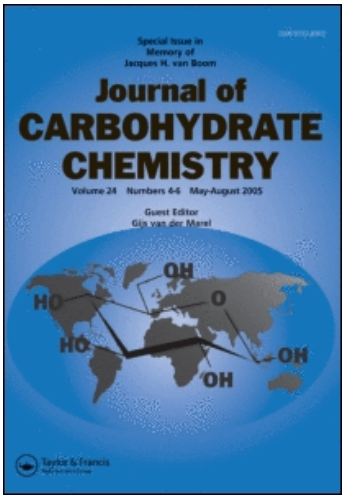

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CROWN ETHER ANALOGS FROM SUCROSE

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CROWN ETHER ANALOGS FROM SUCROSE

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ABSTRACT

A convenient synthesis of 1′,2,3,3′4,4′-hexa-*O*-benzylsucrose (**4**) from the free disaccharide is presented. Diol **4** and previously obtained 1′-*O*-benzyloxymethyl-2,3,3′,4,4′-penta-*O*-benzylsucrose (**3**) served as precursors for chiral crown ether analogs containing a sucrose backbone. Deprotection of macrocyclic compounds (removal of the benzyl blocks) was possible under hydrogenolysis conditions.

INTRODUCTION

Sucrose with eight free hydroxyl groups can be a very demanding compound to work with and selective protection of these groups presents a significant challenge for chemists.[1–3] However, chemical differentiation between the primary and secondary hydroxyl groups is possible and allows preparation of 1′,6,6′-tri-*O*-tritylsucrose in good yield by reaction of sucrose with a large excess of trityl chloride.[4,5] This compound has served as a starting material for the synthesis of 2,3,4,3′,4′-penta-*O*-benzylsucrose[6] (**1**), in which all secondary hydroxyl groups were protected with the blocks easily removable under neutral conditions. We have also conveniently converted **1** into the corresponding mono primary alcohols with free 1′-OH, 6-OH or 6′-OH groups, respectively, in good yields.[3]

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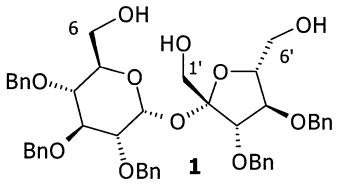

Formula 1.

RESULTS AND DISCUSSION

Having a sucrose derivative with the C-6 and C-6′ positions unprotected offers some interesting synthetic opportunities. Connecting those positions via an oxygen bridge could provide a convenient route to macrocyclic compounds, i.e., analogs of crown ethers with an incorporated sucrose backbone. As yet, there are no examples for the preparation of such sucrose macrocycles, although, chiral crown ethers containing a carbohydrate unit are known.[7]

Recently we prepared diol **3** in which the hydroxyl group at the C-1′ position was protected as a benzyloxymethyl (BOM) ether (Fig. 1).[3] Synthesis of **3** from **1** was rather tedious and required temporary double protection of the most reactive groups at the C-6 and C-6′ positions by a Mitsunobu reaction with *p*-nitrobenzoic acid leading to **2**, followed by conversion of the remaining hydroxyl function (1′-OH) into a BOM ether and deprotection at the C-6 and C-6′positions.[3] Synthesis of hexa-*O*-benzyl sucrose (**4**) by benzylation of **2** with BnBr-Ag_2O gave the desired product, but in very low yield.

Alternatively, it was reasoned that compound **4** could be prepared by benzylation of 6,6′-di-*O*-tritylsucrose (**5**). However, the latter cannot be obtained in reasonable yield. Treatment of sucrose with 2 equivalents of triphenylmethyl chloride gives 6,6′- (27%), 6,1′- (4%) and 1′,6′- (5%) disubstituted derivatives,[8] while tetramolar excess affords 58% of 1′,6,6′-tri-*O*-tritylsucrose and 30% of the

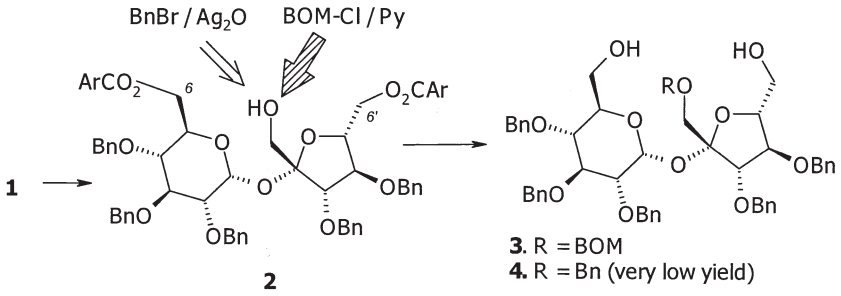

Figure 1. Synthesis of the sucrose diols with free 6,6′-OH groups.

