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PREPARATIVE SYNTHESIS OF *C*-(α-D-GLUCOPYRANOSYL)-ALKENES AND -ALKADIENES: DIELS–ALDER REACTION*

MARIA DE GRACIA GARCIA MARTIN AND DEREK HORTON
Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210 (U.S.A.)

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ABSTRACT

The reaction of 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranose with (*E*)-penta-2,4-dienyltrimethylsilane and boron trifluoride etherate in acetonitrile afforded stereoselectively (*E*)-5-(tetra-*O*-benzyl-α-D-glucopyranosyl)-1,3-pentadiene (**1**) in good yield. The readily available penta-*O*-benzoyl-α-D-glucopyranose reacted with allyltrimethylsilane in the presence of boron trifluoride etherate in acetonitrile to give 3-(tetra-*O*-benzoyl-α-D-glucopyranosyl)-1-propene (**2**) and its β anomer (**5**) in yields of 60% and 2.3%, respectively. Diels–Alder cycloaddition of maleic anhydride to diene **1** afforded the adduct *cis,cis*-3-(tetra-*O*-benzyl-α-D-glucopyranosylmethyl)cyclohex-4-ene-1,2-dicarboxylic anhydride (**9**) in high yield.

INTRODUCTION

The stereoselective synthesis of *C*-(D-glycopyranosyl)alkenes from sugars having non-participating groups at C-2 with allyltrimethylsilane and a Lewis acid has been widely studied[1–5]. A similar kind of reaction led Acton *et al.*[6] to the stereospecific coupling of a pentadienyl chain to C-1 of daunosamine to obtain an α-*C*-glycopyranosyl derivative in >90% yield. Bennek and Gray reported[7] the preparation of *C*-(D-glycopyranosyl)alkenes using methyl per(trimethylsilyl)glycosides and allyltrimethylsilane in the presence of trimethylsilyl trifluoromethanesulfonate.

We now report the extension of the previous work in our laboratory[1] to obtain 3-(α-D-glucopyranosyl)-1-propene (**4**) on a larger scale in an improved yield without chromatographic purification. The synthesis of the very stable diene (*E*)-5-(tetra-*O*-benzyl-α-D-glucopyranosyl)-1,3-pentadiene (**1**) has also been achieved. The latter compound promises to be a good substrate for Diels–Alder cycloaddition reactions, which could be extremely useful for the synthesis of "pseudodisaccharides".

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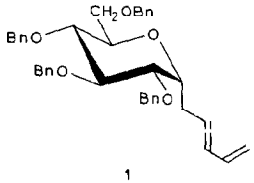
RESULTS AND DISCUSSION

Synthesis of the α-*C*-glucosylalkadiene **1** was achieved by the reaction of tetra-*O*-benzyl-1-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranose with freshly prepared (*E*)-penta-2,4-dienyltrimethylsilane[8] (3 mol eq.) and $BF_3 \cdot OEt_2$ (3 mol eq.) in dry acetonitrile at 0°–room temperature overnight under nitrogen. The compound was purified on a column of silica gel to give a white solid (45% yield). After recrystallization from methanol, long needles having $[\alpha]_D^{28}$ +61.4° in dichloromethane were obtained. At this stage of purity, compound **1** could be stored for long periods of time with no observable decomposition or polymerization. The α-anomeric configuration was established on the basis of its high dextrorotation and the $J_{1',2'}$ value of 5.1 Hz (see ref. 1, $J_{1',2'}$ 5.8 Hz for compound **3**). The coupling constants for the protons of the pentadienyl chain were in accordance[8] with those expected for the (*E*) isomer. Its ^{13}C-n.m.r. spectrum was also as expected for structure **1** (see Experimental).

