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Note

The regioselectivity of the dibutylstannylene-mediated alkylation of α,α-trehalose derivatives

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Chiral molecular receptors incorporating lactose and ethylene glycol units[1] possess heterotopic faces that are inconvenient for studies of receptor–substrate interactions by n.m.r. spectroscopy. α,α-Trehalose has C_2 symmetry and its incorporation into a macrocycle will result in highly symmetric chiral receptors with homotopic faces. Moreover, the conformational features[2,3] of α,α-trehalose are appropriate for the preparation of intermediates bearing concave cavities for the synthesis of macrocyclic receptors. Such intermediates must have one hydroxyl group per glucose residue either unsubstituted or conveniently protected in order to construct the cavity. Numerous derivatives of trehalose are known[4] and unsymmetrical, partially protected trehaloses have been obtained for the synthesis of oligosaccharides of the glycolipid-type antigens isolated from mycobacteria[5], cord factor analogues[6], and substrates and inhibitors of trehalase[7]. However, there have been few regioselective reactions that distinguish between the secondary hydroxyl groups of α,α-trehalose[8,9]. The regioselective benzoylation of trehalose *via* tributylstannyl ethers, to give the 2,3,6,2′,3′,6′-hexabenzoate has been reported[10].

We now report the dibutyltin-mediated alkylation of 4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose[11] (**1**) to give partially alkylated unsymmetrical and symmetrical derivatives.

Treatment[1c] of **1** with 2.5 mol of dibutyltin oxide[12] in acetonitrile in the presence of molecular sieves and then with benzyl bromide in the presence of tetrabutylammonium bromide gave a mixture of 2,3′- (**2**, 12%), 2,2′- (**3**, 33%), and 2-*O*-benzyl (**4**, 15%) derivatives, and 30% of **1** was recovered. When *N*-methylimidazole was used as the catalyst[13], the selectivity was improved and the products were **3** (61%) and **2** (16%), and 11% of **1** was recovered. No **4** was isolated, although it was detected by t.l.c. early in the reaction. When **1** was benzylated in *N,N*-dimethylformamide using barium oxide–barium hydroxide at 0°, a complex mixture of products was obtained without any selectivity. Compounds **2**–**4**

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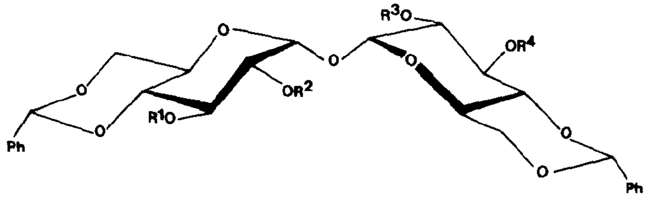
were characterised by their ^{1}H- and ^{13}C-n.m.r. spectra and those of the corresponding acetylated derivatives **2a**–**4a**. The ^{1}H-n.m.r. spectrum of the unsymmetrical derivative **2a**, which could be completely assigned by 2D-COSY experiments, contained signals at 4.87 and 5.54 p.p.m. corresponding to H-2′ and H-3, respectively, that of **3a** contained a signal (t) at 5.51 p.p.m. assigned to H-3 and H-3′, and that of **4a** contained signals (2 t) at 5.65 and 5.53 p.p.m., corresponding to H-3 and H-3′, and at 5.01 p.p.m. (dd) assigned to H-2′.

Allylation of **1** using *N*-methylimidazole as catalyst gave 2,3′- (**5**, 23%), and 2,2′-di-*O*-allyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose (**6**, 75%). The ^{1}H-n.m.r. spectrum of the diacetate (**5a**) of **5** contained signals at 5.49 and 4.82 p.p.m. assigned to H-3 and H-2′ by comparison with the data for **2a**. The diacetate (**6a**) of the symmetrical derivative **6** contained a signal at 5.46 p.p.m. corresponding to H-3 and H-3′.