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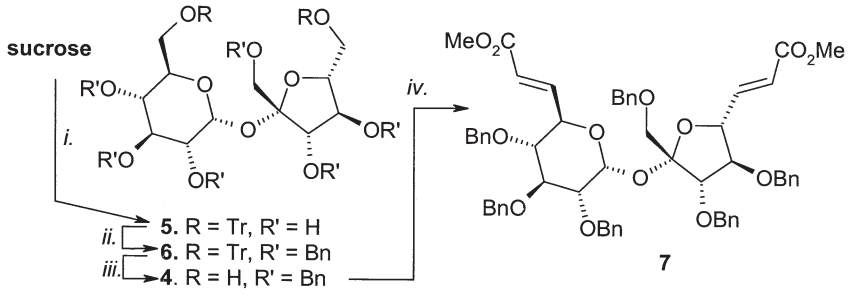
6,6′-disubstituted derivative.[5] It is clearly seen, therefore, that preparation of 6,6′-di-*O*-trityl sucrose in reasonable yield is not a trivial problem, although reactivity of the primary hydroxyl groups at the C-6 and 6-6′-position is much higher than that of the 1′-OH group.[4,5] The low yield of **5** presumably results from the fact that the tritylation is not homogeneous, since sucrose has low solubility in pyridine. Therefore, since the concentration of sucrose in solution is rather low, in contrast to the concentration of the initial tritylation products (*either* OH group), the latter are much more reactive than insoluble sucrose.

We reasoned that if all starting material were dissolved in pyridine initially, the concentration of sucrose would be high enough to take the advantage of the previously established relative reactivity sequence[2] 6-OH ~ 6′-OH > 1′-OH to give the 6,6′-disubstituted derivative **5** as the major product.

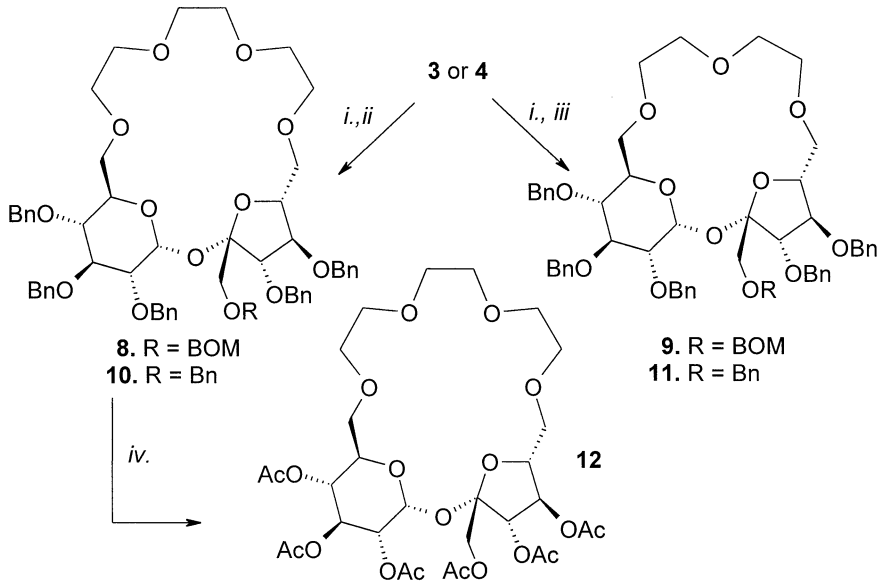
Indeed, reaction of an over-saturated homogeneous solution of sucrose in pyridine with only 2.3 equivalents of triphenylmethyl chloride (3.4 equiv were used in ref.[5]) gave the expected C-6,6′ di-protected derivative **5** as a major product, together with small amounts of the tri- and mono-tritylated derivatives. Simple chromatographic separation gave the desired compound **5** in ca. 50% yield. Standard benzylation (NaH, DMF, BnBr) of the polyol **5** afforded 1′,2,3,3′,4,4′-hexa-*O*-benzyl-6,6′-di-*O*-tritylsucrose[9] (**6**), deprotection of which with wet acetic acid furnished the diol **4**, without hydrolysis of the glycosidic bond (Scheme 1). Compound **4** is targeted for eventual use in the preparation of 'higher sucroses' (e.g., by functionalization of the di-olefin **7** prepared readily from **4**).

