **12** (89 mg, 0.18 mmol) and then acetylation were performed as in the general procedure leading to compound **13** (49 mg, 0.14 mmol, 77%) after column chromatography (*n*-hexane/EtOAc, 6:4): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = +42.3$ (*c* 1.0, $CHCl_3$); HRMS (FAB) Calcd for $C_{16}H_{25}O_9$ $(M+1)^+$: 361.1499. Found: 361.1498; ^{1}H NMR ($CDCl_3$): δ 5.11 (t, $J = 9.3$ Hz, 1H), 5.00 (t, $J = 9.5$ Hz), 4.19 (dd, $J = 4.8$ and 12.4 Hz), 4.04 (dd, $J = 2.0$ and 12.4 Hz), 3.92 (dd, $J = 5.3$ and 10.8 Hz), 3.71 (t, $J = 10.5$ Hz), 3.69 (m, 2H), 3.33 (ddd, $J = 5.3$, 9.9, and 9.9 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.3, 169.7, 99.7, 76.4, 73.4, 71.8, 71.3, 69.0, 62.2, 61.9, 28.8, 20.8, 20.7, 20.6, 18.9. Anal. Calcd for $C_{16}H_{24}O_9$: C, 53.33; H, 6.71. Found: C, 53.29; H, 6.76.

4.39. 2,6-Anhydro-4,5,7-penta-*O*-(*p*-bromobenzoyl)-1,3-*O*-*iso*-propylidene-D-*glycero*-D-*gulo*-heptitol 14

Debenzylation of compound **12** (112 mg, 0.22 mmol) and then *p*-bromobenzoylation as in the general procedure led to **14** (140 mg, 0.18 mmol, 80%) after column chromatography (*n*-hexane/EtOAc, 7.5:2.5): TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = -33.0$ (*c* 1.2, $CHCl_3$); HRMS (FAB) Calcd for $C_{31}H_{27}Br_3O_9$ $(M)^+$: 785.9144. Found: 785.9149; ^{1}H NMR ($CDCl_3$): δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.53–7.44 (m, 6H), 5.61 (t, $J = 9.3$ Hz, 1H), 5.52 (t, $J = 9.5$ Hz, 1H), 4.53 (dd, $J = 2.7$ and 12.2 Hz, 1H), 4.38 (dd, $J = 4.8$ and 12.2 Hz, 1H), 4.06 (ddd, $J = 2.7$, 4.8, and 9.5 Hz, 1H), 4.02 (dd, $J = 5.2$ and 10.5 Hz, 1H), 3.94 (t, $J = 9.5$ Hz, 1H), 3.81 (t, $J = 10.5$ Hz, 1H), 3.56 (ddd, $J = 5.2$, 9.8, and 9.8 Hz, 1H), 1.48 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 165.3, 165.1, 164.6, 131.8–131.2, 128.8, 128.4, 128.3 (×3), 127.5, 99.8, 76.4, 74.0, 72.2, 71.7, 70.3, 63.4, 62.0, 28.8, 19.0; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 254 nm (−18.4), 237 nm (10.5). Anal. Calcd for $C_{31}H_{27}Br_3O_9$: C, 47.54; H, 3.47. Found: C, 47.51; H, 3.60.

4.40. 1-*O*-Acetyl-2,6-anhydro-3,4,5,7-tetra-*O*-benzyl-D-*glycero*-D-*gulo*-heptitol 17

