Carbohydrate Research, 248 (1993) 107–118
Elsevier Science Publishers B.V., Amsterdam

Synthesis of a terminal A-B-C disaccharide fragment of flambamycin, curamycin, and avilamycin

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(Received December 22nd, 1992; accepted April 16th, 1993)

ABSTRACT

Methyl 2,6-dideoxy-4-*O*-[2,6-dideoxy-4-*O*-(3,5-dichloro-4-hydroxy-2-methoxy-6-methylbenzoyl)-β-D-*arabino*-hexopyranosyl]-α-D-*arabino*-hexopyranoside (**25**) corresponds to an A-B-C disaccharide subunit of the title antibiotics. It was synthesized from suitably protected monosaccharide and aromatic precursors. The readily available 4,6-*O*-benzylidene-1,2-*O*-(*R*)-propylidene-α-D-glucopyranose was converted in six steps into 2-*O*-acetyl-4-*O*-benzoyl-3-*O*-benzyl-6-deoxy-α-D-glucopyranosyl bromide, which was condensed with methyl 3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside in the presence of mercury(II) cyanide. Methyl 4-*O*-(2-*O*-acetyl-4-*O*-benzoyl-3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside was converted either into methyl 2,6-dideoxy-4-*O*-(6-deoxy-β-D-glucopyranosyl)-α-D-*arabino*-hexopyranoside by removal of the protective groups or into methyl 3-*O*-benzyl-4-*O*-(3-*O*-benzyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-α-D-*arabino*-hexopyranoside (**22**) by selective deacetylation, Barton deoxygenation, and Zemplén debenzoylation. Disaccharide **22** was deprotonated with butyllithium and treated with 4-benzyloxy-3,5-dichloro-2-methoxy-6-methylbenzoyl chloride to give the title compound **25** after hydrogenolysis.

INTRODUCTION

Flambamycin[1] (**1**), avilamycin A[2] (**2**), and curamycin A[3] (**3**) are oligosaccharides which belong to the orthosomycin[4,5] group of antibiotics. They are produced by *Streptomyces hygroscopicus* DS 23230, *S. viridochromogenes* ETH 23575, and *S. curacoi*, respectively, and exhibit antibacterial activity mainly against Gram-positive strains[1–3,5]; furthermore, flambamycin posseses a low toxicity (LD_{50} = 2500 mg/kg s.c.)[1]. From a structural point of view, spiroortholactone linkages are the common feature of the orthosomycin antibiotics, and it has been shown that the antibiotic activity is associated both with the phenolic hydroxyl group[3] and the central C-D ortho ester[5]. Thus, much effort has concentrated on the synthesis of larger parts of these molecules, including A-B[6,7], B-C[8,9], B-C-D-E[10], E-F[11], and

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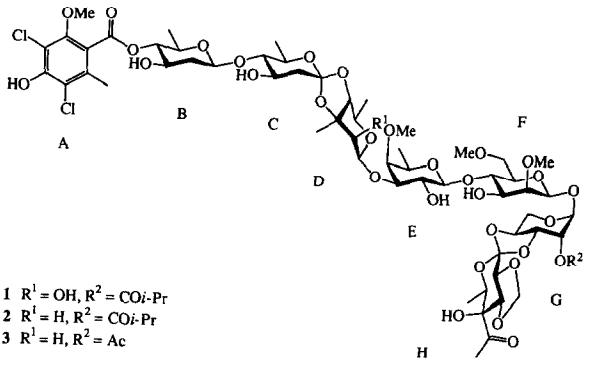


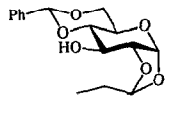
F-G fragments[12]. We report here on the synthesis of an A-B-C fragment of **1–3**, namely methyl 4-*O*-(4-*O*-dichloroisoeverninoyl-β-D-olivosyl)-α-D-olivoside (**25**).

The stereoselective synthesis of 2′-deoxy-β-glycosides like **25** still remains an outstanding problem of carbohydrate chemistry[13], since glycosylation of 2-deoxy-glycosyl donors often leads to anomeric mixtures[14,15]. In the reaction of 2-bromo-2-deoxy-[8,15,16] and 2-arylthio-2-deoxy-glucosyl donors[17], a higher proportion of β-glycosides can be obtained, but chromatographic separations are nevertheless necessary. Recently, glycals have been glycosylated with fairly good β-selectivity after conversion into 1,2-anhydro sugars[18] or by activation with arylbis(arylthio)sulfonium salts[19]. Stereospecific glycosidations can be achieved by the neighbouring group assistance of an ester protective group at HO-2 (e.g., ref 20) and, after selective deoxygenation, the desired deoxysaccharides are accessible[21]. We have used this approach for the synthesis of **25**.

RESULTS AND DISCUSSION

4,6-*O*-Benzylidene-1,2-*O*-(*R*)-propylidene-α-D-glucopyranose (**4**) has been prepared by Collins et al.[22] from D-glucose by Fischer glycosylation with allyl alcohol, followed by benzylidenation, isomerization to the propenyl glycoside, and acid-catalyzed cyclization; **4** was obtained crystalline as one single diastereomer. We chose this compound as starting material and first analyzed its stereochemistry. Thus, the derivative **7** (see below) was subjected to ^{1}H NOE measurements. Irradiation of the acetal proton (H-1′) resulted in an enhancement of H-1 (3%), H-2 (7%), and the ethyl protons (H-2′, 3%; H-3′, 1%), and irradiation of H-3 in an NOE effect at H-2 (8%), H-4 (6%), and H-5 (3%), but not at H-1′. Consequently, all protons of the dioxolane ring are *syn*-oriented and compounds **4–8** have the relative *endo* and absolute *R* configuration at the acetal carbon.

