1.161. This allowed assignment of the signals at δ 1.161 and 2.422 to C21-H and C20-H, respectively. This means that the remaining highly deshielded dimethyl singlet (δ 1.100) must be caused by C28-H and C29-H and the dimethyl doublet (δ 0.933) by C26-H and C27-H.

24,24-Dimethyl-5α-cholesta-7,25-dien-22-yn-3β-ol (6) acetate: mp 138–140 °C; RRT(GC) 1.50, RRT(HPLC) 0.37; MS, *m/z* (assignment, relative intensity) 450.3461 ($C_{31}H_{46}O_2$, M^+, 34, calcd 450.3494), 435.3247 ($C_{30}H_{43}O_2$, 12), 407.2922 ($C_{28}H_{39}O_2$, 4), 475.3064 ($C_{28}H_{39}$, 4), 367.2634 ($C_{25}H_{35}O_2$, 4), 315.2286 ($C_{21}H_{31}O_2$, 18), 313,2114 ($C_{21}H_{29}O_2$, 10), 299.2046 ($C_{20}H_{27}O_2$, 6), 267.2071 ($C_{20}H_{27}$, 2), 255.2102 ($C_{19}H_{27}$, 38), 253.1945 ($C_{19}H_{25}$, 6), 239.1843 ($C_{18}H_{23}$, 6), 229.0000 ($C_{17}H_{25}$, 11), 213.1657 ($C_{16}H_{21}$, 9), 43.0193 ($C_2H_3O_1$, 100). Hydrogenation of **6**-acetate (4 h) afforded a mixture of the acetates of **7** (70%) and **10** (30%), which was separated by HPLC. The MS and ^1H NMR data of these acetates were indistinguishable from those of the hydrogenation products of **5**-acetate.

Decoupling experiments: Irradiation of the methyl doublet at δ 1.170 collapsed the signal at δ 2.468 (1 H, qd) into a doublet (J = 6.8) and irradiation at δ 2.468 collapsed the methyl doublet at δ 1.170. Thus we found C20-H and C22-H.

(22*Z*)-24,24-Dimethyl-5α-cholesta-7,22-dien-3β-ol (7) acetate: mp 195–197 °C; RRT(GC) 1.88, RRT(HPLC) 0.90; MS, *m/z* (assignment, relative intensity) 454.3804 ($C_{31}H_{50}O_2$, M^+, 54), 439.3545 ($C_{30}H_{47}O_2$, 18), 411.3237 ($C_{28}H_{43}O_2$, 18), 394.3556 ($C_{29}H_{46}$, 8), 351.3080 ($C_{26}H_{39}$, 9), 342.2587 ($C_{23}H_{34}O_2$, 14), 315.2308 ($C_{21}H_{31}O_2$, 30), 313.2131 ($C_{21}H_{29}O_2$, 75), 299.2018 ($C_{20}H_{27}O_2$, 7), 288.2065 ($C_{19}H_{28}O_2$, 20), 273.1856 ($C_{18}H_{25}O_2$, 8), 255.2081 ($C_{19}H_{27}$, 67), 253.1962 ($C_{19}H_{25}$, 7), 241.1967 ($C_{18}H_{25}$, 9), 229.1937 ($C_{17}H_{25}$, 37), 213.1684 ($C_{16}H_{21}$, 20), 81.0717 (C_6H_9, 100).

Decoupling experiments: Irradiation at δ 0.983 collapsed the methine signal at δ 2.653 (qdd) into a double doublet (J = 9.6, 7.4), whereas irradiation at δ 2.653 collapsed the methyl doublet at δ 0.983 into a singlet and the methine signal at δ 4.987 (dd) into a doublet (J = 12.5). Further irradiation at δ 4.987 (1 H, dd) collapsed the methine signal at δ 2.653 (qdd) into a quadruple doublet (J = 6.6, 9.4) and the methine doublet at δ 5.053 into a singlet. On the basis of these results the signals at δ 0.983, 2.653, 4.987, and 5.053 were assigned to C21-H, C20-H, C22-H, and C23-H, respectively.

