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New insights into the conformational properties of α-*C*-glucosides

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Abstract—A series of alkyl α-D-*C*-glucopyranosides were synthesized and their conformational properties analyzed by CD and NMR spectroscopy. The conformational analysis revealed that the hydroxymethyl group populations (torsion angle ω, O1–C1–C2–O2) and those around the *C*-glucopyranosidic bond (torsion angle Φ; O2–C6–C7–C8) depend on the structural nature of the *C*-aglycon. The *gt* and the *exo–syn* populations increased as the *C*-aglycon became more substituted. Linear correlations between these rotational populations and proton chemical shifts versus the Taft's steric parameters revealed the significant role of the *C*-aglycon in the overall conformation of *C*-glucosides. The stereoelectronic *exo*-deoxoanomeric effect, affecting the rotation of the hydroxymethyl group, becomes more important as the steric hindrance of motion increases. A *pseudo*-anomer rotational comparison study was also performed.

1. Introduction

The high resistance of *C*-glycosides to degradation by glycosidases combined with their newly identified biological properties[1] give these compounds considerable medical significance, especially as cytotoxic compounds. A number of contributions describe the conformational analysis of *C*-glycosides, especially those carried out by Kishi et al.[2] and Jiménez-Barbero et al.[3]

In a previous study, we reported the conformational properties of a series of alkyl β-*C*-glycosides[4] and showed that the populations around the *C*-glycosidic bond and also the hydroxymethyl group are dependent on the structure of the *C*-aglycon, while the *exo–syn* and *gt* rotamer populations increase with the degree of substitution on the *C*-aglycon. These rotational preferences pointed to a σ_{CH}–σ^*_{CO} stereoelectronic effect (the *exo*-deoxoanomeric effect),[4,5] directly involved in the rotation around the *pseudo*-glycosidic bond and indirectly around the C1–C2 bond (hydroxymethyl group), in addition to non-bonded interactions.

Herein, we report the rotational properties of the *C*-glucosidic bond and the hydroxymethyl group of a series of alkyl α-*C*-glucosides, as well as a *pseudo*-anomer comparison study. Correlations between rotational populations and chemical shifts of prochiral protons H7 and H6 versus Taft's steric parameters support the important role of the *C*-aglycon in the overall conformation of *C*-glucosides.

2. Results and discussion

2.1. Synthesis and characterization

The addition of carbon nucleophiles to activated glycal epoxides has been widely used[6] for the preparation of *C*-glycosides.[7] The addition of Grignard reagents to the 1,2-anhydrosugar,[8] obtained from the addition of dimethyldioxirane (DMDO)[9] to the tri-*O*-benzyl-D-glucal, according to Danishefsky's protocol,[10] led to a mixture of α-and β-D-*C*-glucosides **1a**–**1f** (Scheme 1).

The reaction conditions of Grignard addition are critical for the *pseudo*-anomeric configuration. Thus, we found that a temperature of −40 °C and Et_2O as solvent favored a β-C-glucosidation; while a higher temperature (0 °C) and THF as solvent favored an α-*C*-glucosidation. Deprotection of the benzyl groups with hydrogen and subsequent 4-bromobenzoylation led to the tetra-*O*-(4-bromobenzoyl)-*C*-glucosides **2a**–**2f**.

All these compounds were characterized on the basis of their one- (^1H and ^{13}C) and two-dimensional (COSY-G,

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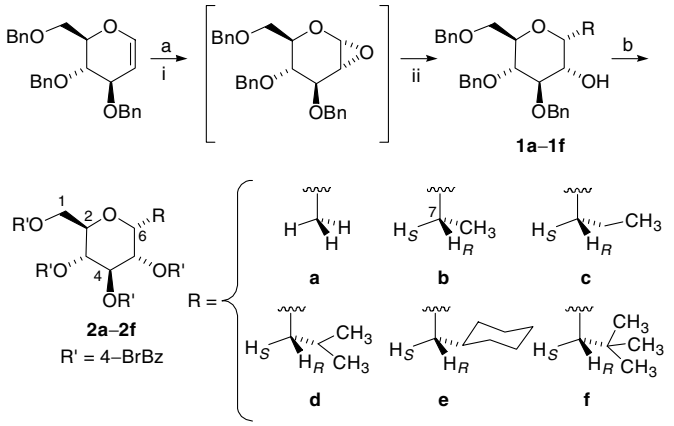


Scheme 1. Synthesis of model α-*C*-glucosides. Reagents and conditions: (a) (i) DMDO, $(CH_3)_2CO/CH_2Cl_2$, 0 °C; (ii) RMgX, THF, 0 °C; (b) (i) H_2, 5% Pd–C, EtOH; (ii) *p*-BrBzCl, DMAP, Py, 60 °C.

HMQC, and T-ROESY) NMR spectra. The stereochemistry at C6 (α axial) of the *C*-glucosides **2a**–**2f** synthesized was established by analyzing the ^{1}H NMR $J_{5,6}$ value (5.8–5.9 Hz). The ^{1}H NMR signals of the prochiral protons of the hydroxymethyl group at C1, H1*R*, and H1*S* were differentiated on the basis of their chemical shifts and coupling constants.[11,12] The assignment of H7*R* and H7*S* was in agreement with the values of the coupling constants $J_{H6,H7R}$ and $J_{H6,H7S}$, as determined by Kishi et al. using specifically deuterated *C*-glycosides,[13] and by means of T-ROESY experiments.[14] For all these compounds, the coupling constants $J_{H6,H7R}$ and $J_{H6,H7S}$ were obtained by analyzing the H6 signals.

2.2. Conformational analysis

Rotation around the ω (O1–C1–C2–O2) and Φ (O2–C6–C7–C8) torsion angles in α-*C*-glucosides led to ideal staggered conformers *gg*, *gt*, *tg*, and *exo–syn*, *exo–anti*, and *non-exo* rotamers, respectively (Fig. 1). The *gg* and the

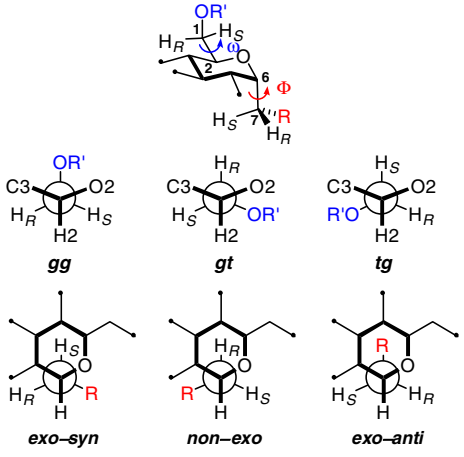


Figure 1. Torsion angle ω around the C1–C2 bond and Φ around the *C*-glucosidic C6–C7 bond (top). Newman projections of the idealized staggered rotamers around the C1–C2 and C6–C7 bonds (central and bottom).