The benzylidene acetal **4** smoothly underwent Hanessian cleavage[23] to give the bromo-benzoate **5** (80%), which was hydrogenolytically reduced to the 6-deoxy



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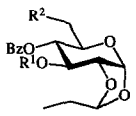
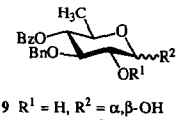
pNBz = 4-Nitrobenzoyl



5 R^1 = H, R^2 = Br
6 R^1 = R^2 = H
7 R^1 = Bz, R^2 = H
8 R^1 = Bn, R^2 = H



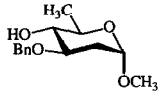
9 R^1 = H, R^2 = α,β-OH
10 R^1 = Ac, R^2 = α,β-OAc
11 R^1 = Ac, R^2 = α-Br
12 R^1 = Ac, R^2 = α,β-OpNBz
13 R^1 = Ac,
R^2 = α-OC(NH)CCl_3

sugar **6** in a yield of 83%. Conventional acylation produced the dibenzoate **7** already mentioned. Silver(I) oxide[24]-mediated benzylation of **6** gave the benzyl ether **8**. This reaction proceeded best with benzene as solvent, whereas we observed ester cleavage and double alkylation when running the reaction in *N*,*N*-dimethylformamide. Acid hydrolysis of **8** gave a quantitative yield of 4-*O*-benzoyl-3-*O*-benzyl-D-quinovose (**9**). Acetylation of **9** gave the diacetate **10** (97%) which, upon treatment with titanium(IV) bromide[25], produced the glycosyl bromide **11** in a yield of 85%. To avoid benzyl ether cleavage, the reaction time had to be carefully controlled.

By applying standard procedures[7,26,27], we also synthesized the glycosyl donors **12** and **13** from **10**, but any attempt to achieve glycosylation with the acceptor methyl 3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside[6,28] (**14**) failed either by activation of **10** and **12** with trimethylsilyl triflate[7,29] or using **13** in the presence of boron trifluoride etherate[27].

On the other hand, **14** was successfully glycosylated by reaction with the glycosyl bromide **11** under modified Königs–Knorr[30] conditions. Best results were achieved by treating a dichloromethane solution of **14** with 2.5 mol equiv of **11** in the presence of the Helferich catalyst[31] mercury(II) cyanide and 4A molecular sieves at room temperature. Previous to work-up, the mixture was treated with hexamethyldisilazane, chloro(trimethyl)silane, and pyridine to silylate residual acceptor **14** and simplify the purification. Disaccharide **15** was thus obtained in 78% yield and anomerically pure. Its β-(1 → 4)-interglycosidic linkage could be proved by the large proton coupling constant, $^3J_{1',2'} = 8.1$ Hz.

We then tried selectively to deacylate the acetate group of **15** without affecting the benzoate. Methods for this purpose include treatment with hydrazine[32], potassium cyanide in alcoholic solvents[33], or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene or methanol[34]. In our hands, solely the last reagent caused predominant acetate cleavage, but even in this case the alcohol **16** was obtained in only 42% yield, together with an approximately equal amount of **17** and **18**. By hydrogenolysis, **18** was converted into methyl 4-*O*-β-D-quinovosyl-α-D-olivoside (**19**), which has already been prepared by deoxygenation of cellobiose[35]. On the other hand, **16** gave the phenyl thionocarbonate **20** upon treatment with *O*-phenyl chlorothioformate (65%). Tributylstannane reduction[36] (to **21**, 70%) followed by Zemplén deacylation produced the tetradeoxydisaccharide **22** in 77% yield.



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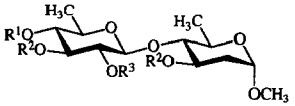
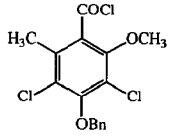


15 R^1 = Bz, R^2 = Bn, R^3 = Ac
16 R^1 = Bz, R^2 = Bn, R^3 = H
17 R^1 = H, R^2 = Bn, R^3 = Ac
18 R^1 = R^3 = H, R^2 = Bn
19 R^1 = R^2 = R^3 = H
20 R^1 = Bz, R^2 = Bn, R^3 = C(S)OPh



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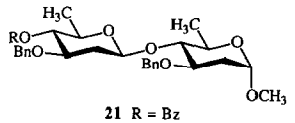
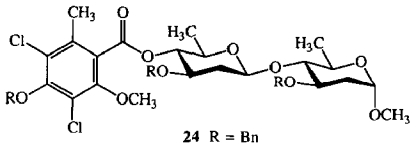


21 R = Bz
22 R = H



24 R = Bn
25 R = H

Sequential treatment of **22** with butyllithium and the acyl chloride[7] **23** furnished the ester **24** (50%), which was finally converted into the title compound **25** by catalytic hydrogenolysis (81%).

In conclusion, the work described here and that reported previously[6,7] present a methodology for he synthesis of orthosomycin fragments containing the dichloroisoeverninic acid ester moiety, which thus fulfil one of the structural requirements for antibiotic activity, the presence of the phenolic hydroxyl group.

EXPERIMENTAL

General methods.—Melting points were determined with a Büchi 510 melting-point apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. NMR spectra were recorded with a Varian VXR 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or VXR 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) instrument. IR spectra were recorded with a Perkin–Elmer FT-IR 1250 spectrophotometer. EIMS were obtained with a Varian MAT 212 spectrometer (70 eV, 1 mA). TLC was performed on Merck Kieselgel 60 F_{254} (detection by charring with 1:1:20 anisaldehyde–H_2SO_4–EtOH) and column chromatography on silica gel (Merck Kieselgel 60). Solvents were dried prior to use. Solutions were concentrated under reduced pressure and at a bath temperature not exceeding 40°C. For optical rotations and elementary analyses, substances were dried in high vacuum (room temperature, 10^{-4} Pa). The following abbreviations are used for solvent

mixtures: 2:3 cyclohexane–EtOAc, eluent *A*; 1:1 cyclohexane–EtOAc, eluent *B*; 3:2 cyclohexane–EtOAc, eluent *C*; 2:1 cyclohexane–EtOAc, eluent *D*, 3:1 cyclohexane–EtOAc, eluent *E*; 4:1 cyclohexane–EtOAc, eluent *F*; 5:1 cyclohexane–EtOAc, eluent *G*; 15:1 cyclohexane–EtOAc, eluent *H*; 30:1 cyclohexane–EtOAc, eluent *I*; 8:1 EtOAc–*i*-PrOH, eluent *J*.