Conventional benzylation of **6** gave 2,2′-di-*O*-allyl-3,3′-di-*O*-benzyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose (**7**, 94%). Deallylation of **7**, using tris(triphenylphosphine)rhodium(I) chloride[14] and mercuric salts[15], gave the 3,3′-di-*O*-benzyl- (**8**, 45%) and the 3,3′-di-*O*-benzyl-2-*O*-propyl (**9**, 20%) derivatives. The ^{1}H-n.m.r. spectrum of the diacetate (**8a**) of **8** contained a signal at 4.86 p.p.m. corresponding to H-2 and H-2′.

Thus, the use of *N*-methylimidazole as catalyst gives 2,2′-di-*O*-alkyl derivatives as the major products. No products with two *O*-alkyl groups in the same glucose ring could be detected, as found for methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[16].



1 $R^1 = R^2 = R^3 = R^4 = H$
1a $R^1 = R^2 = R^3 = R^4 = Ac$
2 $R^1 = R^3 = H$, $R^2 = R^4 = Bn$
2a $R^1 = R^3 = Ac$, $R^2 = R^4 = Bn$
3 $R^1 = R^4 = H$, $R^2 = R^3 = Bn$
3a $R^1 = R^4 = Ac$, $R^2 = R^3 = Bn$
4 $R^1 = R^3 = R^4 = H$, $R^2 = Bn$
4a $R^1 = R^3 = R^4 = Ac$, $R^2 = Bn$
5 $R^1 = R^3 = H$, $R^2 = R^4 = All$
5a- $R^1 = R^3 = Ac$, $R^2 = R^4 = All$
6 $R^1 = R^4 = H$, $R^2 = R^3 = All$
6a $R^1 = R^4 = Ac$, $R^2 = R^3 = All$
7 $R^1 = R^4 = Bn$, $R^2 = R^3 = All$
8 $R^1 = R^4 = Bn$, $R^2 = R^3 = H$
8a $R^1 = R^4 = Bn$, $R^2 = R^3 = Ac$
9 $R^1 = R^4 = Bn$, $R^2 = Pr$, $R^3 = H$

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined on a Kofler block. T.l.c. was performed on Silica Gel GF_{254} (Merck) with detection by charring with sulfuric acid. Column chromatography was performed on silica gel type I (Merck, 70–230 Mesh). The ^1H- and ^{13}C-n.m.r. spectra were recorded with a Varian XL-300 or Bruker AM-200 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Optical rotations were determined with a Perkin–Elmer 141 polarimeter.

*Benzylation of 4,6:4′,6′-*di-O-*benzylidene-α,α-trehalose*[12] (**1**). — *(a) With tetrabutylammonium bromide as catalyst.* A stirred mixture of **1** (100 mg, 0.193 mmol), powdered molecular sieve (3 Å, 0.7 g), and dibutyltin oxide (115 mg, 0.485 mmol) in dry acetonitrile (10 mL) was heated under argon at 120°. After 15 h, benzyl bromide (0.23 mL, 1.93 mmol) and tetrabutylammonium bromide (124 mg, 0.38 mmol) were added. After 4 days at 120°, the molecular sieves were collected and washed with chloroform and methanol. The combined filtrate and washings were concentrated. Column chromatography (hexane–acetone, 7:4) of the residue gave, first, 2,3′-di-*O*-benzyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose (**2**; 16 mg, 0.023 mmol, 12%), isolated as a syrup, $[\alpha]_D$ +76° (*c* 1.1, chloroform). N.m.r. data: ^1H (200 MHz), 7.4–7.2 (m, 20 H, 4 Ph), 5.55 (s, 1 H, PhC*H*), 5.52 (s, 1 H, PhC*H*), 5.20 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.18 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′), 5.98 (d, 1 H, J_{AB} 11.4 Hz, PhCH_2), 4.77 (s, 2 H, PhCH_2), 4.71 (d, 1 H, J_{AB} 11.4 Hz, PhCH_2), 4.31–3.91 (m, 6 H), 3.80–3.46 (m, 6 H); ^{13}C, 136.5–125.1 (Ph), 101.0 (PhCH), 100.3 (PhCH), 94.4 (C-1), 92.9 (C-1′), 81.2, 80.3, 77.9, 77.6, 74.0, 72.4, 70.7, 69.4, 67.9, 62.4, 61.7.