Having access to diol **4**, we were able to synthesize several crown ether analogs containing the sucrose backbone (Scheme 2). Compound **4** and previously prepared diol **3** were converted into di-anions (by action of sodium hydride in DMF) which were then reacted with diethylene- and triethylene glycol ditosylates[10] under standard conditions[7] used for construction of macrocycles, to afford



i. TrCl, py, over-saturated solution; *ii.* BnBr, NaH, DMF; *iii.* AcOH-H_2O 95:5, reflux, 2 h. *iv.* a. Swern oxidation; b. $Ph_3P{=}CHCO_2Me$

Scheme 1.



i. NaH, THF, rt, 30 min; *ii.* $Ts(OCH_2CH_2)_3OTs$ (1.2 equiv), rt, 6 h;
iii. $Ts(OCH_2CH_2)_2OTs$ (1.2 equiv), rt, 6 h; *iv.* H_2, Pd/C, then Ac_2O/py, DMAP.

Scheme 2.

the corresponding macrocyclic derivatives **8–11** in yield of 30–50% (Scheme 2). However, even using the high-dilution technique for cyclization, significant amounts of the monoprotected derivatives (at either C6 or C6′ positions) were formed. The macrocycle product was chromatographically separated from the acyclic products that had been acetylated.

Deprotection of the selected macrocyclic derivative **10** under standard hydrogenolysis conditions (H_2, Pd/C in aqueous ethanol and ethyl acetate) yielded the hexaol in quantitative yield, isolated and characterized as peracetate **12**.

The macrocycles **8–11** as well as their fully deprotected derivatives will be used in a study of enantioselective complexation[11] of chiral amines and their derivatives.

CONCLUSION

This report describes a simple and effective preparation of 6,6′-di-*O*-tritylsucrose (**5**) in much higher yield than previously reported in the literature. Compound **5** was readily converted into 1′,2,3,3′,4,4′-hexa-*O*-benzylsucrose (**4**) by simple benzylation, followed by removal of the trityl protecting groups. Diol **4** and its analog **3** with free hydroxyl groups at the C-6 and C-6′ positions, were then transformed into several *O*-benzylated sucrose crown ether analogs. It was possible to

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de-*O*-benzylate the macrocycle **10** by simple hydrogenolysis over palladium on carbon.

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Varian Gemini 200 or Bruker AM 500 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Most of the proton resonances were assigned by the ^{1}H-^{1}H-correlations and the carbon resonances in **12** by ^{1}H-^{13}C- correlations. Mass spectra (LSIMS; *m*-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added or ESI) were recorded with an AMD-604 or PE SCIEX API 365, or Mariner PerSeptive Biosystems apparatus. Optical rotations were measured with a Digital Jasco polarimeter DIP-360 for solutions in chloroform (*c* 1). Column chromatography was performed on silica gel (Merck, 70–230 or 230–400 mesh). THF and methylene chloride were distilled from potassium or calcium hydride, respectively, prior to use. Dry benzene was stored over sodium wire. For chromatography purposes a fraction of mineral oil with a boiling point in range 70–90 °C was used as mixture of hexanes. Acetylation reactions were performed under standard conditions: acetic anhydride, triethylamine, DMAP as a catalyst in dry methylene chloride. All solutions were dried over anhydrous sodium sulfate.