24,24-Dimethyl-5α-cholest-7-en-3β-ol (10) acetate: mp 180–183 °C; RRT(GC) 2.02, RRT(HPLC) 1.22; MS, *m/z* (relative intensity) 456 (M^+, 100), 441 (18), 413 (3), 396 (59), 381 (12), 315 (11), 288 (8), 273 (9), 255 (67), 229 (20), 213 (29). ^1H NMR data were reported earlier.[22a] The previously unreported ^{13}C NMR data are included in Table I. Assignment of the side-chain ^{13}C signals was made with the aid of ^{13}C NMR data for the relevant model paraffins.[39]

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Registry No. **1**, 118112-67-7; **1** acetate, 118112-68-8; **2**, 118203-79-5; **4**, 82467-98-9; **5**, 118112-69-9; **5** acetate, 118112-73-5; **6**, 118142-17-9; **6** acetate, 118112-71-3; **7**, 118112-70-2; **7** acetate, 118112-72-4; **10**, 105097-81-2; **10** acetate, 105097-84-5.

(39) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.

C-Glycosides. 7.† Stereospecific C-Glycosylation of Aromatic and Heterocyclic Rings

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Stereospecific C-glycosylation of aromatic and heterocyclic rings can be realized by reacting the corresponding organolithium derivatives with benzylated lactones and reducing the so-obtained lactols with triethylsilane in the presence of boron trifluoride etherate at low temperature. Debenzylation proceeds without opening of the ring in pyrano series, but with opening in furano series.

Because of their biological importance, considerable effort has been devoted toward the synthesis of C-glycosides during recent years.[1]

With the goal of devising new and efficient methodologies for the stereocontrolled synthesis of this class of compounds, we are studying the reactivity of several sugar derivatives, diversely activated at the anomeric carbon atom, with a variety of organometallic reagents. Several combinations have already been studied and the results published: glycals with arylpalladium species,[2] peracylated enones[3] and protected 1,2-anhydro sugars[4a] with organocuprates.

We report herein our results concerning the reaction of organolithium derivatives with protected lactones and the reduction of the products so obtained into C-glycosides (Scheme I).

Sugar lactones have previously been employed for that purpose by Kishi et al.[5] to prepare allyl-C-glycosides. In their approach to C-nucleosides, Asbun and Binkley[6] and Ogura et al.[7] effected C–C bond formation in this fashion but were not successful in reduction of the lactol product.

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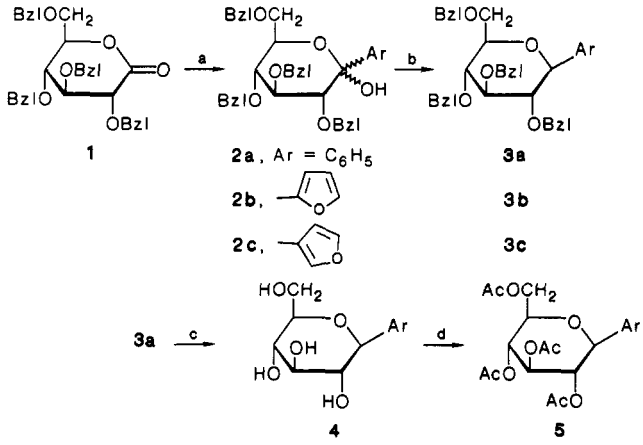
(1) For a recent review, see the special issue of *Carbohydr. Res.* on C-glycoside synthesis: *Carbohydr. Res.* **1987**, *171*.
(2) Czernecki, S.; Dechavanne, V. *Can. J. Chem.* **1983**, *61*(3), 533.
(3) Bellosta, V.; Czernecki, S. *Carbohydr. Res.* **1987**, *171*, 279.
(4) (a) Bellosta, V.; Czernecki, S. *J. Chem. Soc., Chem. Commun.*, in press. (b) Bellosta, V. Thèse, Université P. et M. Curie, Paris, 1987.
(5) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976.
(6) Asbun, W.; Binkley, S. B. *J. Org. Chem.* **1968**, *33*, 140.
(7) Ogura, H.; Takahashi, H. *J. Org. Chem.* **1974**, *39*, 1374.