4-O-Benzoyl-6-bromo-6-deoxy-1,2-O-(R)-propylidene-α-D-glucopyranose (**5**).—A mixture of **4**[22] (15 g, 49 mmol), *N*-bromosuccinimide (10.4 g, 58 mmol), and $BaCO_3$ (29 g, 147 mmol) in CCl_4 (0.5 L) was refluxed with stirring until the colour faded (~ 1 h), filtered, and evaporated. The residue was filtered with eluent *D* upon silica gel to remove polar impurities. Evaporation gave **5** [15 g, 80%; R_f 0.70 (eluent *B*)]. An analytical sample of syrupy **5**, obtained by column chromatography (eluent *C*), had $[\alpha]_D^{22}$ +43.3° (*c* 1, $CHCl_3$); ν_{max}^{liquid} 3480 (OH), 1720 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz): δ 1.06 (t, 3 H, $J_{2',3'}$ 7.6 Hz, H-3'), 1.85 (dq, 2 H, $J_{1',2'}$ 4.9 Hz, H-2'), 3.49 (br s, 1 H, OH), 3.55 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 11.1 Hz, H-6a), 3.68 (dd, 1 H, $J_{5,6b}$ 3.0 Hz, H-6b), 4.16 (ddd, 1 H, $J_{1,2}$ 5.0, $J_{2,3}$ 2.5, $J_{2,4}$ 0.8 Hz, H-2), 4.23 (br s, 1 H, $J_{3,4}$ 2.3 Hz, H-3), 4.32 (ddd, 1 H, $J_{4,5}$ 9.1 Hz, H-5), 4.89 (t, 1 H, H-1'), 4.90 (ddd, 1 H, H-4), 5.69 (d, 1 H, H-1), 7.43–8.06 (m, 5 H, Ph); ^{13}C (75 MHz): δ 8.16 (C-3'), 26.82 (C-2'), 33.13 (C-6), 67.35 (C-5), 70.28 (C-3), 75.87, 76.24 (C-2,4), 96.32 (C-1), 104.75 (C-1'), 128.60, 129.85 (Bz-2,3), 129.05 (Bz-1), 133.77 (Bz-4), 166.78 (CO_2). Mass spectrum; *m/z* 388, 386 (M^+), 359, 357 ($M^+ - C_2H_5$). Anal. Calcd for $C_{16}H_{19}BrO_6$ (387.22): C, 49.63; H, 4.95. Found: C, 49.84; H, 5.01.

4-O-Benzoyl-6-deoxy-1,2-O-(R)-propylidene-α-D-glucopyranose (**6**).—A suspension of **5** (15 g, 39 mmol), Et_3N (11 mL, 79 mmol), and Raney nickel (prepared from 40 g of NiAl alloy) in *i*-PrOH (0.3 L) was hydrogenated for 16 h with vigorous shaking (10^5 Pa H_2). The catalyst was filtered off and the solution concentrated. The residue was treated with water and the aqueous phase extracted with ether. The extract was washed neutral with water, dried ($MgSO_4$), filtered, and concentrated to give syrupy **6** [9.9 g, 83%; R_f 0.69 (eluent *B*)]. An analytical sample of **6**, obtained by column chromatography (eluent *C*), had $[\alpha]_D^{22}$ +73.3° (*c* 0.9, $CHCl_3$); ν_{max}^{liquid} 3475 (OH), 1720 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz): δ 1.05 (t, 3 H, $J_{2',3'}$ 7.6 Hz, H-3'), 1.34 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.83 (dq, 2 H, $J_{1',2'}$ 4.9 Hz, H-2'), 3.51 (br s, 1 H, OH), 4.10 (ddd, 1 H, $J_{1,2}$ 5.0, $J_{2,3}$ 2.7, $J_{2,4}$ 0.7 Hz, H-2), 4.14 (t, 1 H, $J_{3,4}$ 3.3 Hz, H-3), 4.19 (dq, 1 H, $J_{4,5}$ 9.7 Hz, H-5), 4.57 (ddd, 1 H, H-4), 4.86 (t, 1 H, H-1'), 5.60 (d, 1 H, H-1), 7.42–8.07 (m, 5 H, Ph); ^{13}C (75 MHz): δ 8.23 (C-3'), 18.83 (C-6), 26.93 (C-2'), 64.15 (C-5), 71.23 (C-3), 76.74 (C-2), 79.91 (C-4), 96.38 (C-1), 104.22 (C-1'), 128.52, 129.80 (Bz-2,3), 129.37 (Bz-1), 133.57 (Bz-4), 167.25 (CO_2). Mass spectrum: *m/z* 308 (M^+), 279 ($M^+ - C_2H_5$). Anal. Calcd for $C_{16}H_{20}O_6$ (308.33): C, 62.33; H, 6.54. Found: C, 62.30; H, 6.64.

3,4-Di-O-benzoyl-6-deoxy-1,2-O-(R)-propylidene-α-D-glucopyranose (**7**).—A solution of **6** (0.50 g, 1.6 mmol) and benzoyl chloride (0.30 g, 2.1 mmol) in CH_2Cl_2 (2.5 mL) and pyridine (2.5 mL) was stirred for 2 h. Water was added and the mixture extracted with ether. The extract was washed with aq $NaHCO_3$ and water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (eluent *G*)

gave **7** [0.46 g, 69%; R_f 0.58 (eluent *D*)] as a colourless syrup, $[\alpha]_D^{22}$ −53.5° (*c* 1, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1725 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (500 MHz): δ 1.08 (t, 3 H, $J_{2',3'}$ 7.55 Hz, H-3′), 1.34 (d, 3 H, $J_{5,6}$ 6.33 Hz, H-6), 1.89 (dq, 2 H, $J_{1',2'}$ 4.96 Hz, H-2′), 4.17 (ddd, 1 H, $J_{1,2}$ 5.13, $J_{2,3}$ 3.33, $J_{2,4}$ 0.88 Hz, H-2), 4.22 (dq, 1 H, $J_{4,5}$ 9.23 Hz, H-5), 4.92 (t, 1 H, H-1′), 5.10 (ddd, 1 H, $J_{3,4}$ 3.40 Hz, H-4), 5.54 (t, 1 H, H-3), 5.62 (d, 1 H, H-1), 7.40–8.04 (m, 10 H, Ph); NOE experiment: irradiation of H-1′: 2.8% H-1, 7.3% H-2, 2.6% H-2′, 0.7% H-3′; irradiation of H-3: 8% H-2, 6% H-4, 3% H-5; ^{13}C (75 MHz): δ 8.17 (C-3′), 18.73 (C-6), 26.95 (C-2′), 65.08 (C-5), 71.51, 74.06, 74.30 (C-2,3,4), 96.69 (C-1), 104.75 (C-1′), 128.41, 128.42, 129.84, 129.92 (Bz-2,3), 129.28, 129.46 (Bz-1), 133.33, 133.40 (Bz-4), 165.04, 165.47 (CO_2). Mass spectrum: *m/z* 411 ($M^+ - H$), 383 ($M^+ - C_2H_5$). Anal. Calcd for $C_{23}H_{24}O_7$ (412.44): C, 66.98; H, 5.87. Found: C, 66.92; H, 5.89.

