

## Note

### Monomers from sucrose\*†

Navzer D. Sachinvala‡,

*Sugar Technology Department, Hawaiian Sugar Planters' Association, 99-193 Aiea Heights Drive, Aiea, HI 96701 (U.S.A.)*

Walter P. Niemczura,

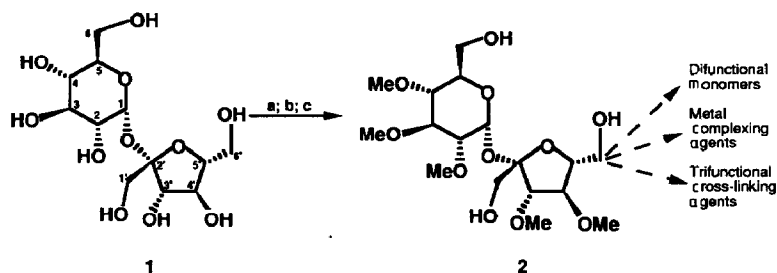
*Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, HI 96822 (U.S.A.)*

and Morton H. Litt

*Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106 (U.S.A.)*

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This laboratory is concerned with developing monomers, polymers, metal complexing agents, and asymmetric auxiliaries for metal-mediated reactions from sucrose. To date, information about the preparation and n.m.r. characterization of monomers and polymers from sucrose is very limited<sup>2,3</sup>. Our strategy (see Scheme I) was to prepare 15–50-g batches of the known 2,3,3',4,4'-penta-*O*-methylsucrose<sup>4,5</sup> (**2**) by a much-improved route and characterize it completely by two-dimensional n.m.r. methods. A previously reported synthesis<sup>5</sup> gave compound **2** on a small scale in 27% yield, and it was partially characterized<sup>6</sup> by n.m.r. We report herein the preparation and structural characterization of three new monomers from sucrose via **2**, namely 2,3,3',4,4'-penta-*O*-methyl-1',6,6'-*O*-(2-methyl-2-propenoyl)sucrose (**3**) 1',2,3,3',4,4'-hexa-*O*-methylsucrose (**7**) and 6,6'-diamino-6,6'-dideoxy-1',2,3,3',4,4'-hexa-*O*-methylsucrose (**9**).



Scheme I

\*Dedicated to Professor Robert G. Salomon.

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‡ To whom correspondence should be addressed.

2,3,3',4,4'-Penta-*O*-methylsucrose (**2**) was prepared (Scheme I) in 3 steps: (a) Sucrose was converted into 1',6,6'-tri-*O*-tritylsucrose by the methods of Hough *et al.*<sup>7</sup>; (b) treatment of the tritryl adduct with sodium hydride in dimethyl sulfoxide at 55° (ref. 8), followed by addition of methyl iodide or dimethyl sulfate, gave 1',6,6'-tri-*O*-trityl-2,3,3',4,4'-penta-*O*-methylsucrose (m.p. 103–108°) in 97% yield when methyl iodide was used and in 89% yield when dimethyl sulfate was used; (c) reductive removal of the trityl groups with lithium in liquid ammonia and tetrahydrofuran<sup>9</sup> generated the desired compound **2** in 97% yield.

Sugar-ring proton assignments were made by homonuclear correlation spectroscopy (H-H COSY)<sup>10</sup> and <sup>13</sup>C assignments by heteronuclear correlation spectroscopy (H-C COSY)<sup>11,12</sup>. Isolated resonances of the *O*-methyl groups were assigned either by

