Tetra-O-benzoylglucosylation: A New ^1H Nuclear Magnetic Resonance Method for Determination of the Absolute Configuration of Secondary Alcohols

Mar Trujillo, Ezequiel Q. Morales, and Jesús T. Vázquez*

Centro de Productos Naturales Orgánicos "Antonio González", Universidad de La Laguna-CSIC, Carretera de La Esperanza 2, 38206 La Laguna, Tenerife, Spain

Received June 17, 1994[⊗]

A new method for determination of the absolute configuration of secondary alcohols based on the anisotropic effect and glycosylation-induced ^1H NMR shifts is described. The tetra-*O*-benzoyl-β-glucosylation of secondary alcohols induces dramatic shifts in the aglycon ^1H NMR peaks. The differences between the proton chemical shifts of the D-glucosylated derivative and the free alcohol ($\Delta\delta = \delta_D - \delta_{ROH}$) or more significantly between their chemical shifts in the D- and L-glucosylated derivatives ($\Delta\delta = \delta_D - \delta_L$) are characteristic of the absolute configuration of the secondary chiral alcohol. Furthermore, in most cases the sign of the chemical shift difference of the carbinyl protons correlates with the absolute configuration of their carbons, namely positive or negative $\Delta\delta$ are obtained for (*R*)- or (*S*)-carbinyl carbons, respectively. Moreover, this method involves the use of one enantiomer and generally a single derivatization is sufficient.

The existent ^1H NMR methods for absolute configuration assignment are based on the fundamental principle that diastereomers are chemically distinct species which exhibit different spectral characteristics.[1] They generally require the formation of a covalent bond between the investigated molecule and a chiral reagent containing a large magnetic anisotropy group such as phenyl or naphthyl, to induce a high NMR chemical shift difference. The well-known Mosher's[2] and *O*-methylmandelate ester methods[3] illustrate this approach for the determination of the absolute configuration of secondary alcohols. Another strategy, involving only one alcohol enantiomer and the derivatizing agent, is based on the tetra-*O*-acetylglucosidation-induced ^1H NMR shifts.[4]

In this paper, we describe a new method for determining the absolute configuration of secondary alcohols, which utilizes a single enantiomer and combines the two approaches mentioned above, namely the anisotropic effect and the glycosylation-induced ^1H NMR shift. Indeed, the conformational properties of the glycopyranosidic linkage[5,6] are well established and the ^1H NMR spectra of tetra-*O*-benzoyl-β-glucosylated secondary alcohols do exhibit large variations compared to the free alcohol.[7]

Results and Discussion

Two sets of chemical shift differences, characteristic of the absolute configuration of the secondary chiral alcohol, can be independently used to denote these variations: (i) the difference between the chemical shift of a proton in the D-glucopyranoside derivative and the free alcohol ($\Delta\delta = \delta_D - \delta_{ROH}$) and (ii) the difference between the chemical shift of a proton in the D- and L-glucopyranoside derivatives ($\Delta\delta = \delta_D - \delta_L$). In both sets, protons *anti* to the endocyclic glucopyranoside oxygen (O-5) are shielded due to the diamagnetic effect of the benzoyl group at C-2 and thus exhibit negative $\Delta\delta$, whereas protons *syn* to that oxygen show positive $\Delta\delta$, due to their proximity to O-5 (Figure 1).[8]

To check the feasibility of the present methodology, we examined the $\Delta\delta$ values corresponding to alcohols **1**–**15** (R = H), the absolute configurations of which are known. In order to obtain the first set of $\Delta\delta$ values ($\delta_D - \delta_{ROH}$) (Figure 2), the D-glucopyranoside derivatives **1D** – **15D** (R = D-glc-Bz_4) were prepared in good yields by coupling the corresponding alcohols to commercial 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide, in the presence of silver trifluoromethanesulfonate as catalyst and 1,1,3,3-tetramethylurea as proton acceptor, using a modified Koenigs–Knorr method.[9,10]

The second set of chemical shift differences ($\delta_D - \delta_L$) has been evaluated for the same series of alcohols (**1**–**15**, R = H); we only report in Figure 3 the values obtained for enantiomers **1**, **3**, **5**, **7**, **12**, and **14**, the corresponding optical antipodes **2**, **4**, **6**, **8**, **13**, and **15**, respectively,

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1994.

(1) Rinaldi, P. L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1982**, *15*, 291.

(2) (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Sullivan, G. R.; Dale, J. A.; Mosher, H. S. *J. Org. Chem.* **1973**, *38*, 2143. (c) Kusumi, T.; Ohtani, I.; Inouye, Y.; Kakisawa, H. *Tetrahedron Lett.* **1988**, *29*, 4731. (d) Ohtani, I.; Kusumi, T.; Ishitsuka, O. M.; Kakisawa, H. *Ibid.* **1989**, *30*, 3147. (e) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Org. Chem.* **1991**, *56*, 1296. (f) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092. (g) Pehk, T.; Lippmaa, E.; Lopp, M.; Paju, A.; Borer, B. C.; Taylor, R. J. K. *Tetrahedron: Asymmetry* **1993**, *4*, 1527.

(3) (a) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 4929. (b) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370. (c) Adamczeski, M.; Quiñoá, E.; Crews, P. *J. Org. Chem.* **1990**, *55*, 240.

(4) Faghih, R.; Fontaine, C.; Horibe, I.; Imamura, P. M.; Lukacs, G.; Olesker, A.; Seo, S. *J. Org. Chem.* **1985**, *50*, 4918.

(5) Lemieux, R. U.; Koto, S. *Tetrahedron* **1974**, *30*, 1933.

(6) There are excellent reviews on this subject. For example, see: (a) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983. (b) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983.

(7) The present method can generalized to glycopyranosides having an equatorial hydroxyl group at C-2, such as galactopyranosides or xylopyranosides.

(8) Hori, H.; Nishida, Y.; Ohrui, H.; Meguro, H.; Uzawa, J. *Tetrahedron Lett.* **1988**, *29*, 4457.

(9) (a) Hanessian, S.; Banoub, J. *Carbohydr. Res.* **1977**, *53*, 13. (b) Banoub, J.; Bundle, D. R. *Can. J. Chem.* **1979**, *57*, 2091. (c) Garegg, P. J.; Norberg, T. *Acta Chem. Scand.* **1979**, *B33*, 116.

(10) Many methods have been developed for the β-glycoside synthesis. There are excellent reviews on this subject. For example, see: (a) Bochkov, A. F.; Zaikov, G. E. *Chemistry of the O-Glycosidic Bond, Formation and Cleavage*; Schuerch, C., Ed.; Pergamon Press: Oxford, 1979. (b) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. (c) Schmidt, R. R. *Ibid.* **1986**, *25*, 212. (d) Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503.