Anal. Calc. for $C_{40}O_{11}H_{42}$: C, 68.75; H, 6.06. Found: C, 68.92; H, 6.33.

The 2′,3-diacetate (**2a**) of **2** was a syrup, $[\alpha]_D$ +78.5° (*c* 1, chloroform). N.m.r. data: ^1H (300 MHz), δ 7.4–7.2 (m, 20 H, 4 Ph), 5.54 (t, 1 H, *J* 9.6 and 9.7 Hz, H-3), 5.47 (s, 1 H, PhC*H*), 5.37 (s, 1 H, PhC*H*), 5.24 (d, 1 H, $J_{1',2'}$ 3.9 Hz, H-1′), 5.10 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.87 (m, 2 H, H-2′ and PhCH_2), 4.75 (m, 3 H, PhCH_2), 4.17–3.91 (m, 5 H, H-3′,5,5′,6*e*,6′*e*), 3.63 (m, 4 H, H-2,4′,6*a*,6′*a*), 3.56 (t, 1 H, *J* 9.6 Hz, H-4), 2.00 (s, 3 H, OAc), 1.99 (s, 3 H, OAc); ^{13}C, 162.3 (CO), 168.8 (CO), 137.6 (C-ipso), 136.2 (C-ipso), 136.0 (C-ipso, double intensity), 128.0–125.1 (Ph), 100.6 (PhCH), 100.5 (PhCH), 93.2 (C-1), 92.6 (C-1′), 80.9, 78.4, 75.5, 75.1, 74.2, 71.5, 69.8, 67.7, 62.1, 20.0 (OAc), 19.7 (OAc).

Anal. Calc. for $C_{44}O_{13}H_{46}$: C, 67.51; H, 5.92. Found: C, 67.81; H, 6.16.

Eluted second was 2,2′-di-*O*-benzyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose (**3**, 44.3 mg, 0.063 mmol, 33%), m.p. 197–199° (from ethyl acetate–hexane), $[\alpha]_D$ +90° (*c* 2, chloroform). N.m.r. data: ^1H (200 MHz), δ 7.4–7.2 (m, 10 H, 2 Ph), 5.47 (s, 1 H, PhC*H*), 5.11 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.7 (s, 2 H, PhCH_2), 4.17–4.03 (m, 3 H), 3.58–3.42 (m, 4 H); ^{13}C, 136.6 (C-ipso), 136.1 (C-ipso), 133.4 (C-ipso), 128.7–125.4 (Ph), 101.0 (PhCH), 93.5 (C-1), 80.3, 78.0, 72.3, 69.3, 67.9, 61.8.

Anal. Calc. for $C_{40}O_{11}H_{42}$: C, 68.75; H, 6.06. Found: C, 68.61; H, 6.31.

The 3,3′-diacetate (**3a**) of **3** was a syrup, $[\alpha]_D$ +80° (*c* 1.2, chloroform).

N.m.r. data: ^{1}H (200 MHz), δ 7.37–7.15 (m, 10 H, 2 Ph), 5.51 (t, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 5.32 (s, 1 H, PhC*H*), 5.09 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.37 (d, 2 H, AB system, PhC*H*$_2$), 4.15 (m, 1 H, H-5), 3.96 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 3.53 (m, 3 H, H-4,6,6′), 1.96 (s, 3 H, OAc); ^{13}C, 169.3 (CO), 137.4 (C-ipso), 137.1 (C-ipso), 128.9–126.3 (Ph), 101.6 (Ph*C*H), 94.1 (C-1), 79.6, 76.7, 72.8, 71.1, 68.8, 62.9, 21.0 (OAc).