0022-3263/89/1954-0610$01.50/0

Scheme I[a]



[a] Key: (a) ArLi (1.05 equiv), THF, −78 °C; (b) Et_3SiH/BF_3·Et_2O/MeCN/−40 °C→room temperature; (c) 10% Pd on C/MeOH/H_2; (d) Ac_2O/pyridine.

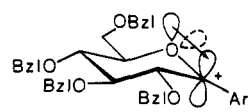
Since very reactive organometallic reagents were employed, stable protective groups (benzyl) were necessary.

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranolactone[8] (**1**) was used as a model compound for examining the stereochemical outcome of the reduction step and verifying that the deprotection by hydrogenolysis would not cleave the O_5–C_1 bond in the resulting C-glycoside **3**.[9]

Reaction of **1** with 1 equiv of phenyllithium in THF (−78 → 20 °C) afforded an α/β mixture of (2,3,4,6-tetra-*O*-benzyl-1-*C*-phenyl)-D-glucopyranose (**2a**) in 85% yield. The reduction of the hemiacetal function of **2a** with triethylsilane in the presence of boron trifluoride etherate[10] (acetonitrile at −40 °C for 1 h) was stereospecific, and the C-glycoside **3a** was isolated in 80% yield. Assignment of stereochemistry was made by examining of the physical constants and spin–spin coupling constants for the ring protons in the 250 MHz ^{1}H NMR spectrum of the tetraacetate **5**, obtained by debenzylation (H_2/Pd–C/MeOH/room temperature) followed by acetylation (Ac_2O/pyridine). The physical constants of **5** were in agreement with the literature data[4b] for the β isomer including the value of 9.7 Hz for $J_{1,2}$.

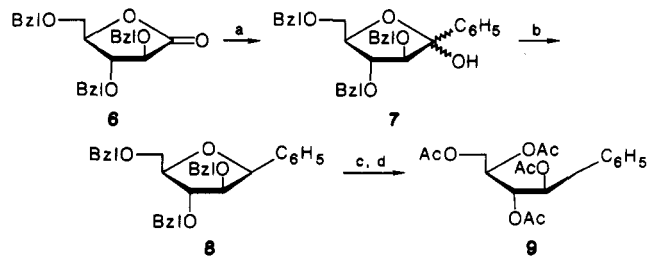
In order to verify the stereospecificity of the reduction step and the absence of the α isomer, hydrogenolysis and acetylation were carried out, without any purification, on crude **3a**. VPC analysis of crude **5** showed only one peak, the retention time of which was identical with that of an authentic sample available in our laboratory.[4b] A mixed injection with the α anomer[4b] gave two well-resolved peaks (see Experimental Section).

The stereospecificity of the reduction may be due to stabilization of the carbenium intermediate by the anomeric effect, favoring hydride attack at the α face.[11]



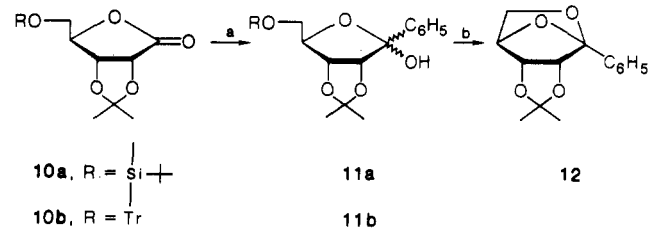
An advantage of our procedure is the fact that the organolithium reagent can be prepared by exchange from the aromatic ring or the corresponding halide allowing a regiospecific C-glycosylation. This was demonstrated by C-glycosylating furan at the 2- and 3-positions by starting respectively from furan and 3-bromofuran. 3-Furyl-C-glycoside subunits are often present in natural compounds, and some of them exhibit interesting biological activities.[12] 2-Furyl-C-glycosides could be useful intermediates in the synthesis of base-modified nucleosides, because the furan ring can be converted into a large number of other heterocyclic systems.[13]

Scheme II[a]



[a] See Scheme I.

