

## Preparation of 2,3-Anhydroalloyranosides Functionalised in the 6-Position

Fritiof Pontén and Göran Magnusson<sup>†</sup>

Organic Chemistry 2, Chemical Center, The Lund Institute of Technology, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Pontén, F. and Magnusson, G., 1994. Preparation of 2,3-Anhydroalloyranosides Functionalised in the 6-Position. – Acta Chem. Scand. 48: 566–569 © Acta Chemica Scandinavica 1994.

Treatment of methyl 2,3-anhydro-6-bromo-6-deoxy- $\alpha$ -D-alloyranoside with sodium phenylsulfinate, decanethiol, and 2-furylmethanethiol gave sugar epoxides carrying sulfone or sulfide functionalities in the 6-position. Oxidation of the sulfides gave the corresponding sulfones.

Ring-contraction of sugar epoxides to yield furanosidic  $\alpha,\beta$ -unsaturated aldehydes<sup>1</sup> (Fig. 1) was the key reaction in our total syntheses of enantiomerically pure botryodiplodin<sup>2</sup> and several lignans.<sup>3</sup> We now report the preparation, from methyl  $\alpha$ -D-glucopyranoside, of the novel sugar epoxides **2–10**, functionalised in the 6-position. These epoxides have the potential for ring-contraction, which would furnish several new enantiomerically pure furanosidic building blocks.

Treatment of methyl  $\alpha$ -D-glucopyranoside with benzaldehyde and zinc chloride gave crude methyl 4,6-*O*-benzylidene- $\alpha$ -D-glucopyranoside,<sup>4</sup> which was treated with *p*-toluenesulfonyl chloride in pyridine to give methyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-toluenesulfonyl- $\alpha$ -D-glucopyranoside<sup>4,5</sup> in 78% overall yield on a 250 g scale. The latter compound was treated with sodium hydroxide–potassium carbonate–tetrabutylammonium hydrogensulfate to give, in 91% yield, methyl 2,3-anhydro-4,6-*O*-benzylidene- $\alpha$ -D-alloyranoside,<sup>5</sup> which was treated with *N*-bromosuccinimide–barium carbonate<sup>6</sup> to furnish methyl 4-*O*-benzoyl-6-bromo-6-deoxy- $\alpha$ -D-alloyranoside<sup>6</sup> (**1**) in 98% yield. Debenzoylation of **1** (Scheme 1) gave crystalline **2** (98%; 68% overall yield from methyl  $\alpha$ -D-glucopyranoside).

Displacement of bromide from **1** or **2**, using various base–thiol combinations<sup>7</sup> (Scheme 1), proceeded in good yields without opening of the epoxide ring (Scheme 1), although thiol-mediated epoxide opening in anhydro sugars has been reported.<sup>8</sup> The recently published<sup>7</sup> use of potassium carbonate in dimethyl formamide (DMF) as promoter was superior compared with cesium carbonate–DMF or –acetonitrile. It is especially rewarding that compound **2** underwent the desired substitution reactions

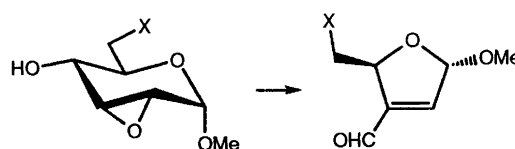


Fig. 1. Pyranosidic sugar epoxides of potential use for the preparation of furanosidic aldehydes.