Anal. Calc. for $C_{44}O_{13}H_{46}$: C, 67.50; H, 5.92. Found: C, 67.83; H, 6.24.

Eluted third was 2-*O*-benzyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose (**4**; 17.5 mg, 0.028 mmol, 15%), m.p. 191–193° (from ethyl acetate–hexane), $[\alpha]_D$ +75° (*c* 1.1, chloroform). N.m.r. data: ^{1}H (300 MHz), δ 7.5–7.1 (m, 15 H, 3 Ph), 5.42 (s, 1 H, PhC*H*), 5.32 (s, 1 H, PhC*H*), 5.03 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.94 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.63 (AB system, 2 H, PhC*H*$_2$), 4.2 (m, 2 H), 3.8 (m, 5 H), 3.44 (m, 8 H); ^{13}C, δ 129.7–126.3 (Ph), 101.9 (Ph*C*H, double intensity), 95.0 (C-1), 93.4 (C-1′), 81.3, 81.0, 79.0, 73.8, 72.3, 71.0, 70.1, 68.9, 68.7, 63.1, 62.9.

Anal. Calc. for $C_{33}O_{11}H_{36}$: C, 65.12; H, 5.96. Found: C, 64.93; H, 5.93.

The 2′,3,3′-triacetate (**4a**) of **4** was a syrup. N.m.r. data: ^{1}H (300 MHz), δ 7.33–7.17 (m, 15 H, Ph), 5.65 (t, 1 H, *J* 9.9 Hz, H-3 or H-3′), 5.57 (t, 1 H, *J* 9.6 Hz, H-3′ or H-3), 5.47 (s, 1 H, PhC*H*), 5.43 (s, 1 H, PhC*H*), 5.33 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′), 5.15 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.01 (dd, 1 H, $J_{2',3'}$ 9.8 Hz, H-2′), 4.65 (2 H, AB system, PhC*H*$_2$), 4.27 (m, 1 H, H-5 or H-5′), 4.10 (m, 2 H, H-6a,6b), 3.98 (m, 1 H, H-5′ or 5), 3.72–3.62 (m, 4 H, H-2,4 or 4′,6′a,6′b), 3.57 (t, 1 H, *J* 9.6 Hz, H-4 or 4′), 2.04 (s, 3 H, OAc), 1.97 (s, 6 H, OAc); ^{13}C, 169.4 (CO), 168.4 (CO, double intensity), 136.3 (C-ipso), 135.9 (C-ipso, double intensity), 128.0–125.2 (Ph), 100.7 (Ph*C*H, double intensity), 93.5 (C-1), 92.4 (C-1′), 78.4, 78.2, 75.4, 72.1, 71.1, 70.0, 68.0, 67.8, 67.6, 62.1, 61.9, 20.0 (OAc), 19.0 (OAc), 19.6 (OAc).

Eluted last was **1** (30%) characterised as the tetra-acetate **1a**.

(b) With N-*methylimidazole as catalyst.* A stirred mixture of **1** (1 g, 1.93 mmol), powdered molecular sieves (3 Å, 5 g), and dibutyltin oxide (1.2 g, 4.82 mmol) in dry acetonitrile (100 mL) was heated under argon at 120° for 1 day. Benzyl bromide (2.3 mL, 19.3 mmol) and *N*-methylimidazole (0.30 mL, 3.8 mmol) were added. After 3 days at 110°, the molecular sieves were collected and washed with chloroform and methanol. The combined filtrate and washings were concentrated. Column chromatography (hexane–acetone, 7:4) of the residue gave, first, **2** (0.2 g, 0.286 mmol, 16%) and then **3** (0.78 g, 1.086 mmol, 61%); 11% of **1** was recovered.

