ELSEVIER

Carbohydrate Research 337 (2002) 2377–2381

CARBOHYDRATE RESEARCH

www.elsevier.com/locate/carres

Regioselective sulfonylation of 6,1′,6′-tri-*O*-tritylsucrose through dibutylstannylation: synthesis of 4′-*O*-sulfonyl derivatives of sucrose

A. S. Muhammad Sofian,[a,*] Cheang Kuan Lee,[a] Anthony Linden[b]

[a]*Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260*
[b]*Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH 8057 Zurich, Switzerland*

Received 5 July 2002; accepted 10 September 2002

Abstract

3-*O*-Mesyl-1,6-di-*O*-trityl-β-D-fructofuranosyl-(2→1)-6-*O*-trityl-α-D-glucopyranoside (**3**) was synthesized via stannylation of 6,1′,6′-tri-*O*-tritylsucrose with dibutyltin oxide in benzene, followed by treatment of the crude product with methanesulfonyl chloride in the presence of triethylamine in dichloromethane at 0 °C. A similar treatment of the tri-tritylsucrose in toluene, instead of benzene, yielded 4-*O*-mesyl-1,6-di-*O*-trityl-β-D-fructofuranosyl-(2→1)-6-*O*-trityl-α-D-glucopyranoside (**4**) as the major product. The X-ray crystal structure of the corresponding acetyl derivative, 3-*O*-acetyl-4-*O*-mesyl-1,6-di-*O*-trityl-β-D-fructofuranosyl-(2→1)-2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside (**5**), confirms the position and stereochemistry of the methanesulfonyl group at C-4 of the fructofuranosyl ring.

Keywords: Stannylation; Methanesulfonate; Trifluoromethanesulfonate; Sucrose

1. Introduction

The use of organotin reagents for the selective activation of hydroxyl groups in carbohydrates has enabled the introduction of protecting groups and other substituents in a regioselective manner.[1,2] Ogawa and Matsui[3] reported that 1,6-di-*O*-benzoyl-β-D-fructofuranosyl-(2→1)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (**1**) could be prepared (87% yield) by treating sucrose with bis(tributyltin)oxide in toluene at 140 °C for 4 h, followed by benzoylation at ambient temperature. Interestingly, Holzapfel and co-workers[4] reported the synthesis of 3-*O*-benzoyl-1,6-di-*O*-trityl-β-D-fructofuranosyl-(2→1)-6-*O*-trityl-α-D-glucopyranoside[5] (**2**) by treatment of 6,1′,6′-tri-*O*-tritylsucrose[5] in benzene with dibutyltin oxide, followed by benzoylation at room temperature.

In our attempt to synthesize 3-*O*-mesyl-1,6-di-*O*-trityl-β-D-fructofuranosyl-(2→1)-6-*O*-trityl-α-D-glucopyranoside (**3**) using the method of Holzapfel and co-workers,[4] we found that in addition to **3**, a small amount of the C-4′ mesyl derivative (**4**) was also formed. We now describe the regioselective sulfonylation of 6,1′,6′-tri-*O*-tritylsucrose via its dibutylstannylene derivative.

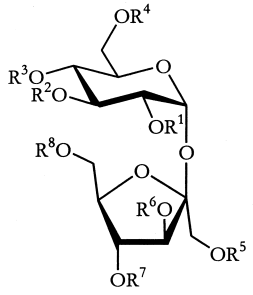
2. Results and discussion

When a mixture of 6,1′,6′-tri-*O*-tritylsucrose and dibutyltin oxide (1 mol equiv) in benzene was refluxed for 16 h, and then treated with mesyl chloride (2 mol equiv) in dichloromethane in the presence of triethylamine (2 mol equiv) for 30 min at 0 °C, we found that, in addition to **3** (34%), ~10% of the C-4′ mesyl derivative (**4**) was also formed. However, when the stannylation was carried out in toluene, instead of benzene, mesylation gave **4** as the major product in ~50% yield; **3** was formed in only ~15%.

The structures of **3** and **4** were consistent with their NMR data. The ^{1}H NMR spectrum of **3** showed that H-3′ appeared as a downfield doublet at δ 5.07 ($J_{3',4'}$ 8.4 Hz), being due to the electron withdrawing mesyl

* Corresponding author. Fax: +65-67-791-691
E-mail address: scip8192@nus.edu.sg (A.S.M. Sofian).