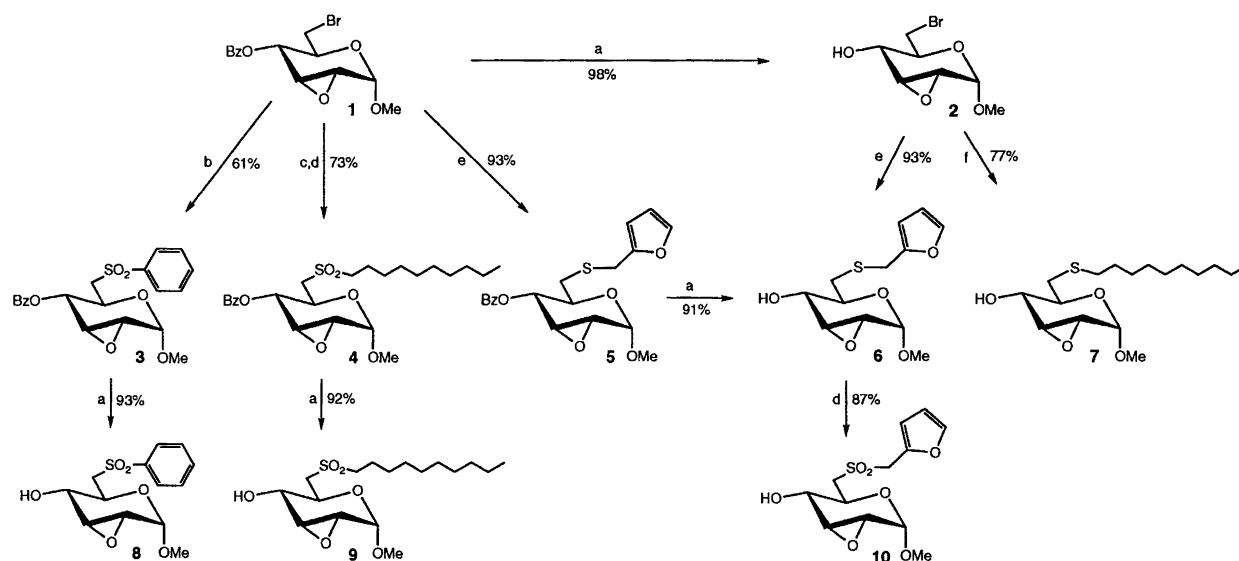
in high yields, since this gives directly the functionalised epoxy alcohols needed for ring-contraction to furanosidic aldehydes.<sup>1</sup>

Treatment of **1** with sodium phenylsulfinate<sup>9</sup> in DMF for 16 h at room temperature and 30 h at 60°C, gave the sulfone epoxide **3** (61%). The yield decreased both when the reaction was performed only at room temperature or only at 60°C. In the latter case, NMR spectral analysis indicated that the epoxide ring had been opened. Treatment of **2** under similar conditions was unsuccessful.

Treatment of **1** with decanethiol in DMF–cesium carbonate at room temperature, followed by oxidation with *m*-chloroperbenzoic acid, gave the sulfone epoxide **4** (73%). It was found that formation of by-products in the substitution step was significantly reduced if the DMF was kept at ~15 mmHg for a few min before use. Presumably, volatile contaminants (e.g. dimethylamine and carbon monoxide) were removed from the DMF by the evacuation. In a similar reaction, **2** was transformed, using cesium carbonate in acetonitrile, into the sulfide epoxide **7** (77%).

Treatment of **1** or **2** with 2-furylmethanethiol in DMF–potassium carbonate gave the sulfide epoxides **5** (93%) and **6** (93%), respectively. Compound **5** was transformed into **6** (91%) by debenzoylation.

<sup>†</sup> To whom correspondence should be addressed.



Scheme 1. (a) MeONa–MeOH, 22 °C; (b) PhSO<sub>2</sub>Na–DMF, 16 h at r.t., then 30 h at 60 °C; (c) C<sub>10</sub>H<sub>21</sub>SH–Cs<sub>2</sub>CO<sub>3</sub>–DMF, 22 °C; (d) MCPBA–EtOAc, 22 °C; (e) 2-2-furylmethanethiol–K<sub>2</sub>CO<sub>3</sub>–DMF, 22 °C; (f) C<sub>10</sub>H<sub>21</sub>SH–Cs<sub>2</sub>CO<sub>3</sub>–CH<sub>3</sub>CN, 22 °C.