Allylation of **1** *with* N-*methylimidazole as catalyst.* — The procedure in (*b*) was followed, but using allyl bromide (1.7 mL, 19.3 mmol) instead of benzyl bromide. Column chromatography (hexane–acetone, 7:4) of the product yielded 2,3′-di-*O*-allyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose (**5**; 0.265 g, 0.443 mmol, 23%), isolated as a syrup, $[\alpha]_D$ +52° (*c* 1.5, chloroform). N.m.r. data: ^{1}H (200 MHz), δ 7.53–7.34 (m, 10 H, 2 Ph), 6.02–5.84 (m, 2 H, 2 C*H*=CH$_2$), 5.54 (s, 1 H, PhC*H*), 5.52 (s, 1 H, PhC*H*), 5.4–5.15 (m, 6 H, H-1,1′, 2 CH=C*H*$_2$), 4.55–4.10 (m, 10 H), 3.9–3.5 (m, 6 H), 2.60 (bs, 1 H, OH), 2.33 (bs, 1 H, OH); ^{13}C, 137.4 (C-ipso), 137.1 (C-ipso), 134.8 (*C*H=CH$_2$), 134.0 (*C*H=CH$_2$), 129.2–126.1 (Ph), 118.3

(CH=CH_2), 117.3 (CH=CH_2), 101.9 (Ph*C*H), 101.4 (Ph*C*H), 95.6 (C-1), 93.9 (C-1′), 82.2, 81.3, 79.0, 73.8, 72.2, 71.6, 70.1, 68.9, 63.2, 62.8, 62.7.

Anal. Calc. for $C_{32}O_{11}H_{38}$: C, 64.20; H, 6.39. Found: C, 63.88; H, 6.39.

The 2,3′-diacetate (**5a**) of **5** had m.p. 174–176°, $[\alpha]_D$ +93° (*c* 1.2, chloroform). N.m.r. data: ^{1}H (200 MHz), δ 7.18 (m, 10 H, 2 Ph), 5.82–5.78 (m, 2 H, 2 *CH*=CH_2), 5.49 (t, 1 H, *J* 9.7 Hz, H-3), 5.46 (s, 1 H, PhC*H*), 5.39 (s, 1 H, PhC*H*), 5.39–5.09 (m, 6 H, H-1,1′, 2 CH=CH_2), 4.82 (dd, 1 H, $J_{1',2'}$ 3.9 Hz, $J_{2',3'}$ 9.7 Hz, H-2′), 4.4–3.9 (m, 9 H), 3.7–3.4 (m, 5 H), 2.07 (s, 3 H, OAc), 2.04 (s, 3 H, OAc); ^{13}C, 170.1 (CO), 169.6 (CO), 137.1 (C-ipso), 136.8 (C-ipso), 134.7 (*C*H=CH_2), 133.7 (*C*H=CH_2), 129.8–126.0 (Ph), 117.8 (CH=CH_2), 116.3 (CH=CH_2), 101.8 (Ph*C*H), 101.4 (Ph*C*H), 94.0 (C-1), 93.4 (C-1′), 81.8, 79.2, 77.4, 75.5, 73.7, 72.3, 72.0, 70.6, 65.6 (double intensity), 62.9, 62.7, 20.8 (OAc), 20.6 (OAc).

Anal. Calc. for $C_{36}O_{13}H_{42}$: C, 63.33; H, 6.20. Found: C, 63.08; H, 6.53.

Further elution gave 2,2′-di-*O*-allyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose (**6**), m.p. 180–181°, $[\alpha]_D$ +83° (*c* 0.2, chloroform). N.m.r. data: ^{1}H (300 MHz), δ 7.44–7.18 (m, 5 H, Ph), 5.85 (m, 1 H, *CH*=CH_2), 5.44 (s, 1 H, PhC*H*), 5.28 (dd, 1 H, J_{trans} 17.2 Hz, CH=CH_2), 5.17 (dd, 1 H, J_{cis} 8.9 Hz, CH=CH_2), 5.12 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.13 (m, 5 H), 3.62 (t, 1 H, H-3), 3.44 (t, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 3.39 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2); ^{13}C, 133.0 (C-ipso), 128.8 (*C*H=CH_2), 128.2–125.0 (Ph), 117.0 (CH=CH_2), 101.1 (Ph*C*H), 93.4 (C-1), 80.2, 78.0, 71.0, 68.9, 67.9, 61.6.