0008-6215/02/$ - see front matter
PII: S0008-6215(02)00347-6



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
1	Bz	Bz	H	Bz	Bz	H	H	Bz
2	H	H	H	Tr	Tr	Bz	H	Tr
3	H	H	H	Tr	Tr	Ms	H	Tr
4	H	H	H	Tr	Tr	H	Ms	Tr
5	Ac	Ac	Ac	Tr	Tr	Ac	Ms	Tr
6	H	H	H	Tr	Tr	H	Tf	Tr

group. The singlet at δ 2.68 confirmed the presence of only one mesyl group. This is also evident from its ^{13}C NMR spectrum (δ 37.8).

Similarly, the ^1H NMR spectrum of **4** showed the H-4′ signal at δ 5.45 ($J_{3',4'} = J_{4',5'}$ 8.5 Hz) and the methyl protons (OSO_2CH_3) at δ 2.69. The structure of **4** was further confirmed by X-ray diffraction of the acetyl derivative, **5** (Fig. 1), which clearly showed the position and configuration of the mesyl group at C-4 of the fructofuranosyl ring; the conformation of this ring is $^4T_3$, as indicated by the Cremer and Pople parameters[6] ($\varphi_2 = 124.7°$, $Q_2 = 0.290$).

A similar treatment of 6,1′,6′-tri-*O*-tritylsucrose with dibutyltin oxide and then with trifluoromethanesulfonic anhydride gave the C-4′ triflate, **6** in ~40% yield. This was characterized as its 4′-bromo-4-deoxy derivative (**7**) by treatment with lithium bromide in acetone, followed by acetylation (Scheme 1). Similar treatment of the C-4′-mesyl derivative **4** with lithium bromide or lithium chloride in boiling *N*,*N*-dimethylformamide gave instead the 3′,4′-lyxo-epoxide.[7]

Stannylene reactions always occur through acetals, and it is normally considered that trans-diols on five-membered rings do not form acetals readily.[8] However, the Sn–O bonds in stannylene acetals are much longer than the C–O bonds in normal acetals, and thus probably allow its formation. Nevertheless, it is interesting that substitution occurs on the trans-diol in the furanose ring rather than on one of the trans-diol units in the pyranose ring since stannylene acetals do form across the latter diols.[2] The reaction thus appears to occur where the stannylene acetal is less stable.

Bazin and co-workers[9] reported that C-4′ of 6-*O*-acyl-sucrose could be regioselectively sulfonated directly using the $Pyr{\cdot}SO_3$ complex in pyridine in 70% yield. It was proposed that regioselectivity was probably due to the presence of the long acyl substituent at C-6 of the glucopyranosyl ring.[9] We are presently not