Scheme III[a]



[a] See Scheme I.

Reduction of the furan adducts proceeded smoothly at low temperature, affording only one isomer **3b** or **3c**, whose anomeric configurations were also found to be β, since $J_{1,2}$ was 9.7 Hz for **3b** and 10.0 Hz for **3c**. An anomeric mixture of furyl-C-glycosides was obtained by Maeba et al.[14] by reaction of 2,3,5-tri-*O*-benzyl-D-ribofuranosyl bromide with 2-(chloromercurio)furan.

The extension of this methodology for glycosylation of aromatic rings with pentofuranosyl moieties was also studied since it would provide a new route to C-nucleosides when applied to heterocycles.

The same sequence of reactions was performed on *O*-benzyl-protected arabinolactone **6** (Scheme II).

When submitted to catalytic hydrogenation and acetylation, the intermediate **8**[15] was transformed into 1,2,3,4-tetraacetoxy-5-phenyl-(2*R*,3*S*,4*R*)-pentane (**9**). The presence of four singlets ($\delta \simeq 2$ ppm, 12 H) and of an ABX multiplet for two benzylic hydrogens in the ^{1}H NMR spectrum of **9** clearly indicated that the O_4–C_1 bond was cleaved during deprotection. This reduction cleavage of the carbohydrate ring could not be avoided by using other solvents (AcOEt or THF).[16]

In order to circumvent the problem of ring opening in the furano series, other blocking groups, stable to organolithium reagents, were evaluated with the commercially

(8) Kuzuhara, H.; Fletcher, H. G., Jr. *J. Org. Chem.* **1967**, *32*, 2531.
(9) While this paper was in preparation, a similar approach appeared: Kraus, G. A.; Molina, M. T. *J. Org. Chem.* **1988**, *53*, 752.
(10) Frainnet, E.; Esclamadon, C. *C. R. Hebd. Seances Acad. Sci.* **1962**, *254*, 1814.
(11) *Anomeric Effect: Origin and Consequences*; Szarek, W. A., Horton, D., Eds.; American Chemical Society: Washington, DC., 1979; ACS Symposium Series 87.
(12) (a) Kawakami, Y.; Nagai, Y. Nezu, Y.; Sato, T.; Kumi, T.; Kagei, K. *Chem. Pharm. Bull.* **1987**, *35*, 4839. (b) Harde, C.; Bohlman, F. *Tetrahedron* **1988**, *44*(1), 81.
(13) Van der Plas, H. C. *Ring Transformations of Heterocycles*; Academic Press: New York, 1973; Vol. 1, p 151.
(14) Maeba, I.; Iwata, K.; Usami, F.; Furukawa, H. *J. Org. Chem.* **1983**, *48*, 2998.
(15) One isomer was isolated in 85% yield, but the anomeric configuration was not firmly established; it is written as β for convenience of reading.
(16) Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1983**, *48*, 4144.

available ribonolactone (Scheme III).

Reaction of **10a** and **10b** with phenyllithium afforded the hemiacetals **11a** and **11b** (90% and 81% yield, respectively). Reduction of these compounds as above led to the same product **12**, the stucture of which was determined by spectroscopic methods. In this case, with acid-labile protective groups at C-5, a cyclization is possible, and it took place faster than the reduction. Such a propensity to form 1,5-anhydro derivatives from ribofuranosyl compounds has been already observed.[17]

The procedure described herein constitutes a very convenient method for the C-glycosylation of aromatic and heterocyclic rings with pyranosyl moieties. Further studies with other protective groups are currently in progress in our laboratory to extend it to the furano series.