Anal. Calc. for $C_{32}O_{11}H_{38}$: C, 64.20; H, 6.39. Found: C, 64.51; H, 6.20.

The 3,3′-diacetate (**6a**) of **6** was a syrup, $[\alpha]_D$ +101° (*c* 0.7, chloroform). N.m.r. data: ^{1}H (200 MHz), δ 7.40–7.18 (m, 5 H, Ph), 5.76 (m, 1 H, *CH*=CH_2), 5.46 (t, 1 H, *J* 9.7 Hz, H-3), 5.37 (s, 1 H, PhC*H*), 5.20–5.10 (m, 2 H, CH=CH_2), 5.13 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.18–4.03 (m, 4 H, H-2,5, 2 *CH*=CH_2), 3.64–3.46 (m, 4 H), 2.01 (s, 3 H, OAc); ^{13}C, 169.3 (CO), 137.0 (*C*H=CH_2), 134.0 (C-ipso), 128.9–126.3 (Ph), 117.7 (CH=CH_2), 101.6 (Ph*C*H), 94.9 (C-1), 79.5, 76.8, 72.0, 70.9, 68.9, 62.7, 20.9 (OAc).

Anal. Calc. for $C_{36}O_{13}H_{42}$: C, 63.33; H, 6.20. Found: C, 63.40; H, 6.42.

2,2′-Di-O-allyl-3,3′-di-O-benzyl-4,6:4′,6′-di-O-benzylidene-α,α-trehalose (**7**). — To a stirred mixture of **6** (700 mg, 1.2 mmol) and sodium hydride (112 mg, 4.7 mmol) in dry *N,N*-dimethylformamide was added benzyl bromide (1.2 mL). After 3 h, methanol (1 mL) was added, and the mixture was diluted with chloroform, washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–acetone, 7:2) of the residue yielded **7** (94%), isolated as a syrup, $[\alpha]_D$ +52° (*c* 3.7, chloroform). N.m.r. data: ^{1}H (300 MHz), δ 7.54-7.25 (m, 10 H, 2 Ph), 5.91 (m, 1 H, *CH*=CH_2), 5.57 (s, 1 H, PhC*H*), 5.36–5.19 (m, 2 H, CH=CH_2), 5.16 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.87 (AB system, 2 H, PhCH_2), 4.25 (m, 3 H), 4.05 (t, 1 H, *J* 9.3 Hz and *J* 9.3 Hz, H-3 or H-4), 3.67 (m, 3 H), 3.53 (dd, 1 H, $J_{2,3}$ 9.3 Hz, H-2); ^{13}C, 136.4 (C-ipso), 133.5 (*C*H=CH_2), 127.8–125.0 (Ph), 116.3 (CH=CH_2), 100.2 (Ph*C*H), 94.0 (C-1), 81.1, 77.9, 77.4, 74.2, 72.5, 68.0, 62.7.

Anal. Calc. for $C_{46}O_{11}H_{50}$: C, 70.93; H, 6.47. Found: C, 71.20; H, 6.69.