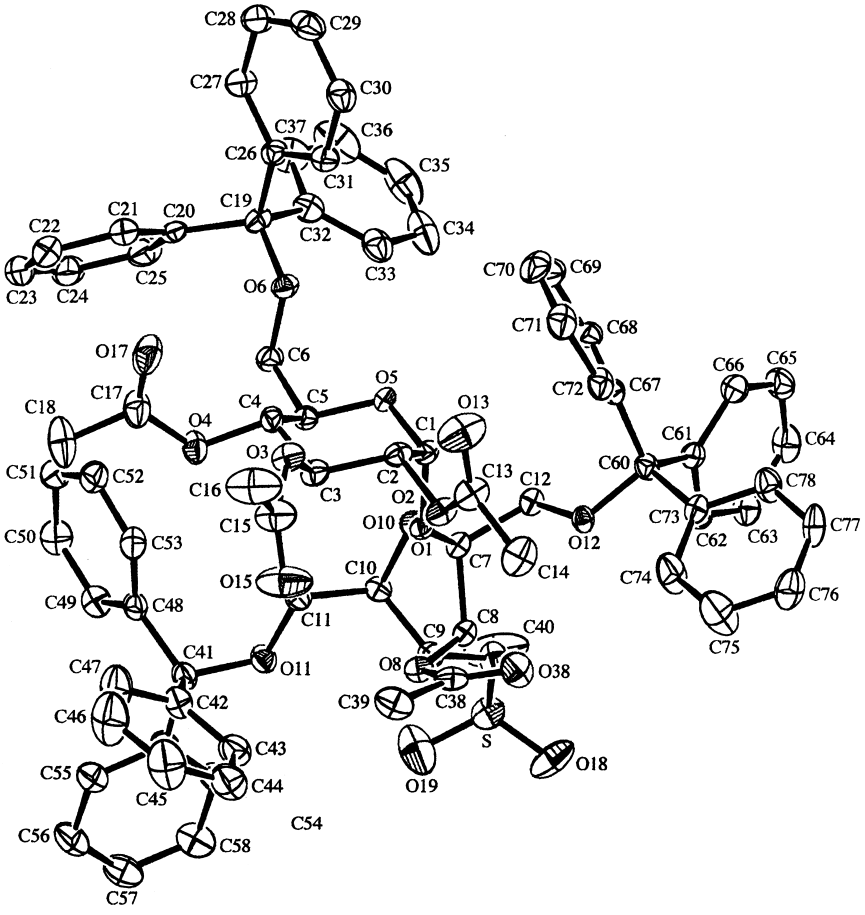
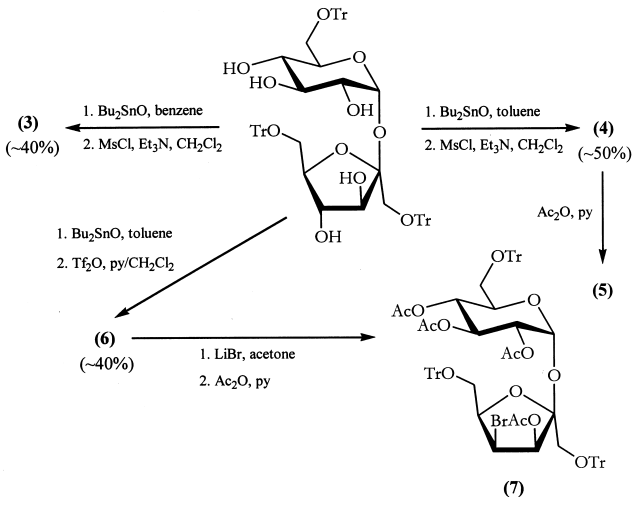


Fig. 1. ORTEP drawing of **5**.



Scheme 1.

very clear as to the reason for the observed regioselectivity in our reaction. It is possible that the 3′-*O*-benzoate obtained by Holzapfel and co-workers[4] resulted from O-4′ to O-3′ benzoyl migration since the benzoylation reaction was carried out at room temperature. Such migration has been observed in benzoylation reactions of stannylene acetals derived from acyclic diols.[10] However, Bredenkamp and Spies[11] showed that it is rather unlikely in the trans configuration. The migration of the mesyl group in our study can also be ruled out since the reaction was carried out at low temperature. The main difference between the two experiments is the temperature of the reaction (refluxing benzene vs toluene). It is probable that different structures of the stannylene acetal (dimers or oligomers) are formed in these solvents, since formation of these are dependent on the temperature of the reaction between dibutyltin oxide and the polyol.[2] The X-ray structure suggests that there is no obstruction to the formation of extended structures from the furanose oxygen atoms. The formation of an extended structure from the oxygen atoms of the pyranose ring, on the other hand, would be hindered by the furanose ring. It is not certain whether this extends to the solution conformations (Table 1).

Our preliminary investigations appear to indicate that sulfonyl halides and anhydrides react at C-4′ (when the stannylene acetal was formed in toluene), while other reagents, including trialkylsilyl halides, react mainly at C-3′ (regardless whether the stannylene acetal was formed in benzene or toluene). Although it is possible that the nature and structure of the electrophile may exert some influence over regioselectivity,[9] we are not yet in a position to confirm this.