Experimental Section

General Methods. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. IR spectra (film, KBr disk) were recorded on a Unicam SP3-300 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ or C_6D_6, using Me_4Si as internal standard, at 90 MHz with a Varian EM-390 instrument or at 250 MHz with a Brucker apparatus operating in the FT mode. Gas chromatographic analysis was carried out on a Girdel 75 FD 2 instrument equipped with flame-ionization detectors and fitted with a 1-m 3% w/w phenyldiethanolamine succinate (PDEAS) on Chromosorb W AW DMCS column at 155 °C. Analytical TLC was performed on precoated alumina plates (E. Merck silica gel $60F_{254}$). For flash chromatography, E. Merck silica gel 60 (230–400 mesh) and anhydrous solvents were used. Mass spectra (MS) were obtained on a Nermag R10-10 spectrometer using chemical ionization (NH_3).

General Procedure. (2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)benzene (5). The following preparation illustrates the typical procedure.

Arylation. Lactone 1[8] (1.08 g, 2 mmol) was dissolved in 5 mL of THF, and the mixture was cooled to −78 °C under argon. Phenyllithium (1.25 mL of 1.7 M, 2.1 mmol) was then added, and the mixture was stirred for 2 h at −78 °C. The temperature was then allowed to rise to room temperature while the mixture was further stirred for 2 h. After hydrolysis, extraction with ether, and drying over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure, yielding 1.056 g (85.7% yield) of **2a** as a colorless oil, pure by TLC (R_f 0.45 with ether–pentane, 2:1): IR 3400 (br), 3090, 3060, 3030, 2970, 2920, 2860, 1595, 1450, 1360, 1210, 1090, 1025, 910, 735, and 695 cm^{-1}.

Reduction. To a solution of 616 mg (1 mmol) of **2a** in 10 mL of acetonitrile, cooled to −40 °C, was added 320 μL (2 molar equiv) of triethylsilane and 140 μL (1 molar equiv) of $BF_3{\cdot}Et_2O$. After the solution had been stirred at −40 °C for 1 h, 1 mL of a saturated aqueous solution of K_2CO_3 was added, and the mixture was stirred for 1 h at room temperature. The aqueous layer was extracted with ether, and the organic phase was dried over anhydrous Mg_2SO_4. Evaporation of the solvent afforded 540 mg of a yellowish oil, which was purified by column chromatography on silica (pentane–ether), yielding 480 mg (0.8 mmol; 80% yield) of pure **3a**: $[\alpha]^{20}_D$ 29.4° (*c* 1.5, $CHCl_3$); IR 3090, 3060, 3030, 2900, 2860, 1600, 1580, 1490, 1450, 1360, 1210, 1090, 1065, 1030, 1000, 910, 735, and 695 cm^{-1}. Anal. Calcd for $C_{40}H_{40}O_5$: C, 79.97; H, 6.71. Found: C, 79.59; H, 6.82.

Debenzylation. Compound **3a** (120 mg, 0.2 mmol) was dissolved in 5 mL of methanol, and 20 mg of 10% palladium on charcoal was added. The mixture was vigorously stirred in a hydrogenation apparatus. After completion of the reaction (6 h), the catalyst was filtered off and the solvent was evaporated, yielding 44 mg (0.18 mmol; 90% yield) of chromatographically homogeneous product **4a** (R_f 0.22 with AcOEt): mp 49–50 °C; $[\alpha]^{20}_D$ 30.3° (*c* 1.9, CH_3OH); ^1H NMR [$(CD_3)_2SO$] δ 3.17 (dd, 1 H, H-2, $J_{1,2}$ = 9.3 Hz, $J_{2,3}$ = 10.1 Hz), 3.20–3.29 (m, 4 H, H-3, H-4, H-5, OH), 3.46 (dd, 1 H, H-6, $J_{5,6}$ = 5.4 Hz, $J_{6,6'}$ = 11.6 Hz), 3.70 (dd + br s, 2 H, H-6′, OH, $J_{5,6'}$ = 1.3 Hz), 4.01 (d, 1 H, H-1), 4.83 (br s, 3 H, OH), 7.06–7.30 (m, 5 H, aromatic H).