The sulfone epoxides **3** and **4** were debenzoylated to give the sulfone epoxy alcohols **8** (93%) and **9** (92%), respectively. Oxidation of **6** gave the sulfone epoxy alcohol **10** (87%).

The most characteristic feature of the epoxy sugars is the NMR signals for H-2 and H-3. However, with deuteriochloroform solutions, the H-4,5,6-signals often obscure the spectrum, where the chemical shifts of H-2–H-6 were found in the region 3.5–3.9 ppm. In deuteriobenzene solution the signals were separated over a larger region (2.8–3.8 ppm). The coupling constants for H-2 and H-3 were of similar magnitude in all the compounds.

In summary, nine new epoxy saccharides (**2**–**10**), functionalized in the 6-position, have been prepared from the known precursor **1**, which in turn was prepared in 68% yield over four steps (all intermediates were crystalline) from commercially available methyl  $\alpha$ -D-glucopyranoside. It should be pointed out that all compounds, except **3** and **5**, shown in Scheme 1 are crystalline, which greatly facilitates their large-scale preparation. Ring-contraction to furanosidic  $\alpha,\beta$ -unsaturated aldehydes will be reported in due course.

## Experimental

NMR spectra were recorded at 23 °C with a Varian XL-300 spectrometer operating at 300 MHz proton frequency using CDCl<sub>3</sub> as the solvent and CHCl<sub>3</sub> as an internal standard ( $\delta$  7.26 from Me<sub>4</sub>Si). Optical rotations were measured with a Perkin-Elmer 141 polarimeter. For TLC analysis Merck SiO<sub>2</sub> 60 F<sub>254</sub> precoated aluminium sheets were used and the spots were visualised with UV light, I<sub>2</sub> in SiO<sub>2</sub>, or by charring with 5% anisaldehyde in sulfuric acid and ethanol. Liquid chromatography was performed on Matrex SiO<sub>2</sub> 60 (35–70  $\mu$ m) silica gel.

**Methyl 2,3-anhydro-6-bromo-6-deoxy- $\alpha$ -D-allopyranoside (2).** To a stirred solution of **1** (7.44 g, 21.7 mmol) in dry methanol (250 ml) was added sodium methoxide in methanol (5.0 ml, 0.5 M). After 3 h, SiO<sub>2</sub> (5 g) was added and the stirring was continued until the mixture was neutral. Filtration (Celite), concentration, and drying *in vacuo* gave a solid (7.23 g), which gave **2** (5.11 g, 98%) after recrystallisation from toluene. M.p. 108–109 °C,  $[\alpha]_D^{25} + 127^\circ$  (*c* 1.4, CHCl<sub>3</sub>). Anal. C<sub>7</sub>H<sub>11</sub>BrO<sub>4</sub>: C, H. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.36 (d, 1 H, *J* 2.9 Hz, H-1), 3.74 (ddd, 1 H, *J* 2.2, 6.9, 9.2 Hz, H-5), 3.48 (dd, 1 H, *J* 2.2, 11.0 Hz, H-6), 3.40 (br d, 1 H, *J* 9.3 Hz, H-4), 3.25 (dd, 1 H, *J* 6.8, 11.0 Hz, H-6), 3.24 (s, 3 H, OMe), 2.88 (dd, 1 H, *J* 2.9, 4.2 Hz, H-2), 2.84 (dd, 1 H, *J* 1.7, 4.2 Hz, H-3). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  94.6, 68.6, 68.1, 56.0, 55.9, 54.1, 33.5.