1′,2,3,3′,4,4′-Hexa-*O*-benzylsucrose (4). Sucrose (12.0 g; 35 mmol) was dissolved in pyridine (200 mL) containing DMAP (ca 50 mg) at reflux. After cooling to room temperature, triphenylmethyl chloride (22.0 g; 79 mmol) was added in one portion (contrary to ref.[5] were 3.4 equiv of TrCl were added dropwise) to the clear solution and the mixture was stirred at rt for 48 h (TLC monitoring in MeOH–acetone–water–$CHCl_3$, 20:20:3:57). Water (200 mL) was added and the products were extracted with ethyl acetate (500 mL). The organic phase was washed with water (2 × 150 mL), brine (150 mL), dried, concentrated, and the oily residue was purified by column chromatography (hexane–ethyl acetate, 1:2, then ethyl acetate–methanol–water, 100:5:2) to afford 6,6′-di-*O*-tritylsucrose (**5**, 15.5 g, 19 mmol, 54%) contaminated with small amounts of other regioisomers. This crude product was used for the next reaction without further purification. For analytical purposes, a small amount of this material was acetylated and the desired 1′,2,3,3′,4,4′-hexa-*O*-acetyl-6,6′-di-*O*-tritylsucrose was isolated by column chromatography (hexane–ethyl acetate, 3:1 to 1:1): $[\alpha]_D$ +69.5° (lit.[5] $[a]_D$ = +64.6°); *m/z:* 1101 [$M(C_{62}H_{62}O_{17}) + Na^+$]. NMR (500 MHz) δ7.50 − 7.00 (m, 30H, Ar-H), 5.70 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.35 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 4.0 Hz, H-4′), 5.26 (d, 1H, H-3′) 5.29 − 5.17 (m, 2H, H-3 and H-4), 4.82 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 4.40 and 4.27 (AB system of both H-1′, $J_{A,B}$ = 12.6 Hz), 4.21 − 4.14 (m, 1H, H-5′), 4.07 − 4.01 (m, 1H, H-5), 3.41 and 3.27 (AB system of both H-6′, $J_{5',6'}$ = 6.1 and 6.7 Hz, $J_{A,B}$ = 9.7 Hz), 3.15 and 2.92 (AB system of both H-6, $J_{5,6}$ = 1.7 and 4.1 Hz, $J_{A,B}$ = 10.5 Hz), 2.09, 2.08, 2.07, 2.00, 1.95, 1.64 (6×s, 6×3H, 6×OAc). ^{13}C NMR (50 MHz) δ170.1 (double intensity), 169.8, 169.5, 169.3,

168.8 (6×CO), 143.6, 143.4 (2×C), 104.9 (C-2′), 90.4 (C-1), 86.9, 86.3, 81.0, 70.7, 70.0, 69.6, 68.4 (7×CH), 63.5, 61.9, 61.1 (3×CH_2), 20.8, 20.7, 20.6, 20.5, 20.4, 20.3 (6×OAc).

To a stirred solution of the above prepared **5** in DMF (200 mL), was added sodium hydride (50% dispersion in mineral oil; 8.55 g, 0.17 mol), and the mixture was stirred for 30 min at rt. Benzyl bromide (16.2 mL, 0.13 mol) was added dropwise, and the mixture was stirred at rt for another 2 h. Excess of hydride was decomposed carefully with water and the mixture was partitioned between water and ethyl acetate. The organic phase was separated, washed with water, dried, concentrated and the product, 1′,2,3,3′,4,4′-hexa-*O*-benzyl-6,6′-di-*O*-tritylsucrose (**6**, 19.7 g, 76 %) was isolated by column chromatography (hexane–ethyl acetate, 99:1 to 6:1). $[\alpha]_D$ +20.6°; *m/z:* 1389 [M($C_{92}H_{86}O_{11}$) + Na^+]. ^{1}H NMR (500 MHz) d 6.57 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1) ^{13}C NMR (125 MHz) d 144.6, 144.2, 140.0, 139.4, 139.3, 139.1, 138.4, 138.1 (quaternary C, 2×Tr and 6×Bn), 104.9 (C-2′), 96.4 (C-1), 89.5 (CH), 87.5 and 86.7 (2×*C*Ph_3), 84.8, 82.7, 81.19, 81.17, 79.5, 78.5 (6×CH), 75.8, 75.0, 73.73, 73.68, 73.3, 72.7, 72.3, 71.6, 63.4, 62.7 (10×OCH_2).

Anal. Calcd for $C_{92}H_{86}O_{11}$: C, 80.79; H, 6.34. Found: C, 80.8; H, 6.4.