3,3′-Di-O-benzyl-4,6:4′,6′-di-O-benzylidene-α,α-trehalose (**8**). — A mixture of **7** (750 mg, 0.964 mmol), tris(triphenylphosphine)rhodium(I) chloride (178.4 mg, 0.192 mmol) and diazabicyclo[2.2.2]octane (71.79 mg, 0.64 mmol) in aq. 10% ethanol was heated under reflux for 1 h, then concentrated, diluted with dichloromethane, and poured into water. The organic layer was concentrated, and a solution of the residue in 10:1 acetone–water (20 mL) was treated with mercury(II) oxide (521 mg, 2.4 mmol) then dropwise with a solution of mercury(II) chloride (523 mg, 1.92 mmol) in 10:1 acetone–water (10 mL). The mixture was heated for 30 min at 100°, then filtered through Celite, and concentrated. The residue was diluted with dichloromethane, washed with aq. potassium iodide (20 mL), dried, and concentrated. Column chromatography (hexane–acetone, 7:3) of the residue gave **8** (300 mg, 0.439 mmol, 45%), isolated as a syrup, $[\alpha]_D$ +77° (*c* 2.6, chloroform). N.m.r. data: ^{1}H (200 MHz), δ 7.53–7.26 (m, 10 H, 2 Ph), 5.58 (s, 1 H, PhCH), 5.20 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.89 (AB system, 2 H, PhCH_2), 4.29 (m, 1 H, H-6a), 4.13 (m, 1 H, H-5), 3.9–3.6 (m, 4 H, H-2,3,4,6b), 2.29 (bs, 2 H, 2 OH); ^{13}C, 138.3 (C-ipso), 137.3 (C-ipso), 128.9–126.0 (Ph), 101.2 (PhCH), 95.2 (C-1), 82.1, 78.6, 74.9, 71.7, 68.9, 63.3.

Anal. Calc. for $C_{32}O_{11}H_{38}$: C, 64.20; H, 6.39. Found: C, 64.48; H, 6.65.

The 2,2′-diacetate (**8a**) of **8** was a syrup, $[\alpha]_D$ +91° (*c* 0.9 chloroform). N.m.r. data: ^{1}H (300 MHz), δ 7.4–7.1 (m, 10 H, 2 Ph), 5.52 (s, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.88 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 4.86 (d, AB system, 1 H, PhCH_2), 4.66 (d, AB system, 1 H, PhCH_2), 4.11 (m, 1 H, H-6a), 3.99 (t, 1 H, J 9.5 Hz, H-3 or H-4), 3.88 (m, 1 H, H-6b), 3.72–3.63 (m, 2 H, H-4 or H-3, H-5), 2.15 (s, 3 H, OAc); ^{13}C, 170.0 (CO), 138.4 (C-ipso), 137.2 (C-ipso), 129.0–125.9 (Ph), 101.4 (PhCH), 93.4 (C-1), 81.7, 76.2, 74.9, 72.4, 68.7, 20.7 (OAc).

Anal. Calc. for $C_{44}O_{13}H_{46}$; C, 67.50; H, 5.92. Found: C, 67.69; H, 6.10.

Eluted second was 3,3′-di-*O*-benzyl-4,6:4′,6′-di-*O*-benzylidene-2-*O*-propyl-α,α-trehalose (**9**), isolated as a syrup (150 mg, 0.192 mmol, 20%), $[\alpha]_D$ +60° (*c* 0.78, chloroform). N.m.r. data: ^{1}H (300 MHz), δ 7.55–7.24 (m, 10 H, 2 Ph), 5.54 (s, 1 H, PhCH), 5.53 (s, 1 H, PhCH), 5.23 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.17 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.03–4.74 (m, 4 H, 2 PhCH_2), 4.33–4.13 (m, 4 H), 4.03–3.94 (m, 2 H), 3.79–3.49 (m, 8 H), 2.35 (s, 1 H, OH), 1.69 (m, 2 H, $\mathrm{OCH_2C}H_2\mathrm{CH_3}$), 1.02 (t, 3 H, $\mathrm{OCH_2CH_2C}H_3$); ^{13}C, 137.7 (C-ipso), 137.3 (C-ipso), 136.3 (double intensity, C-ipso), 127.8–124.5 (Ph), 100.2 (PhCH), 100.0 (PhCH), 94.4 (C-1), 93.1 (C-1), 81.1, 80.9, 78.9, 77.5, 77.2, 73.9, 73.8, 72.5, 70.6, 67.9, 67.8, 62.0, 61.8, 22.2 (CH_2), 9.5 (CH_3).

Anal. Calc. for $C_{43}H_{48}O_{11}$: C, 69.71; H, 6.53. Found: C, 69.45; H, 6.71.

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