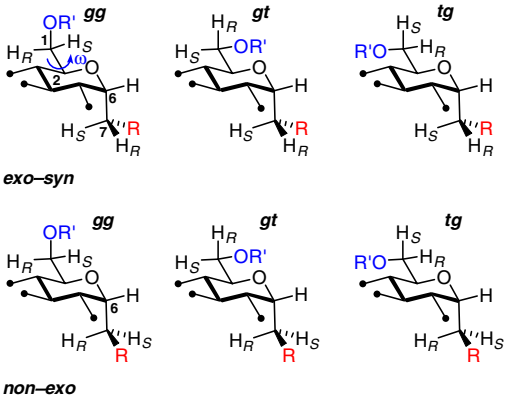


Figure 2. Plausible orientations of α-*C*-glucosyl compounds.

exo–syn rotamers were found to be the most stable, while the *exo–anti* rotamer is not significant due to severe steric interactions. Therefore, rotation around these two torsion angles can be simplified to the six ideal staggered conformers shown in Figure 2.

2.2.1. Conformational analysis of the *C*-glucosidic bond. High values of $J_{H6,H7S}$ (8.9–10.1 Hz) and moderate values of $J_{H6,H7R}$ (3.1–4.0 Hz) were observed in our model compounds **2b**–**2f**. These data confirm the *exo–syn* rotamer as the most populated in all cases (Table 1). The rotamer populations were calculated using the Serianni-equations,[15,16] and fixing a nil *exo–anti* population. In addition, for compounds **2b**–**2e**, Table 1 shows a decreases in $J_{H6,H7R}$ values from 4.0 to 3.1 Hz, and of $J_{H6,H7S}$ from 9.6 to 8.9 Hz, as the size of the aglycon increases. This behavior involves a decrease in the population of the *non-exo* rotamer and an increase in the *exo–syn*. As for compound **2f**, since $J_{H6,H7R}$ was undetectable and $J_{H6,H7S}$ had the biggest value of the series (10.1 Hz), a single glycosidic conformation can be assumed, slightly distorted from the ideal *exo–syn* staggered conformer (H6–C6–C7–H7*R* ≈ 90°).

2.2.2. *pseudo*-Anomer *C*-glucosidic bond comparison. Although both epimer series have the *exo–syn* rotamer as the most stable, a straight dependence of the populations around the *C*-glucosidic bond on the *pseudo*-anomeric configuration was observed (Table 1). The rotational populations around the C6–C7 bond were more dependent on the *C*-aglycon in the β-series than in the α-series. Thus, for compounds with a linear aglycon, **2b** or **2c**, greater flexibility was observed for the β-epimers (only 60–70% of *exo–syn*) than for the α-epimers (80% of *exo–syn*). However, this behavior drastically changed with compounds having branched aglycons (**2d** and **2e**), where the β-epimers exhibited high rigidity.

2.2.3. Conformational analysis of the *C*-aglycosidic bond. T-ROESY experiments were also performed with compounds **2b**–**2f**. The main cross-peaks observed for the model α-*C*-glucosides are shown on the three most stable rotamers around the Ψ dihedral bond (C6–C7–C8–C9) in Figure 3. These cross-peaks are in complete agreement with conformer **A**, the most stable rotamer obtained from

Table 1. $J_{H6,H7}$ coupling constants ($CDCl_3$) and calculated rotamer populations (%) around the C6–C7 bond for the model α-D-*C*-glucopyranosides **2b**–**2f** and β-**2b**–**2f**

Compd.	$J_{H6,H7S}$	$J_{H6,H7R}$	*exo–syn*	*non-exo*	Compd.	$J_{H6,H7S}$	$J_{H6,H7R}$	*exo–syn*	*exo–anti*	*non-exo*
2b	9.6	4.0	80	20	β-**2b**	3.0	8.0	69	24	7
2c	9.2	3.5	83	17	β-**2c**	3.8	7.1	57	27	16
2d	9.2	3.4	84	16	β-**2d**	2.2	9.9	91	9	0
2e	8.9	3.1	86	14	β-**2e**	2.3	9.7	89	11	0
2f	10.1	N.D.[a]	100	0	β-**2f**	N.D.[a]	8.8	100	0	0

[a] N.D.: Not detected.

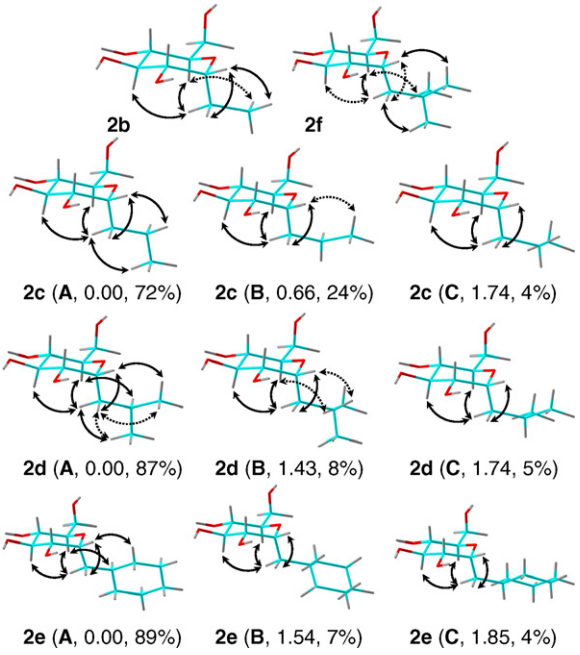


Figure 3. Main cross-peaks observed for the model α-*C*-glucosides **2b**–**2f** in the T-ROESY experiments ($CDCl_3$) shown on the three most stable rotamers **A**–**C**. Solid line: strong cross-peak; dash line: weak cross-peak.

molecular mechanics,[17] and with Kishi's extended zig-zag conformation.[2]

2.2.4. Conformational analysis of the hydroxymethyl group. The rotamer populations of the hydroxymethyl group were calculated using the Serianni-equations.[15] Analysis of the coupling constants of the prochiral protons at C1, or their calculated rotamer populations, revealed a relationship with the structure of the *C*-aglycon. On the one hand, the $J_{H1R,H2}$ coupling constants increased as the substitution in the aglycon increased, from **2a** (4.9 Hz) to **2e** (6.1 Hz), except for compound **2f** (5.5 Hz) (Table 2). On the other hand, the coupling constant $J_{H1S,H2}$ displayed the opposite behavior, from **2b** (3.8 Hz) to **2f** (3.1 Hz). These experimental NMR data correlate with an increased *gt* population and with decreased *gg* and *tg* populations, as shown in Figure 4. Compound **2f** deserves particular consideration; its bulky *neo*-pentyl group coming near to the hydroxymethyl group could generate non-bonded interactions between these two groups, therefore decreasing the *gt* population in favor of the *gg*. This exception also suggests that there are no non-bonded interactions between the aglycon and the hydroxymethyl groups in the rest of the compounds (see below).