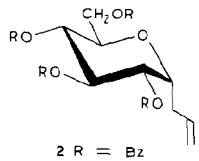
The reaction of penta-*O*-benzoyl-α-D-glucopyranose with allyltrimethylsilane (10 mol. eq.) and $BF_3 \cdot OEt_2$ (10 mol eq.) in dry acetonitrile under nitrogen at 80° yielded the glucosylpropene **2**. This reaction required a longer time (~1 day) than that already described to form the acetylated analog **3** starting from penta-*O*-acetyl-α-D-glucopyranose under the same reaction conditions. The mixture was processed as previously described[1], and treatment of the residue with ethanol gave crystalline compound **2** (43%) which showed $[\alpha]_D^{25}$ +66° in dichloromethane. The ^{1}H-n.m.r. spectrum of **2** presented a doubled doublet of doublets ($J_{1',2'}$ 5.3 Hz) for H-1′ at δ 4.58 which indicates the α-D-*gluco* configuration. The structure of **2** was confirmed by its transformation into the known[1,7] deprotected compound **4** by *O*-debenzoylation with sodium methoxide–methanol. Additional amounts of **2** were obtained (60% total yield) by evaporating the mother liquor followed by chromatography on a column of silica gel.

An amorphous solid (~2.5%) which was characterized as the β anomer of **2** (**5**) was also isolated from the column. Compound **5** showed a specific rotation of +34° in dichloromethane. The β-anomeric configuration was assigned on the basis of the ^{1}H-n.m.r. data for H-1′, which resonated as a doubled doublet of doublets at δ 3.84 and had $J_{1',2'}$ 9.6 Hz (see ref. 1, $J_{1',2'}$ 9.5 Hz for the β anomer of **3**); the lower δ value for H-1′ of **5** indicates that is axially oriented. The large values of $J_{2',3'} = J_{3',4'} = J_{4',5'}$ (8.5 Hz for **2** and 9.6 Hz for **5**) are in accordance with the $^4C_1$ D-glucopyranose conformation. The chemical-shift values found for C-1′ in compounds **2** and **5**, 71.78 and 77.84 p.p.m., respectively, are also in accordance with those previously observed[1] for the corresponding α and β anomers.

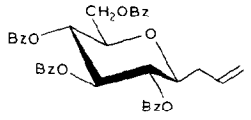
Attempts to obtain *C*-(D-glycopyranosyl)alkenes of 2-amino-2-deoxy-D-glucose by the same procedure, using several different protecting groups for the amino function, were unsuccessful. It is worth noting that the reaction of tetra-*O*-acetyl-2-deoxy-2-(*p*-toluenesulfonamido)-α,β-D-glucopyranose with allyltrimethylsilane and $BF_3 \cdot OEt_2$ in acetonitrile afforded a product formulated as the



1



2 R = Bz
3 R = Ac
4 R = H



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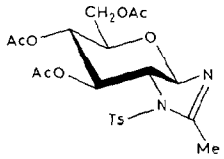

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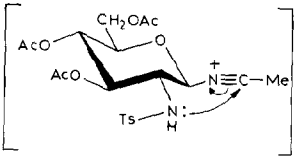

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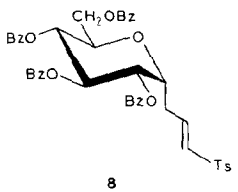

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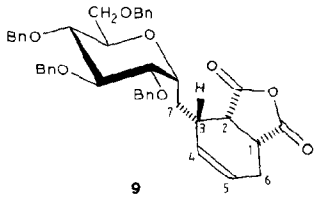

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imidazoline **6** in ~20% yield. The same compound was obtained in almost quantitative yield when allyltrimethylsilane was not present in the reaction mixture.

The structure assigned to **6** was based on its elemental analysis and spectroscopic data (see Experimental section). The strong levorotation indicates the β-anomeric configuration, and the ^{1}H-n.m.r. data suggest a distorted, chair-like conformation ("normal" values of $J_{2,3}$ and $J_{3,4}$, but low values of 5 Hz for $J_{1,2}$ and $J_{4,5}$, indicative of *trans* ring-fusion[9]), rather than the skew conformation (high $J_{1,2}$ and $J_{4,5}$ values, low $J_{2,3}$ and $J_{3,4}$ values) found[10] for structurally related, dextrorotatory oxazolines having the α-anomeric configuration (*cis* ring-fusion). The formation of **6** may be rationalized on the basis of reaction of an oxonium ion, formed from the sugar by the Lewis acid, with acetonitrile to give a nitrilium ion* **7**, which then undergoes nucleophilic attack by the tosylamino group.