Acetylation. The hydroxyl groups were acetylated by using a classical procedure (Ac_2O–pyridine), giving 62 mg (0.15 mmol; 84% yield) of pure **5**. The crude product was analyzed by VPC on a 5% PDEAS on 45–50 mesh Chromosorb W NAW column (1 m × 0.375 in.) at 155 °C. The retention time of the observed peak was 23.8 min, identical with that of an authentic sample available in our laboratory.[4b] A mixed injection with the α isomer gave two well-resolved peaks (retention time of α: 19.8 min): $[\alpha]^{20}_D$ −20° (*c* 1.1, $CHCl_3$); mp 156–157 °C. Anal. Calcd for $C_{20}H_{24}O_9$: C, 58.82; H, 5.88. Found: C, 58.88; H, 5.84.

2′-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)furan (3b) was obtained in 77% yield (454 mg) by the same sequence, by condensing of 2-furyllithium[18] with **1** (540 mg; 1 mmol) and was characterized as follows: mp 111 °C;[19] $[\alpha]^{20}_D$ 10.42°[19] (*c* 1.2, CH_2Cl_2); MS, *m/z* (relative abundance) 591 (M + 1, 45), 561 (M − HCO, 100); ^1H NMR (C_6D_6) δ 3.47 (ddd, 1 H, H-5, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 3.8 Hz, $J_{5,6'}$ = 5.6 Hz), 3.56 (m, 2 H, H-6, H-6′), 3.62–3.95 (m, 2 H, H-3, H-4), 3.97 (t, 1 H, H-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.2 Hz), 4.10–5.00 (8 d, 8 H, benzylic CH_2), 4.30 (d, 1 H, H-1), 6.05 (dd, 1 H, H-4′, $J_{3',4'}$ = 3.2 Hz, $J_{4',5'}$ = 1.8 Hz), 6.25 (dd, 1 H, H-3′), $J_{3',5'}$ = 0.7 Hz), 7.05–7.37 (m, 21 H, aromatic H and H-5′). Anal. Calcd for $C_{38}H_{38}O_6$: C, 77.29; H, 6.44. Found: C, 77.32; H, 6.54.

3′-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)furan (3c) was similarly obtained in 30% yield (177 mg) by condensation of 3-furyllithium[20] with **1** (540 mg; 1 mmol) and characterized as follows: mp 140–141 °C; $[\alpha]^{20}_D$ −9.4° (*c* 0.1, $CHCl_3$); MS, *m/z* (relative abundance) 591 (M + 1, 4), 561 (M − HCO, 100); ^1H NMR (C_6D_6) δ 3.21 (dd, 1 H, H-2, $J_{1,2}$ = 10 Hz, $J_{2,3}$ = 9.3 Hz), 3.30–3.42 (m, 2 H, H-6, H-6′, $J_{6,6'}$ = 11.6 Hz), 3.43 (dd, 1 H, H-4, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 10 Hz), 4.02 (t, 1 H, H-3), 4.07 (m, 1 H, H-5), 4.50–5.02 (8 d, 8 H, benzylic H), 4.96 (d, 1 H, H-1), 5.26 (d, 1 H, H-4′, $J_{4',5'}$ = 3.4 Hz), 7.16–7.20 (m, 2 H, H-2′, H-5′), 7.28–7.40 (m, 20 H, aromatic H). Anal. Calcd for $C_{38}H_{38}O_6$: C, 77.29; H, 6.44. Found: C, 77.18; H, 6.31.