The conformation of the hydroxymethyl group was also investigated by means of T-ROESY experiments. However, only compound **2f** showed clear cross-peaks between H1*R* and H2, and between H1*S* and H2. The double intensity observed for H1*S* and H2 compared to H1*R* and H2 means much higher *gt* than *tg* populations for this compound.

2.2.5. Circular dichroism analysis. The high sensitivity and simple spectral interpretation of the circular dichroic exciton chirality method[18] provides further conformational data. The CD spectra (Fig. 5) were analyzed taking into account the additivity principle,[19] the interchromophoric distances and the dihedral angles of the electric transition moments of the chromophores, namely, the *p*-bromobenzoates. The *tetra*-chromophoric compounds **2a**–**2f** exhibited exciton Cotton effects around 251 and 234 nm in the CD spectra in CH_3CN. The intensity of the first Cotton effect gradually decreased from compound **2a** (17.9), **2b** (11.7), **2c** (10.9), **2d** (8.5), to **2e** (4.8), and then increased with compound **2f** (9.2). These intensities are consistent with decreased positive contributions from the pairwise interactions between the chromophore at the 1-position (*gg* rotamer) and those at the 3- and 4-positions, and increased negative contributions from the interactions between the chromophore at the 1-position (*gt* rotamer) and those at the 3 and 5-positions, for compounds **2a**–**2e** (Fig. 6). The intensity of the first Cotton effect of com-

Table 2. $J_{H1,H2}$ coupling constants ($CDCl_3$) and calculated rotamer populations (%) around the C1–C2 bond for the model α-D-*C*-glucopyranosides **2a**–**2f** as well as the corresponding rotational populations for the already reported β-D-*C*-glucopyranosides **2a**–**2f**[4]

Compd.	$J_{H1S,H2}$	$J_{H1R,H2}$	*gg*	*gt*	*tg*	Compd.	*gg*	*gt*	*tg*
2a	3.3	4.9	54	37	9	β-**2a**	57	37	6
2b	3.8	5.3	46	39	15	β-**2b**	54	40	6
2c	3.8	5.4	45	40	15	β-**2c**	51	41	8
2d	3.5	5.5	46	42	12	β-**2d**	47	46	7
2e	3.1	6.1	43	50	7	β-**2e**	44	50	6
2f	3.1	5.5	49	44	7	β-**2f**	39	56	5

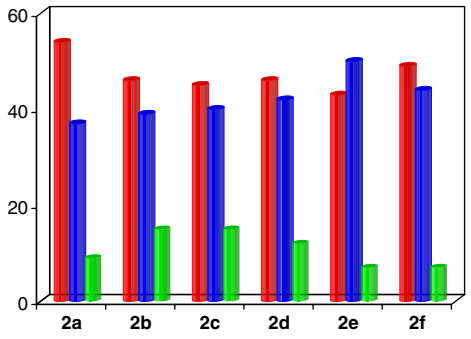


Figure 4. Rotational populations (%) around the C1–C2 bond, calculated from the $J_{H1,H2}$ coupling constants of compounds **2a**–**2f** ($CDCl_3$); *gg*/*gt*/*tg* rotamers (red/blue/green).

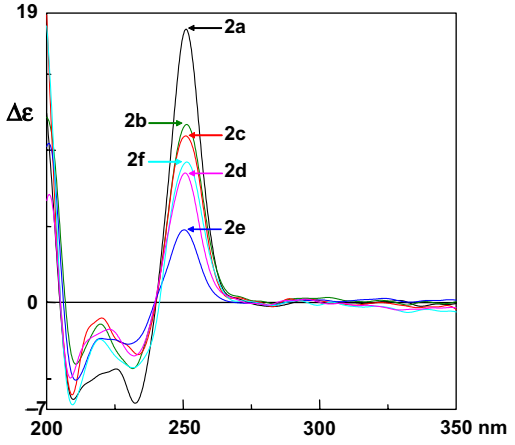


Figure 5. CD spectra comparison of compounds **2a**–**2f** (CH_3CN).

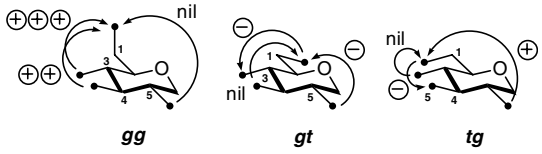
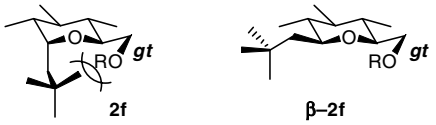


Figure 6. 1/3, 1/4, and 1/5 pairwise interactions involving the chromophore at the 1-position in each of the three stable rotamers (*gg*, *gt*, and *tg*) for the glucopyranosyl system.

pound **2f**, in between **2c** and **2d**, is in excellent agreement with the $J_{H1,H2}$ coupling constants obtained from NMR for these compounds and already explained on the basis of steric interactions. Therefore, NMR and CD data of compounds **2a**–**2f** are in total agreement.

2.2.6. *pseudo*-Anomers hydroxymethyl comparison. Applying the same set of equations for comparative analysis of the rotational populations of the hydroxymethyl group between these compounds and their epimers at C-6 (β-*pseudo*-anomers)[4,15] revealed that independent of the *pseudo*-anomeric configuration, the population of the *gt* rotamer increases as the substitution in the *C*-aglycon increases. However, depending on that configuration, the rotamer that decreases changed only the *gg* rotamer for the β-anomers and both the *gg* and *tg* for the α-anomers. Moreover, the rotational populations of compounds with an unbranched aglycon **2a**–**c** show a clear dependence on the *pseudo*-anomeric configuration. That is, compounds with an α-configuration showed lesser/higher *gg*/*tg* populations than their corresponding β-anomers, as can be observed in Table 2. In addition, a comparative analysis between the *neo*-pentyl epimers **2f** and β-**2f** revealed higher *gg* and smaller *gt* populations for the α-anomer than for the β. In fact, *gg* is the most populated rotamer in the α-epimer, as is the *gt* rotamer in the β. As already explained, these results are made clear by the existence of non-bonded interactions between aglycon and the hydroxymethyl group in its *gt* rotamer in the α-anomer, missing in the β.