0022-3263/94/1959-6637$04.50/0

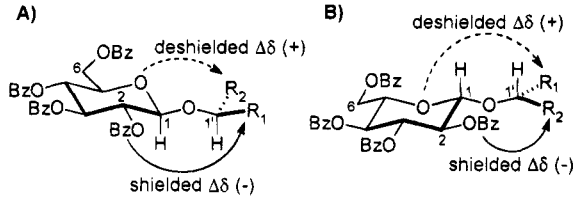

Figure 1. Configurational correlation models for secondary alcoholic (A) β-D-glucopyranosides and (B) β-L-glucopyranosides.

having opposite Δδ values. For practical purposes, the chemical shifts of the L-glucopyranoside derivatives of alcohols **1**, **3**, **5**, **7**, **12**, and **14** were obtained from the ^{1}H NMR spectra of their enantiomeric D-glucopyranosides **2D**, **4D**, **6D**, **8D**, **13D**, **15D** (R = D-glc-Bz$_4$), respectively. The L-glucopyranosides **9L**−**11L** (R = L-glc-Bz$_4$) were synthesized from the corresponding alcohols and the readily prepared 2,3,4,6-tetra-*O*-benzoyl-α-L-glucopyranosyl bromide,[11] using the same modified Koenigs−Knorr reaction.

These model compounds were characterized on the basis of their one- (^{1}H and ^{13}C)[12] and two-dimensional (COSY and HMQC) NMR spectra as well as UV and CD spectroscopy.[13]

Figures 2 and 3 show the two sets of Δδ values, $\delta_D - \delta_{ROH}$ and $\delta_D - \delta_L$, respectively. In both cases, the Δδ signs allowed us to assign the correct absolute configuration for the 15 secondary alcohols studied and to verify the general rules summarized in Figure 1; namely, the protons of the aglycon are *syn* or *anti* to the endocyclic glucopyranoside oxygen (O-5) when the Δδ is positive or negative, respectively.

In some cases, the $\delta_D - \delta_{ROH}$ value of a proton has a sign opposite to the expected one; as shown for compound **11** (Figure 2), the H-16α exhibits a negative instead of a positive Δδ; however, this does not affect the determination of the absolute configuration, since all the other Δδ signs follow the general concept shown in Figure 1.

Although the $\delta_D - \delta_{ROH}$ values (Figure 2) are generally enough for absolute configuration determination, the $\delta_D - \delta_L$ values (Figure 3) provide an unambiguous and rapid control. Indeed, the latter values are much larger than the former, and their signs follow the general rule much better. Thus, in compound **5**, the equatorial H-6 has a positive $\delta_D - \delta_{ROH}$ value but, as expected, a negative $\delta_D - \delta_L$value.

In the tetra-*O*-benzoyl-β-glucosylated and the tetra-*O*-acetylglucosylated secondary alcohols, the chemical shift of the carbinyl protons of the *R*-alcoholic glucopyranosides appeared at lower field than those of the *S*-alcoholic glucopyranoside counterparts. In contrast to the acetylglucosylated analogs, the signs of the chemical shift difference of the carbinyl protons of the benzoylated derivatives correlate with the absolute configuration of their carbons. Thus, positive Δδ are obtained for (*R*)-carbinyl carbons while negative Δδ are obtained for (*S*)-carbinyl carbons (Table 1). However, this correlation failed in the case of cholesterol and cholestanol (Δδ = 0.00), probably due to the absence of substituents at the β-positions which confer to the aglycon moiety a higher degree of conformational freedom, and in the case of dimethyl D- and L-malate (**12** and **13**, respectively), which possess two carbonyl groups that might modify the anisotropic effect coming from the glucosyl system. Methyl (*S*)-3-hydroxybutyrate (**15**) having one carbonyl group showed a positive $\delta_D - \delta_{ROH}$ value, but a predicted negative $\delta_D - \delta_L$value.

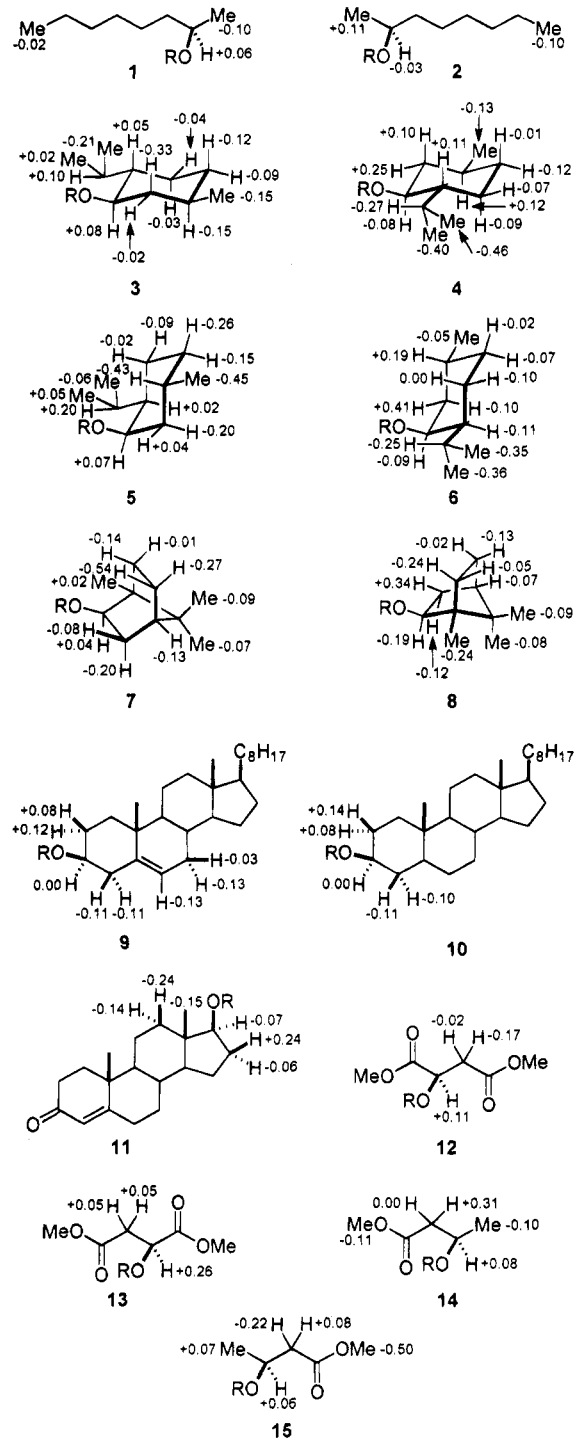

Figure 2. $\delta_D - \delta_{ROH}$ values (in ppm; room temperature; solvent $CDCl_3$) obtained for (−)- and (+)-2-octanol (**1** and **2**, respectively), (−)- and (+)-menthol (**3** and **4**), (−)- and (+)-neomenthol (**5** and **6**), (−)- and (+)-borneol (**7** and **8**), cholesterol (**9**), cholestanol (**10**), testosterone (**11**), dimethyl D- and L-malate (**12** and **13**), and (−)- and (+)-methyl 3-hydroxybutyrate (**14** and **15**).