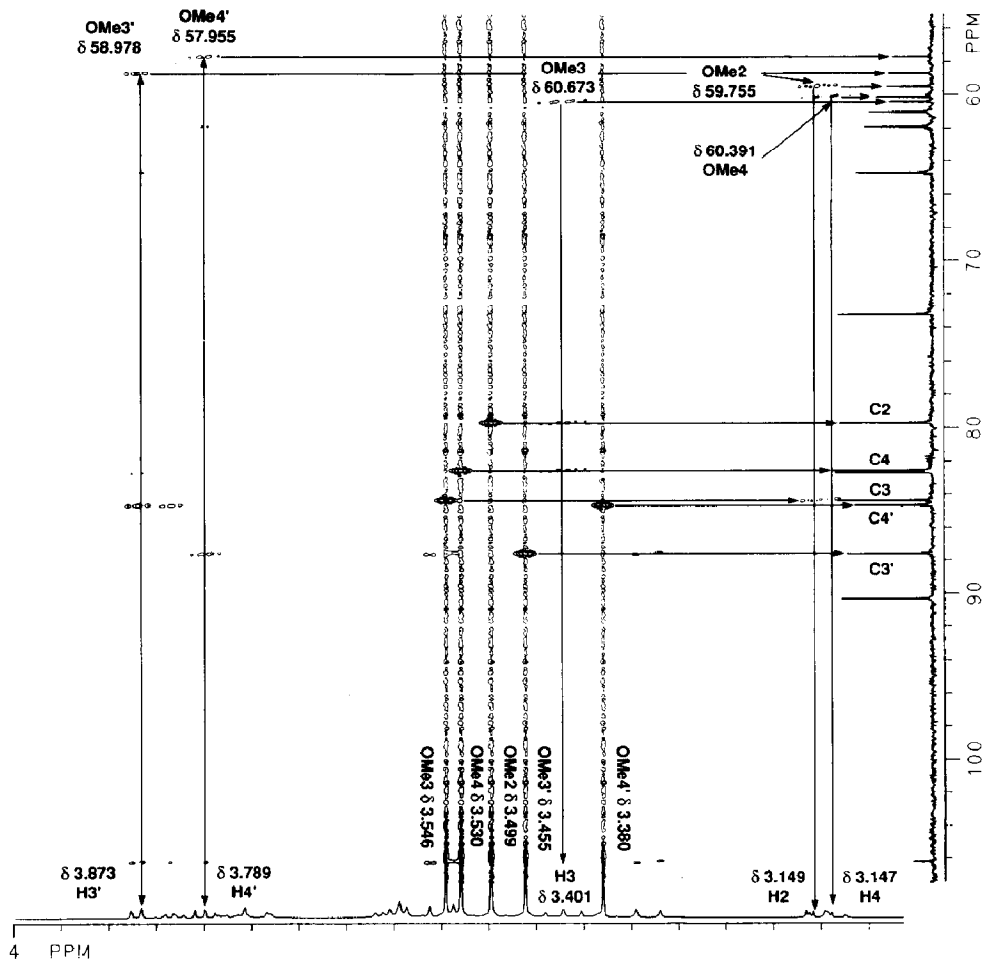
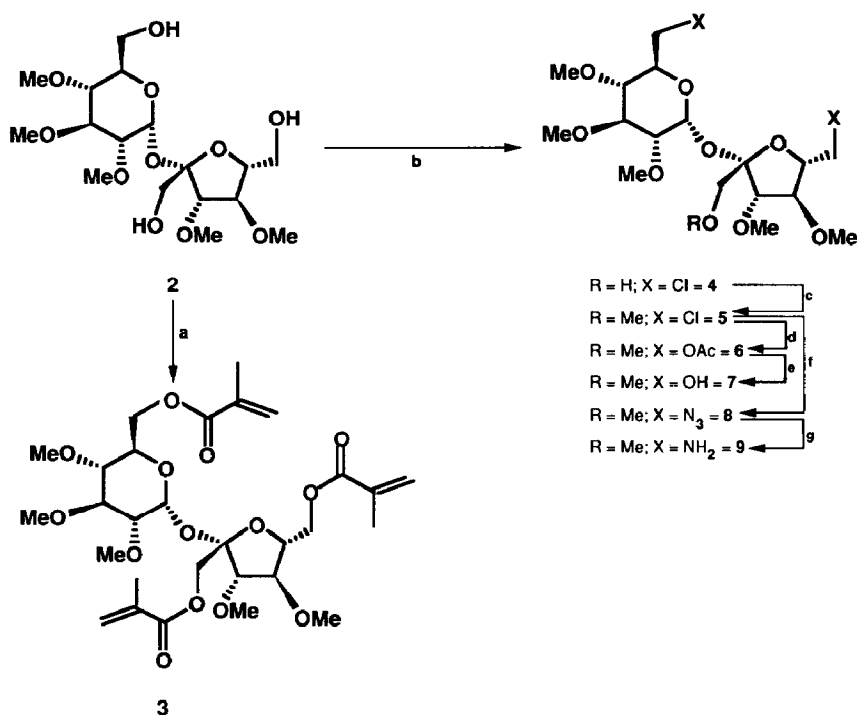


Fig. 1. Heteronuclear multiple bond connectivity (HMBC) experiment on 2,3,3',4,4'-penta-*O*-methylsucrose (**5**). The pulse sequence used was identical to that proposed by Bax and Sommers<sup>14</sup>. Specifically, 512-K blocks of 64 scans were recorded using a delay of 80 ms, for the evolution of the long-range coupling and a 3.6-ms delay for the removal of the direct correlation. The final data-set was multiplied by a sine-bell function in both domains and zero filled to yield a 1 K × 1 K real-data matrix. The sample temperature was regulated at 25°, and the sample was not spun.

long-range heteronuclear correlation spectroscopy (H-C COLOC)<sup>13</sup> or by proton-detected heteronuclear multiple-bond connectivity (HMBC) experiments<sup>14</sup>. Fig. 1 shows the HMBC experiment performed on 2,3,3',4,4'-penta-*O*-methylsucrose (**2**). Correlations can be seen from the *O*-methyl carbons (between 57 and 62 p.p.m.) and the sugar-ring protons. In addition, correlations are observed between the methyl protons and the adjacent ring carbons. This double correlation permitted an additional check not only on the methyl-group assignments but also on the carbon assignments from the H-C COSY experiment.

Scheme II shows methods for preparing compounds **3–9** from **2**. (a) Treatment of penta-*O*-methylsucrose with triethylamine and methacryloyl chloride in tetrahydrofuran provided 2,3,3',4,4'-penta-*O*-methyl-1',6,6'-tri-*O*-(2-methyl-2-propenoyl)sucrose (**3**) in 50% yield; (b) selective manipulation of **2** in pyridine with triphenylphosphine and carbon tetrachloride<sup>15</sup> generated 6,6'-dichloro-6,6'-dideoxy-2,3,3',4,4'-penta-*O*-methylsucrose (**4**, 91% yield); (c) once the dihalide **4** had been prepared the 1'-hydroxyl group in **4** was permanently blocked as its methyl ether **5**, by using diazomethane, and boron trifluoride etherate, in dichloromethane, at  $-10^{\circ}$ , in 99% yield<sup>16</sup>. Subsequently the diol monomer **7** was prepared in two steps; (d) treatment of the hexamethoxy dichloride **5** with cesium acetate<sup>17</sup> in DMF, followed by (e) hydrolysis with 2M sodium methoxide in methanol<sup>18</sup> at ambient temperature, produced the desired diol **7** in 80% overall yield from **5**. Similarly, the diamine **9** was produced (in 86% yield over 2 steps) by



Scheme II

(f) displacement of the dihalide in **5** by sodium azide<sup>19</sup>, followed by (g) reduction of **8** with lithium aluminum hydride in tetrahydrofuran<sup>19</sup> or with 10% palladium on carbon and hydrogen 60 lb in<sup>-2</sup> in ethanol<sup>20</sup>.