2.2.7. Origin of the conformational preferences. The decreases in the *non-exo* rotamer populations as the *C*-aglycon became more substituted can be explained by an increase in the steric interactions between the *C*-aglycon and the substituent at the 2-position (see Fig. 1 or 2). However, this conformational behavior can also be explained by steric hindrances to motion. As seen from Figure 7, there is an excellent linear correlation between the *exo–syn* and *non-exo* rotational populations of compounds **2a**–**2f** with the corresponding Taft's steric parameters.[20] The E_S values are composite terms, derived from both potential energy steric effects (steric strains) and kinetic energy steric effects (steric hindrances to motions). According to Taft,[20] the introduction of a straight-chain alkyl group in place of the standard hydrogen substituent raises the activation energy due to steric hindrance. Therefore, the bulkier alkyl groups freeze out the rotation of the more stable *exo–syn* rotamer, increasing its population. These two steric factors, that between the *C*-aglycon and the substituent at the 2-position, and due to steric hindrances to motions, are probably both simultaneously involved in the conformational behavior around the *C*-glucosidic bond.

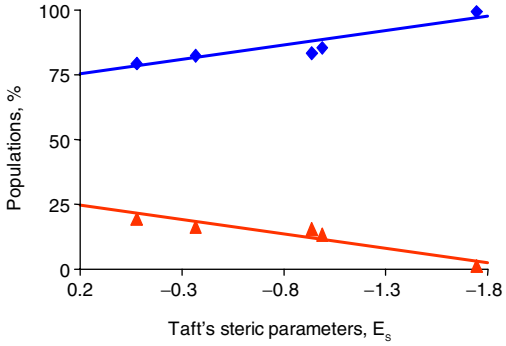


Figure 7. Rotational populations of *exo–syn* and *non-exo* rotamers (blue/red) versus corresponding E_S values for aliphatic substituents.

Conversely, the conformational behavior of the hydroxymethyl group cannot be explained in general by means of

non-bonded interactions, since as the *C*-aglycon became more substituted or branched the population of the *gt* rotamer, nearest to the *exo–syn*, increases. However, the plot of the rotational populations of the hydroxymethyl group of compounds **2a**–**2f** versus the corresponding Taft's steric parameters[20] reveals some relationship between them, except for compound **2f** (Fig. 8). In fact, this exception indicates that for this compound at least two different effects are acting simultaneously, one of them due to direct non-bonded interactions between the *neo*-pentyl and the hydroxymethyl group.

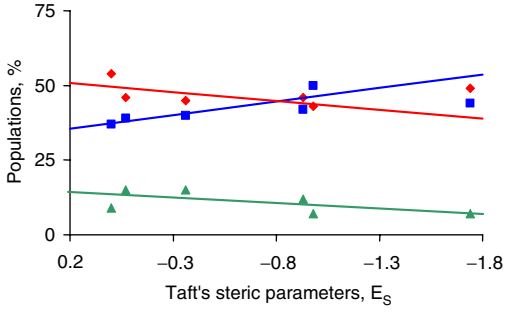


Figure 8. Rotational populations of *gg*/*gt*/*tg* rotamers (red/blue/green) versus corresponding E_S values for aliphatic substituents.

Recently, we have proposed that a stereoelectronic σ_{CH}–σ^*_{CO} interaction (*exo*-deoxoanomeric effect) is involved in the rotational preferences of the hydroxymethyl group of β-*C*-glycosides.[4] This effect could also apply to the α-series, by a favorable stereoelectronic σ_{CH}–σ^*_{CO} interaction between the C7–H7*R* bonding orbital in the *exo–syn* conformation and the C6–O2 antibonding orbital, since σ_{CH} is a moderate donor and σ^*_{CO} a good acceptor (Fig. 9).[21] The σ_{CC}–σ^*_{CO} interaction (*non-exo* conformer) is not considered, since the σ_{CC} orbital is a much worse donor than σ_{CH}.[22]

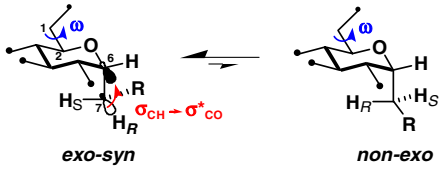


Figure 9. Molecular orbitals involved in the *exo*-deoxoanomeric effect.

The σ_{CH}–σ^*_{CO} interaction increases as the *exo–syn* population increases, due to the above steric factors. Analysis of the ^{1}H and ^{13}C NMR chemical shifts of the *pseudo*-anomeric and prostereogenic protons, H6, H7*R* and H7*S*, and carbons C6 and C7 (Table 3) revealed some noteworthy behavior as the C-aglycon became branched. The prochiral hydrogens H7*R* and H6 showed a displacement toward higher and lower fields, respectively. As for the carbons, the chemical shifts of C6 and C7 were, respectively, shielded and deshielded. The observed shielding for H7*R* and C6 can be attributed to greater electron densities around such nuclei. These behavior patterns are summarized in Figure 10.

Table 3. Some ^{1}H and ^{13}C NMR chemical shifts ($CDCl_3$) for the alkyl α-*C*-glucosides **2b**–**2f**

Compd.	H6	C6	C7	H7*S*	H7*R*
2b	4.35	74.1	18.8	2.03	1.71
2c	4.45	72.6	27.5	2.02	1.55
2d	4.55	71.2	33.9	2.03	1.35
2e	4.58	70.6	34.1	1.98	1.37
2f	4.65	71.2	36.9	1.96	1.48

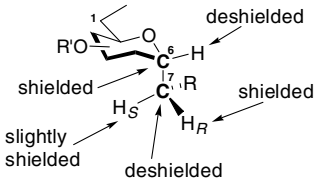


Figure 10. ^{1}H and ^{13}C NMR chemical shift characteristics of α-*C*-glucosides as the substituent *R* increases in size.