(11) The chiral derivatizing agents can be prepared in high yields from D-(+)- and L-(−)-glucose in two steps. Ness, R. K.; Fletcher, Jr., H. G.; Hudson, C. S. *J. Am. Chem. Soc.* **1950**, *72*, 2200.

(12) The coupling constant between H-1 and H-2 (J = 7.8−8.0 Hz) is critical for confirming the right anomeric configuration of the β-*O*-glucopyranoside derivatives.

(13) Morales, E. Q.; Padrón, J. I.; Trujillo, M.; Vázquez, J. T. Manuscript in preparation.

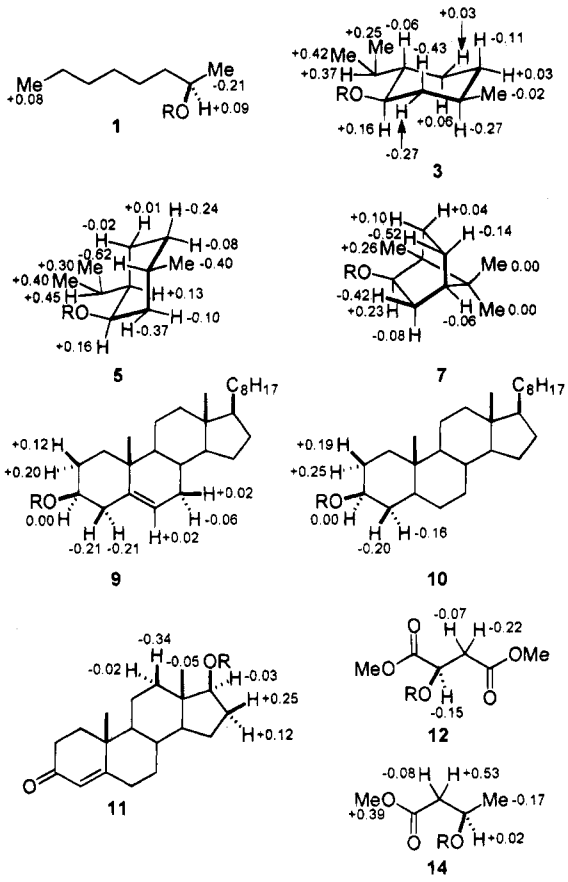

Figure 3. $\delta_D - \delta_L$ values (in ppm; room temperature; solvent $CDCl_3$) obtained for (−)-2-octanol (**1**), (−)-menthol (**3**), (−)-neomenthol (**5**), (−)-borneol (**7**), cholesterol (**9**), cholestanol (**10**), testosterone (**11**), dimethyl D-malate (**12**), and (−)-methyl 3-hydroxybutyrate (**14**).

Table 1. Relationship between the Absolute Configuration of the Carbinylic Carbon (C-1′) and the Sign of Δδ (ppm) of Its Corresponding Hydrogen

compd	carbinyl carbon config (C-1′)	$\delta_D - \delta_{ROH}$	$\delta_D - \delta_L$
(−)-2-Octanol (**1**)	*R*	+0.06	+0.09
(+)-2-Octanol (**2**)	*S*	−0.03	−0.09
(−)-Methanol (**3**)	*R*	+0.08	+0.16
(+)-Menthol (**4**)	*S*	−0.08	−0.16
(−)-Neomenthol (**5**)	*R*	+0.07	+0.16
(+)-Neomenthol (**6**)	*S*	−0.09	−0.16
(−)-Borneol (**7**)	*R*	+0.04	+0.23
(+)-Borneol (**8**)	*S*	−0.19	−0.23
(3β)-Cholesterol (**9**)	*S*	0.00	0.00
(3β)-Cholestanol (**10**)	*S*	0.00	0.00
(17β)-Testosterone (**11**)	*S*	−0.07	−0.03
dimethyl D-malate (**12**)	*R*	+0.12	−0.14
dimethyl L-malate (**13**)	*S*	+0.26	+0.14
(−)-methyl 3-hydroxy-butyrate (**14**)	*R*	+0.08	+0.02
(+)-methyl 3-hydroxy butyrate (**15**)	*S*	+0.06	−0.02

In Figure 4 we compare the results we obtained with (−)-menthol to those acquired by the advanced Mosher's method.[2d] The larger $\delta_D - \delta_L$ values resulting from the benzoylglucosylation can be useful in some cases. In addition, they allow this method to be used when high-field FT-NMR spectrometers are not available.

We have also found[13] that the intensity of the Cotton effect around 233 nm, or the *A* value[14] of the exciton CD curves[15] of the tetra-*O*-benzoyl-β-glucosylated secondary alcohols, is characteristic of the absolute configuration

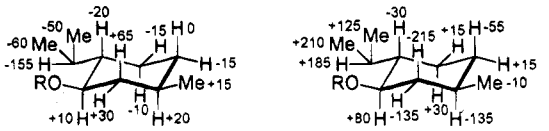

Figure 4. Comparison of the $\delta_S - \delta_R$ and the $\delta_D - \delta_L$ values (in hertz; 500 MHz; room temperature; solvent $CDCl_3$) of the MTPA[2d] (left) and the tetra-*O*-benzoylglucopyranoside (right) derivatives of (−)-menthol, respectively.

of the chiral alcohol. Thus, a slightly higher intensity is observed for all the β-D-glucosylated derivatives having an *R* absolute configuration at the carbinylic carbon than for those with an *S* absolute configuration.[16] Furthermore, the CD data of the β-L-glucosylated derivatives **9L**−**11L** seem to follow the opposite correlation, as expected, due to their diastereoisomeric relationship. Thus, β-L-glucosylated derivatives **9L** and **10L** exhibit a negative Cotton effect around 233 nm of −7.8 and −7.2 both of a higher intensity, in absolute value, than their diasteromers **9D** (+7.4) and **10D** (+6.2), respectively. For intensity comparison of testosterone derivatives **11D** and **11L** subtraction of the overlapping CD contribution at 234 nm (+7.7) of the $\pi \rightarrow \pi^*$ transition of the enone system (**11**, R = H) is required.