The above prepared 1′,2,3,3′,4,4′-hexa-*O*-benzyl-6,6′-di-*O*-tritylsucrose (**6**, 13,0 g; 9,5 mmol) was dissolved in toluene (60 mL) to which water (13.5 mL) and glacial acetic acid were added (170 mL) and this mixture was boiled under reflux for 2 h (TLC monitoring in hexane–ethyl acetate, 4:1). Water was added (200 mL), the mixture was cooled to room temperature, the phases were separated and the aqueous phase was extracted thrice with ethyl acetate–ether (150 mL : 50 mL). The combined organic phases were placed in a flask containing water (100 mL). The pH of the aqueous layer was adjusted to 14 by addition of concd NaOH and the mixture was stirred for 12 h. The organic phase was separated, washed with water, brine, dried, concentrated, and 1′,2,3,3′,4,4′-hexa-*O*-benzylsucrose (**4**, 4.4 g, 52%) was isolated by column chromatography (hexane–ethyl acetate, 4:1 to 1:1). It was possible to remove all impurities at this stage. $[\alpha]_D$ +40.8°; *m/z*: 905 [M($C_{54}H_{58}O_{11}$) + Na^+].

Anal. Calcd for $C_{54}H_{58}O_{11}$: C, 73.45; H, 6.62. Found: C, 73.0; H, 6.8.

This compound was characterised as diacetate: $[\alpha]_D$ +50.6°; *m/z*: 989 [M($C_{58}H_{62}O_{13}$) + Na^+]. ^{1}H NMR (200 MHz) d 5.66 (d, 1 H, $J_{1,2}$ = 3.1 Hz, H-1), 1.97 (s, 6H, 2×CH_3). ^{13}C NMR (50 MHz) d 170.5, 170.5 (2×CO), 104.6 (C-2′), 89.7 (C-1), 83.6, 81.8, 81.7, 79.6, 78.2, 77.2 (6×CH), 75.5, 74.8, 73.4, 72.9, 72.6, 72.3, 71.0 (6×OCH_2Ph and C-1′), 69.7 (1×CH), 65.4, 63.6 (2× *C*H_2OAc), 20.8 and 20.7 (2×OAc).

Methyl [methyl (*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*gluco*-oct-2-en-1,5-pyranosiduronat-1-yl]-(1(7)-(*E*)-5,6,8-tri-*O*-benzyl-2,3-dideoxy-(D-*lyxo*-oct-2-en-7-ulo-4,7-furanosidonate (7). To a solution of oxalyl chloride (0.3 mL) in CH_2Cl_2 (20 mL), DMSO (1.0 mL) was added dropwise at −78 °C followed by a solution of **4** (958 mg, 1.08 mmol) in CH_2Cl_2 (5 mL). After stirring for 15 min, triethylamine (2 mL) was added and stirring was prolonged for 1 h.

The mixture was partitioned between brine (15 mL) and ether (20 mL), the organic phase was separated, washed with water (10 mL), dried and concentrated. The residue was dissolved in dry benzene (15 mL) to which was added methoxycarbonylmethylene triphenylphosphorane (1.5 g, 4.94 mmol) and the mixture was stirred at rt for 3 h. Chromatographic purification (hexanes–ethyl acetate, 4:1) afforded **7** (860 mg, 80%). $[\alpha]_D$ +65.3°; *m/z*: 1013 [M($C_{60}H_{62}O_{13}$) + Na^+]. ^{1}H NMR (500 MHz) δ6.96 (dd, 1H, $J_{5',6'}$ = 6.1 Hz, $J_{6',7'}$ = 15.7 Hz, H-6′), 6.95 (dd, 1H, $J_{5,6}$ = 7.8 Hz, $J_{6,7}$ = 15.8 Hz, H-6), 6.05 (dd, 1H, $J_{5',7'}$ = 1.3 Hz, $J_{6',7'}$ = 15.7 Hz, H-7′), 6.01 (dd, 1H, $J_{5,7}$ = 1.7 Hz, $J_{6,7}$ = 15.8 Hz, H-7), 5.56 (s, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.65−4.30 (m, 8H, positions of H-5 at d 4.65 and H-5′ at d 4.40 were assigned from ^{1}H-^{1}H- correlations), 4.071-11411^{1}1-11411^1 (dd, 1H, $J_{3',4'}$ = 8.1 Hz, $J_{4',5'}$ = 8.1 Hz, H-4′), 4.00 (dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{2,3}$ = 9.5 Hz, H-3), 3.51 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.21 (dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.9 Hz, H-4). ^{13}C NMR (50 MHz,) δ168.6, 168.1 (2×CO), 144.7, 144.4, 122.4, 121.2 (2×*C*H═*C*H-CO_2Me), 138.5, 138.0, 137.82, 137.77, 137.6 (double intensity; 6×Bn), 104.1 (C-2′), 89.9 (C-1), 84.5, 83.1, 81.8, 81.7, 79.5, 79.1 (6×CH), 75.7, 75.2, 73.4, 73.2, 72.8 (double intensity), 70.9 (6× *C*H_2Ph and C-1′), 69.9 (CH), 51.6, 51.5 (2×CH_3).