Sucrose is an abundant and inexpensive starting material<sup>21</sup>. Using the methods discussed herein, we are able to generate monomers in quantities useful for the practical development of thermoset acrylic polymers as well as linear polyesters and polyamides from sucrose.

## EXPERIMENTAL

**General methods.** — All reactions were conducted in dry glassware under an inert atmosphere. Proton nuclear magnetic resonance (n.m.r.) spectra were recorded at 500.11 MHz using a General Electric GN Omega-500 instrument. The <sup>13</sup>C-spectra were obtained at 125.76 MHz. Fast-atom bombardment (f.a.b.) mass spectra were obtained on VG Instruments (Model 70 SE) using xenon as the bombarding gas. Molecular ions were verified as [M + I]<sup>+</sup>, [M + K]<sup>+</sup>, or [M + Na]<sup>+</sup> by addition of potassium or sodium iodides to the sample matrix. All organic reagents and solvents (reagent grade, Aldrich Chemical Co.) were purified and dried before use according to procedures outlined by Perrin *et al.*<sup>22</sup>. Column chromatography refers to flash column chromatography, performed according to Still *et al.*<sup>23</sup> on silica gel (230–400 mesh). Reverse-phase chromatography was performed using the Spectrum<sup>®</sup> m.p.l.c. apparatus on C<sub>18</sub> gels (40 μm). Compounds were detected on t.l.c. plates (silica gel 60, F 254, 0.25 mm, E. M. Science) by u.v. or by spraying with 10% phosphomolybdic acid in EtOH; *R<sub>F</sub>* recorded here were determined on 10-cm strips of these plates. Melting points were recorded with an Electrothermal digital melting-point apparatus and are uncorrected. Optical rotations were obtained on a Jasco DIP-370 polarimeter at 598 nm. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

**2,3,3',4,4'-Penta-O-methyl-1',6,6'-tri-O-tritylsucrose<sup>8</sup>.** — To a stirred suspension of NaH (60% in oil, 150 g, 1250 mmol washed free of oil with pentane) in dry Me<sub>2</sub>SO (800 mL) at 50°, was added a solution of 1',6,6'-tri-O-tritylsucrose<sup>7</sup> (50 g, 46.76 mmol, dissolved in dry Me<sub>2</sub>SO, 200 mL, added dropwise over 2 h). The temperature of the reaction was monitored internally and maintained between 50 and 55°. After hydrogen evolution had ceased, the burgundy-red solution was cooled to 25° and treated with Me<sub>2</sub>SO<sub>4</sub> (147.5 g, 1175 mmol, 111 mL, added dropwise over 90 min). The mixture was stirred for 24 h, at room temperature, treated with aq. NaOH (10% solution, 500 mL) and stirred for 3 h. The mixture was then diluted with water (500 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 300 mL). The combined organic extracts were then washed with water and brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was flash-chromatographed over a column of silica gel (10 × 15 cm) and eluted with 1:1 hexane–CH<sub>2</sub>Cl<sub>2</sub> (2 L), then CH<sub>2</sub>Cl<sub>2</sub> (2 L), followed by 5% EtOAc in CH<sub>2</sub>Cl<sub>2</sub> (2 L), at a flow rate of ~200 mL/min. The isolated product, yield 47.1 g (41.35 mmol, 89%) had (m.p. 103–108°; [α]<sub>D</sub><sup>27</sup> +47.7° (c 0.34, CH<sub>2</sub>Cl<sub>2</sub>); *R<sub>F</sub>* 0.15 in CH<sub>2</sub>Cl<sub>2</sub>; <sup>1</sup>H-n.m.r. (500.11 MHz, acetone-*d*<sub>6</sub>): δ 3.04 (dd, *J* 3.5, 9.5 Hz, H-2), 3.06 (d, *J* 10 Hz, H-1'a), 3.07 (dd, *J* 3,