Conclusions

In conclusion, the present ^1H NMR method constitutes a versatile and reliable tool for the determination of the absolute configuration of secondary acyclic and cyclic alcohols. It involves the use of one enantiomer, and in most cases a single derivatization is sufficient. An attractive application of this method would be the determination of the absolute configuration of natural glycosides.

Experimental Section

General. ^1H NMR spectra were recorded at 400 MHz, and ^{13}C NMR were recorded 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. Optical rotations were measured on a digital polarimeter in a 1-dm cell. UV and CD spectra were recorded at room temperature in spectroscopic grade CH_3CN in the range 400−200 nm and by using 10 mm cells. Prior to measurement of CD spectra, all compounds were purified by HPLC by using a μ-Porasil column, 300 × 7.8 mm i.d., 254 nm, HPLC grade *n*-hexane/EtOAc solvent systems. Except for the testosterone derivatives the concentrations of the CD samples were ascertained from the UV spectra by using the experimentally determined value of 44 300 at 229 nm (CH_3CN) for the tetra-*O*-benzoyl-glucopyranosides.

Flash column chromatography was performed using silica gel 60 (0.015−0.04 mm) obtained from Merck. For analytical and preparative thin-layer chromatography silica gel F 1500/LS 254 ready-foils and G 1510/LS glass-backed plates (1 mm) (Schleicher & Schuell) were used, respectively. All reagents as well as the chiral alcohols **1**−**10** (R = H) were obtained from

(14) The amplitude (*A*) of split CD Cotton effects is defined as: $A = \Delta\epsilon_1 - \Delta\epsilon_2$ where $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are intensities of the first and second Cotton effects, respectively. Most of these glucopyranoside derivatives exhibited only the first Cotton effect, the second Cotton effect being masked by a strong background ellipticity.

(15) For a monograph on exciton CD spectroscopy see: Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.

(16) A high purity is required to apply the present CD results to determine absolute configurations since the Δε differences for the pair of glucosylated alcohols are small.

commercial sources and used without further purification. Solvents were dried and distilled before use. All reactions were performed under a dry argon atmosphere. While the α-D-glucopyranosyl bromide tetrabenzoate is commercially available, its enantiomer (L-series) was prepared by a procedure similar to that reported previously,[11] as described in the following.

2,3,4,6-Tetra-*O*-benzoyl-α-L-glucopyranosyl Bromide. This compound was obtained in two steps from L-glucose. First, a solution of L-glucose in dry pyridine with DMAP as catalyst, under Ar and at room temperature, was treated with 7.5 equiv of benzoyl chloride. The resulting solution was heated at 60 °C and stirred overnight. The reaction was quenched with MeOH and the excess solvent removed under reduced pressure in the presence of toluene. The residue was purified by flash column chromatography (*n*-hexane/EtOAc, 85:15) to give 1,2,3,4,6-penta-*O*-benzoyl-L-glucopyranoside as an α:β anomer mixture (ratio 3:1), yield 93%. α-Anomer: ^{1}H NMR ($CDCl_3$) δ 4.51 (1 H, m), 4.63 (1 H, m), 4.63 (1 H, dd, *J* = 13.1 and 2.7 Hz), 5.69 (1 H, dd, *J* = 10.0 and 3.8 Hz), 5.87 (1 H, t, *J* = 10.0 Hz), 6.33 (1 H, t, *J* = 10.0 Hz), 6.86 (1 H, d, *J* = 3.7 Hz), 7.29–7.57 (15 H), 7.88–8.18 (10 H). β-Anomer: ^{1}H NMR ($CDCl_3$) δ 4.42 (1 H, m), 4.52 (1 H, dd, *J* = 12.3 and 4.7 Hz), 4.67 (1 H, dd, *J* = 12.3 and 2.9 Hz), 5.84 (1 H, t, *J* = 9.5 Hz), 5.87 (1 H, dd, *J* = 9.5 and 8.0 Hz), 6.05 (1 H, t, *J* = 9.5 Hz), 6.31 (1 H, d, *J* = 8.0 Hz), 7.28–7.63 (15 H), 7.85–8.12 (10 H). Second, to a solution of the anomer mixture 1,2,3,4,6-penta-*O*-benzoyl-L-glucopyranoside in dry CH_2Cl_2 (3 mL/mmol) under Ar atmosphere was added 4 equiv of 30% (w/w) HBr/AcOH and the reaction mixture kept under stirring at room temperature. Once the reaction was finished, the excess solvent was removed under reduced pressure in the presence of toluene. The residue obtained was purified by flash column chromatography (*n*-hexane/EtOAc, 85:15), yield 85%: TLC R_f 0.52 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ −125.9° (*c* 0.4, $CHCl_3$); mp 127.9–129.8 °C; ^{1}H NMR ($CDCl_3$) δ 4.58 (1 H, dd, *J* = 12.6 and 4.4 Hz), 4.73 (1 H, dd, *J* = 12.6 and 2.5 Hz), 4.81 (1 H, m), 5.43 (1 H, dd, *J* = 9.9 and 4.0 Hz), 5.92 (1 H, t, *J* = 9.9 Hz), 6.35 (1 H, t, *J* = 9.9 Hz), 6.94 (1 H, d, *J* = 4.0 Hz), 7.28–7.58 (12 H), 7.92, 8.00, 8.05, 8.11 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 61.90, 67.95, 70.58, 71.43, 72.68, 86.85, 128.32–133.76, 165.04, 165.26, 165.52, 165.98.

General Procedure for Preparation of β-*O*-Glucopyranosides. To a solution of 2,3,4,6-tetra-*O*-benzoyl-α-glucopyranosyl bromide in dry CH_2Cl_2 (10 mL/mmol) under Ar and at room temperature were added 0.5 equiv of the chiral alcohol and 0.5 equiv of 1,1,3,3-tetramethylurea. The reaction mixture was cooled at 0 °C in an ice bath, and 1 equiv of the promoter AgOTf was then added in the dark under rigorously anhydrous conditions. The reaction was usually complete within 30 min (TLC). After the reaction was quenched with a few drops of water and filtration through a bed of Celite with CH_2Cl_2, the filtrate was evaporated under diminished pressure, and preparative TLC or flash column chromatography (*n*-hexane/EtOAc solvent systems) gave the purified product, yield 50–80%. The following *O*-glucopyranosides were prepared according to this method.