In order to engage the unactivated alkene **2** as a dienophile in Diels–Alder reactions, we converted it into activated derivatives by the temporary introduction of suitable substituents. For example, the tolyl vinyl sulfone derivative **8** was prepared in almost quantitative yield by the reaction of **2** with the readily available *Se*-phenyl *p*-tolueneselenosulfonate[12] in boiling chloroform, followed by oxidation of the resulting selenol derivatives with excess *m*-chloroperoxybenzoic acid[13] in dichloromethane. However, attempts to react **8** either with Danishefsky's diene [1-

*For the general structure **7** the β configuration has been proposed[11] to be the more stable through operation of the antianomeric effect.

methoxy-3-(trimethylsilyloxy)-1,3-butadiene] or benzyl *trans*-1,3-butadiene-1-carbamate were unsuccessful.

Diene **1** was found to undergo Diels–Alder addition of maleic anhydride to give a single compound, adduct **9**, in ~80% yield after recrystallization from ethanol. The reaction took place smoothly at ~80–90° in toluene during 8 h, after which time no starting sugar was present. The stereochemical course of the cycloaddition to the prochiral diene **1** from the *re* face was *endo*, as expected.

The highly functionalized adduct **9** might be further elaborated in order to prepare the corresponding chiral cyclohexane derivatives.

EXPERIMENTAL

General methods. — Evaporations were conducted under diminished pressure. T.l.c. was performed on precoated plates of Silica Gel 60F-254 (E. Merck); components were detected by u.v. light and by spraying the plates with 10% sulfuric acid and subsequent heating. Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Specific rotations were determined with a Perkin–Elmer 141 polarimeter. I.r. spectra were recorded with a Matteson Polaris FT-IR spectrometer. ^{1}H-N.m.r. and ^{13}C-n.m.r. spectra were obtained at 500 MHz and 125 MHz, respectively, with a Bruker AM-500 spectrometer by Dr. C. E. Cottrell. Chemical shifts refer to an internal standard of tetramethylsilane (δ = 0.00). Chemical-ionization (c.i.) and fast-atom-bombardment (f.a.b.) mass spectra were recorded at The Ohio State University Chemical Instrument Center with Kratos MS-30 and VG 70-250S mass spectrometers. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Georgia.

5-(Tetra-O-benzyl-α-D-glucopyranosyl)-(E)-1,3-pentadiene (**1**). — A solution of 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranose[14] (500 mg, 0.72 mmol) in dry MeCN (10 mL) was cooled to 0° and $BF_3 \cdot OEt_2$ (0.26 mL, 2.16 mmol) and freshly prepared (*E*)-penta-2,4-dienyltrimethylsilane (0.39 mL, 2.16 mmol) were added. The mixture was stirred overnight under nitrogen and the solvent was removed under diminished pressure. The residue was dissolved in CH_2Cl_2 and the solution was washed successively with water, saturated $NaHCO_3$ solution, and water, dried (anhydrous $MgSO_4$), and evaporated to a syrup, which was chromatographed on a column of silica gel (9:1 petroleum ether–Et_2O). The main product was isolated as a white solid (192.8 mg, 45%) which gave long needles, m.p. 79–80°, on recrystallization from MeOH; $[\alpha]_D^{28}$ +61.4° (c 1.7, CH_2Cl_2); ν_{max}^{NaCl} 1600 (C=C aliphat.), 1500, and 1450 (C=C aromat.) cm^{-1}; n.m.r. data (^{1}H, 500 MHz, $CDCl_3$): δ 7.27–7.34 (m, C*H*$_2$Ph), 6.31 (ddd, 1 H, H-2), 6.12 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 15.2 Hz, H-3), 5.70 (dt, 1 H, $J_{4,5a}$ 7.0, $J_{4,5b}$ 14.6 Hz, H-4), 5.09 (dd, 1 H, $J_{1a,1b}$ <1, $J_{1b,2}$ 16.7 Hz, H-1b), 4.98 (dd, 1 H, $J_{1a,2}$ 10.4 Hz, H-1a), 4.12 (dt, 1 H, $J_{1',2'}$ 5.1, $J_{1',5a}$ 10.3, $J_{1',5b}$ 10.3 Hz, H-1'), 4.45–4.82 (4 dd, 8 H, $J_{A,B}$ 11–12 Hz, C*H*$_2$Ph), 3.61–3.81 (m, 6 H, H-2',3',4',5',6'a,6'b), and 2.52 (m, 2 H, H-5a and H-5b); (^{13}C, 125 MHz, $CDCl_3$): δ 115.34 (C-1), 137.08, 133.05, 130.67 (C-2,3,4), 28.65 (C-5), 82.36 (C-1'),