10 Hz, H-6a), 3.14 (s, OMe-3'), 3.16 (s, OMe-4'), 3.19 (s, OMe-2), 3.21 (t,  $J$  9.5 Hz, H-3), 3.31 (s, OMe-4), 3.36 (d,  $J$  10 Hz, H-1'b), 3.41 (s, OMe-3), 3.41 (dd,  $J$  2, 10 Hz, H-6b), 3.51 (m, H-6'a), 3.53 (dd,  $J$  9.5, 10 Hz, H-4), 3.55 (m, H-6'b), 3.88 (ddd,  $J$  2, 3, 10 Hz, H-5), 4.17 (d,  $J$  8.5 Hz, H-3), 4.29 (t,  $J$  8.5 Hz, H-4'), 4.41 (m, H-5'), and 5.98 (d,  $J$  3.5 Hz, H-1), 7.34 (30 H, arom), 7.52 (15 H, arom);  $^{13}\text{C}$ -n.m.r. (125.76 MHz, acetone- $d_6$ ):  $\delta$  57.73 (OMe-3'), 58.36 (OMe-4'), 58.68 (OMe-2), 60.46 (OMe-4), 60.60 (OMe-3), 62.97 (CH<sub>2</sub>-6'), 63.89 (CH<sub>2</sub>-6), 67.86 (CH<sub>2</sub>-1'), 71.41 (CH-5), 79.52 (CH-5'), 80.17 (CH-4), 81.50 (CH-4'), 82.35 (CH-2), 84.52 (CH-3), 86.74 (1'-C-trityl methine), 86.93 (CH-3'), 87.51 (6-C-trityl methine), 87.68 (6'-C-trityl methine), 88.92 (CH-1), 104.66 (CH-2'), 127.22 (CH), 127.43 (2 CH), 128.07 (2 CH), 128.23 (3 CH), 128.27 (CH), 129.03 (2 CH), 129.14 (4 CH), 144.05 (C), and 144.32 (2 C); f.a.b. mass for C<sub>74</sub>H<sub>74</sub>O<sub>11</sub> calc. 1138.33; found  $M^+ + 1 = 1139$ ,  $M^+ - H + K^+ = 1177$ ,  $M^+ + K^+ = 1178$ .

*Anal.* Calc. for C<sub>74</sub>H<sub>74</sub>O<sub>11</sub>: C, 78.0; H, 6.5. Found: C, 77.5; H, 6.5.

*2,3,3',4,4'-Penta-O-methylsucrose* (**2**). — To a solution of the preceding product (45.6 g, 40 mmol) in dry tetrahydrofuran (1 L) and liquid NH<sub>3</sub> (2 L) at  $-70^\circ$  were added small pieces of Li wire (4 g) over 50 min. The deep-red solution was stirred for 3 h at  $-70^\circ$ . The excess of Li was decomposed by adding EtOH (60 mL), and small pieces of solid CO<sub>2</sub> were added to aid in the evaporation of NH<sub>3</sub> as the solution attained room temperature. The resulting mixture was filtered, the inorganic retentate washed thoroughly with acetone (5  $\times$  300 mL), and the effluent concentrated to a thick yellow oil. Flash column chromatography of the oil on a column of silica gel (10  $\times$  15 cm) using 50% EtOAc in CH<sub>2</sub>Cl<sub>2</sub> (at 200 mL/min) separated the Ph<sub>3</sub>CH and other nonpolar components of the mixture. The column was then charged with 10% EtOH in CH<sub>2</sub>Cl<sub>2</sub> to elute the desired compound; yield 16.11 g (39.10 mmol, 97%);  $[\alpha]_D^{27} + 50.6^\circ$  ( $c$  7.8, acetone);  $R_F$  of **2** in 5% EtOH in CH<sub>2</sub>Cl<sub>2</sub> 0.31;  $^1\text{H}$ -n.m.r. (500.11 MHz, acetone- $d_6$ ):  $\delta$  3.15 (t,  $J_{3,4}$  9.8,  $J_{4,5}$  9.0 Hz, H-4), 3.15 (dd,  $J_{1,2}$  3.7,  $J_{2,3}$  9.8 Hz, H-2), 3.33 (d,  $J_{1'a,1'b}$  12.5 Hz, H-1'a), 3.38 (s, OMe-4'), 3.40 (t,  $J_{3,4}$  9.8 Hz, H-3), 3.46 (s, OMe-3'), 3.50 (s, OMe-2), 3.53 (s, OMe-4), 3.55 (s, OMe-3), 3.55 (d, H-1'b), 3.59 (m,  $J_{6'a,6'b}$  12.0 Hz, H-6'a), 3.60 (dd,  $J_{5,6a}$  5.0,  $J_{6a,6b}$  10.6 Hz, H-6a), 3.61 (m,  $J_{6'a,6'b}$  12 Hz, H-6'b), 3.75 (dd,  $J_{5,6b}$  2.1,  $J_{6a,6b}$  10.6 Hz, H-6b), 3.78 (m,  $J_{5,6a}$  5,  $J_{5,6b}$  2.1 Hz, H-5), 3.80 (t,  $J_{3',4'}$  5.1  $J_{4',5'}$  5.8 Hz, H-4'), 3.84 (m,  $J_{5',6'a}$  4.2,  $J_{5',6'a}$  6.3 Hz, H-5'), 3.87 (d,  $J_{3',4'}$  5.1 Hz, H-3'), and 5.45 (d,  $J_{1,2}$  3.7 Hz, H-1);  $^{13}\text{C}$ -n.m.r. (125.76 MHz, acetone- $d_6$ ):  $\delta$  57.96 (OMe-4'), 58.98 (OMe-3'), 59.76 (OMe-2), 60.29 (CH<sub>2</sub>-6), 60.39 (OMe-4), 60.67 (OMe-3), 61.79 (CH<sub>2</sub>-6'), 64.63 (CH<sub>2</sub>-1'), 73.12 (CH-5), 79.53 (CH-2), 82.48 (CH-4), 82.59 (CH-5'), 84.24 (CH-3), 84.52 (CH-4'), 87.48 (CH-3'), 90.17 (CH-1), and 106.80 (C-2'), f.d.-m.s. for C<sub>17</sub>H<sub>32</sub>O<sub>11</sub> calc. 412.43; found  $[M + 1]^+ = 413$ .

*Anal.* Calc. for C<sub>17</sub>H<sub>32</sub>O<sub>11</sub>: C, 49.5; H, 7.5. Found: C, 49.2; H, 7.8.

