Note

Sucrochemistry
Part II[1]. 6,6′-Di-*O*-tritylsucrose

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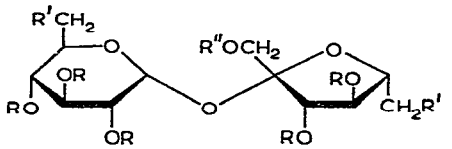
Selective tosylation of sucrose affords, after column chromatography, 6,6′-di-*O*-tosylsucrose[1] in ~20% yield, which undergoes displacement reactions with various nucleophiles to give bifunctional derivatives of sucrose. As an alternative route, the synthesis of 6,6′-di-*O*-tritylsucrose (**1**) was explored, in view of the previous observations[1] on the enhanced reactivity of the primary hydroxyl groups at C-6 and C-6′.



1 R,R″=H, R′=OTr
2 R=H, R′=OTr, R″=Tr
3 R=Bz, R′=OTr, R″=Tr
4 R, R″=Ac, R′=OTr
5 R, R″=Bz, R′=OTr
6 R,R″=Bz, R′=OH
7 R,R″=Bz, R′=OTs
8 R,R″=Bz, R′=I
9 R=Ac, R′=OTr, R″=Tr

Tri-*O*-tritylsucrose (**2**) was first reported crystalline by Josephson[2], but later workers obtained a colourless glass that was reported to be a mixture of tri-*O*-tritylsucrose, products of lower trityl content, reducing sugar fragments, and triphenylmethanol[3]. Tritylation of sucrose with four mol. of reagent in pyridine yielded a mixture which was separated by column chromatography to give crystalline 1′,6,6′-tri-*O*-tritylsucrose (**2**) and 6,6′-di-*O*-tritylsucrose (**1**) in 58 and 30% yield, respectively. Acetylation of **2** gave the known[3] penta-acetate **9** and benzoylation gave a crystalline pentabenzoate **3**. Likewise, the di-*O*-trityl derivative **1** afforded the corresponding hexa-acetate **4** and hexabenzoate **5** as crystalline derivatives. The location of the trityl groups at the 6- and 6′-positions was determined by their selective cleavage from the hexabenzoate derivative **5**, by using either hydrobromic acid in glacial acetic acid

at 5–10° or boiling, aqueous acetic acid, to give the diol **6** which on tosylation gave the known 6,6′-di-*O*-tosylsucrose hexabenzoate (**7**)[1]. The identification was confirmed by conversion of **7** into the 6,6′-di-iodo derivative **8** by treatment with sodium iodide in butanone[1].

Thus, the primary hydroxyl groups of sucrose at C-6 of the D-glucopyranosyl unit and at C-6′ of the D-fructofuranosyl unit react preferentially with trityl chloride. Unlike acetyl substituents, the benzoyl groups of 1′,2,3,3′,4,4′-hexa-*O*-benzoylsucrose (**6**) did not migrate upon detritylation of **5**, thus providing a new route to 6,6′-bifunctional derivatives of sucrose. The ^{1}H-n.m.r. spectra of the hexa-*O*-acetyl (**4**) and hexa-*O*-benzoyl (**5**) derivatives of 6,6′-di-*O*-tritylsucrose and of 6,6′-di-iodosucrose hexabenzoate are recorded in Table I.

TABLE I

FIRST-ORDER CHEMICAL SHIFTS[a] (τ VALUES) AND COUPLING CONSTANTS (Hz) AT 100 MHz

Derivative: *Solvent:*	*Acetate* **4** *Chloroform-d*	*Benzoate* **5** *Acetone-d_6*	*Di-iodide* **8** *Chloroform-d*
H-1	4.3d	3.76d	3.9d
H-2	5.18q	4.7q	4.56q
H-3		4.1t	3.81t
H-3′	4.67d	3.86d	4.03d
H-4		4.5t	4.5t
H-4′	4.71t	3.68t	4.15t
Ac	7.93s, 7.94s. 7.95s, 8.0s, 8.05s, 8.36s		
Tr	2.53–2.87 m		
Bz			1.8–2.98 m
$J_{1,2}$	3.5	3.5	3.0
$J_{2,3}$	9.5	10.0	10.0
$J_{3,4}$		10.0	10.0
$J_{4,5}$		10.0	10.0
$J_{3',4'}$	7.0	7.5	6.0
$J_{4',5'}$	7.0	7.5	6.0

[a]s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet.

EXPERIMENTAL

The general experimental data are as described in Part I.

6,6′-Di-O-tritylsucrose (**1**) *and 1′,6,6′-tri-O-tritylsucrose* (**2**). — To a solution of sucrose (15 g) in pyridine (225 ml) was added, dropwise during 0.5 h, a solution of trityl chloride (41.5 g) in pyridine (50 ml). The reaction mixture was then stirred at room temperature for 2 days. Concentration of the solution gave a brown syrup which was dissolved in chloroform, and this solution was washed successively with 2M hydrochloric acid and water, and then dried (Na_2SO_4). The chloroform was distilled off to give a syrup (35 g) which showed on t.l.c. (chloroform–acetone, 2:1) a fast-moving, yellow spot (triphenylmethanol) and two slower-moving products.