78.15 (C-2'), 80.08 (C-3'), 71.26 (C-4'), 73.84 (C-5'), 69.03 (C-6'), 73.11, 73.44, 75.03, 75.04 (4 CH_2Ph), 138.11, 138.21, 138.76 (4 $CH_2C_6H_5$), and 127.57–128.42 (9 signals for 4 $CH_2C_6H_5$); *m/z* 591 $(M + H)^+$.

Anal. Calc. for $C_{39}H_{42}O_5$: C, 79.29; H, 7.16. Found: C, 79.37; H, 7.21.

3-(Tetra-O-benzoyl-α-D-glucopyranosyl)-1-propene (**2**) *and its β anomer* (**5**). — Penta-*O*-benzoyl-α-D-glucopyranose (5.0 g, 7.14 mmol) was dissolved in dry MeCN (50 mL) at 80° and allyltrimethylsilane (11.3 mL, 71.4 mmol) and $BF_3 \cdot OEt_2$ (9. 0mL, 71.4 mmol) were added under nitrogen. The mixture was heated for 27 h at 80° under nitrogen. Evaporation gave a brown residue which was dissolved in CH_2Cl_2 and processed conventionally to give a brown foam (4.40 g). This was dissolved in abs. EtOH, anhydrous Et_2O was added, and the mixture was kept in a freezer for several h to give the title compound **2** (1.90 g, 43.18%) in two crops, m.p. 121–122° (from EtOH), $[\alpha]_D^{25}$ +66° (*c* 0.65, CH_2Cl_2); ν_{max}^{NaCl} 1735 (C=O), 1600 (C=C aliphat.), 1580, 1450 (C=C aromat.), and 1260 (C=O) cm^{-1}; n.m.r. data (^1H, 500 MHz, $CDCl_3$): δ 7.30–8.05 (m, 20 H, $OCOC_6H_5$), 5.99 (t, 1 H, $J_{3',4'}$ 8.5 Hz, H-3'), 5.80 (dddd, 1 H, $J_{2,3a}$ 4.5, $J_{2,3b}$ 7.5, $J_{1a,2}$ 10.3, $J_{1b,2}$ 17.1 Hz, H-2), 5.54 (t, 1 H, $J_{4',5'}$ 8.5 Hz, H-4'), 5.51 (dd, 1 H, $J_{2',3'}$ 8.5 Hz, H-2'), 5.17 (dd, 1 H, $J_{1a,1b}$ 1.1, $J_{1b,2}$ 17.1, $J_{1b,3a} = J_{1b,3b}$ ~1 Hz, H-1b), 5.02 (dd, 1 H, $J_{1a,2}$ 10.3 Hz, $J_{1a,3a} = J_{1a,3b}$ ~1 Hz, H-1a), 4.58 (ddd, 1 H, $J_{1',2'}$ 5.3, $J_{1',3b}$ 10.8, $J_{1',3a}$ 4.5 Hz, H-1'), 4.59 (dd, 1 H, $J_{5',6'b}$ 6.2 Hz, H-6'b), 4.58 (dd, 1 H, $J_{5',6'a}$ 3.3, $J_{6'a,6'b}$ −12.0 Hz, H-6'a), 4.35 (ddd, 1 H, H-5'), 2.80 (dddt, 1 H, $J_{2,3b}$ 7.5, $J_{3a,3b}$ 15.3 Hz, H-3b), 2.49 (ddt, 1 H, H-3a); (^{13}C, 125 MHz, $CDCl_3$): δ 117.99 (C-1), 133.04 (C-2), 31.16 (C-3), 71.78 (C-1'), 70.28 (C-2'), 70.93 (C-3'), 69.67 (C-4'), 69.48 (C-5'), 63.05 (C-6'), 166.19, 165.84, and 165.33 (4 $OCOC_6H_5$); *m/z* 621 $(M + H)^+$, 579 $(M - allyl)^+$, 500 $(M - OBz + H)^+$, and 499 $(M - OBz)^+$.