3. Experimental

General methods.—Melting points were measured with a Thermo–Galen Hot Stage Microscope. Optical rotations were taken with a Perkin–Elmer 241 polarimeter at 26 °C. NMR spectra were recorded at 298 K in $CDCl_3$ (unless otherwise specified) on a Bruker DPX 300 spectrometer (300.13 MHz for ^1H and 75.47 MHz for ^{13}C). Mass spectra were recorded on a Finnigan TSQ 7000 (ion trap) spectrometer using electrospray-ionization (ESI) with a spray voltage of 4.5 kV. The elemental composition of ions was determined with a resolution of 7000 (10% valley definition). Microanalyses were carried out using a Perkin–Elmer 2400 Elemental Analyzer. Flash chromatography was performed on Silica Gel 60 (0.63–0.200 nm, E. Merck). Thin-layer chromatography was run on glass plates precoated with silica gel $60F_{254}$ (E. Merck, Darmstadt, Germany); detection was effected by observation under short wavelength UV light (254 nm), then spraying with 10% sulfuric acid in ethanol and charring them on a hot plate.

Table 1
Crystal data collection and refinement data for **5**

Crystallized from	Diethyl ether
Empirical formula	$C_{78}H_{74}O_{17}S$
Formula weight (g mol^{-1})	1315.49
Crystal color, habit	colorless, prism
Crystal dimensions (mm)	$0.17\times0.25\times0.30$
Temperature (K)	160 (1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Z	4
Reflections for cell determination	7356
θ range for cell determination (°)	2–26
Unit cell parameters	
a (Å)	14.5747 (1)
b (Å)	20.1994 (1)
c (Å)	23.2186 (2)
V (Å^3)	6835.56 (8)
$F(000)$	2776
Calculated density (g cm^{-3})	1.278
μ(Mo K$_\alpha$) (mm^{-1})	0.119
Scan type	ϕ and ω
$\theta_{(max)}$ (°)	26
Total reflections measured	116533
Symmetry-independent reflections	13384
R_{int}	0.070
Reflections used in refinement $[I>2\sigma(I)]$	9797
Parameters refined	866
R [on F]	0.0453
wR [on F]	0.0400
Weights	$[\sigma^2(F_o)+(0.01F_o)^2]^{-1}$
Goodness of fit	1.887
Secondary extinction coefficient	$3.5\ (3)\times10^{-7}$
Absolute structure parameter	0.02(5)
Final Δ_{max}/σ	0.0007
$\Delta\rho$ (max; min) (e Å^{-3})	0.44; −0.3

3-O-*Mesyl*-*1,6*-*di*-O-*trityl*-*β*-D-*fructofuranosyl*-(*2*→*1*)-*6*-O-*trityl*-*α*-D-*glucopyranoside* (**3**).—To a solution of 6,1′,6′-tri-*O*-tritylsucrose (1.49 g, 1.39 mmol) in benzene (20 mL) was added dibutyltin oxide (0.35 g, 1.41 mmol). The reaction mixture was heated under azeotropic distillation overnight and then concentrated under reduced pressure. The residue was taken up in dichloromethane (20 mL) and Et_3N (0.21 mL, 2.08 mmol), and cooled (0 °C), and then MsCl (0.25 mL, 2.18 mmol) was added dropwise under argon. When TLC (1:1 EtOAc–hexane) showed that the reaction was complete (~0.5 h), workup in the usual way, followed by flash column chromatography (1:1 EtOAc–hexane), gave **3** (0.54 g, 34%) as a colorless syrup: $[\alpha]_D^{26}$ +18.0° (*c* 0.50, $CHCl_3$); ^{1}H NMR: δ 2.68 (s, 3H, OSO_2CH_3), 2.98–3.51 (m, 9H, H-2,3,4,1′a,b,6′a,b and 6a,b), 3.70–3.75 (m, 1H, H-5), 3.95–4.00 (m, 1H, H-5′), 4.45–4.52 (m, 1H, H-4′), 5.07 (d, 1H, $J_{3',4'}$ 8.4 Hz, H-3′), 5.53 (d, 1H, $J_{1,2}$ 4.2 Hz, H-1) and 7.14–7.40 (m, 45H, Ar-H). ^{13}C NMR: δ 143.6, 143.5, 143.2, 128.7, 128.6, 127.9, 127.2, 127.1 (Ar-*C*), 102.7 (C-2′), 91.0 (C-1), 87.3, 87.2, 87.1 (CPh_3), 83.1 (C-5′), 79.6 (C-3′), 74.4 (C-4′), 71.9, 71.4, 71.1, 70.9 (C-2,3,4,5), 64.9, 63.5, 63.1 (C-1′,6,6′) and 37.8 (OSO_2CH_3). HRESIMS (positive mode): calcd for $[C_{70}H_{66}O_{13}S+Na]^+$ 1169.4122. Found 1169.4162. Anal. Calcd for $C_{70}H_{66}O_{13}S$: C, 73.27; H, 5.80; S, 2.79. Found: C, 73.10; H, 5.69; S, 2.52.