**Methyl 2,3-anhydro-4-O-benzoyl-6-deoxy-6-phenylsulfonyl- $\alpha$ -D-allopyranoside (3).** To a stirred solution of **1** (301 mg, 0.88 mmol) in DMF (5.0 ml) was added sodium benzenesulfinate (361 mg, 2.20 mmol). The mixture was kept for 16 h at 22 °C and at 60 °C for 30 h. After concentration at 50 °C, the residue was dissolved in water (75 ml) and the solution was extracted with diethyl ether (3  $\times$  25 ml), then dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and concentrated and the residue was chromatographed (heptane–EtOAc 2:1) to give **3** (217 mg, 61%) as an oil;  $[\alpha]_D^{25} + 170^\circ$  (*c* 4.8, CDCl<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.89 (m, 4 H, Ph), 7.51–7.67 (m, 5 H, Ph), 7.43 (t, 1 H, *J* 7.8 Hz, Ph), 5.10 (dd, 1 H, *J* 1.3, 9.8 Hz, H-4), 4.93 (d, 1 H, *J* 3.1 Hz, H-1), 4.58 (ddd, 1 H, *J* 2.8, 6.4, 9.9 Hz, H-5), 3.62 (dd, 1 H, *J* 1.6, 4.2 Hz, H-3), 3.58 (m, 1 H, *J* 3.0 Hz, H-2), 3.57 (s, 3 H, OMe), 3.34 (m, 2 H, H-6). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  165.7, 139.8, 133.8, 133.7, 129.9, 129.4, 128.7, 128.6, 127.9, 94.8, 70.1, 61.9, 57.7, 56.6, 54.5, 50.8.

*Methyl 2,3-anhydro-4-O-benzoyl-6-decylsulfonyl-6-deoxy- $\alpha$ -D-allopyranoside (4)*. To a stirred solution of **1** (259 mg, 0.75 mmol) in DMF (7.5 ml) was added decanethiol (230  $\mu$ l, 1.57 mmol) and  $\text{Cs}_2\text{CO}_3$  (366 mg, 1.90 mmol). After 20 h, the reaction mixture was added to ice-water (50 ml) and the mixture was extracted with ether (4  $\times$  20 ml). The extract was dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and concentrated to give crude **7** (430 mg). The crude material was dissolved in EtOAc (20 ml) and *m*-chloroperbenzoic acid (Fluka 55%, 950 mg, 3.03 mmol) was added. After 40 h, the solution was filtered through basic  $\text{Al}_2\text{O}_3$  (activity grade II–III) and concentrated, and the residue was chromatographed (heptane–EtOAc 2:1) to give **4** (251 mg, 73%), which crystallized upon standing.

M.p. 73–75°C;  $[\alpha]_{\text{D}}^{23} + 140^\circ$  (*c* 1.9;  $\text{CDCl}_3$ ). Anal.  $\text{C}_{24}\text{H}_{36}\text{O}_7\text{S}$ : C, H.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.04 (d, 2 H, *J* 1.3 Hz, Ph), 7.62 (m, 1 H, *J* 7.4 Hz, Ph), 7.47 (m, 2 H, Ph), 5.20 (dd, 1 H, *J* 1.7, 9.8 Hz, H-4), 4.97 (d, 1 H, *J* 3.0 Hz, H-1), 4.67 (ddd, 1 H, *J* 3.2, 9.0, 9.3 Hz, H-5), 3.67 (dd, 1 H, *J* 1.5, 4.2 Hz, H-3), 3.62 (dd, 1 H, *J* 3.0, 4.2 Hz, H-2), 3.57 (s, 3 H, OMe), 3.17 (d, 1 H, *J* 8.5 Hz, H-6), 3.15 (d, 1 H, *J* 3.0 Hz, H-6), 3.06 (dd, 2 H, *J* 2.7, 8.0 Hz,  $\text{SO}_2\text{CH}_2\text{CH}_2$ ), 1.82 (m, 2 H,  $\text{SO}_2\text{CH}_2\text{CH}_2$ ), 1.40–1.20 [m, 14 H,  $(\text{CH}_2)_7$ ], 0.88 (dd, 3 H, *J* 6.5, 7.5 Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  165.9, 133.9, 130.0, 128.7, 95.0, 70.0, 62.6, 56.6, 54.9, 54.5, 54.2, 50.9, 31.8, 29.4, 29.2, 29.0, 28.5, 22.6, 21.8, 14.1.