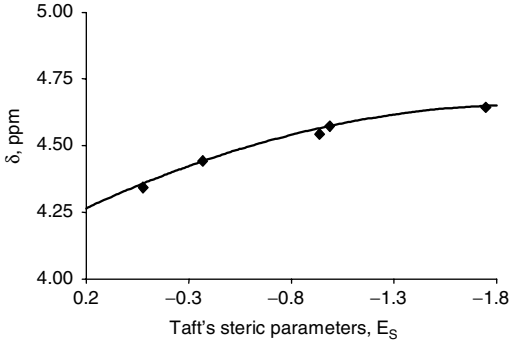


Figure 11. Chemical shifts of the *pseudo*-anomeric proton H6 versus corresponding E_S values for aliphatic substituents.

Plots of the chemical shifts of the *pseudo*-anomeric proton H6 and of prochiral protons H7, for compounds **2b**–**2f**, versus the corresponding Taft's steric parameters[20] are shown in Figures 11 and 12, respectively. The correlations between these parameters and the chemical shifts are good in all cases but H7*R* of compound **2f**, due to direct non-

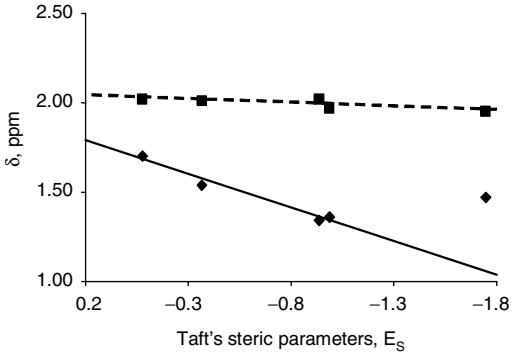


Figure 12. Chemical shifts of prochiral protons H7*S* (dashed line) and H7*R* (solid line) versus corresponding E_S values for aliphatic substituents.

bonded interactions between the *neo*-pentyl and hydroxymethyl groups. This exception correlates with the irregular intensity of the first CD cotton effect and the rotational populations derived from NMR for this compound. It thus supports a relationship between the hydroxymethyl group and the electron densities around the *pseudo*-anomeric carbon and therefore with the *exo*-deoxoanomeric effect.

3. Conclusions

On the basis of the ^{1}H NMR coupling constant values and CD spectral data, we conclude that the conformational preferences of the hydroxymethyl group and of the *C*-glucosidic bond in α-*C*-glucosides depend on the structure of the *C*-aglycon. The population of the *exo–syn* rotamer increased and that of the *non-exo* decreased as the substitution of the *C*-aglycon increased, due to interactions between the *C*-aglycon and the substituent at the 2-position and/or to steric hindrances to motions. The correlation between these rotational populations and Taft's steric parameters is highly satisfactory.

The hydroxymethyl group populations of the *gt* rotamer increased and those of the *tg* and *gg* decreased, as the degree of substitution of the *C*-aglycon increased. The correlation between the hydroxymethyl group populations (Table 2), the CD data (Fig. 5), and the chemical shifts (Table 3) of compounds **2b**–**2f**, supports the proposal of the influence of the *C*-aglycon on the rotational behavior of the hydroxymethyl group through the stereoelectronic *exo*-deoxoanomeric effect.

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 of carbon NMR. Optical rotations were measured on a digital polarimeter in a 1 dm cell. UV and CD spectra were recorded in the range 350–200 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: *tetrakis*-(4-bromobenzoate) = 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 obtained from commercial sources and used without further purification. 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-G, HMQC, and T-ROESY) NMR spectra, as well as by elemental analysis, HRMS, UV, and CD spectroscopy.

4.2. General procedure for the preparation of α-*C*-glucosides

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-glucal 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 THF (10 mL/mmol) under dry nitrogen, cooled at 0 °C and the corresponding Grignard reagent added. When the reaction was completed, it was diluted with Et_2O, quenched with NH_4Cl saturated solution and extracted three times with Et_2O. The combined organic layers were washed with a saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuum. The product was purified by silica gel column chromatography.

4.3. General procedure for the debenzylation and *p*-bromobenzoylation

To a solution of the substrate in dry ethanol (10 mL/mmol) were 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. The crude reaction mixture was then dissolved in dry pyridine (10 mL/mmol), and 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.

4.4. 2,6-Anhydro-1,3,4-tri-*O*-benzyl-7-deoxy-D-*glycero*-L-*gulo*-heptitol 1a

Following the general procedure for the preparation of α-*C*-glucosides, 351 mg of tri-*O*-benzyl-D-glucal yielded 281 mg of **1a** (0.63 mmol, 74%) as an epimer mixture α/β = 1, after flash column chromatography (*n*-hexane/EtOAc, 7:3). Spectroscopy data were in agreement with previously reported information.[6c]

4.5. 2,6-Anhydro-1,3,4-tri-*O*-benzyl-7,8-dideoxy-D-*glycero*-L-*gulo*-octitol 1b

Following the general procedure for the preparation of α-*C*-glucosides, 238 mg of tri-*O*-benzyl-D-glucal yielded 177 mg of **1b** (0.38 mmol, 67%) as an epimer mixture α/β = 2, after flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5). Spectroscopy data were in agreement with those previously reported.[23]

4.6. 2,6-Anhydro-1,3,4-tri-*O*-benzyl-7,8,9-trideoxy-D-*glycero*-L-*gulo*-nonitol 1c

Following the general procedure for the preparation of α-*C*-glucosides, 700 mg of tri-*O*-benzyl-D-glucal yielded 603 mg of **1c** (1.27 mmol, 75%) as an epimer mixture α/

β = 4, after flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +29.5$ (*c* 1.0, $CHCl_3$); HRMS (EI): $(M-C_7H_7)^+$ calcd for $C_{23}H_{29}O_5$, 385.2015; found, 385.2017; ^1H NMR ($CDCl_3$) δ 7.41–7.30 (m, 15H), 4.78 (d, $J = 11.7$ Hz, 1H), 4.74 (d, $J = 10.7$ Hz, 1H), 4.71 (d, $J = 11.7$ Hz, 1H), 4.68–4.62 (m, 2H), 4.60 (d, $J = 12.1$ Hz, 1H), 4.05 (m, H-2), 3.99 (m, H-6), 3.90 (dd, $J = 5.5$ and 10.2 Hz, H-1), 3.85–3.78 (m, 3H), 3.73 (t, $J = 5.5$ Hz, H-3), 3.07 (br s, OH), 1.78 (m, 1H), 1.68–1.57 (m, 2H), 1.46 (m, 1H), 1.04 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.0 (s), 138.0 (s), 137.4 (s), 128.3–127.4, 78.5 (d, C-4), 75.4 (d, C-3), 73.4 (t), 73.1 (t), 72.9 (t), 72.8 (d, C-2), 71.7 (d, C-6), 69.9 (d, C-5), 68.2 (t, C-1), 29.6 (t, C-7), 18.5 (t, C-8), 13.9 (q, C-9); Anal. Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.59; H, 7.86.