Anal. Calc. for $C_{37}H_{32}O_9$: C, 71.60; H, 5.19. Found: C, 71.62; H, 5.20.

The mother liquor of compound **2** was concentrated to a residue, which was chromatographed on a column of silica gel (50:1 PhMe–EtOAc) to afford an additional crop of **2** (0.55 g), leading to a 60% total yield.

Some fractions from the column were found to contain the β anomer of **2** (**5**) (0.10 g, 2.3%). Compound **5** was a foam, $[\alpha]_D^{25}$ +34° (*c* 0.7, CH_2Cl_2); ν_{max}^{NaCl} 1735 (C=O), 1600 (C=C aliphat.), 1500, and 1450 (C=C aromat.) cm^{-1}; n.m.r. data (^1H, 500 MHz, $CDCl_3$): δ 7.32–8.03 (m, 20 H, $OCOC_6H_5$), 5.87 (m, 2 H, $J_{2,3a}$ 6.8, $J_{2,3b}$ 8.0 Hz, H-2 and H-3'), 5.62 (t, 1 H, $J_{3',4'} = J_{4',5'}$ 9.6 Hz, H-4'), 5.43 (t, 1 H, $J_{2',3'}$ 9.6 Hz, H-2'), 5.07 (dd, 1 H, $J_{1a,1b}$ 1.6, $J_{1b,2}$ 17.2, $J_{1b,3a} = J_{1b,3b}$ ~1 Hz, H-1b), 5.02 (dd, 1 H, $J_{1a,2}$ 10.3, $J_{1a,3a} = J_{1a,3b}$ ~1 Hz, H-1a), 4.60 (dd, 1 H, $J_{5',6'b}$ 3.1 Hz, H-6'b), 4.45 (dd, 1 H, $J_{5',6'a}$ 5.5, $J_{6'a,6'b}$ −12.0 Hz, H-6'a), 4.08 (ddd, 1 H, H-5'), 3.84 (ddd, 1 H, $J_{1',2'}$ 9.6 Hz, H-1'), 2.37–2.47 (m, 2 H, $J_{3a,3b}$ 15.2 Hz, H-3a and H-3b); (^{13}C, 125 MHz, $CDCl_3$): δ 117.93 (C-1), 133.04 (C-2), 35.82 (C-3), 77.84 (C-1'), 74.57 (C-2'), 76.08 (C-3'), 72.28 (C-4'), 70.07 (C-5'), 63.47 (C-6'), 166.16, 165.97, 165.36, and 165.27 ($OCOC_6H_5$); *m/z* 621 $(M + H)^+$, 579 $(M - allyl)^+$, 500 $(M - OBz + H)^+$, and 499 $(M - OBz)^+$.

Anal. Calc. for $C_{37}H_{32}O_9$: C, 71.60; H, 5.19. Found: C, 71.49; H, 5.22.

3-(α-D-Glucopyranosyl)-1-propene (**4**). — A solution of the tetrabenzoate **2** (1.5 g, 2.4 mmol) in dry MeOH (20 mL) was treated with 4.4M NaOMe in MeOH (0.11 mL) overnight and neutralized with Amberlite IR-120 (H^+) resin. The resin was filtered off, washed with MeOH, and the filtrate was evaporated to a solid (0.49 g, 100%), m.p. 150–151° (from 2-propanol) (lit.[1] m.p. 150–151°).