Separation of these components by elution from silica gel (500 g, Mallinckrodt) with chloroform–acetone (4:1) gave initially 1′,6,6′-tri-*O*-tritylsucrose[1,2] (**2**, 27.1 g, 58%), m.p. 128–130° (from chloroform–light petroleum), $[\alpha]_D^{23}$ +62.2° (*c* 0.87, chloroform); lit.[2] m.p. 127–129°, $[\alpha]_D^{23}$ +43.4° (ethanol) (Found: C, 77.5; H, 5.8. $C_{69}H_{64}O_{11}$ calc.: C, 77.7; H, 6.2%). Acetylation, in the usual way, gave the penta-acetate **9**, m.p. 229–230°, $[\alpha]_D^{23}$ +66.7° (*c* 1.03, chloroform); lit.[3] m.p. 235–236°, $[\alpha]_D^{17}$ +68.9° (*c* 2.45, chloroform).

6,6′-Di-*O*-tritylsucrose (**1**, 12.1 g, 30%) was then eluted and isolated as a syrup which crystallised from chloroform–light petroleum; m.p. 134–136°, $[\alpha]_D^{23}$ +43° (*c* 0.2, chloroform) (Found: C, 71.8; H, 6.5. $C_{50}H_{50}O_{11}$ calc.: C, 72.6; H, 6.05%).

2,3,3′,4,4′-Penta-O-*benzoyl-1′,6,6′-tri*-O-*tritylsucrose* (**3**). — Benzoyl chloride (4 ml) was added to a cooled solution of **1** (3.2 g) in dry pyridine (20 ml) which was then left at room temperature for 24 h. Isolation in the usual way, by pouring onto ice–water followed by chloroform extraction, gave the pentabenzoate **3** (2.9 g, 60%), m.p. 129–131° (from methanol), $[\alpha]_D^{23}$ +14.9° (*c* 0.91, chloroform) (Found: C, 78.3; H, 5.2. $C_{104}H_{84}O_{11}$ calc.: C, 78.8; H, 5.5%).

1′,2,3,3′,4,4′-Hexa-O-*benzoyl-6,6′-di*-O-*tritylsucrose* (**5**). — Benzoylation of **2** (1.8 g) as above gave the hexabenzoate **5** (2.6 g, 82%), m.p. 107–110° (from ethanol), $[\alpha]_D$ +3° (*c* 0.2, chloroform) (Found: C, 75.6; H, 5.2. $C_{92}H_{74}O_{17}$ calc.: C, 76.1; H, 5.1%).

1,2,3,3′,4,4′-Hexa-O-*acetyl-6,6′-di*-O-*tritylsucrose* (**4**). — Conventional acetylation of **2** (3 g) with acetic anhydride (4.5 ml) in pyridine (100 ml) at room temperature for 2 days gave the hexa-acetate **4** (3 g, 77%), m.p. 104–105° (from methanol), $[\alpha]_D^{23}$ +64.6° (*c* 0.2, chloroform) (Found: C, 68.6; H, 6.15. $C_{62}H_{62}O_{17}$ calc.: 69.0; H, 5.75%).

1′,2,3,3′,4,4′-Hexa-O-*benzoylsucrose* (**6**). — (*a*) A solution of the 6,6′-dityrityl ether **5** (6 g) in glacial acetic acid (6 ml) was mixed at 5° with 45% hydrobromic acid in glacial acetic acid (6 ml) and shaken for 5 min. Triphenylmethanol was immediately filtered off, and the filtrate was collected in ice–aqueous sodium hydrogen carbonate and extracted with chloroform. The extract was dried (Na_2SO_4) and concentrated, and the residual syrup was eluted from silica gel (30 g), using ether–light petroleum (3:1), to give the hexabenzoate **6** as a syrup (2.5 g, 76%), $[\alpha]_D^{23}$ +23° (*c* 0.61, chloroform) (Found: C, 66.7; H, 4.8. $C_{54}H_{46}O_{17}$ calc.: C, 67.1; H, 4.8 %).

(*b*) A solution of the dityrityl ether **5** (2.5 g) in glacial acetic acid (50 ml) was heated to the boiling point, water (1 ml) was added, and the mixture was refluxed for 1 h. Removal of the solvents by co-distillation with toluene gave a syrup which was purified by elution from silica gel (30 g) with ether–light petroleum (3:1). The product co-chromatographed on t.l.c. with that prepared in (*a*), showed identical i.r. spectra, and gave[1] the 6,6′-di-*O*-tosyl derivative **7** (68% yield), m.p. and mixed m.p. 93–96°, $[\alpha]_D$ +24.1° (*c* 2.5, chloroform) (Found: C, 63.9; H, 4.7; S, 5.1. $C_{68}H_{58}O_{21}S_2$ calc.: C, 64.0; H, 4.5; S, 5.2%).

Treatment of **7** with sodium iodide in butanone in the usual way[1] gave the 6,6′-di-iodo derivative **8** (31%), m.p. and mixed m.p. 178–179°, $[\alpha]_D$ +0.2° (*c* 2.8,

chloroform) (Found: C, 54.5; H, 3.8; I, 21.0. $C_{54}H_{44}I_2O_{15}$ calc.: C, 54.6; H, 3.7; I, 21.4%).

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REFERENCES

1 Part I: C. H. BOLTON, L. HOUGH, AND R. KHAN, *Carbohyd. Res.*, 21 (1972) 133.
2 K. JOSEPHSON, *Ann.* 472 (1929) 230.
3 G. G. MCKEOWN, R. S. E. SERENIUS, AND L. D. HAYWARD, *Can. J. Chem.*, 35 (1957) 28.