*Methyl 2,3-anhydro-4-O-benzoyl-6-deoxy-6-furfurylthio- $\alpha$ -D-allopyranoside (5)*. To a stirred solution of **1** (1.00 g, 2.92 mmol) in dry, degassed DMF (12 ml) was added 2-furylmethanethiol (0.36 ml, 3.20 mmol) and  $\text{K}_2\text{CO}_3$  (602 mg, 4.36 mmol). After 2.5 h, the mixture was poured into water (60 ml) and the mixture was extracted with diethyl ether (4  $\times$  20 ml). The extract was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. Residual DMF was removed *in vacuo*. The residue was chromatographed (heptane–toluene–EtOAc 3:3:1) to give **5** (566 mg, 93%).  $[\alpha]_{\text{D}}^{23} + 194^\circ$  (*c* 1.1,  $\text{CHCl}_3$ ); Anal.  $\text{C}_{19}\text{H}_{20}\text{O}_6\text{S}$ : C, H.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.03 (m, 2 H, Ph), 7.61 (m, 1 H, Ph), 7.47 (m, 2 H, Ph), 7.23 (dd, 1 H, *J* 0.9, 1.9 Hz, fur-H-5), 6.16 (dd, 1 H, *J* 1.9, 3.2 Hz, fur-H-4), 6.09 (dd, 1 H, *J* 0.7, 3.2 Hz, fur-H-3), 5.25 (dd, 1 H, *J* 1.7, 9.5 Hz, H-4), 4.96 (d, 1 H, *J* 3.2 Hz, H-1), 4.18 (br dt, 1 H, *J* 2.6, 9.0 Hz, H-5), 3.80, 3.72 (AB system, 2 H, *J* 14.7 Hz,  $\text{CH}_2\text{-fur}$ ), 3.66 (dd, 1 H, *J* 1.7, 4.3 Hz, H-3), 3.60 (dd, 1 H, *J* 3.1, 4.2 Hz, H-2), 3.57 (s, 3 H, OMe), 2.78 (dd, 1 H, *J* 2.6, 14.3 Hz, H-6), 2.58 (dd, 1 H, *J* 8.6, 14.2 Hz, H-6).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  165.9, 151.2, 142.2, 133.6, 129.9, 129.8, 129.3, 128.5, 128.2, 110.2, 107.8, 94.6, 70.8, 66.4, 55.9, 54.8, 51.5, 32.7, 28.8.

*Methyl 2,3-anhydro-6-deoxy-6-furfurylthio- $\alpha$ -D-allopyranoside (6)*. To a stirred solution of **2** (1.50 g, 6.27 mmol) in dry, degassed DMF (28 ml) was added 2-furylmethanethiol (0.97 ml, 9.56 mmol) and  $\text{K}_2\text{CO}_3$  (1.31 g, 9.41 mmol). After 15 h, the mixture was poured into water (170 ml) and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$