4-O-*Mesyl*-*1,6*-*di*-O-*trityl*-*β*-D-*fructofuranosyl*-(*2*→*1*)-*6*-O-*trityl*-*α*-D-*glucopyranoside* (**4**).—A solution of 6,1′,6′-tri-*O*-tritylsucrose (4.16 g, 3.89 mmol) in toluene (40 mL) was treated with dibutyltin oxide (0.99 g, 3.98 mmol) and then MsCl (0.50 mL, 4.37 mmol) in the presence of Et_3N (0.50 mL, 4.95 mmol), as described above to give, after flash column chromatography (1:1 EtOAc–hexane), **4** (2.51g, 56%) which crystallized from MeOH: mp 104–107 °C (dec.); $[\alpha]_D^{26}$ +25.3° (*c* 1.02, acetone); ^{1}H NMR: δ 2.69 (s, 3H, OSO_2CH_3), 2.72–2.80 (m, 1H, H-2), 3.15–3.54 (m, 7H, H-3,4,5,1′a,b and 6′a,b), 3.86–4.01 (m, 3H, H-3′, 6′a,b), 4.50 (dd, 1H, $J_{4'5'}$ 8.5 $J_{5'6'}$ 11.6 Hz, H-5′), 5.45 (t, 1H, $J_{3',4'}=J_{4',5'}$ 8.5 Hz, H-4′), 6.00 (d, 1H, $J_{1,2}$ 4.2 Hz, H-1) and 7.22–7.50 (m, 45H, Ar-H). ^{13}C NMR: δ 143.4, 143.4, 128.9, 128.7, 127.3, 127.1 (Ar-*C*), 105.2, (C-2′), 91.4 (C-1), 87.5, 87.3, 87.3 (CPh_3), 82.6, (C-5′), 76.5, 76.2 (C-3′,4′), 73.7, 72.3, 70.5, 70.3 (C-2,3,4,5), 65.7, 65.4, 64.0 (C-1′,6,6′) and 38.6 (OSO_2CH_3). HRESIMS (positive mode): calcd for $[C_{70}H_{66}O_{13}S+Na]^+$ 1169.4122. Found: 1169.4114. Anal. Calcd for $C_{70}H_{66}O_{13}S$: C, 73.27; H, 5.80; S, 2.79. Found: C, 73.12; H, 5.76; S, 2.55.

3-O-*Acetyl*-*4*-O-*mesyl*-*1,6*-*di*-O-*trityl*-*β*-D-*fructofuranosyl*-(*2*→*1*)-*2,3,4*-*tri*-O-*acetyl*-*6*-O-*trityl*-*α*-D-*glucopyranoside* (**5**).—Conventional treatment of **4** (2.3 g, 2.00 mmol) with pyridine and Ac_2O gave crystalline **5** (2.3 g, 86%): mp 178–180 °C (dec.) (from Et_2O); $[\alpha]_D^{26}$ +47.7° (*c* 0.95, $CHCl_3$); ^{1}H NMR: δ 1.52, 1.83, 1.89, 1.90 (s, 12H, $COCH_3$), 2.68 (dd, 1H, $J_{5,6a}$ 3.1 $J_{6a,6b}$ 10.0 Hz, H-6a), 2.75 (s, 3H, OSO_2CH_3), 3.08 (dd, 1H, $J_{5,6b}$ 1.0 $J_{6a,6b}$ 10.0 Hz, H-6b), 3.22–3.32 (m, 4H, H-1′a,b and H-6′a,b), 3.88–3.92 (m, 1H, H-5), 4.11–4.16 (m, 1H, H-5′), 4.71 (dd, 1H, $J_{1,2}$ 3.8 $J_{2,3}$ 9.7 Hz, H-2), 5.08–5.22 (m, 3H, H-3,4,4′), 5.25 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 5.92 (d, 1H, $J_{3'4'}$ 4.9 Hz, H-3′) and 7.10–7.40 (m, 45H, Ar-H). ^{13}C NMR: δ 170.2, 169.7, 169.1, 168.8 ($COCH_3$), 143.6, 143.3, 143.1, 128.7, 127.9, 127.7, 127.1, 126.8, (Ar-*C*), 105.1 (C-2′), 90.2 (C-1), 87.3, 87.2, 86.1 (CPh_3), 81.0 (C-5′), 79.6 (C-4′), 75.7 (C-3′), 70.6, 69.9, 69.4, 68.3 (C-2,3,4,5), 63.0, 62.4, 60.8 (C-1′,6,6′), 38.2 (OSO_2CH_3) and 20.7, 20.5, 20.3, 20.3 ($COCH_3$). HRESIMS (positive mode): calcd for $[C_{78}H_{74}O_{17}S+Na]^+$ 1337.4544. Found: 1337.4532. Anal. Calcd for $C_{78}H_{74}O_{17}S$: C, 71.21; H, 5.67; S, 2.43. Found: C, 71.05; H, 5.70; S, 2.59.