*2-Methyl-3-*p*-tolylsulfonyl-(3,4,6-tri-O-acetyl-1,2-dideoxy-β-D-glucopyrano)-[2,1-*d*]-1-imidazoline* (**6**). — A mixture of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(*p*-toluenesulfonamido)-α,β-D-glucopyranose[15] (1.5 g, 3.0 mmol), MeCN (8 mL), and $BF_3 \cdot OEt_2$ (4 mL) was boiled for 19 h under N_2. The solution was evaporated to dryness and diluted with $CHCl_3$. The solution was washed successively with water, saturated $NaHCO_3$ solution, and water, and dried over anhydrous $MgSO_4$. Evaporation gave a brown foam, which after treatment with MeOH afforded the title compound as a white solid (1.25 g, 87%), m.p. 104–105° (from methanol), $[\alpha]_D^{25}$ −250° (*c* 1, chloroform); ν_{max}^{NaCl} 1735 (C=O), 1650 (C=N), 1375 (S=O), and 1240 (C=O) cm^{-1}; n.m.r. data (^1H, 500 MHz, $CDCl_3$): δ 7.77 (d, 2 H, *J* 8.2 Hz, C_6H_4), 7.40 (d, 2 H, *J* 8.2 Hz, C_6H_4), 5.50 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 5.50 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 4.95 (dd, 1 H, $J_{4,5}$ 4.7 Hz, H-4), 4.29 (dd, 1 H, $J_{5,6b}$ 5.4, $J_{6a,6b}$ −12.2 Hz, H-6b), 4.14 (dd, 1 H, $J_{5,6a}$ 2.9 Hz, H-6a), 3.90 (dd, 1 H, $J_{2,3}$ 8.4 Hz, H-2), 3.72 (ddd, 1 H, H-5), 2.45, and 2.43 (s, 6 H, N=CCH_3 and $C_6H_4CH_3$), 2.11 (s, 3 H, OAc), and 2.07 (s, 6 H, 2 OAc); (^{13}C, 125 MHz): δ 91.63 (C-1), 68.23 (C-2), 77.25 (C-3), 57.79 (C-4), 76.99 (C-5), 63.17 (C-6), 160.43 (N–*C*=N), 145.31, 134.83, 130.31, 127.28 ($SO_2C_6H_4$), 170.54, 169.59 (3 CH_3CO), 21.54, 20.80, 20.66, and 17.48 (3 CH_3CO, $SO_2C_6H_4CH_3$, and N=CCH_3); *m/z* 483 $(M + H)^+$ and 423 $(M - Ac - H_2O)^+$.

Anal. Calc. for $C_{21}H_{26}N_2O_9S$: C, 52.27; H, 5.43; N, 5.80; S, 6.64. Found: C, 52.19; H, 5.44; N, 5.76; S, 6.69.

trans-*3-(Tetra-O-benzoyl-α-D-glucopyranosyl)-1-(*p*-tolylsulfonyl)-1-propene* (**8**). — A solution of compound **2** (100 mg, 0.16 mmol) and *Se*-phenyl *p*-tolueneselenolsulfonate (54.7 mg, 0.17 mmol) in $CHCl_3$ (4 mL) was boiled for 48 h. The solvent was removed, and the residue was treated with EtOH to give two crops of a white solid material (136 mg, 90%) which showed two spots on t.l.c. (R_F 0.27 and 0.19, 30:1 PhMe–EtOAc). Eighty mg (0.08 mmol) of this material was dissolved in CH_2Cl_2 (0.6 mL) and a solution of *m*-chloroperoxybenzoic acid (34 mg, 0.19 mmol) in CH_2Cl_2 (3.0 mL) was added during 5 min. The mixture was washed with 5% Na_2CO_3 solution, then water, dried over anhydrous $MgSO_4$, and evaporated to dryness to afford 66 mg (99%) of the title compound, m.p. 90–95° (from EtOH), $[\alpha]_D^{26}$ +54.3° (*c* 0.35, CH_2Cl_2); ν_{max}^{NaCl} 1735 (C=O), 1600 (C=C aliphat.), 1450, 1500 (C=C aromat.), 1325, and 1150 (S=O) cm^{-1}; n.m.r. data (^1H, 500 MHz, $CDCl_3$): δ 7.24–8.08 (m, aromatic), 7.02 (ddd, 1 H, $J_{1,2}$ 15.1, $J_{2,3a}$ 2.3, $J_{2,3b}$ 6.8 Hz, H-2), 6.51 (d, 1 H, $J_{1,2}$ 15.1 Hz, H-1), 5.90 (t, 1 H, $J_{2',3'}$ 8.1 Hz, H-3'), 5.54 (t, 1 H, $J_{3',4'}$ 8.1 Hz, H-4'), 5.48 (dd, 1 H, $J_{1',2'}$ 5.1 Hz, H-2'), 4.65 (ddd, 1 H, $J_{1',3a}$ 4.0, $J_{1',3b}$ 8.8 Hz, H-1'), 4.54 (dd, 1 H, $J_{5',6'a}$ 6.2 Hz, H-6'a), 4.45 (dd, 1 H, $J_{5',6'b}$ 3.5, $J_{6'a,6'b}$ 12.1 Hz, H-6'b), 4.30 (ddd, 1 H, $J_{4',5'}$ 8.1 Hz, H-5'), 2.97 (m, 1 H,