(5  $\times$  35 ml). The organic extract was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. Residual DMF was removed *in vacuo* overnight. The residue was dissolved in diethyl ether, and ligroin (b.p. 80–110°C) was added. The mixture was left for 15 h, which gave crystalline **6** (1.60 g, 93%). M.p. 69–71°C,  $[\alpha]_{\text{D}}^{23} + 124^\circ$  (*c* 0.8,  $\text{CHCl}_3$ ). Anal.  $\text{C}_{12}\text{H}_{16}\text{O}_5\text{S}$ : C, H.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.36 (dd, 1 H, *J* 0.6, 2.0 Hz, fur-H-5), 6.30 (dd, 1 H, *J* 2.0, 3.1 Hz, fur-H-4), 6.18 (dd, 1 H, *J* 0.6, 3.2 Hz, fur-H-3), 4.89 (d, 1 H, *J* 3.2 Hz, H-1), 3.83 (br d, 1 H, *J* 9.9 Hz, H-4), 3.79 (s, 2 H,  $\text{CH}_2\text{-fur}$ ), 3.72 (ddd, 1 H, *J* 2.8, 7.6, 9.3 Hz, H-5), 3.57 (dd, 1 H, *J* 3.2, 4.1 Hz, H-2), 3.50 (s, 3 H, OMe), 3.46 (dd, 1 H, *J* 1.7, 4.1 Hz, H-3), 2.94 (dd, 1 H, *J* 2.9, 14.2 Hz, H-6), 2.64 (dd, 1 H, *J* 7.6, 14.2 Hz, H-6), 2.01 (br s, 1 H, OH).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  151.4, 142.3, 110.4, 107.8, 94.5, 69.0, 68.8, 55.9, 55.8, 54.0, 33.1, 29.1.

*Methyl 2,3-anhydro-6-deoxy-6-furfurylthio- $\alpha$ -D-allopyranoside (6)*. To a stirred solution of **5** (456 mg, 1.21 mmol) in dry MeOH (35 ml) was added MeONa–MeOH (0.5 ml, 0.5 M). After 3 h,  $\text{SiO}_2$  (1 g) was added and the mixture was stirred until it was neutral, then filtered (Celite) and concentrated. The residue was chromatographed to give **6** (301 mg, 91%), which crystallised upon standing. Analytical and spectroscopic data were identical with those of **6** prepared from **2**.

*Methyl 2,3-anhydro-6-decylthio-6-deoxy- $\alpha$ -D-allopyranoside (7)*. To a stirred solution of **2** (244 mg, 1.0 mmol) in dry  $\text{CH}_3\text{CN}$  (56 ml) was added decanethiol (0.255 ml, 1.2 mmol) and  $\text{Cs}_2\text{CO}_3$  (387 mg, 1.2 mmol). After 90 h, the mixture was filtered and concentrated. The residue was chromatographed (heptane–EtOAc 2:1) to give **7** (260 mg, 77%), which crystallised upon standing. M.p. 56–58°C;  $[\alpha]_{\text{D}}^{23} + 105^\circ$  (*c* 3.2,  $\text{CDCl}_3$ ). Anal.  $\text{C}_{17}\text{H}_{32}\text{O}_4\text{S}$ : C, H.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.90 (d, 1 H, *J* 3.2 Hz, H-1), 3.85 (ddd, 1 H, *J* 1.7, 9.2, 9.5 Hz, H-4), 3.73 (ddd, 1 H, *J* 3.2, 7.5, 9.2 Hz, H-5), 3.58 (dd, 1 H, *J* 3.2, 4.2 Hz, H-2), 3.50 (s, 3 H, OMe), 3.46 (dd, 1 H, *J* 1.7, 4.1 Hz, H-3), 2.95 (dd, 1 H, *J* 3.2, 13.9 Hz, H-6), 2.66 (dd, 1 H, *J* 7.5, 13.9 Hz, H-6), 2.57 (t, 2 H, *J* 7.6 Hz,  $\text{SO}_2\text{CH}_2\text{CH}_2$ ), 1.98 (d, 1 H, *J* 9.5 Hz, OH), 1.58 (quintet, 2 H, *J* 7.3 Hz,  $\text{SO}_2\text{CH}_2\text{CH}_2$ ), 1.40–1.20 [m, 14 H,  $(\text{CH}_2)_7$ ], 0.88 (t, 3 H, *J* 6.8 Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  94.5, 69.0, 68.7, 55.8, 55.7, 54.1, 34.0, 33.1, 31.9, 29.6(0), 29.5(6), 29.5(3), 29.3, 29.2, 28.9, 22.7, 14.1.