4.7. 2,6-Anhydro-1,3,4-tri-*O*-benzyl-7,8,9-trideoxy-8-methyl-D-*glycero*-L-*gulo*-nonitol 1d

Following the general procedure for the preparation of α-*C*-glucosides, 500 mg of tri-*O*-benzyl-D-glucal yielded 413 mg of **1d** (0.84 mmol, 70%) as an epimer mixture α/β = 5, after flash column chromatography (*n*-hexane/EtOAc, 8.5:1.5): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +22.2$ (*c* 1.4, $CHCl_3$); HRMS (EI): $(M-C_7H_7)^+$ calcd for $C_{24}H_{31}O_5$, 399.2172; found, 399.2199; ^1H NMR ($CDCl_3$) δ 7.41–7.29 (m, 15H), 4.78 (d, $J = 11.6$ Hz, 1H), 4.74–4.62 (m, 4H), 4.59 (d, $J = 12.1$ Hz, 1H), 4.10 (m, H-6), 4.05 (dd, $J = 5.5$ and 10.0 Hz, H-2), 3.91 (dd, $J = 5.1$ and 10.0 Hz, H-1), 3.76–3.71 (m, 4H), 3.05 (br s, OH), 1.92–1.77 (m, 2H), 1.42 (m, 1H), 1.04 (d $J = 6.7$ Hz, 3H); 1.02 (d $J = 6.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.0 (s), 138.0 (s), 137.4 (s), 128.3–127.4, 78.6 (d, C-4), 75.3 (d, C-3), 73.4 (t), 73.1 (t), 72.9 (t), 72.8 (d, C-2), 70.1 (d, C-6), 70.1 (d, C-5), 68.2 (t, C-1), 36.2 (t, C-7), 24.0 (d, C-8), 23.4 (q), 21.7 (q); Anal. Calcd for $C_{31}H_{38}O_5$: C, 75.89; H, 7.81. Found: C, 75.84; H, 7.99.

4.8. 2,6-Anhydro-1,3,4-tri-*O*-benzyl-7-cyclohexyl-7-deoxy-D-*glycero*-L-*gulo*-heptitol 1e

Following the general procedure for the preparation of α-*C*-glucosides, 230 mg of tri-*O*-benzyl-D-glucal yielded 131 mg of compound α-**1e** (0.24 mmol, 45%), after flash column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 8.5:1.5); $[\alpha]_D = +26.9$ (*c* 1.0, $CHCl_3$); HRMS (EI): $(M-C_7H_7)^+$ calcd for $C_{27}H_{35}O_5$, 439.2484; found, 439.2469; ^1H NMR ($CDCl_3$) δ 7.37–7.26 (m, 15H), 4.74 (d, $J = 11.7$ Hz, 1H), 4.69–4.61 (m, 4H), 4.56 (d, $J = 12.2$ Hz, 1H), 4.10 (m, H-6), 4.05 (m, H-2), 3.87 (m, H-1), 3.79–3.74 (m, 2H), 3.68–3.66 (m, 2H), 2.91 (br s, OH), 1.86 (br d, $J = 12.1$ Hz, 1H), 1.74–1.67 (m, 5H), 1.52 (m, 1H), 1.40 (m, 1H), 1.31–1.20 (m, 3H), 1.03 (t, $J = 11.4$ Hz, 1H); 0.93 (t, $J = 11.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 138.1 (s), 138.0 (s), 137.5 (s), 128.4–127.5, 78.4 (d, C-4), 75.4 (d, C-3), 73.5 (t), 73.2 (t), 73.0 (d, C-2), 72.9 (t), 70.1 (d, C-5), 69.3 (d, C-6), 68.3 (t, C-1), 35.2 (t, C-7), 34.1 (t), 33.5 (d), 32.6 (t), 26.5 (t), 26.2 (t), 26.1 (t); Anal. Calcd for $C_{34}H_{42}O_5$: C, 76.95; H, 7.98. Found: C, 76.86; H, 7.81.

4.9. 2,6-Anhydro-1,3,4-tri-*O*-benzyl-7,8,9-trideoxy-8,8-dimethyl-D-*glycero*-L-*gulo*-nonitol 1f

Following the general procedure for the preparation of α-*C*-glucosides, 500 mg of tri-*O*-benzyl-D-glucal yielded 361 mg of compound α-**1f** (0.72 mmol, 60%), after flash column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +24.2$ (*c* 2.2, $CHCl_3$); HRMS (EI): $(M-C_7H_7)^+$ calcd for $C_{25}H_{33}O_5$, 413.2328; found, 413.2311; ^1H NMR ($CDCl_3$) δ 7.37–7.24 (m, 15H), 4.75 (d, $J = 11.7$ Hz, 1H), 4.68 (d, $J = 11.4$ Hz, 1H), 4.64 (d, $J = 11.4$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 4.58 (d, $J = 11.7$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.14 (m, H-6), 4.03 (m, H-2), 3.83 (dd, $J = 5.1$ and 10.0 Hz, H-1), 3.75–3.72 (m, 2H), 3.69–3.63 (m, 2H), 2.86 (d, $J = 7.0$ Hz, OH), 1.68 (dd, $J = 9.6$ and 14.9 Hz, H-7), 1.46 (d, $J = 14.9$ Hz, H-7), 1.00 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.1 (s), 138.0 (s), 137.6 (s), 128.5–127.6, 78.2 (d, C-4), 75.4 (d, C-3), 73.6 (t), 73.3 (t), 73.1 (d, C-2), 72.8 (t), 70.9 (d, C-5), 69.8 (d, C-6), 68.3 (t, C-1), 40.2 (t, C-7), 30.1 (s, C-8), 29.9 (q), 29.9 (q), 29.9 (q); Anal. Calcd for $C_{32}H_{40}O_5$: C, 76.16; H, 7.99. Found: C, 76.16; H, 8.11.