*4-O-Benzoyl-3-O-benzyl-6-deoxy-1,2-O-(*R*)-propylidene-α-*D*-glucopyranose* (**8**).—A mixture of **6** (13.0 g, 39 mmol), benzyl bromide (18 mL), silver(I) oxide[24] (24 g), and benzene (0.15 L) was stirred for 1 day in the dark. The silver salts were filtered off, the solution evaporated, and the residue placed on 150 g of silica gel. Elution with solvent *I* removed nonpolar impurities and elution with solvent *H* gave syrupy **8** [12.8 g, 76%; R_f 0.55 (eluent *F*)], $[\alpha]_D^{22}$ +39.3° (*c* 1.1, $CHCl_3$); ν_{max}^{liquid} 1725 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz): δ 1.05 (t, 3 H, $J_{2',3'}$ 7.6 Hz, H-3′), 1.31 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.84 (dq, 2 H, $J_{1',2'}$ 5.0 Hz, H-2′), 3.87 (t, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 3.1 Hz, H-3), 4.09 (ddd, 1 H, $J_{1,2}$ 5.2, $J_{2,4}$ 0.9 Hz, H-2), 4.13 (dq, 1 H, $J_{4,5}$ 8.9 Hz, H-5), 4.73, 4.83 (2 d, 2 H, *J* 12.1 Hz, CH_2Ph), 4.89 (t, 1 H, H-1′), 5.04 (ddd, 1 H, H-4), 5.59 (d, 1 H, H-1), 7.22–8.05 (m, 10 H, Ph); ^{13}C (75 MHz): δ 8.21 (C-3′), 18.95 (C-6), 26.99 (C-2′), 65.06 (C-5), 71.70 (*C*H_2Ph), 74.29, 75.34, 76.27 (C-2,3,4), 96.89 (C-1), 104.50 (C-1′), 127.75 (Bn-4), 127.94, 128.33, 128.42, 129.74 (Ph-2,3), 129.87 (Bz-1), 133.25 (Bz-4), 137.64 (Bn-1), 165.73 (CO_2). Mass spectrum: *m/z* 398 (M^+), 369 ($M^+ - C_2H_5$). Anal. Calcd for $C_{23}H_{26}O_6$ (398.45): C, 69.33; H, 6.58. Found: C, 69.37; H, 6.79.

*4-O-Benzoyl-3-O-benzyl-6-deoxy-α,β-*D*-glucopyranose* (**9**).—A solution of **8** (12.0 g, 30 mmol) in 10% H_2SO_4 (60 mL) and THF (240 mL) was refluxed for 3 days, concentrated, treated with water, and extracted with CH_2Cl_2. The extract was washed with aq $NaHCO_3$ and then aq NaCl, dried ($MgSO_4$), filtered, and concentrated; **9** [10.7 g, 99%; R_f 0.31 (eluent *B*)] was obtained as a colourless solid. Crystallization from EtOAc produced the pure β anomer, mp 141.5–142.5°C, $[\alpha]_D^{22}$ −65.0° (initial) → −39.9° (42 h, *c* 1, MeOH); ν_{max}^{KBr} 3425 (OH), 1720 cm^{-1} (C=O). NMR data (CD_3OD): ^1H (300 MHz), α anomer: δ 1.12 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 3.68 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.5 Hz, H-2), 3.95 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.19 (dq, 1 H, $J_{4,5}$ 9.8 Hz, H-5), 4.60, 4.82 (2 d, 2 H, *J* 11 Hz, CH_2Ph), 4.90 (t, 1 H, H-4), 5.12 (d, 1 H, H-1), 7.02–8.00 (m, 10 H, Ph); β anomer: δ 1.18 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 3.45 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 9.1 Hz, H-2), 3.68 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.69 (dq, 1 H, $J_{4,5}$ 9.6 Hz, H-5), 4.60 (d, 1 H, H-1), 4.62, 4.84 (2 d, 2 H, *J* 11.5 Hz, CH_2Ph), 4.95 (t, 1 H, H-4), 7.02–7.99 (m, 10 H, Ph); ^{13}C (125 MHz), α anomer: δ 18.04 (C-6), 66.21 (C-5), 74.54 (C-3), 75.95 (*C*H_2Ph), 77.36 (C-4), 80.80 (C-2), 94.07 (C-1),

128.42 (Bn-4), 128.98, 129.04, 129.66, 130.70 (Ph-2,3), 131.24 (Bz-1), 134.44 (Bz-4), 139.77 (Bn-1), 167.26 (CO_2); β anomer: δ 18.06 (C-6), 71.12 (C-5), 75.73 (CH_2Ph), 76.87, 77.10 (C-3,4), 83.37 (C-2), 98.23 (C-1), 128.45 (Bn-4), 128.97, 129.07, 129.67, 130.71 (Ph-2,3), 131.14 (Bz-1), 134.51 (Bz-4), 139.64 (Bn-1), 167.21 (CO_2). Mass spectrum: *m/z* 358 (M^+), 341 ($M^+ - OH$). Anal. Calcd for $C_{20}H_{22}O_6$ (358.39): C, 67.03; H, 6.19. Found: C, 67.08; H, 6.15.