(2*R*)-(−)-2-Octyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (1D): TLC R_f 0.47 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ +1.0° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.82 (3 H, t, *J* = 6.9 Hz), 1.03 (3 H, d, *J* = 6.2 Hz), 1.17–1.38 (10 H, m), 3.80 (1 H, m), 4.14 (1 H, ddd, *J* = 9.7, 5.6 and 3.3 Hz), 4.50 (1 H, dd, *J* = 12.0 and 5.6 Hz), 4.62 (1 H, dd, *J* = 12.0 and 3.3 Hz), 4.89 (1 H, d, *J* = 7.9 Hz), 5.48 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.64 (1 H, t, *J* = 9.7 Hz), 5.89 (1 H, d, *J* = 9.7 Hz), 7.28–7.55 (12 H, m), 7.83, 7.90, 7.95 and 8.01 (each: 2 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.96, 19.67, 22.43, 25.13, 29.01, 31.65, 36.76, 63.29, 70.01, 71.95, 72.04, 73.06, 76.25, 99.52, 128.06–133.28, 164.94, 165.16, 165.75, 166.00; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 234 (7.3), 220 nm (−0.9). Anal. Calcd for $C_{42}H_{44}O_{10}$: C, 71.17; H, 6.26. Found: C, 71.41; H, 6.51.

(2*S*)-(+)-2-Octyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (2D): TLC R_f 0.49 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ +14.9° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.74 (3 H, t, *J* = 6.9 Hz), 0.81–1.12 (10 H, m), 1.24 (3 H, d, *J* = 6.2 Hz), 3.71 (1 H, m), 4.15 (1 H, ddd, *J* = 9.7, 5.8, and 3.2 Hz), 4.50 (1 H, dd, *J* = 12.0 and 5.8 Hz), 4.63 (1 H, dd, *J* = 12.0 and 3.2 Hz), 4.88 (1 H, d, *J* = 7.9 Hz), 5.52 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.62 (1 H, t, *J* = 9.7 Hz), 5.90 (1 H, t, *J* = 9.7 Hz), 7.28–7.55 (12 H, m), 7.83, 7.90, 7.96, and 8.01 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.99, 21.79, 22.48, 25.24, 29.22, 31.50, 36.87, 63.45, 70.09, 72.06, 72.10, 73.03, 78.89, 101.70, 128.28–133.39, 164.98, 165.26, 165.86, 166.12; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 235 (6.3), 220 nm (−0.6). Anal. Calcd for $C_{42}H_{44}O_{10}$: C, 71.17; H, 6.26. Found: C, 70.90; H, 6.54.

(1*R*,2*S*,5*R*)-(−)-1-Menthyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (3D): TLC R_f 0.52 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ −26.7° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.68 (1 H, m), 0.71 (3 H, d, *J* = 7.0 Hz), 0.72 (1 H, m), 0.75 (3 H, d, *J* = 6.6 Hz), 0.82 (3 H, d, *J* = 7.0 Hz), 0.89 (1 H, m), 1.15 (1 H, br t, *J* = 10.6 Hz), 1.26 (1 H, m), 1.56 (2 H, m), 1.94 (1 H, br d, *J* = 12.2 Hz), 2.25 (1 H, m), 3.48 (1 H, dt, *J* = 10.6 and 4.1 Hz), 4.13 (1 H, ddd, *J* = 9.7, 5.7, and 3.3 Hz), 4.48 (1 H, dd, *J* = 12.0 and 5.7 Hz), 4.62 (1 H, dd, *J* = 12.0 and 3.3 Hz), 4.93 (1 H, d, *J* = 7.9 Hz), 5.48 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.63 (1 H, t, *J* = 9.7 Hz), 5.89 (1 H, t, *J* = 9.7 Hz), 7.26–7.55 (12 H, m), 7.83, 7.90, 7.96, and 8.00 (each: 2 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 15.61, 20.77, 22.00, 23.03, 25.13, 31.37, 34.09, 40.76, 47.32, 63.47, 70.20, 72.01, 72.15, 73.22, 79.07, 98.99, 128.27–133.36, 165.06, 165.30, 165.86, 166.13; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 232 nm (5.8).

(1*S*,2*R*,5*S*)-(+)-1-Menthyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (4D): TLC R_f 0.51 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ +23.0° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.40 (3 H, d, *J* = 6.9 Hz), 0.46 (3 H, d, *J* = 6.9 Hz), 0.77 (3 H, d, *J* = 6.4 Hz), 0.83 (2 H, m), 1.11 (1 H, q, *J* = 12.2 Hz), 1.21 (1 H, m), 1.53 (3 H, m), 1.88 (1 H, m), 2.21 (1 H, br d, *J* = 12.2 Hz), 3.32 (1 H, dt, *J* = 4.3 and 10.6 Hz), 4.19 (1 H, ddd, *J* = 9.7, 6.8, and 3.1 Hz), 4.50 (1 H, dd, *J* = 12.0 and 6.8 Hz), 4.63 (1 H, dd, *J* = 12.0 and 3.1 Hz), 4.88 (1 H, d, *J* = 8.0 Hz), 5.55 (1 H, dd, *J* = 9.7 and 8.0 Hz), 5.57 (1 H, t, *J* = 9.7 Hz), 5.91 (1 H, t, *J* = 9.7 Hz), 7.28–7.54 (12 H, m), 7.83, 7.91, 7.95 and 8.02 (each: 2 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 15.42, 20.57, 22.09, 22.67, 24.66, 31.64, 34.10, 42.98, 48.01, 63.66 , 70.16, 72.00 and 72.08, 72.99, 83.36, 102.70, 128.21–133.42, 164.99, 165.31, 165.87, 166.09; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 230 nm (4.2).

(1*R*,2*R*,5*S*)-(−)-1-Neomenthyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (5D): TLC R_f 0.54 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ −21.1° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.36 (1 H, d, *J* = 6.6 Hz), 0.67 (1 H, m), 0.81 (1 H, m), 0.83 (3 H, d, *J* = 6.7 Hz), 0.84 (1 H, m), 0.90 (3 H, d, *J* = 6.7 Hz), 1.21 (2 H, m), 1.41 (1 H, m), 1.51 (1 H, br dd, *J* = 12.9 and 3.3 Hz), 1.68 (1 H, m), 1.82 (1 H, br d, *J* = 13.9 Hz), 4.10 (1 H, br s), 4.14 (1 H, ddd, 9.7, 5.7 and 3.3 Hz), 4.48 (1 H, dd, *J* = 12.0 and 5.7 Hz), 4.64 (1 H, dd, *J* = 12.0 and 3.3 Hz), 4.88 (1 H, d, *J* = 7.9 Hz), 5.53 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.64 (1 H, t, *J* = 9.7 Hz), 5.92 (1 H, t, *J* = 9.7 Hz), 7.26–7.53 (12 H), 7.84, 7.91, 7.95 and 8.00 (each: 2 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.59, 20.89, 21.68, 24.28, 25.76, 28.32, 34.76, 38.11, 47.80, 63.39, 70.19, 71.94, 71.99, 73.13, 74.88, 98.79, 128.28–133.36, 164.95, 165.29, 165.85, 166.11; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 233 nm (6.6).