4.10. 2,6-Anhydro-1,3,4,5-tetra-*O*-(*p*-bromobenzoyl)-7-deoxy-D-*glycero*-L-*gulo*-heptitol 2a

Debenzylation of compound **1a** (101 mg, 0.23 mmol) and then *p*-bromobenzoylation was performed as in the general procedure, giving compound **2a** (192 mg, 0.21 mmol, 94%) after column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.6$ (*n*-hexane/EtOAc, 7.5:2.5); $[\alpha]_D = +49.6$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.87 (d, $J = 8.5$ Hz, 2H), 7.80 (d, $J = 8.5$ Hz, 2H), 7.74 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.48 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 5.93 (t, $J = 9.3$ Hz, H-4), 5.53 (t, $J = 9.2$ Hz, H-3), 5.45 (dd, $J = 5.8$ and 9.5 Hz, H-5), 4.66 (dddd, $J = 5.8$, 6.9, 6.9, and 6.9 Hz, H-6), 4.55 (dd, $J = 3.3$ and 12.0 Hz, H-1_{proS}), 4.51 (dd, $J = 4.9$ and 12.0 Hz, H-1_{proR}), 4.31 (ddd, $J = 3.3$, 4.9, and 9.2 Hz, H-2), 1.47 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$)δ 165.4 (s), 165.1 (s), 164.6 (s), 164.5 (s), 131.9–131.2, 128.9 (s), 128.9 (s), 128.8 (s), 128.4 (s), 128.4 (s), 127.7 (s), 127.6 (s), 127.6 (s), 71.5 (d, C-5), 70.7 (d, C-4), 70.0 (d, C-3), 69.1 (d, C-6), 69.0 (d, C-2), 63.3 (t, C-1), 12.8 (q, C-7); UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (17.9), 234 nm (−6.6); Anal. Calcd for $C_{35}H_{26}Br_4O_9$: C, 46.19; H, 2.88. Found: C, 46.19; H, 3.07.

4.11. 2,6-Anhydro-1,3,4,5-tetra-*O*-(*p*-bromobenzoyl)-7,8-dideoxy-D-*glycero*-L-*gulo*-octitol 2b

Debenzylation of compound **1b** (121 mg, 0.26 mmol) and then *p*-bromobenzoylation was performed as in the general procedure, giving compound **2b** (216 mg, 0.23 mmol, 89%) after column chromatography (*n*-hexane/EtOAc, 8:2): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +29.3$ (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.87 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 8.6$ Hz, 2H), 7.75–7.71 (m, 4H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 5.92 (t, $J = 9.2$ Hz, H-4), 5.50 (t, $J = 9.2$ Hz, H-3), 5.48 (dd, $J = 5.8$ and

9.5 Hz, H-5), 4.53 (dd, $J = 3.8$ and 12.1 Hz, H-1_{proS}), 4.50 (dd, $J = 5.3$ and 12.1 Hz, H-1_{proR}), 4.35 (ddd, $J = 4.0$, 5.8, and 9.6 Hz, H-6), 4.22 (ddd, $J = 3.8$, 5.3, and 9.2 Hz, H-2), 2.03 (ddddd, $J = 7.3$, 7.3, 7.3, 9.6, and 14.5 Hz, H-7_{proS}), 1.71 (ddddd, $J = 4.0$, 7.3, 7.3, 7.3, and 14.5 Hz, H-7_{proR}), 1.02 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.4 (s), 165.1 (s), 164.5 (s), 164.5 (s), 131.9–131.1, 128.9 (s), 128.9 (s), 128.8 (s), 128.4 (s), 128.4 (s), 127.7 (s), 127.6 (s), 127.6 (s), 74.1 (d, C-6), 71.5 (d, C-5), 70.9 (d, C-4), 70.0 (d, C-3), 68.8 (d, C-2), 63.5 (t, C-1), 18.8 (t, C-7), 9.4 (q, C-8); UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (11.7), 234 nm (−4.3); Anal. Calcd for $C_{36}H_{28}Br_4O_9$: C, 46.78; H, 3.05. Found: C, 46.81; H, 3.00.

4.12. 2,6-Anhydro-1,3,4,5-tetra-*O*-(*p*-bromobenzoyl)-7,8,9-trideoxy-D-*glycero*-L-*gulo*-nontitol 2c

Debenzylation of compound **1c** (156 mg, 0.33 mmol) and then *p*-bromobenzoylation, performed as in the general procedure, led to compound **2c** (303 mg, 0.32 mmol, 99%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.5$ (*n*-hexane/EtOAc, 8:2); $[\alpha]_D = +37.5$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.87 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 8.6$ Hz, 2H), 7.74 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H), 7.56 (d, $J = 8.6$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 5.92 (t, $J = 9.3$ Hz, H-4), 5.51 (t, $J = 9.2$ Hz, H-3), 5.47 (dd, $J = 5.8$ and 9.6 Hz, H-5), 4.52 (dd, $J = 3.8$ and 12.1 Hz, H-1_{proS}), 4.49 (dd, $J = 5.4$ and 12.1 Hz, H-1_{proR}), 4.45 (ddd, $J = 3.5$, 5.8, and 9.2 Hz, H-6), 4.23 (ddd, $J = 3.8$, 5.4, and 9.2 Hz, H-2), 2.02 (m, H-7_{proS}), 1.60–1.50 (m, 2H), 1.38 (m, H-8), 0.96 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.4 (s), 165.1 (s), 164.6 (s), 164.6 (s), 132.0–131.2, 128.9 (s), 128.9 (s), 128.8 (s), 128.4 (s), 128.4 (s), 127.8 (s), 127.6 (s), 127.6 (s), 72.6 (d, C-6), 71.5 (d, C-5), 70.9 (d, C-4), 70.0 (d, C-3), 68.9 (d, C-2), 63.5 (t, C-1), 27.5 (t, C-7), 18.2 (t, C-8), 13.7 (q, C-9); UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (10.9), 234 nm (−3.4); Anal. Calcd for $C_{37}H_{30}Br_4O_9$: C, 47.36; H, 3.22. Found: C, 47.40; H, 3.47.