1,2-Di-O-acetyl-4-O-benzoyl-3-O-benzyl-6-deoxy-α,β-D-glucopyranose (**10**).—A solution of **9** (10.0 g, 28 mmol) in CH_2Cl_2 (150 mL) and pyridine (50 mL) was treated with Ac_2O (10.6 mL, 110 mmol) at 0°C. The mixture was stirred overnight at room temperature, treated with iced water, and extracted with ether. The extract was washed with dil H_2SO_4, aq $NaHCO_3$, and water, dried ($MgSO_4$), filtered, and concentrated. Syrupy **10** [12.0 g, 97%; R_f 0.49 and 0.53 (eluent *D*)] was obtained as an approximately equimolar mixture of anomers. The β anomer of **10** was analogously prepared from anomerically pure **9** and had mp 101.5–102°C (from EtOH), $[\alpha]_D^{22}$ −31.9° (*c* 0.5, $CHCl_3$); ν_{max}^{KBr} 1760, 1750, 1720 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz), α anomer: δ 1.24 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 2.00, 2.19 (2 s, 6 H, $COCH_3$), 4.06 (t, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.8 Hz, H-3), 4.07 (dq, 1 H, $J_{4,5}$ 9.7 Hz, H-5), 4.61, 4.65 (2 d, 2 H, *J* 11.8 Hz, CH_2Ph), 5.12 (dd, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 5.17 (t, 1 H, H-4), 6.32 (d, 1 H, H-1), 7.08–8.05 (m, 10 H, Ph); β anomer: δ 1.28 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.98, 2.11 (2 s, 6 H, $COCH_3$), 3.77 (dq, 1 H, $J_{4,5}$ 9.6 Hz, H-5), 3.87 (t, 1 H, $J_{2,3}$ 9.4, $J_{3,4}$ 9.4 Hz, H-3), 4.56, 4.59 (2 d, 2 H, *J* 11.5 Hz, CH_2Ph), 5.19 (t, 1 H, H-4), 5.21 (dd, 1 H, $J_{1,2}$ 8.1 Hz, H-2), 5.70 (d, 1 H, H-1), 7.08–8.03 (m, 10 H, Ph); ^{13}C (75 MHz), α anomer: δ 17.45 (C-6), 20.61, 20.96 ($COCH_3$), 68.48 (C-5), 71.95, 74.93, 76.78 (C-2,3,4), 74.62 (CH_2Ph), 89.61 (C-1), 127.58, 127.60, 128.20, 128.47, 129.75 (Ph-2,3, Bn-4), 129.54 (Bz-1), 133.36 (Bz-4), 137.78 (Bn-1), 165.23, 169.03, 169.61 (CO_2); β anomer: δ 17.41 (C-6), 20.74, 20.91 ($COCH_3$), 71.42 (C-5), 72.02, 74.78 (C-3,4), 74.04 (CH_2Ph), 79.80 (C-2), 92.08 (C-1), 127.74 (Bn-4), 127.85, 128.28, 128.51, 129.76 (Ph-2,3), 129.41 (Bz-1), 133.42 (Bz-4), 137.44 (Bn-1), 165.18, 169.13, 169.40 (CO_2). Mass spectrum: *m/z* 383 ($M^+ - CH_3CO_2$). Anal. Calcd for $C_{24}H_{26}O_8$ (442.46): C, 65.15; H, 5.92. Found: C, 65.49; H, 5.90.

2-O-Acetyl-4-O-benzoyl-3-O-benzyl-6-deoxy-α-D-glucopyranosyl bromide (**11**).—A solution of **10** (7.0 g, 16 mmol) and titanium(IV) bromide (11.6 g, 32 mmol) in CH_2Cl_2 (75 mL) and EtOAc (15 mL) was stirred for 1 h in the dark. Powdered sodium acetate (35 g) and MeCN (200 mL) were added, and the mixture was stirred until it was colourless (~ 1 h). Ether (300 mL) was added and stirring continued for 1 h. The salts were filtered off and the solution concentrated. Ether and solid $NaHCO_3$ were added, and the suspension was stirred for 2 h, when the salts were again filtered off. Activated 4A molecular sieves were added to the clear filtrate and filtered off after 2 h. The solution was concentrated to give **11** (6.2 g, 85%) as a colourless syrup of ca. 95% purity which was immediately used for glycosylation. NMR data ($C_6D_5CD_3$): ^1H (300 MHz): δ 1.09 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6), 1.64 (s, 3 H, $COCH_3$), 4.20 (t, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 9.3 Hz, H-3), 4.22 (dq, 1 H,

$J_{4,5}$ 10.0 Hz, H-5), 4.48, 4.52 (2 d, 2 H, J 11.9 Hz, CH_2Ph), 4.74 (dd, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 5.26 (dd, 1 H, H-4), 6.63 (d, 1 H, H-1), 6.91–7.98 (m, 10 H, Ph); ^{13}C (75 MHz): δ 16.93 (C-6), 20.17 ($COCH_3$), 71.55 (C-5), 73.85, 74.37, 77.85 (C-2,3,4), 74.94 (CH_2Ph), 89.95 (C-1), 127–129 (Bz-1, Ph-2,3, Bn-4), 133.23 (Bz-4), 138.46 (Bn-1), 165.03, 169.13 (CO_2).