*2,3,3',4,4'-Penta-O-methyl-1',6,6'-tri-O-(2-methyl-2-propenoyl)sucrose* (**3**). — To a solution of **2** (3.88 g, 9.42 mmol) in dry tetrahydrofuran (100 mL) at  $0^\circ$  was added Et<sub>3</sub>N (freshly distilled over Na, 10 mL, 7.4 g, 73.3 mmol, 15 equiv.), followed by methacryloyl chloride (freshly distilled over 3 Å molecular sieves, 5.52 mL, 5.91 g, 56.5 mmol, 6 equiv. added dropwise over 15 min). The suspension was stirred at  $4^\circ$  and monitored by t.l.c. using 50% EtOAc in hexane. After 3 h at  $4^\circ$ , the volatiles were removed *in vacuo* at  $4^\circ$ ,

then the residue was redissolved in EtOAc in hexane (1:1, 20 mL), the mixture filtered to remove the ammonium salt, and the filtrate treated with aq.  $\text{NaHCO}_3$  (0.2M, 10 mL). Following the usual workup and concentration *in vacuo*, the residue was chromatographed on a column (5  $\times$  15 cm) of silica gel using 20% EtOAc in hexane to provide the desired triester **3** as an oil; yield 2.91 g (4.71 mmol, 50%);  $[\alpha]_D^{26}$  45.73° (*c* 2.9, acetone);  $R_F$  **3** in 50% EtOAc in hexane 0.42;  $^1\text{H}$ -n.m.r. (500.11 MHz, acetone- $d_6$ ):  $\delta$  1.90 (m, 3 H, methacryloyl), 1.93 (m, 3 H, methacryloyl), 1.95 (m, 3 H, methacryloyl), 3.07 (dd, *J* 4.3, 9.5 Hz, H-2), 3.12 (t, *J* 9.5 Hz, H-4), 3.40 (s, OMe-2), 3.41 (t, *J* 9.5 Hz, H-3), 3.45 (s, OMe-3'), 3.50 (s, OMe-4), 3.52 (s, OMe-4'), 3.54 (s, OMe-3), 3.96 (t, *J* 7 Hz, H-4'), 3.99 (d, *J* 7 Hz, H-3'), 4.02 (ddd, *J* 4, 5.5, 7 Hz, H-5'), 4.06 (ddd, *J* 2, 5, 10 Hz, H-5), 4.20 (d, *J* 12 Hz, H-1'a), 4.25 (d, *J* 12 Hz, H-1'b), 4.27 (dd, *J* 5, 11.5 Hz, H-6a), 4.33 (dd, *J* 5.5, 12 Hz, H-6'a), 4.41 (dd, *J* 4, 12 Hz, H-6'b), 4.43 (dd, *J* 2, 11.5 Hz, H-6b), 5.46 (d, *J* 4.3 Hz, H-1), 5.57 (m, 1 H), 5.63 (m, 1 H), 5.65 (m, 1 H), 6.09 (m, 1 H), 6.11 (m, 1 H), and 6.14 (m, 1 H);  $^{13}\text{C}$ -n.m.r. (125.76 MHz, acetone- $d_6$ ):  $\delta$  18.09 (2  $\text{CH}_3$ , methacryloyl), 18.15 ( $\text{CH}_3$ , methacryloyl), 58.21 (2  $\text{CH}_3$ , OMe-2, OMe-3'), 58.74 (OMe-4'), 60.21 (OMe-4), 60.39 (OMe-3), 63.53 ( $\text{CH}_2$ -6), 64.94 ( $\text{CH}_2$ -6'), 65.62 ( $\text{CH}_2$ -1'), 70.03 (CH-5), 78.87 (CH-5'), 79.93 (CH-4), 82.12 (CH-2), 83.82 (CH-3), 83.96 (CH-3'), 86.54 (CH-4'), 89.59 (CH-1), 103.84 (C-2'), 125.49 (1 CH, methacryloyl), 125.90 (2 CH, methacryloyl), 136.72 (2 C, methacryloyl), 136.99 (C, methacryloyl), 166.50 (C, methacryloyl), and 166.81 (2 C, methacryloyl); e.i.-m.s. for  $\text{C}_{29}\text{H}_{44}\text{O}_{14}$  calc. 616.2785; found 616.2768, 617.2696 (a  $^{13}\text{C}$  isotope).

*Anal.* Calc. for  $\text{C}_{29}\text{H}_{44}\text{O}_{14}$ : C, 56.4; H, 7.3. Found: C, 56.5; H, 7.4.

**6,6'-Dichloro-6,6'-dideoxy-1',2,3,3',4,4'-hexa-O-methylsucrose (5).** — To a solution containing compound **2** (6.2 g, 15.04 mmol) in pyridine (150 mL) was added  $\text{Ph}_3\text{P}$  (14.16 g, 54 mmol, 3.6 equiv.) followed by  $\text{CCl}_4$  (8.31 g, 5.19 mL, 54 mmol) at 25°. The contents were stirred vigorously and allowed to attain a temperature of 60° during 40 min, and then maintained at that temperature for an additional 30 min. To this mixture was added MeOH (100 mL), and then the contents were cooled to room temperature and concentrated to a paste *in vacuo*. The residue was redissolved in EtOAc and washed with 10%  $\text{H}_2\text{O}_2$  (3  $\times$  100 mL). The organic layer was then absorbed onto silica gel (100 g) and further concentrated to a dry, free-flowing powder. The silica gel-coated mixture was carefully poured onto a column (5  $\times$  15 cm) and eluted with 30% EtOAc in hexane to provide 6,6'-dichloro-6,6'-dideoxy-2,3,3',4,4-penta-O-methylsucrose (**4**) as an oil; yield 6.2 g (13.8 mmol, 91.7%);  $[\alpha]_D^{26}$  + 40.13° (*c* 1.2, acetone);  $R_F$  0.29 (50% EtOAc in hexane). This compound was used immediately without further characterization.