3-O-*Acetyl*-*4*-*bromo*-*4*-*deoxy*-*1,6*-*di*-O-*trityl*-*β*-D-*tagatofuranosyl*-(*2*→*1*)-*2,3,4*-*tri*-O-*acetyl*-*6*-O-*trityl*-*α*-D-*glucopyranoside* (**7**).—6,1′,6′-Tri-*O*-tritylsucrose (7.35 g, 6.88 mmol) was treated with dibutyltin oxide (1.71 g, 6.87 mmol) as described for **3**. The crude stannylene acetal was stirred in CH_2Cl_2 (100 mL) and pyridine (7 mL) at −60 °C and trifluoromethanesulfonic anhydride (2.2 mL, 13.4 mmol) was added dropwise under argon. The temperature was then allowed to rise to 0 °C, and stirring was continued for 10 min. Work up in the usual manner, followed by flash column chromatography (1:1 EtOAc–hexane), gave the corresponding 4′-*O*-trifluoromethanesulfonyl-6,1′,6′-tri-*O*-tritylsucrose.

A mixture of the 4′-*O*-triflate and lithium bromide (0.44 g) in acetone (50 mL) was stirred at rt for ~15 h when TLC (1:1 EtOAc–hexane) revealed that all starting material had reacted. The mixture was concentrated, taken up in dichloromethane and filtered. The organic layer was washed with brine, dried (Na_2SO_4), filtered, concentrated, and acetylated using Ac_2O in pyridine. Workup in the usual manner, followed by column chromatography (1:2 EtOAc–hexane), gave **7** as a yellowish syrup (2.2 g, 25%): $[\alpha]_D^{26}$ +72.3° (*c* 1.20, $CHCl_3$); ^{1}H NMR: δ 1.54, 1.71, 1.89, 1.89 (s, 12H, $COCH_3$), 2.69 (dd, 1H, $J_{5,6a}$ 2.0 $J_{6a,6b}$ 10.0 Hz, H-6a), 3.18 (dd, 1H, $J_{5,6b}$ 2.0 $J_{6a,6b}$ 10.0 Hz, H-6b), 3.25 (s, 2H, H-1′a,b), 3.32 (dd, 1H, $J_{5'6'a}$ 4.9 $J_{6'a,6'b}$ 10.1 Hz, H-6′a), 3.40 (dd, 1H, $J_{5'6'b}$ 6.6 $J_{6'a,6'b}$ 10.1 Hz, H-6′b), 4.01–4.04 (m, 1H, H-5), 4.19–4.25 (m, 1H, H-5′), 4.52 (t, 1H, $J_{3',4'}=J_{4',5'}$ 5.0 Hz, H-4′), 4.80 (dd, 1H, $J_{1,2}$ 3.5 $J_{2,3}$ 9.7 Hz, H-2), 5.19–5.30 (m, 3H, H-3,3′,4), 5.44 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1) and 7.08–7.33 (m, 45H, Ar-H). ^{13}C NMR: δ 170.3, 169.9, 169.8, 169.0 ($COCH_3$), 143.7, 143.2, 128.7, 128.0, 127.8, 127.3, 126.8 (Ar-*C*), 104.7 (C-2′), 90.4 (C-1), 87.4, 87.1, 86.1 (CPh_3), 78.7 (C-5′), 73.0 (C-3′), 70.8 (C-3), 70.6 (C-2), 69.4 (C-5), 68.6 (C-4), 65.4 (C-6′), 64.7 (C-1′), 60.7 (C-6), 50.0 (C-4′) and 20.8, 20.6, 20.5, 20.4 ($COCH_3$). HRESIMS (positive mode): calcd for $[C_{77}H_{71}O_{14}Br+Na]^+$ 1321.3925: 1323.3905.