Methyl 4-O-(2-O-acetyl-4-O-benzoyl-3-O-benzyl-6-deoxy-β-D-glucopyranosyl)-3-O-benzyl-2,6-dideoxy-α-D-arabino-hexopyranoside (**15**).—With exclusion of light and under dry Ar, a mixture of **14**[6,28] (1.20 g, 4.8 mmol), mercury(II) cyanide (2.4 g, 9.5 mmol), and activated 4A molecular sieves (1 g) in CH_2Cl_2 (20 mL) was stirred for 30 min. A solution of **11** (2.9 g, 6.3 mmol) in CH_2Cl_2 (30 mL), which had been stirred overnight with activated 4A molecular sieves in the dark, was added and stirring continued for 4 h. A second portion of mercury(II) cyanide (2.4 g) and **11** (2.6 g, 5.6 mmol) dissolved in CH_2Cl_2 (30 mL) was added. After 4 h, pyridine (0.5 mL), hexamethyldisilazane (0.5 mL), and chloro(trimethyl)silane (0.1 mL) were added followed by MeOH (1 mL) 15 min later. The mixture was filtered and the filtrate concentrated. Column chromatography (eluent *E*) gave **15** [2.35 g, 78%; R_f 0.42 (eluent *D*)] as a colourless foam, $[\alpha]_D^{22}$ +19.6° (*c* 1, $CHCl_3$); ν_{max}^{KBr} 1755, 1730 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz): δ 1.14, 1.28 (2 d, 6 H, $J_{5,6}$ 6.1, $J_{5',6'}$ 6.1 Hz, H-6,6'), 1.66 (ddd, 1 H, $J_{1,2a}$ 3.6, $J_{2a,2e}$ 13.3, $J_{2a,3}$ 11.3 Hz, H-2*a*), 2.00 (s, 3 H, $COCH_3$), 2.22 (ddd, 1 H, $J_{1,2e}$ 1.4, $J_{2e,3}$ 5.1 Hz, H-2*e*), 3.18 (s, 3 H, OCH_3), 3.34 (dd, 1 H, $J_{3,4}$ 8.4, $J_{4,5}$ 9.3 Hz, H-4), 3.44 (dq, 1 H, $J_{4',5'}$ 9.6 Hz, H-5'), 3.68 (dq, 1 H, H-5), 3.77 (t, 1 H, $J_{2',3'}$ 9.4, $J_{3',4'}$ 9.6 Hz, H-3'), 3.90 (ddd, 1 H, H-3), 4.53, 4.56 (2 d, 2 H, J 11.6 Hz, CH_2Ph), 4.63, 4.72 (2 d, 2 H, J 11.6 Hz, CH_2Ph), 4.70 (br s, 1 H, H-1), 4.79 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1'), 5.12 (dd, 1 H, H-2'), 5.15 (t, 1 H, H-4'), 7.07–8.01 (m, 15 H, Ph); ^{13}C (75 MHz): δ 17.52, 17.96 (C-6,6'), 20.96 ($COCH_3$), 35.54 (C-2), 54.51 (OCH_3), 66.33 (C-5), 70.25 (C-5'), 71.77, 73.56 (CH_2Ph), 73.66, 75.22, 75.64 (C-3,3',4'), 80.16 (C-2'), 84.44 (C-4), 98.04 (C-1), 101.13 (C-1'), 127.13, 127.85, 128.18, 128.19, 128.44, 129.67 (Ph-2,3), 127.26, 127.59 (Bn-4), 129.59 (Bz-1), 133.27 (Bz-4), 137.66, 139.06 (Bn-1), 165.19, 169.14 (CO_2). Mass spectrum: m/z 574 ($M^+ - CH_3COOH$), 543 ($M^+ - C_7H_7$), 383 ([ring B]$^+$). Anal. Calcd for $C_{36}H_{42}O_{10}$ (634.72): C, 68.12; H, 6.67. Found: C, 68.07; H, 6.61.

Methyl-4-O-(4-O-benzoyl-3-O-benzyl-6-deoxy-β-D-glucopyranosyl)-3-O-benzyl-2,6-dideoxy-α-D-arabino-hexopyranoside (**16**).—A solution of **15** (1.40 g, 2.2 mmol) and 1.8-diazabicyclo[5.4.0]undec-7-ene (2.35 g, 15.4 mmol) in benzene (20 mL) and MeOH (20 mL) was stirred for 20–22 h, until the conversion was complete (TLC). Water was added and the solution extracted with ether. The extract was washed with water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (eluent *F*) gave at first **16** [0.55 g, 42%; R_f 0.38 (eluent *D*)] and then a mixture of **17** and **18** [0.45 g; R_f 0.22–0.28 (eluent *D*)]; **16** was a colourless glass and had $[\alpha]_D^{22}$ +12.6° (*c* 1.8, $CHCl_3$); ν_{max}^{KBr} 3445 (OH), 1730 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz): δ 1.17, 1.37 (2 d, 6 H, $J_{5,6}$ 6.1, $J_{5',6'}$ 6.1 Hz, H-6,6'), 1.69 (ddd, 1 H, $J_{1,2a}$ 3.6, $J_{2a,2e}$ 13.0, $J_{2a,3}$ 11.3 Hz, H-2*a*), 2.30 (ddd, 1 H, $J_{1,2e}$ 0.9, $J_{2e,3}$ 4.9 Hz, H-2*e*), 3.06 (br s, 1 H, OH), 3.31 (s, 3 H, OCH_3), 3.50 (t, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 9.2 Hz,

H-4), 3.51 (dq, 1 H, $J_{4',5'}$ 9.4 H, H-5'), 3.60 (t, 1 H, $J_{2',3'}$ 9.1, $J_{3',4'}$ 9.1 Hz, H-3'), 3.69 (dd, 1 H, $J_{1',2'}$ 7.8 Hz, H-2'), 3.76 (dq, 1 H, H-5), 3.92 (ddd, 1 H, H-3), 4.59 (d, 1 H, H-1'), 4.63, 4.71 (2 d, 2 H, J 11.5 Hz, CH_2Ph), 4.64 (s, 2 H, CH_2Ph), 4.74 (br s, 1 H, H-1), 5.04 (t, 1 H, H-4'), 7.11–8.00 (m, 15 H, Ph); ^{13}C (75 MHz): δ 17.57, 18.38 (C-6,6'), 35.43 (C-2), 54.53 (OCH_3), 67.04 (C-5), 70.46 (C-5'), 71.41, 74.22 (CH_2Ph), 74.32, 75.05, 75.06 (C-3,3',4'), 81.13, 81.60 (C-2',4), 97.99 (C-1), 102.00 (C-1'), 127.45, 127.59 (Bn-4), 127.69, 127.86, 128.15, 128.32, 128.38, 129.72 (Ph-2,3), 129.81 (Bz-1), 133.14 (Bz-4), 138.20, 138.25 (Bn-1), 165.49 (CO_2). Mass spectrum: m/z 501 ($M^+ - C_7H_7$), 341 ([ring B]$^+$), 251 ([ring C]$^+$). Anal. Calcd for $C_{34}H_{40}O_9$ (592.68): C, 68.90; H, 6.80. Found: C, 69.14; H, 6.82.