A solution of **4** (6.2 g, 13.8 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) at  $-10^\circ$  was treated with  $\text{BF}_3\cdot\text{OEt}_2$  (70  $\mu\text{L}$ ), with subsequent addition of an excess of  $\text{CH}_2\text{N}_2$  in  $\text{CH}_2\text{Cl}_2$  ( $\sim 0.7\text{M}$ , 100 mL, 70 mmol). After  $\sim 5$  min, the cold solution was filtered and washed serially with saturated  $\text{NaHCO}_3$ , water, and brine. The organic layer was dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo* to provide the dichlorohexamethyl ether **5** as an oil; yield 6.33 g (13.66 mmol, 99%);  $[\alpha]_D^{25}$  + 58.15° (*c* 2.7 MeOH); this compound needed no further purification;  $R_F$  of **5** in 50% EtOAc in hexane 0.48;  $^1\text{H}$ -n.m.r. (500.11 MHz, acetone- $d_6$ ):  $\delta$  3.07 (dd, *J* 9, 9.5 Hz, H-4), 3.08 (dd, *J* 3.5, 9.5 Hz, H-2), 3.36 (d, *J* 11 Hz, H-1'b), 3.38 (t,

$J$  9.5 Hz, H-3), 3.38 (s, OMe-1'), 3.43 (s, OMe-2), 3.46 (s, OMe-4'), 3.47 (s, OMe-3'), 3.53 (s, OMe-4), 3.53 (s, OMe-3), 3.58 (d,  $J$  11 Hz, H-1'a), 3.75–3.92 (m, 6 H), 4.01 (d,  $J$  7 Hz, H-3'), 4.01 (ddd,  $J$  2.5, 5, 9.5 Hz, H-5), and 5.51 (d,  $J$  3.5 Hz, H-1);  $^{13}\text{C}$ -n.m.r. (125.76 MHz, acetone- $d_6$ ):  $\delta$  45.60 ( $\text{CH}_2$ -6), 46.25 ( $\text{CH}_2$ -6'), 58.20 (OMe-2), 58.31 (OMe-4'), 58.49 (OMe-3'), 59.08 (OMe-1'), 60.33 (OMe-3), 60.35 (OMe-4), 71.03 (CH-5), 73.99 ( $\text{CH}_2$ -1'), 80.56 (CH-4), 81.10 (CH-5), 82.21 (CH-2), 83.75 (CH-3), 85.75 (CH-4'), 85.98 (CH-3'), 89.96 (CH-1), and 105.2 (C-2').

*Anal.* Calc. for  $\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{O}_9$ : C, 45.6; H, 6.9; Cl, 15.5. Found: C, 45.7; H, 6.9; Cl, 15.2.

**6,6'-Di-O-acetyl-1',2,3,3',4,4'-hexa-O-methylsucrose (6).** — To a suspension of cesium acetate<sup>17</sup> (2.48 g, 12.95 mmol, 6 equiv.) in dry DMF (5 mL) was added the dichloride **5** (1.0 g, 2.15 mmol in 2 mL DMF). The mixture was allowed to stir for 24 h at 130°, and then cooled to room temperature, diluted with water, and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic extracts were washed with water and then brine, dried ( $\text{MgSO}_4$ ), and concentrated *in vacuo*. Silica gel chromatography on a column (5 × 18 cm) using 50% EtOAc in hexane (flow rate ~100 mL/min) provided the desired diacetate **6** as an oil (0.98 g) in 90% yield;  $R_f$  0.29 in 50% EtOAc in hexane;  $^1\text{H}$ -n.m.r. (500.11 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.05 (s, Me of acetate-6), 2.05 (s, Me of acetate-6'), 3.03 (t,  $J$  9.1, 9.9 Hz, H-4), 3.09 (dd,  $J$  3.9, 9.7 Hz, H-2), 3.35 (d,  $J$  10.9 Hz, H-1'a), 3.39 (t,  $J$  9.1, 9.7 Hz, H-3), 3.39 (s, OMe-1'), 3.42 (s, OMe-3'), 3.44 (s, OMe-4'), 3.47 (s, OMe-2), 3.49 (s, OMe-4), 3.53 (d,  $J$  10.9 Hz, H-1'b), 3.56 (s, OMe-3), 3.79 (t,  $J$  7.7 Hz, H-4'), 3.91 (m,  $J$  4.5, 6.3, 7.8 Hz, H-5'), 3.97 (m,  $J$  2.2, 4.9, 9.9 Hz, H-5), 4.01 (d,  $J$  7.7 Hz, H-3'), 4.15 (dd,  $J$  4.9, 11.8 Hz, H-6a), 4.26 (dd,  $J$  2.2, 11.8 Hz, H-6b), 4.26 (m, H-6'a), 4.27 (m, H-6'b), and 5.47 (d,  $J$  3.9 Hz, H-1);  $^{13}\text{C}$ -n.m.r. (125.76 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  20.93 (Me of acetate-6'), 20.98 (Me of acetate-6), 58.56 (OMe-3'), 58.65 (OMe-4'), 58.80 (OMe-2), 59.48 (OMe-1'), 60.58 (OMe-4), 60.71 (OMe-3), 63.77 ( $\text{CH}_2$ -6), 65.54 ( $\text{CH}_2$ -6'), 69.43 (CH-5), 74.17 ( $\text{CH}_2$ -1'), 78.47 (CH-5'), 79.98 (CH-4), 81.87 (CH-2), 83.45 (CH-3), 83.79 (CH-4'), 85.46 (CH-3'), 89.52 (CH-1), 104.47 (C-2'), 170.90 (CO of acetate 6'), and 170.94 (CO of acetate 6).