H-3b), 2.61 (m, 1 H, $J_{3a,3b}$ 16.5 Hz, H-3a), and 2.38 (s, 3 H, $C_6H_4CH_3$); *m/z* 776 $(M + H)^+$, 775 $(M)^+$, 653 $(M - OBz - H)^+$.

Anal. Calc. for $C_{44}H_{38}SO_{11}$: C, 68.20; H, 4.94; S, 4.13. Found: C, 68.07; H, 4.97; S, 4.20.

cis-cis-*3-(Tetra-O-benzyl-α-D-glucopyranosylmethyl)cyclohex-4-ene-1,2-dicarboxylic anhydride* (**9**). — A solution of diene **1** (66 mg, 0.11 mmol) and maleic anhydride (21 mg, 0.21 mmol) in PhMe (1 mL) was heated at 80–90° for 8 h under N_2. The solution was evaporated to a colorless residue which solidified after treatment with abs. EtOH. Recrystallization from EtOH gave the title compound, 60 mg (78%), m.p. 129–130°, $[\alpha]_D^{30}$ +51° (*c* 0.45, $CHCl_3$); ν_{max}^{NaCl} 1775 (C=O, anhydride); n.m.r. data (^1H, 500 MHz, $CDCl_3$): δ 7.46–8.16 (m, C_6H_5), 5.95 (ddd, 1 H, H-5), 5.80 (dt, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 9.3 Hz, H-4), 4.99–4.43 (4 dd, 8 H, $J_{A,B}$ 11–12 Hz, $CH_2C_6H_5$), 4.58 (m, 1 H, $J_{1',2'}$ 4.7 Hz, H-1'), 3.84–3.46 (m, 7 H, H-2',3',4',5',6'a,6'b,2), 3.21 (t, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 2.61 (dd, 1 H, $J_{4,6a} = J_{1,6a}$ <1, $J_{5,6a}$ 8.4, $J_{6a,6b}$ 14.1 Hz, H-6a), 2.45 (m, 1 H, H-3), 2.30 (ddd, 1 H, $J_{1',7a}$ 3.8, $J_{3,7a}$ 11.6, $J_{7a,7b}$ 15.0 Hz, H-7a), 2.20 (ddd, 1 H, $J_{3,7b}$ 4.8, $J_{1',7b}$ 12.0 Hz, H-7b), 1.98 (m, 1 H, H-6b); (^{13}C, 125 MHz, $CDCl_3$): δ 41.00, 41.70 (C-1,2), 30.93 (C-3), 134.14 (C-4,5), 24.24 (C-6), 26.15 (CH_2), 82.18 (C-1'), 78.06 (C-2'), 79.64 (C-3'), 70.38 (C-4'), 71.77 (C-5'), 69.66 (C-6'), 72.67, 73.51, 75.00, 75.47 ($CH_2C_6H_5$), 174.32, 171.98 (C=O), 137.94, 138.02, 138.05, 138.67 ($CH_2C_6H_5$), 127.63–128.40 (6 signals for C-4/C-5 and 4 $CH_2C_6H_5$); *m/z* 689 $(M)^+$.

Anal. Calc. for $C_{43}H_{44}O_8$: C, 74.98; H, 6.44. Found: C, 74.87; H, 6.46.

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