Two equivalents (25 mg, 0.99 mmol) of sodium hydride was added to a solution of substrate **8** in dry DMF (5 mL/mmol) under a nitrogen atmosphere. After 15 min, 2 equiv of benzyl bromide (120 μl, 0.99 mmol) was added dropwise. When the reaction was complete, it was quenched with water and the mixture extracted with CH_2Cl_2. The combined organic layers were washed with saturated NH_4Cl solution, saturated $NaHCO_3$ solution, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Then the residue was submitted to the reductive ozonolysis and acetylation procedure to give compound **17** (255 mg, 0.43 mmol, 87%), after column chromatography (*n*-hexane/EtOAc, 7.5:2.5): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = -6.0$ (*c* 0.5, $CHCl_3$); HRMS (FAB) Calcd for $C_{37}H_{41}O_7$ $(M+1)^+$: 597.2852. Found: 597.2846; ^{1}H NMR ($CDCl_3$): δ 7.34–7.26 (m, 18H), 7.16 (m, 2H), 4.95–4.88 (m, 2H), 4.87 (d, $J = 11.0$ Hz, 1H), 4.82 (d, $J = 10.8$ Hz, 1H), 4.63-4.57 (m, 3H), 4.55 (d, $J = 12.2$ Hz, 1H), 4.38 (dd, $J = 1.8$ and 11.9 Hz, 1H), 4.21 (dd, $J = 4.6$ and 11.9 Hz, 1H), 3.76–3.68 (m, 3H), 3.63 (t, $J = 9.3$ Hz, 1H), 3.55–3.51 (m, 2H), 3.47 (ddd, $J = 2.1$, 4.1, and 9.6 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.8, 138.5, 138.2, 138.0, 137.7, 128.5–127.6, 87.2, 79.2, 78.3, 78.1, 77.0, 75.6, 75.1, 75.0, 73.5, 68.9, 63.5, 20.9. Anal. Calcd for $C_{37}H_{40}O_7$: C, 74.47; H, 6.76. Found: C, 74.41; H, 6.89.

4.41. 1-*O*-Acetyl-2,6-anhydro-3,4,5,7-tetra-*O*-(*p*-bromobenzoyl)-D-*glycero*-D-*gulo*-heptitol 18 and 2,6-anhydro-1,3,4,5,7-penta-*O*-(*p*-bromobenzoyl)-D-glycero-D-*gulo*-heptitol 19

Debenzylation of compound **17** (234 mg, 0.39 mmol) and then *p*-bromobenzoylation as in the general procedure led to **18** (240 mg, 0.25 mmol, 63%) and **19** (102 mg, 0.092 mmol, 23%) after column chromatography (*n*-hexane/EtOAc, 7.5:2.5).

Compound **18**: TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 6:4); $[\alpha]_D = +32.9$ (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.72 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.56–7.52 (m, 4H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.44 (d, $J = 8.6$ Hz, 2H),

5.82 (t, $J = 9.6$ Hz, 1H), 5.61 (t, $J = 9.7$ Hz, 1H), 5.54 (t, $J = 9.7$ Hz, 1H), 4.58 (dd, $J = 3.1$ and 12.2 Hz, 1H), 4.46 (dd, $J = 4.9$ and 12.2 Hz, 1H), 4.29 (dd, $J = 5.0$ and 12.3 Hz, 1H), 4.24 (dd, $J = 2.9$ and 12.3 Hz, 1H), 4.11 (ddd, $J = 3.1$, 4.9, and 9.8 Hz, 1H), 4.01 (ddd, $J = 2.9$, 5.0, and 9.7 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.4, 165.2, 165.0, 164.4 (×2), 131.8–131.1, 128.9 (×2), 128.7, 128.3, 128.2, 127.4, 127.3 (×2), 76.0, 75.8, 74.4, 69.6, 69.3, 63.2, 62.4, 20.6; UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (20.9), 234 nm (−6.6). Anal. Calcd for $C_{37}H_{28}Br_4O_{11}$: C, 45.90; H, 2.91. Found: C, 45.91; H, 2.88.

Compound **19**: TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 6:4); HRMS (FAB) Calcd for $C_{42}H_{29}Br_5O_{11}$ $(M)^+$: 1113.7524. Found: 1113.7495; ^{1}H NMR ($CDCl_3$): δ 7.80 (d, $J = 8.6$ Hz, 4H), 7.73 (d, $J = 8.6$ Hz, 4H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.51–7.48 (m, 8H), 7.43 (d, $J = 8.6$ Hz, 2H), 5.86 (t, $J = 9.6$ Hz, 1H), 5.61 (t, $J = 9.8$ Hz, 2H), 4.60 (dd, $J = 3.0$ and 12.2 Hz, 2H), 4.44 (dd, $J = 5.2$ and 12.2 Hz, 2H), 4.15 (ddd, $J = 3.0$, 5.2, and 9.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 165.2 (×2), 165.1, 164.4 (×2), 131.8–131.1, 129.0 (×2), 128.8, 128.4 (×2), 128.3 (×2), 127.3 (×3), 75.9 (×2), 74.4, 69.6 (×2), 63.2 (×2); UV (CH_3CN) λ_{max} 245 nm. Anal. Calcd for $C_{42}H_{29}Br_5O_{11}$: C, 45.48; H, 2.64. Found: C, 45.48; H, 2.59.

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