*Anal.* Calc. for  $\text{C}_{22}\text{H}_{38}\text{O}_{13}$ : C, 51.8; H, 7.4. Found: C, 51.8; H, 7.4.

**1',2,3,3',4,4'-Hexa-O-methylsucrose (7).** — To a solution of the diacetate **6** (1.08 g, 2.11 mmol) in MeOH (40 mL) was added 2M NaOMe in MeOH<sup>18</sup> (8 mL) dropwise over 15 min. The pale-yellow solution was stirred for 2 h at room temperature, and then concentrated *in vacuo*, diluted with water, and acidified to pH 7 by dropwise addition of M HCl. The mixture was concentrated to a residue that was applied directly on a column (5 × 15 cm) of silica gel that was eluted with 19:1 EtOAc– $\text{CH}_2\text{Cl}_2$  (flow rate ~100 mL/min) to provide the diol **7** as an oil; yield 800 mg (90%);  $[\alpha]_D^{22} + 61.7^\circ$  ( $c$  1.12, acetone);  $R_f$  0.21 (9:1 EtOAc– $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$ -n.m.r. (500.11 MHz, acetone- $d_6$ ):  $\delta$  3.04 (dd,  $J$  3.7, 9.6 Hz, H-2), 3.09 (t,  $J$  9.3, 9.6 Hz, H-4), 3.34 (d,  $J$  10.9 Hz, H-1'a), 3.36 (t,  $J$  9.3, 9.6 Hz, H-3), 3.37 (s, OMe-1'), 3.41 (s, OMe-4'), 3.44 (s, OMe-2), 3.44 (s, OMe-3'), 3.48 (s, OMe-4), 3.52 (s, OMe-3), 3.53 (d,  $J$  10.9 Hz, H-1'b), 3.59 (dd,  $J$  4.1, 13.4 Hz, H-6a), 3.63 (dd,  $J$  4.5, 12.4 Hz, H-6'a), 3.71 (dd,  $J$  2.5, 13.4 Hz, H-6'b), 3.73 (dd,  $J$  6.4, –12.4 Hz, H-6'b), 3.74 (m,  $J$  4.5, 6.4, 7.7 Hz, H-5'), 3.79 (m,  $J$  2.5, 4.1, 9.6 Hz, H-5), 3.92 (t,  $J$  7.7, 7.8

Hz, H-4'), 4.00 (d,  $J$  7.8 Hz, H-3'), 5.51 (d,  $J$  3.6 Hz, H-1);  $^{13}\text{C}$ -n.m.r. (125.76 MHz, acetone- $d_6$ ):  $\delta$  58.42 (OMe-3'), 58.44 (OMe-4'), 58.66 (OMe-2), 59.41 (OMe-1'), 60.36 (OMe-4), 60.57 (OMe-3), 61.68 ( $\text{CH}_2$ -6'), 62.48 ( $\text{CH}_2$ -6), 73.04 (CH-5), 75.02 ( $\text{CH}_2$ -1'), 80.00 (CH-4), 81.86 (CH-5'), 82.50 (CH-2), 82.79 (CH-4'), 84.14 (CH-3), 85.97 (CH-3'), 90.23 (CH-1), and 104.50 (C-2).

*Anal.* Calc. for  $\text{C}_{18}\text{H}_{34}\text{O}_{11}$ : C, 50.7; H, 8.0. Found: C, 50.9; H, 8.3.