*Methyl-2,6-dideoxy-4-*O*-(6-deoxy-β-*D*-glucopyranosyl)-α-*D*-*arabino*-hexopyranoside* (**19**).—A suspension of **18** (0.29 g, 0.59 mmol, obtained from a mixture of **17** and **18** by Zemplén deacylation) and 10% Pd–C (40 mg) in EtOAc (50 mL) was hydrogenated (10^5Pa H_2) for 1 day with vigorous shaking. The catalyst was filtered off and the solution concentrated. Column chromatography (eluent *J*) gave **19** [0.12 g, 66%; R_f 0.41 (eluent *J*)], mp 50–51°C, $[\alpha]_D^{22}$ +58.0° (*c* 1, acetone); lit.[35] $[\alpha]_D^{20}$ +47.7° (*c* 0.79, acetone).

*Methyl-4-*O*-(4-*O*-benzoyl-3-*O*-benzyl-2,6-dideoxy-β-*D*-*arabino*-hexopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-*D*-*arabino*-hexopyranoside* (**21**).—A solution of **16** (0.50 g, 0.84 mmol), *O*-phenyl chlorothioformate (0.44 g, 2.5 mmol), pyridine (0.7 mL), and catalytic amounts of 4-dimethylaminopyridine in CH_2Cl_2 (20 mL) was stirred for 2 days. Water was added and the solution extracted with ether. The extract was washed with dilute HCl, water, aq $NaHCO_3$, and water, dried ($MgSO_4$), filtered, and concentrated. The residue was placed on silica gel; elution with eluent *G* removed nonpolar impurities and elution with eluent *E* gave crude thionocarbonate **20** [0.40 g, 65%; R_f 0.52 (eluent *D*)] which was immediately dissolved in toluene (20 mL) and treated with tributylstannane (0.32 g, 1.1 mmol) and 2,2'-azobisisobutyronitrile (18 mg). The solution was refluxed for 30 min and concentrated. Column chromatography (eluent *F*) gave syrupy **21** [0.22 g, 70%; R_f 0.51 (eluent *D*)], $[\alpha]_D^{22}$ +24.8° (*c* 0.9, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1725 cm^{-1} (C=O). NMR data ($CDCl_3$): ^{1}H (300 MHz): δ 1.19, 1.29 (2 d, 6 H, $J_{5,6}$ 6.1, $J_{5',6'}$ 6.1 Hz, H-6,6'), 1.69 (ddd, 1 H, $J_{1,2a}$ 3.7, $J_{2a,2e}$ 13.2, $J_{2a,3}$ 11.1 Hz, H-2*a*), 1.75 (ddd, 1 H, $J_{1',2'a}$ 9.8, $J_{2'a,2'e}$ 12.3, $J_{2'a,3'}$ 11.7 Hz, H-2'*a*), 2.24 (ddd, 1 H, $J_{1,2e}$ 1.4, $J_{2e,3}$ 5.1 Hz, H-2*e*), 2.39 (ddd, 1 H, $J_{1',2'e}$ 2.1, $J_{2'e,3'}$ 4.9 Hz, H-2'*e*), 3.30 (s, 3 H, OCH_3), 3.32 (dd, $J_{3,4}$ 8.6, $J_{4,5}$ 9.5 Hz, H-4), 3.41 (dq, 1 H, $J_{4',5'}$ 9.5 Hz, H-5'), 3.64 (ddd, 1 H, $J_{3',4'}$ 9.2 Hz, H-3'), 3.72 (dq, 1 H, H-5), 3.89 (ddd, 1 H, H-3), 4.45, 4.59 (2 d, 2 H, J 12.2 Hz, CH_2Ph), 4.62, 4.76 (2 d, 2 H, J 11.8 Hz, CH_2Ph), 4.72 (br d, 1 H, H-1), 4.75 (dd, 1 H, H-1'), 5.01 (t, 1 H, H-4'), 7.14–8.03 (m, 15 H, Ph); ^{13}C (75 MHz): δ 17.80, 18.30 (C-6,6'), 35.78 (C-2), 37.03 (C-2'), 54.51 (OCH_3), 66.69 (C-5), 70.44 (C-5'), 70.84, 72.10 (CH_2Ph), 75.61, 75.74, 76.29 (C-3,3',4'), 83.37 (C-4), 98.14 (C-1), 100.18 (C-1') 127.36, 127.47, 127.48, 127.52, 128.22, 128.25, 128.37, 129.74 (Ph-2,3, Bn-4), 130.04 (Bz-1), 133.08 (Bz-4), 138.03, 139.02 (Bn-1), 165.72 (CO_2). Mass spectrum:

m/z 576 (M^+), 325 ([ring B]$^+$), 251 ([ring C]$^+$). Anal. Calcd for $C_{34}H_{40}O_8$ (576.69): C, 70.81; H, 6.99. Found: C, 70.46; H, 7.17.