4.13. 2,6-Anhydro-1,3,4,5-tetra-*O*-(*p*-bromobenzoyl)-7,8,9-trideoxy-8-methyl-D-*glycero*-L-*gulo*-nontitol 2d

Debenzylation of compound **1d** (510 mg, 1.04 mmol) and then *p*-bromobenzoylation, performed as in the general procedure, led to compound **2d** (955 mg, 1.00 mmol, 96%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 9:1); $[\alpha]_D = +32.3$ (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$)δ 7.86 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 8.6$ Hz, 2H), 7.75 (d, $J = 8.6$ Hz, 2H), 7.72 (d, $J = 8.6$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 5.92 (t, $J = 9.3$ Hz, H-4), 5.51 (t, $J = 9.2$ Hz, H-3), 5.47 (dd, $J = 5.9$ and 9.7 Hz, H-5), 4.55 (ddd, $J = 3.4$, 5.8, and 9.2 Hz, H-6), 4.52 (dd, $J = 3.5$ and 12.0 Hz, H-1_{proS}), 4.48 (dd, $J = 5.5$ and 12.0 Hz, H-1_{proR}), 4.23 (ddd, $J = 3.5$, 5.5, and 9.2 Hz, H-2), 2.03 (ddd, $J = 4.5$, 9.2, and 14.7 Hz, H-7_{proS}), 1.80 (m, H-8), 1.35 (ddd, $J = 3.4$, 9.5, and 14.7 Hz, H-7_{proR}), 0.99 (d, $J = 6.7$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.4 (s), 165.2 (s), 164.6 (s), 164.6 (s), 132.0–131.2, 128.9 (s), 128.9 (s), 128.8 (s), 128.4 (s), 128.4 (s), 127.8 (s), 127.6 (s), 127.5 (s), 71.5 (d, C-5), 71.2 (d, C-6), 71.0 (d, C-4), 70.1 (d, C-3), 69.0 (d, C-2), 63.6 (t, C-1), 33.9 (t, C-7), 24.2 (d, C-8), 23.5 (q), 21.3 (q); UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (8.5), 234 nm (−3.5); Anal. Calcd for $C_{38}H_{32}Br_4O_9$: C, 47.93; H, 3.39. Found: C, 48.03; H, 3.43.

4.14. 2,6-Anhydro-1,3,4,5-tetra-*O*-(*p*-bromobenzoyl)-7-cyclohexyl-7-deoxy-D-*glycero*-L-*gulo*-heptitol 2e

Debenzylation of compound **1e** (75 mg, 0.14 mmol) and then *p*-bromobenzoylation, performed as in the general procedure, led to compound **2e** (134 mg, 0.14 mmol, 96%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 9:1); $[\alpha]_D = +26.7$ (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.90 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.72 (d, $J = 8.6$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 5.92 (t, $J = 9.4$ Hz, H-4), 5.48 (t, $J = 9.2$ Hz, H-3), 5.45 (dd, $J = 5.8$ and 9.7 Hz, H-5), 4.58 (ddd, $J = 3.1$, 5.8, and 8.9 Hz, H-6), 4.51 (dd, $J = 3.1$ and 12.0 Hz, H-1_{proS}), 4.46 (dd, $J = 6.1$ and 12.0 Hz, H-1_{proR}), 4.25 (ddd, $J = 3.1$, 6.1, and 9.3 Hz, H-2), 1.98 (ddd, $J = 3.6$, 8.9, and 14.9 Hz, H-7_{proS}), 1.77 (m, 2H), 1.68–1.53 (m, 3H), 1.48 (m, 1H), 1.37 (ddd, $J = 3.1$, 9.5, and 14.9 Hz, H-7_{proR}), 1.15–0.97 (m, 4H), 0.83 (m, 1H); ^{13}C NMR ($CDCl_3$) 165.3 (s), 165.1 (s), 164.5 (s), 164.5 (s), 131.9–131.1, 128.9 (s), 128.8 (s), 128.7 (s), 128.4 (s), 128.4 (s), 127.7 (s), 127.6 (s), 127.5 (s), 71.5 (d, C-5), 70.9 (d, C-4), 70.6 (d, C-6), 70.1 (d, C-3), 68.9 (d, C-2), 63.7 (t, C-1), 34.1 (t, C-7), 33.4 (d), 32.5 (t), 32.0 (t), 26.3 (t), 26.3 (t), 25.9 (t); UV (CH_3CN) λ_{max} 245 nm; CD (CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (4.8), 234 nm (−2.7); Anal. Calcd for $C_{41}H_{36}Br_4O_9$: C, 49.62; H, 3.66. Found: C, 49.59; H, 3.74.

4.15. 2,6-Anhydro-1,3,4,5-tetra-*O*-(*p*-bromobenzoyl)-7,8,9-trideoxy-8,8-dimethyl-D-*glycero*-L-*gulo*-nonitol 2f

Debenzylation of compound **1f** (384 mg, 0.76 mmol) and then *p*-bromobenzoylation, performed as in the general procedure, gave compound **2f** (601 mg, 0.62 mmol, 82%) after column chromatography (*n*-hexane/EtOAc, 9:1): TLC $R_f = 0.3$ (*n*-hexane/EtOAc, 9:1); $[\alpha]_D = +23.6$ (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.48 (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.6$ Hz, 2H), 5.84 (t, $J = 9.4$ Hz, H-4), 5.52 (t, $J = 9.3$ Hz, H-3), 5.41 (dd, $J = 5.9$ and 10.1 Hz, H-5), 4.65 (dd, $J = 5.9$ and 10.1 Hz, H-6), 4.53 (dd, $J = 3.1$ and 12.0 Hz, H-1_{proS}), 4.45 (dd, $J = 5.5$ and 12.0 Hz, H-1_{proR}), 4.35 (ddd, $J = 3.1$, 5.5, and 9.3 Hz, H-2), 1.96 (dd, $J = 10.1$ and 15.0 Hz, H-7_{proS}), 1.48 (d, $J = 15.0$ Hz, H-7_{proR}), 0.95 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 165.4 (s), 165.1 (s), 164.5 (s), 164.5 (s), 132.0–131.1, 128.8 (s), 128.8 (s), 128.7 (s), 128.4 (s), 128.3 (s), 127.7 (s), 127.5 (s), 127.5 (s), 71.5 (d, C-5), 71.2 (d, C-6), 70.8 (d, C-4), 70.1 (d, C-3), 68.7 (d, C-2), 63.7 (t, C-1), 36.9 (t, C-7), 30.4 (s, C-8), 29.6 (q), 29.6 (q), 29.6 (q); UV (CH_3CN) λ_{max} 245 nm; CD

(CH_3CN) λ_{ext} ($\Delta\varepsilon$) 251 nm (9.2), 234 nm (−4.3); Anal. Calcd for $C_{39}H_{34}Br_4O_9$: C, 48.48; H, 3.55. Found: C, 48.49; H, 3.61.

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