**6,6'-Diazido-6,6'-dideoxy-1',2,3,3',4,4'-hexa-O-methylsucrose (8).** — To a stirred solution of **5** (9.8 g, 21.14 mmol) in dry *N,N*-dimethylformamide (200 mL) was added  $\text{NaN}_3$  (27.5 g, 423 mmol, added portionwise via a solids addition-funnel). The contents were then allowed to attain a temperature of 120° and stirred for 12 h. Subsequently, the mixture was cooled, diluted with water (500 mL), and extracted with EtOAc ( $2 \times 100$  mL). The organic layer was washed with water and then with brine, dried ( $\text{MgSO}_4$ ), and chromatographed to provide the diazide **8** as an oil; yield 8.8 g (18.47 mmol, 87.3%); (usually the azide was purified by fast filtration through silica gel);  $[\alpha]_D^{25} + 66.7^\circ$  ( $c$  1.44, EtOAc);  $R_F$  0.42 (1:1 EtOAc–hexane);  $^1\text{H}$ -n.m.r. (500.11 MHz, acetone- $d_6$ ):  $\delta$  3.01 (dd,  $J$  9, 9.5 Hz, H-4), 3.11 (dd,  $J$  3.5, 9 Hz, H-2), 3.34 (dd,  $J$  5, 10.5 Hz, H-6a), 3.37 (t,  $J$  9 Hz, H-3), 3.38 (d,  $J$  11 Hz, H-1'a), 3.39 (s, OMe-1'), 3.43 (s, OMe-4'), 3.43 (dd,  $J$  3.5, 13 Hz, H-6'a), 3.45 (s, OMe-2), 3.47 (s, OMe-3'), 3.49 (s, OMe-4), 3.53 (s, OMe-3), 3.60 (dd,  $J$  2.5, 10.5 Hz, H-6b), 3.61 (d,  $J$  11 Hz, H-1'b), 3.74 (dd,  $J$  7.5, 13 Hz, H-6'b), 3.83 (t,  $J$  7.5 Hz, H-4'), 3.88 (ddd,  $J$  3.5, 7.5, 7.5 Hz, H-5'), 3.94 (ddd,  $J$  2.5, 5, 9.5 Hz, H-5), 4.03 (d,  $J$  7.5 Hz, H-3'), and 5.52 (d,  $J$  3.5 Hz, H-1);  $^{13}\text{C}$ -n.m.r. (125.76 MHz, acetone- $d_6$ ):  $\delta$  51.37 ( $\text{CH}_2$ -6), 53.15 ( $\text{CH}_2$ -6'), 57.23 (OMe-4'), 57.33 (OMe-2), 57.40 (OMe-3'), 58.18 (OMe-1'), 59.27 (OMe-4), 59.35 (OMe-3), 69.99 (CH-5), 73.14 ( $\text{CH}_2$ -1'), 78.99 (CH-5'), 79.72 (CH-4), 81.29 (CH-2), 82.73 (CH-3), 84.02 (CH-4'), 84.62 (CH-3'), 88.94 (CH-1), and 104.06 (C-2').

*Anal.* Calc. for  $\text{C}_{18}\text{H}_{32}\text{O}_9\text{N}_6$ : C, 45.4; H, 6.7; N, 17.6. Found: C, 45.3; H, 7.0; N, 17.5.

**6,6'-Diamino-6,6'-dideoxy-1',2,3,3',4,4'-hexa-O-methylsucrose (9).** — To a suspension of  $\text{LiAlH}_4$  (2.86 g, 75.4 mmol, 6 equiv.) in dry tetrahydrofuran (60 mL) was added dropwise a solution of the diazide **8** (6 g, 12.6 mmol) in tetrahydrofuran (30 mL) over 60 min. The contents were then boiled under reflux for 3 h, cooled to 5°, and treated with dropwise addition of water (2.9 mL), 15% aq. NaOH (2.9 mL), and water (8.6 mL). After 1 h, the mixture was filtered, the residue washed with hot MeOH, and the effluent concentrated and poured on a column (5  $\times$  10 cm) of O.D.S. silica gel (J. T. Baker, 40  $\mu\text{m}$ ) and eluted under pressure with MeOH to afford the desired diamine **9** as an oil; yield 5.4 g (99%);  $[\alpha]_D^{27} + 54.8^\circ$  ( $c$  4.42, MeOH). The O.D.S. gel was cleaned by washing with hot water, then with hot MeOH and was reused.  $^1\text{H}$ -n.m.r. [500.11 MHz,  $\text{DCON}(\text{CD}_3)_2$ ]:  $\delta$  1.20 (m,  $\text{NH}_2$ -6'), 1.35 (m,  $\text{NH}_2$ -6), 2.57 (m, H-6'a), 2.68 (m, H-6a), 2.71 (m, H-6b), 2.78 (m, H-6'b), 2.99 (dd,  $J$  3.7, 9 Hz, H-2), 3.02 (t,  $J$  9 Hz, H-4), 3.26 (t,  $J$  9 Hz, H-3), 3.31 (d,  $J$  11 Hz, H-1'a), 3.31 (s, OMe-1'), 3.34 (s, OMe-4'), 3.35 (s, OMe-2), 3.37 (s, OMe-3'), 3.42 (s, OMe-4), 3.44 (s, OMe-3), 3.46 (d,  $J$  11 Hz, H-1'b), 3.58 (m, H-5'), 3.60 (m, H-5), 3.71 (t,  $J$  7.5 Hz, H-4'), 3.88 (d,  $J$  7.5 Hz, H-3'), and 5.39 (d,  $J$  3.5 Hz, H-1);  $^{13}\text{C}$ -n.m.r. [125.76 MHz,  $\text{DCON}(\text{CD}_3)_2$ ]:  $\delta$  42.23 ( $\text{CH}_2$ -6), 44.64 ( $\text{CH}_2$ -6'), 57.60



(OMe-4'), 57.72 (OMe-3'), 57.76 (OMe-2), 58.77 (OMe-1'), 59.63 (OMe-4), 59.71 (OMe-3), 71.66 (CH-5), 73.49 (CH<sub>2</sub>-1'), 79.71 (CH-4), 81.20 (CH-2), 81.67 (CH-5'), 82.56 (CH-3), 83.71 (CH-4'), 84.87 (CH-3'), 88.88 (CH-1), and 103.44 (C-2'); f.a.b. mass calc. for C<sub>18</sub>H<sub>36</sub>N<sub>2</sub>O<sub>9</sub>: 424.49; observed [M + H]<sup>+</sup> = 425, [M + K]<sup>+</sup> = 463.

*Anal.* Calc. for C<sub>18</sub>H<sub>36</sub>N<sub>2</sub>O<sub>9</sub>·H<sub>2</sub>O: C, 48.9; H, 8.5; N, 6.3; O, 36.2. Found: C, 49.3; H, 8.2; N, 6.1; O, 36.2

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