*Methyl 3-O-benzyl-4-O-(3-O-benzyl-2,6-dideoxy-β-*D*-arabino-hexopyranosyl)-2,6-dideoxy-α-*D*-arabino-hexopyranoside* (**22**).—Compound **21** (205 mg, 355 μmol) was dissolved in a solution of a catalytic amount of Na in MeOH (20 mL). After 2 days, an excess of weakly acidic cation-exchanger (Bayer, Lewatit CNP 80) was added and the mixture stirred until it was neutral. The resin was filtered off and the solution concentrated. Column chromatography (eluent *D*) gave syrupy **22** [129 mg, 77%; R_f 0.34 (eluent *D*)], $[\alpha]_D^{22}$ +38.4° (*c* 0.6, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3460 cm^{-1} (OH). NMR data ($CDCl_3$): ^1H (300 MHz): δ 1.27, 1.28 (2 d, 6 H, $J_{5,6}$ 6.1, $J_{5',6'}$ 6.1 Hz, H-6,6′), 1.53 (ddd, 1 H, $J_{1',2'a}$ 9.8, $J_{2'a,2'e}$ 12.2, $J_{2'a,3'}$ 11.5 Hz, H-2′*a*), 1.68 (ddd, 1 H, $J_{1,2a}$ 3.8, $J_{2a,2e}$ 13.2, $J_{2a,3}$ 11.1 Hz, H-2*a*), 2.23 (ddd, 1 H, $J_{1,2e}$ 1.5, $J_{2e,3}$ 5.1 Hz, H-2*e*), 2.34 (ddd, 1 H, $J_{1',2'e}$ 2.1, $J_{2'e,3'}$ 4.8 Hz, H-2′*e*), 2.41 (br s, 1 H, OH), 3.15–3.39 (m, 4 H, H-3′,4,4′,5′), 3.30 (s, 3 H, OCH_3), 3.70 (dq, 1 H, $J_{4,5}$ 9.4 Hz, H-5), 3.88 (ddd, 1 H, $J_{3,4}$ 8.4 Hz, H-3), 4.46, 4.60, 4.66, 4.73 (4 d, 4 H, *J* 11.5 and 11.5 Hz, CH_2Ph), 4.72 (br d, 1 H, H-1), 4.73 (dd, 1 H, H-1′), 7.22–7.39 (m, 10 H, Ph); ^{13}C (75 MHz): δ 17.98, 18.30 (C-6,6′), 35.69 (C-2), 36.32 (C-2′), 54.50 (OCH_3), 66.68 (C-5), 70.91, 72.01 (CH_2Ph), 71.77 (C-5′), 75.64, 75.82 (C-3,3′), 79.01 (C-4′), 82.98 (C-4), 98.14 (C-1), 100.16 (C-1′), 127.38, 127.93 (Bn-4), 127.46, 127.74, 128.21, 128.57 (Bn-2,3), 138.06, 138.98 (Bn-1). Mass spectrum: *m/z* 472 (M^+), 381 ($M^+ - C_7H_7$), 251 ([ring C]$^+$), 221 ([ring B]$^+$). Anal. Calcd for $C_{27}H_{36}O_7$ (472.58): C, 68.62; H, 7.68. Found: C, 68.72; H, 7.76.

*Methyl 2,6-dideoxy-4-O-[2,6-dideoxy-4-O-(3,5-dichloro-4-hydroxy-2-methoxy-6-methylbenzoyl)-β-*D*-arabino-hexopyranosyl]-α-*D*-arabino-hexopyranoside* (**25**).—A solution of **22** (74 mg, 157 μmol) in tetrahydrofuran (8 mL) was treated with activated 4A molecular sieves and stirred for 2 h. With a syringe, the solution was transferred into a reaction flask under dry Ar. A hexane solution of butyllithium (0.29 mL; 1.6 M; 0.47 mmol) was added and the solution stirred for 1 h. A solution of **23**[7] (338 mg, 940 μmol) in THF (2 mL) was added and stirring continued for 4 h. Brine was added and the mixture extracted with ether. The extract was washed with water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (eluent *G*) gave **24** [62 mg, 50%; R_f 0.48 (eluent *D*)] which was dissolved in EtOAc (50 mL) and treated with 10% Pd–C (30 mg). The suspension was hydrogenated (10^5 Pa H_2) for 6 h with vigorous shaking. The catalyst was filtered off and the solution evaporated. Column chromatography (eluent *A*) gave **25** [33 mg, 81%; R_f 0.39 (eluent *B*)], mp 175–176°C (from diisopropyl ether), $[\alpha]_D^{22}$ +39.8° (*c* 0.8, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3440 (OH), 1730 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (500 MHz): δ 1.26 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 1.38 (d, 3 H, $J_{5',6'}$ 6.4 Hz, H-6′), 1.63 (ddd, 1 H, $J_{1,2a}$ 3.7, $J_{2a,2e}$ 13.1, $J_{2a,3}$ 11.7 Hz, H-2*a*), 1.83 (ddd, 1 H, $J_{1',2'a}$ 9.8, $J_{2'a,2'e}$ 12.8, $J_{2'a,3'}$ 11.9 Hz, H-2′*a*), 2.21 (ddd, 1 H, $J_{1,2e}$ 1.2, $J_{2e,3}$ 5.3 Hz, H-2*e*), 2.36 (s, 3 H, PhCH_3), 2.38 (ddd, 1 H, $J_{1',2'e}$ 2.1, $J_{2'e,3'}$ 4.9 Hz, H-2′*e*), 2.72 (br s, 1 H, OH), 3.01 (dd, 1 H, $J_{3,4}$ 8.5, $J_{4,5}$ 9.5 Hz, H-4), 3.32 (s, 3 H, OCH_3), 3.56 (dq, 1 H, $J_{4',5'}$ 9.8 Hz, H-5′), 3.70 (dq, 1 H, H-5), 3.85 (br s, 1 H, $J_{3',4'}$ 8.9 Hz,

H-3′), 3.89 (s, 3 H, PhOCH_3), 3.92 (ddd, 1 H, H-3), 4.31 (s, 1 H, OH), 4.57 (dd, 1 H, H-1′), 4.74 (br d, 1 H, H-1), 4.82 (t, 1 H, H-4′), 6.17 (br s, 1 H, PhOH); ^{13}C (75 MHz): δ 17.34, 17.49, 17.71 (C-6,6′, PhCH_3), 36.81 (C-2), 38.93 (C-2′), 54.68 (OCH_3), 62.46 (PhOCH_3), 65.54, 66.85, 69.65, 70.02 (C-3,3′,5,5′), 79.26 (C-4′), 89.30 (C-4), 98.23 (C-1), 100.91 (C-1′), 112.89, 117.65, 122.70 (C-1″,3″,5″), 132.95 (C-6″), 149.93, 152.04 (C-2″,4″), 166.35 (CO_2). Mass spectrum: m/z 494, 492 ($M^+ - CH_3OH$), 367, 365, 363 ([rings A and B]$^+$), 237, 235, 233 ([ring A]$^+$). Anal. Calcd for $C_{22}H_{30}Cl_2O_{10}$ (525.38): C, 50.30; H, 5.76. Found: C, 50.84; H, 5.76.

ACKNOWLEDGMENTS

We thank Dr. J. Runsink for recording the NMR spectra, and the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie for supporting this work.

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