1,2,3,4-Tetraacetoxy-5-phenyl-(2*R*,3*S*,4*R*)-pentane (9) was obtained from 2,3,5-tri-*O*-benzyl-D-arabinofuranolactone (**6**)[21] (836 mg; 2 mmol) in 58% overall yield (306 mg) by using the phenylation/reduction/hydrogenolysis/acetylation sequence already described for the preparation of **5** and was characterized as follows: mp 106 °C; $[\alpha]^{20}_D$ 43.7° (*c* 1.2, $CHCl_3$); ^1H NMR (CCl_4) δ 1.95, 2.02, 2.04, 2.18 (4 s, 12 H, 4 CH_3CO), 2.76 (dd, 1 H, H-5, $J_{5,5'}$ = 13.5 Hz, $J_{4,5}$ = 8.1 Hz), 2.83 (dd, 1 H, H-5′, $J_{4,5'}$ = 5.3 Hz), 4.12 (dd, 1 H, H-1, $J_{1,2}$ = 5.1 Hz, $J_{1,1'}$ = 12.5 Hz), 4.23 (dd, 1 H, H-1′, $J_{1',2}$ = 2.8 Hz), 5.14 (ddd, 1 H, H-2, $J_{2,3}$ = 8 Hz), 5.32 (dd, 1 H, H-3, $J_{3,4}$ = 2.6 Hz), 5.39 (dd, 1 H, H-4), 7.08–7.27 (m, 5 H, aromatic H). Anal. Calcd for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36. Found: C, 60.00; H, 6.32.

1,5-Anhydro-2,3-*O*-isopropylidene-1-*C*-phenyl-β-D-ribofuranose (12) was obained from 5-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-ribofuranolactone[22] (**10a**) (604 mg; 2 mmol) by using the same phenylation/reduction sequence in 51% overall yield (253 mg) and characterized as follows: mp 118 °C; $[\alpha]^{20}_D$ −87.9° (*c* 1.4, $CHCl_3$); MS, *m/z* (relative abundance) 249 (M + 1, 100), 105 (M − PhCO, 70); ^1H NMR (CCl_4) δ 1.22, 1.42 (2 s, 6 H, 2 CH_3), 3.46 (d, 1 H, H-2, $J_{2,3}$ = 7.5 Hz), 3.60 (dd, 1 H, H-3, $J_{3,4}$ = 3.7 Hz), 4.29, 4.44 (2 d, 2 H, H-5, H-5′, $J_{5,5'}$ = 5.5 Hz, $J_{4,5}$ = $J_{4,5'}$ = 0 Hz), 4.75 (d, 1 H, H-4), 7.40–7.55 (m, 5 H, aromatic H). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.68; H, 6.54.

Preparation of 12 from 5-*O*-trityl-2,3-*O*-isopropylidene-D-ribofuranolactone (10b)[23] (860 mg; 2 mmol) was carried out by using the same technique, in 36% overall yield (178 mg).

(17) (a) Barker, G. R.; Lock, M. V. *J. Chem. Soc.* **1950**, 23. (b) Vis, E.; Fletcher, H. G., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 1182. (c) Kraska, B.; Lichtentaler, F. W. *Chem. Ber.* **1981**, *114*, 1636. (d) Izquierdo Cubero, I.; Garcia Poza, D. *Carbohydr. Res.* **1985**, *138*, 139.

(18) Ramanathan, V.; Levine, R. *J. Org. Chem.* **1962**, *27*, 1216.

(19) Grynkiewicz, G.; BeMiller, J. N. *Carbohydr. Res.* **1984**, *131*, 273. The differences in physical constants of **3b** between our results and those reported in this paper, mp 94 °C and $[\alpha]^{20}_D$ 71° (*c* 1, CH_2Cl_2), are likely due to an incorrect assignment of anomeric configuration by the authors.

(20) Gilman, H.; Melstrom, D. S. *J. Am. Chem. Soc.* **1948**, *70*, 1655.

(21) Rabinsohn, Y.; Fletcher, H. G., Jr. *J. Org. Chem.* **1967**, *32*, 3452.

(22) Cheng, J. C.; Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1985**, *50*, 2778.

(23) Camps, P.; Cardellach, J.; Font, J.; Ortuño, R. M.; Ponsati, O. *Tetrahedron* **1982**, *38*(15), 2395.