(1*S*,2*S*,5*R*)-(+)-Neomenthyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (6D): TLC R_f 0.53 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ +8.6° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.50 (3 H, d, *J* = 6.6 Hz), 0.53 (3 H, d, *J* = 6.6 Hz), 0.71 (1 H, m), 0.75 (1 H, m), 0.76 (3 H, d, *J* = 6.7 Hz), 0.91 (1 H, m), 1.23 (2 H, m), 1.50 (1 H, br dd, *J* = 13.0 and 3.4 Hz), 1.65 (1 H, br d, *J* = 12.9 Hz), 1.83 (1 H, m), 2.19 (1 H, br d, *J* = 13.2 Hz), 3.94 (1 H, br s), 4.15 (1 H, m), 4.47 (1 H, dd, *J* = 12.0 and 5.9 Hz), 4.65 (1 H, dd, *J* = 12.0 and 3.3 Hz), 4.86 (1 H, d, *J* = 7.9 Hz), 5.57 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.63 (1 H, t, *J* = 9.7 Hz), 5.91 (1 H, t, *J* = 9.7 Hz), 7.28–7.56 (12 H), 7.83, 7.91, 7.93 and 8.02 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 20.55, 20.92, 22.16, 24.68, 25.93, 28.07, 34.95, 41.23, 48.51, 63.47, 70.14, 72.03, 73.05, 79.70, 103.01, 128.17–133.39, 165.02, 165.30, 165.87, 166.09; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 232 nm (6.2).

[(1*S*)-*endo*]-(−)-2-Bornyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (7D): TLC R_f 0.57 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ −3.5° (*c* 2.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.69 (1 H, m), 0.75 (3 H, s), 0.77 (3 H, s), 0.85 (1 H, m), 0.86 (3 H, s), 1.09 (1 H, m), 1.45 (1 H, m), 1.48 (1 H, m), 1.86 (1 H, m), 2.06 (1 H, m), 4.04 (1 H, br d, *J* = 9.1 Hz), 4.12 (1 H, m), 4.52 (1 H, dd, *J* = 12.0 and 5.7 Hz), 4.61 (1 H, dd, *J* = 12.0 and 3.6 Hz), 4.80 (1 H, d, *J* = 7.9 Hz), 5.53 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.65 (1 H, t, *J* = 9.7 Hz), 5.90 (1 H, t, *J* = 9.7 Hz), 7.27−7.53 (12 H), 7.85, 7.90, 7.98 and 8.00 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.25, 18.73, 19.60, 26.33, 27.80, 35.85, 44.77, 47.83, 49.00, 63.37, 70.25, 72.03, 72.91, 83.81, 99.97, 128.26−133.35, 164.99, 165.24, 165.82, 166.07; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 232 nm (8.7). Anal. Calcd for $C_{44}H_{44}O_{10}$: C, 72.12; H, 6.05. Found: C, 71.85; H, 6.09.

[(1*R*)-*endo*]-(+)-2-Bornyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (8D): TLC R_f 0.51 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ +13.1° (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.60 (3 H, s), 0.75 (3 H, s), 0.76 (3 H, s), 0.99 (1 H, br t, *J* = 11.1 Hz), 1.21 (1 H, m), 1.27 (1 H, dd, *J* = 13.6 and 3.2 Hz), 1.54 (1 H, m), 1.59 (1 H, m), 1.82 (1 H, m), 2.14 (1 H, m), 3.81 (1 H, br d, *J* = 9.6 Hz), 4.12 (1 H, m), 4.52 (1 H, dd, *J* = 12.0 and 5.8 Hz), 4.61 (1 H, dd, *J* = 12.0 and 3.2 Hz), 4.82 (1 H, d, *J* = 7.9 Hz), 5.57 (1 H, dd, *J* = 9.6 and 7.9 Hz), 5.64 (1 H, t, *J* = 9.6 Hz), 5.89 (1 H, t, *J* = 9.6 Hz), 7.27−7.53 (12 H), 7.84, 7.90, 7.95, and 8.01 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.35, 18.61, 19.49, 26.29, 27.82, 37.07, 44.89, 47.30, 49.28, 63.33, 70.14, 72.00, 72.10, 72.92, 87.59, 102.79, 128.15−133.32, 164.98, 165.20, 165.78, 166.00; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 233 (7.5), 215 nm (−0.3).

Cholesteryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (9D): TLC R_f 0.54 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ +13.5 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.65 (3 H, s), 0.86 (3 H, d, *J* = 6.6 Hz), 0.87 (3 H, d, *J* = 6.6 Hz), 0.89 (3 H, s), 0.91 (3 H, d, *J* = 6.5 Hz), 1.56 (1 H, m), 1.92 (2 H, m), 2.15 (2 H, m), 3.53 (1 H, m), 4.15 (1 H, m), 4.52 (1 H, dd, *J* = 12.0 and 5.9 Hz), 4.60 (1 H, dd, *J* = 12.0 and 3.3 Hz), 4.94 (1 H, d, *J* = 7.9 Hz), 5.22 (1 H, d, *J* = 5.0 Hz), 5.49 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.62 (1 H, t, *J* = 9.7 Hz), 5.89 (1 H, t, *J* = 9.7 Hz), 7.28−7.54 (12 H), 7.83, 7.90, 7.95, and 8.01 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 11.82, 18.71, 19.25, 21.00, 22.55, 22.80, 23.80, 24.26, 28.01, 28.21, 29.57, 29.68, 31.81, 31.90, 35.76, 36.18, 36.62, 37.09, 38.81, 39.51, 39.77, 42.30, 50.12, 56.15, 56.75, 63.39, 70.10, 72.09, 73.06, 80.46, 100.15, 121.94, 128.27−133.40, 140.34, 165.09, 165.25, 165.84, 166.09; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 233 nm (7.4).