Found: 1321.3900: 1323.3927 (1:1). Anal. Calcd for $C_{77}H_{71}BrO_{14}$: C, 71.66; H, 5.55; Br, 6.20. Found: C, 73.12; H, 5.76; Br, 6.20.

X-ray crystal structure determination and refinement for ***5****.—A view of the molecule is shown in Fig. 1. All measurements were made on a Nonius Kappa CCD diffractometer[12] using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack.[13] The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using SIR92[14] which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions [d(C–H) = 0.95 Å] and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. Refinement of the structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. A correction for secondary extinction was applied. Ten reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter[15] confirmed that the model represents the true enantiomorph. Neutral atom scattering factors for non-hydrogen atoms were taken from Maslen, Fox and O'Keefe,[16] and the scattering factors for H-atoms were taken from Stewart, Davidson and Simpson.[17] Anomalous dispersion effects were included in F_c;[18] the values for f' and f'' were those of Creagh and McAuley.[19] The values of the mass attenuation coefficients are those of Creagh and Hubbel.[20] All calculations were performed using the teXsan crystallographic software package,[21] and Fig. 1 was drawn using ORTEPII.[22]*

4. Supplementary material

The crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 163883. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033; email: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank the National University of Singapore for financial support for this research.

References

1. Wagner, D.; Verheyden, J. P. H; Moffatt, J. G. *J. Org. Chem.* **1974**, *39*, 24–30.
2. Grindley, T. B. *Adv. Carbohydr. Chem. Biochem.* **1998**, *53*, 17–142.
3. Ogawa, T.; Matsui, M. *Tetrahedron* **1981**, *37*, 2363–2369.
4. Holzapfel, C. W.; Koekemoer, J. M.; Marais, M. F. *S. Afr. J. Chem.* **1984**, *37*, 57–61.
5. McKeown, G. G.; Serenius, R. S. E.; Hayward, L. D. *Can. J. Chem.* **1957**, *35*, 28–36.
6. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
7. Khan, R.; Jenner, M. R.; Lindseth, R. J.; Mufti, K. S.; Patel, G. *Carbohydr. Res.* **1987**, *162*, 199–207.
8. Stoddart, J. F. *Stereochemistry of Carbohydrates*; Wiley-Interscience: New York, 1971; p 205.
9. Bazin, H. G.; Polat, T.; Linhardt, R. J. *Carbohydr. Res.* **1998**, *309*, 189–205.
10. Roelens, S. *J. Org. Chem.* **1996**, *61*, 5257–5263.
11. Bredenkamp, M. W.; Spies, H. S. C. *Tetrahedron. Lett.* **2000**, *41*, 543–546.
12. Hooft, *KappaCCD Collect Software*, Nonius BV: Delft, The Netherlands, 1999.
13. Otwinowski, Z.; Minor, W. *Methods Enzymol., Macromol. Crystallogr.*, Part A; Academic Press: New York, 1997; Vol. 276, pp 307–326.
14. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.
15. (a) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr., Sect. A* **1999**, *55*, 908–915;
(b) Flack, H. D.; Bernardinelli, G. *J. Appl. Crystallogr.* **2000**, *33*, 1143–1148.
16. Maslen, E. N.; Fox, A. G.; O'Keefe M. A. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, Table 6.1.1.1, pp 477–486.
17. Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.
18. Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781–782.
19. Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, Table 4.2.6.8, pp 219–222.
20. Creagh, D. C.; Hubbell, J. H. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, Table 4.2.4.3, pp 200–206.
21. *teXsan: Single Crystal Structure Analysis Software*, Version 1.10, Molecular Structure Corporation: The Woodlands, TX, 1999.
22. Johnson, C. K., ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.