Anal. Calcd for $C_{60}H_{62}O_{13}$: C, 72.71; H, 6.31. Found: C, 72.5; H, 6.4.

General procedure for the coupling of the O-6 and O-6′ positions in sucrose diols 3 or 4. Diol **3** or **4** was dissolved in an amount of dry THF to keep the concentration ca. 10^{-2} M/L. Sodium hydride (60 % dispersion in mineral oil, 4 equiv) and catalytic amounts of imidazole (ca. 10 mg) were added and the mixture was stirred at room temperature for 30 min. Then the corresponding ethylene ditosylate (1.2 equiv) was added and stirring was prolonged at rt for another 6 h. Excess of sodium hydride was carefully decomposed with water and the products were extracted with ethyl acetate. The organic phase was washed with water, brine, dried, and acetylated. Chromatographic isolation of the product afforded the desired macrocycles **8–11**.

2,3,3′,4,4′-Penta-*O*-benzyl-1′-*O*-benzyloxymethyl-6,6′-*O*-diethoxyethylenesucrose (8). Yield 47%. $[\alpha]_D$ +29.9°; *m/z:* 1049 [M($C_{61}H_{70}O_{14}$) + Na^+]. ^{1}H NMR (500 MHz) δ5.67 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1). ^{13}C NMR (125 MHz) δ104.0 (C-2′), 94.8 (OCH_2O), 89.5 (C-1), 83.7, 82.1, 82.0 79.9, 79.7, 77.7, 70.8 (7×CH), 75.4, 74.8, 72.6 (triple intensity), 72.0, 71.3, 71.1, 70.9, 70.70, 70.66, 70.57, 69.62, 69.59, 69.50 (5×OCH_2Ph, OBOM, 3×OCH_2CH_2O, C-6, C-1′ and C-6′).

Anal. Calcd for $C_{61}H_{70}O_{14}$: C, 71.33; H, 6.87. Found: C, 71.3; H, 7.0.

1′,2,3,3′,4,4′-Hexa-*O*-benzyl-6,6′-*O*-diethoxyethylenesucrose (10). Yield 31%. $[\alpha]_D$ +46.1°; *m/z:* 1014 [M($C_{60}H_{68}O_{13}$) + NH_4^+]. ^{1}H NMR (500 MHz) d 5.68 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1). ^{13}C NMR (125 MHz) δ104.3 (C-2′), 89.6 (C-1), 83.7, 82.1, 82.0, 79.8, 77.7, 77.3 (6×CH), 75.4, 74.8, 73.4, 72.6, 72.5, 72.4, 72.2,

71.6, 71.2, 71.1, 70.89, 70.86 (12×CH_2), 70.81 (1×CH), 70.6, 70.5, 69.5 (3×CH_2).

Anal. Calcd for $C_{60}H_{68}O_{13}$: C, 72.27; H, 6.87. Found: C, 72.2; H, 7.0.

2,3,3′,4,4′-Penta-*O*-benzyl-1′-*O*-benzyloxymethyl-6,6′-*O*-ethoxyethylenesucrose (9). Yield 51%. $[\alpha]_D$ +37.3°; *m/z:* 1005 [M($C_{59}H_{66}O_{13}$) + Na^+]. ^{1}H NMR (500 MHz) δ5.39 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 3.51 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.35 (dd, 1H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 10.1 Hz, H-4). ^{13}C NMR (125 MHz) δ103.6 (C-2′), 94.8 (OCH_2O), 90.0 (C-1), 84.1, 83.4, 82.1 80.1, 79.7, 78.9, 70.6 (7×CH), 75.4, 74.7, 73.6, 73.4, 72.9, 72.3, 72.2, 70.9, 70.5, 70.3, 69.9, 69.4, 69.0 (5×OCH_2Ph, OBOM, 2×OCH_2CH_2O, C-6, C-1′, C-6′).