Cholesteryl 2,3,4,6-tetra-*O*-benzoyl-β-L-glucopyranoside (9L): TLC R_f 0.59 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ −26.1° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.65 (3 H, s), 0.85 (6 H, d, *J* = 6.6 Hz), 0.85 (3 H, d, *J* = 6.6 Hz), 0.90 (3 H, s), 1.44 (1 H, m), 1.49 (1 H, m), 1.72 (1 H, m), 1.90 (1 H, m), 2.36 (2 H, m), 3.53 (1 H, m), 4.16 (1 H, m), 4.50 (1 H, dd, *J* = 12.0 and 6.1 Hz), 4.62 (1 H, dd, *J* = 12.0 and 3.1 Hz), 4.94 (1 H, d, *J* = 7.9 Hz), 5.20 (1 H, br d, *J* = 4.7 Hz), 5.49 (1 H, dd, *J* = 9.6 and 7.9 Hz), 5.61 (1 H, t, *J* = 9.6 Hz), 5.89 (1 H, t, *J* = 9.6 Hz), 7.28−7.54 (12 H), 7.83, 7.91, 7.95 and 8.02 (each: 2 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 11.83, 18.71, 19.24, 22.55, 22.80, 28.27, 36.98, 40.16, 63.46, 70.07, 72.14, 73.02, 80.78, 100.32, 122.01, 128.27−133.40, 140.34, 165.06, 165.26, 165.84, 166.12; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 232 nm (−7.8).

Cholestanyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (10D): TLC R_f 0.51 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ +24.8° (*c* 2.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.62 (3 H, s), 0.67 (3 H, s), 0.86 (6 H, d, *J* = 6.6 Hz), 0.90 (3 H, d, *J* = 6.5 Hz), 1.18 (1 H, m), 1.45 (1 H, m), 1.51 (1 H, m), 1.86 (1 H, br d, *J* = 10.5 Hz), 3.59 (1 H, m), 4.15 (1 H, m), 4.52 (1 H, dd, *J* = 12.0 and 6.0 Hz), 4.60 (1 H, dd, *J* = 12.0 and 3.4 Hz), 4.94 (1 H, d, *J* = 7.9 Hz), 5.48 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.61 (1 H, t, *J* = 9.7 Hz), 5.89 (1 H, t, *J* = 9.7 Hz), 7.28−7.54 (12 H), 7.83, 7.90, 7.95, and 8.01 (each: 2 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 12.02, 12.15, 18.65, 21.17, 22.54, 22.79, 24.17, 42.57, 44.68, 54.31, 63.43, 70.14, 72.05, 72.16, 73.08, 80.07, 99.97, 128.16−133.38, 165.05, 165.25, 165.84, 166.08; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 233 (6.2), 215 nm (−0.9).

Cholestanyl 2,3,4,6-tetra-*O*-benzoyl-β-L-glucopyranoside (10L): TLC R_f 0.59 (*n*-hexane/EtOAc, 8:2); $[\alpha]^{25}_D$ −6.9° (*c* 1.6, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.62 (3 H, s), 0.69 (3 H, s), 0.86 (6 H, d, *J* = 6.6 Hz), 0.89 (3 H, d, *J* = 6.6 Hz), 1.38 (1 H, m), 1.61 (1 H, m), 1.32 (1 H, m), 1.61 (1 H, m), 3.58 (1 H, m), 4.16 (1 H, m), 4.51 (1 H, dd, *J* = 12.0 and 6.1 Hz), 4.60 (1 H, dd, *J* = 12.0 and 3.2 Hz), 4.93 (1 H, d, *J* = 7.9 Hz), 5.47 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.61 (1 H, t, *J* = 9.7 Hz), 5.88 (1 H, t, *J* = 9.7 Hz), 7.28−7.54 (12 H), 7.83, 7.90, 7.95, and 8.01 (each: 2 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 12.04, 12.20, 18.66, 21.17, 22.55, 22.80, 24.20, 42.58, 44.88, 54.35, 63.52, 70.14, 72.09, 72.19, 73.05, 80.32, 100.19, 128.23−133.40, 165.07, 165.28, 165.86, 166.12; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 233 nm (−7.2).

Testosterone 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (11D): TLC R_f 0.45 (*n*-hexane/EtOAc, 6:4); $[\alpha]^{25}_D$ +65.5° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.64 (3 H, s), 0.82 (1 H, m), 0.95 (1 H, br t, *J* = 12.4 Hz), 1.10 (3 H, s), 1.22 (1 H, m), 1.34 (1 H, br d, *J* = 11.3), 1.49 (1 H, m), 1.61 (1 H, m), 1.70 (1 H, m), 1.78 (1 H, m), 1.94 (1 H, dd, *J* = 13.4 and 3.7 Hz), 2.00 (1 H, m), 2.30 (4 H), 3.58 (1 H, t, *J* = 8.4 Hz), 4.12 (1 H, m), 4.51 (1 H, dd, *J* = 12.0 and 5.6 Hz), 4.62 (1 H, dd, *J* = 12.0 and 3.1 Hz), 4.85 (1 H, d, *J* = 7.9 Hz), 5.52 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.63 (1 H, t, *J* = 9.7 Hz), 5.70 (1 H, s), 5.89 (1 H, t, *J* = 9.7 Hz), 7.28−7.54 (12 H), 7.83, 7.90, 7.96 and 8.01 (each: 2 H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 11.38, 17.31, 20.36, 23.28, 28.76, 31.45, 32.68, 33.89, 35.24, 35.66, 36.88, 38.53, 42.74, 50.09, 53.78, 63.35, 70.07, 72.10, 72.87, 90.03, 101.94, 123.82, 128.27−133.41, 164.98, 165.24, 165.82, 166.05, 171.06, 199.43; UV (CH_3CN) λ_{max} 229.0 nm; CD (CH_3CN) λ_{ext} (Δε) 328 nm (−1.5), 235 (15.7).