Anal. Calcd for $C_{59}H_{66}O_{13}$: C, 72.08; H, 6.77. Found: C, 71.8; H, 6.8.

1′,2,3,3′,4,4′-Hexa-*O*-benzyl-6,6′-*O*-ethoxyethylenesucrose (11). Yield 40%. $[\alpha]_D$ +41.2°; *m/z:* 975 [M($C_{58}H_{64}O_{12}$) + Na^+]. ^{1}H NMR (500 MHz) d 5.41 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1). ^{13}C NMR (125 MHz) d 138.8, 138.7, 138.5, 138.4, 138.2, 138.1 (6× CH_2Ph), 103.7 (C-2′), 89.9 (C-1), 83.9, 83.2, 82.0, 79.89, 79.87, 78.6 (6×CH), 75.4, 74.7, 73.45, 73.40, 73.2, 72.8, 72.4, 72.2, 71.3, 71.0 (10×CH_2), 70.6, 70.4, 70.3, 69.8 (4×CH_2).

Anal. Calcd for $C_{58}H_{64}O_{12}$: C, 71.33; H, 6.87. Found: C, 71.3; H, 7.0.

1′,2,3,3′,4,4′-Hexa-*O*-acetyl-6,6′-*O*-diethoxyethylenesucrose (12). 1′,2,3,3′,4,4′-Hexa-*O*-benzyl-6,6′-*O*-diethoxyethylsucrose (10, 50 mg, 0.05 mmol) was dissolved in ethanol (10 mL), water (0.25 mL) and ethyl acetate (2 mL). Palladium on carbon (10%, 10 mg) was added and the mixture was stirred under a hydrogen atmosphere for 24 h. Solvents were evaporated under vacuum and traces of water were removed by co-evaporation with toluene. Pyridine (10 mL) was added to the residue followed by acetic anhydride (1.5 mL) and DMAP (5 mg), the mixture was stirred for 15 min at room temperature, concentrated and the product, hexaacetate **12**, was isolated by column chromatography (100% ethyl acetate) and then further purified by HPLC (100% ethyl acetate). Yield 35 mg (quant.) mp 148–149 °C. $[\alpha]_D$ +61.0°; *m/z*: 731.2315 [M($C_{30}H_{44}O_{19}$) + Na^+ requires 731.2369]. ^{1}H NMR (500 MHz) δ5.71 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.44 (dd, 1H, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 9.9 Hz, H-3), 5.40 (d, 1H, $J_{3',4'}$ = 5.3 Hz, H-3′), 5.36 (dd, 1H, $J_{4',5'}$ = 5.3 Hz, H-4′), 5,19 (dd, 1H, $J_{3,4}$ = 9.9 Hz, $J_{4,5}$ = 9.9 Hz, H-4), 4.85 (dd, 1 H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4,24 − 4.11 (m, 4H, $J_{A,B}$ = 12.3, H-5, H-5′ and AB system of both H-1′), 3.90 [1H of the AB system of -C(6′)H_2O-, $J_{A,B}$ = 11.0 Hz, $J_{5',6'}$ = 7.6 Hz), 3.80 [1H of the AB system of -C(6)H_2O-, $J_{A,B}$ = 11.1 Hz, $J_{5,6}$ = 3.9 Hz], 3.74 − 3.53 [m, 14H, 6×CH_2O, second proton of the AB system of -C(6′)H_2O- and -C(6)H_2O-], 2.19 (s, 3H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 2.07 (s, 3 H, CH_3CO), 2.04 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO). ^{13}C NMR (125 MHz) δ170.1 (double intensity), 169.9, 169.8, 169.6, 169.4 (6×CO), 103.9 (C-2′), 89.7 (C-1), 81.3 (C-5′), 76.0 (C-3′), 75.6 (C-4′), 71.6 (C-6′), 71.4, 71.1, 70.9 (3×CH_2O), 70.5 (triple intensity: C-2, 2×CH_2O), 70.4 (CH_2O), 70.1 (C-3), 69.5 (C-5), 69.3 (C-6), 68.8 (C-4), 62.7 (C-1′), 20.84, 20.79, 20.74, 20.64, 20.57 (double intensity) (6×OAc).

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