Testosterone 2,3,4,6-tetra-*O*-benzoyl-β-L-glucopyranoside (11L): TLC R_f 0.50 (*n*-hexane/EtOAc, 6:4); $[\alpha]^{25}_D$ +23.2° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.69 (3 H, s), 0.87 (1 H, m), 0.97 (1 H, m), 1.10 (3 H, s), 1.17 (1 H, m), 1.45 (1 H, m), 1.49 (1 H, m), 1.88 (1 H, m), 1.95 (1 H, m), 3.61 (1 H, t, *J* = 8.4 Hz), 4.16 (1 H, m), 4.57 (2 H, d, *J* = 4.7 Hz), 4.78 (1 H, d, *J* = 7.8 Hz), 5.49 (1 H, dd, *J* = 9.7 and 7.8 Hz), 5.61 (1 H, t, *J* = 9.7 Hz), 5.70 (1 H, s), 5.89 (1 H, t, *J* = 9.7 Hz), 7.27−7.54 (12 H), 7.84, 7.91, 7.94, and 8.02 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 11.41, 17.25, 20.32, 22.89, 27.38, 31.42, 32.63, 33.85, 35.27, 35.60, 36.31, 38.49, 42.41, 50.48, 53.79, 63.50, 70.07, 72.13, 72.82, 89.59, 100.98, 123.70, 128.21−133.38, 164.97, 165.23, 165.73, 165.96, 171.15, 199.45; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 328 (−1.4), 236 (−0.4), 215 nm (10.1).

Glucoside 12D (R = D-glc-Bz_4): TLC R_f 0.50 (*n*-hexane/EtOAc, 6:4); $[\alpha]^{25}_D$ +8.3° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.68 (1 H, dd, *J* = 4.8 and 16.8 Hz), 2.75 (1 H, dd, *J* = 16.8 and 8.7 Hz), 3.26 (3 H, s), 3.63 (3 H, s), 4.16 (1 H, m), 4.44 (1 H, dd, *J* = 12.0 and 5.6 Hz), 4.60 (1 H, dd, *J* = 8.7 and 4.8 Hz), 4.60 (1 H, dd, *J* = 12.0 and 3.5 Hz), 5.07 (1 H, d, *J* = 7.9 Hz), 5.58 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.66 (1 H, t, *J* = 9.7 Hz), 5.89 (1 H, t, *J* = 9.7 Hz), 7.27−7.55 (12 H), 7.82, 7.90, 7.96, 8.03 (each: 2 H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 37.18, 51.53, 52.33, 62.91, 69.52, 71.56, 72.41, 72.75, 75.71, 101.78, 128.25−133.42, 164.79, 165.13, 165.68, 166.00, 169.90, 170.64; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 234 nm (8.0).

Glucoside 13D (R = D-glc-Bz_4): TLC R_f 0.42 (*n*-hexane/EtOAc, 6:4); $[\alpha]^{25}_D$ +5.2° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.82 (1 H, dd, *J* = 16.2 and 6.3 Hz), 2.90 (1 H, dd, *J* = 16.2 and 6.3 Hz), 3.45 (3 H, s), 3.59 (3 H, s), 4.14 (1 H, m), 4.48 (1 H, dd, *J* = 12.2 and 5.0 Hz), 4.63 (1 H, dd, *J* = 12.2 and 3.2 Hz), 4.75 (1 H, t, *J* = 6.3 Hz), 5.11 (1 H, d, *J* = 7.9 Hz), 5.52 (1 H, dd, *J* = 9.7 and 7.9 Hz), 5.68 (1 H, t, *J* = 9.7 Hz), 5.90 (1 H, t, *J* = 9.7 Hz), 7.27−7.57 (12 H), 7.83, 7.89, 7.99, 8.03 (each: 2 H, d, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 37.58, 51.86, 52.19, 62.92, 69.60, 71.68, 72.33, 72.71, 73.69, 100.64, 128.30−133.44, 165.02, 165.16, 165.74, 166.10; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} (Δε) 234 nm (5.8).

Glucoside 14D (R = D-glc-Bz_4): TLC R_f 0.55 (*n*-hexane/EtOAc, 6:4); $[\alpha]^{25}_D$ +14.9° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.13 (3 H, d, *J* = 6.2 Hz), 2.42 (1 H, dd, *J* = 15.8 and 7.0 Hz), 2.81 (1 H, dd, *J* = 15.8 and 6.0 Hz), 3.60 (3 H, s), 4.13 (1 H, m), 4.28 (1 H, m), 4.47 (1 H, dd, *J* = 12.1 and 5.2 Hz), 4.61 (1 H, dd, *J* = 12.1 and 3.3 Hz), 4.96 (1 H, d, *J* = 7.9 Hz), 5.48 (1

H, dd, J = 9.7 and 7.9 Hz), 5.66 (1 H, t, J = 9.7 Hz), 5.89 (1 H, t, J = 9.7 Hz), 7.28–7.56 (12 H), 7.83, 7.89, 7.96, 8.02 (each: 2 H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.30, 42.09, 51.51, 63.12, 69.76, 71.93, 72.06, 72.92, 73.71, 100.51, 128.24–133.37, 164.99, 165.15, 165.78, 166.09, 171.35; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} ($\Delta\epsilon$) 233 nm (10.8).

Glucoside 15D (R = D-glc-Bz$_4$): TLC R_f 0.52 (*n*-hexane/EtOAc, 6:4); $[\alpha]^{25}_D$ +4.7° (*c* 2.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.30 (3 H, d, J = 6.3 Hz), 2.28 (1 H, dd, J = 16.3 and 4.0 Hz), 2.50 (1 H, dd, J = 16.3 and 8.8 Hz), 3.21 (3 H, s), 4.17 (1 H, m), 4.26 (1 H, m), 4.49 (1 H, dd, J = 11.9 and 5.6 Hz), 4.62 (1 H, dd, J = 12.0 and 3.2 Hz), 5.03 (1 H, d, J = 7.9 Hz), 5.48 (1 H, dd, J = 9.7 and 7.9 Hz), 5.66 (1 H, t, J = 9.7 Hz), 5.91 (1 H, t, J = 9.7 Hz), 7.24–7.56 (10 H), 7.81, 7.91, 7.96, 8.02 (each: 2 H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.83, 41.62, 51.08, 63.21, 69.90, 71.89, 72.03, 72.89, 101.84, 128.13–133.38, 164.94, 165.22, 165.73, 166.05, 171.24; UV (CH_3CN) λ_{max} 229 nm; CD (CH_3CN) λ_{ext} ($\Delta\epsilon$) 234 (6.2), 220 nm (−0.8).

Acknowledgment. Support of this work by the Dirección General de Investigación Científica y Técnica (DGICYT), Ministerio de Educación y Ciencia (Spain), through grant PB93-0559 is gratefully acknowledged. We thank Prof. Julio D. Martín (University of La Laguna) for his valuable support and interest in this work and Dr. Fadila Derguini (Columbia University) for revisions of this manuscript. E.Q.M. thanks the Ministerio de Educación y Ciencia (Spain) for a fellowship.

Supplementary Material Available: A full listing of ^{1}H NMR spectral data and peak assignments of the β-glucopyranoside derivatives, as well as copies of the ^{1}H NMR spectra (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.