*Methyl 2,3-anhydro-6-deoxy-6-phenylsulfonyl- $\alpha$ -D-allopyranoside (8)*. To a stirred solution of **3** (156 mg, 0.39 mmol) in dry MeOH (5.0 ml) was added MeONa–MeOH (0.05 ml, 0.5 M). After 16 h, the mixture was neutralised (Amberlite  $\text{H}^+$  resin) and the solvent was removed *in vacuo*. The residue was chromatographed to give **8** (108 mg, 93%), which crystallized upon standing. M.p. 140–142°C;  $[\alpha]_{\text{D}}^{23} + 123^\circ$  (*c* 0.5,  $\text{CDCl}_3$ ); Anal.  $\text{C}_{13}\text{H}_{16}\text{O}_6\text{S}$ : C, H.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.93 (dd, 2 H, *J* 7.0, 1.3 Hz, Ph), 7.66 (m, 1 H, Ph), 7.57 (m, 2 H, Ph), 4.86 (d, 1 H, *J* 3.1 Hz, H-1), 4.17 (ddd, 1 H, *J* 1.9, 8.9,

9.1 Hz, H-5), 3.71 (m, 1 H, H-4), 3.62 (dd, 1 H,  $J$  2.0, 14.6 Hz, H-6), 3.57 (dd, 1 H,  $J$  3.1, 4.1 Hz, H-2), 3.50 (s, 3 H, OMe), 3.46 (dd, 1 H,  $J$  1.6, 4.0 Hz, H-3), 3.29 (dd, 1 H,  $J$  8.6, 14.6 Hz, H-6), 1.96 (br d, 1 H,  $J$  9.5 Hz, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  139.8, 133.8, 129.4, 127.9, 94.6, 68.6, 64.3, 57.8, 56.4, 55.6, 53.3.

*Methyl 2,3-anhydro-6-decylsulfonyl-6-deoxy- $\alpha$ -D-allopyranoside (9)*. To a stirred solution of **4** (250 mg, 0.53 mmol) in dry MeOH (15 ml) was added MeONa–MeOH (0.1 ml, 0.5 M). After 22 h,  $\text{SiO}_2$  (1.3 g) was added and the mixture was stirred until it was neutral. The mixture was filtered (Celite) and concentrated, and the residue was chromatographed (heptane–EtOAc 1:2) to give **9** (180 mg, 92%), which crystallised upon standing. M.p. 95–96°C,  $[\alpha]_{\text{D}}^{23} + 83^\circ$  ( $c$  2.6,  $\text{CDCl}_3$ ). Anal.  $\text{C}_{17}\text{H}_{32}\text{O}_6\text{S}$ : C, H.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.88 (d, 1 H,  $J$  3.0 Hz, H-1), 4.20 (dt, 1 H,  $J$  1.8, 9.3 Hz, H-5), 3.79 (br dd, 1 H,  $J$  1.2, 1.7 Hz, H-4), 3.59 (dd, 1 H,  $J$  3.1, 4.2 Hz, H-2), 3.51 (m, 4 H, OMe, H-3), 3.48 (dd, 1 H,  $J$  1.0, 15.0 Hz, H-6), 3.16 (dd, 1 H,  $J$  9.1, 15.0 Hz, H-6), 3.05 (dd, 2 H,  $J$  5.6, 8.0 Hz,  $\text{SO}_2\text{CH}_2\text{CH}_2$ ), 2.60 (br d, 1 H,  $J$  7.4 Hz, OH), 1.82 (m, 2 H,  $\text{SO}_2\text{CH}_2\text{CH}_2$ ), 1.40–1.20 [m, 14 H,  $(\text{CH}_2)_7$ ], 0.87 (t, 3 H,  $J$  7.0 Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  94.9, 68.2, 64.9, 56.4, 55.4, 54.7, 54.2, 53.4, 31.8, 29.5, 29.2, 29.1, 28.5, 22.6, 21.8, 21.8, 14.1.

*Methyl 2,3-anhydro-6-deoxy-6-(furfurylsulfonyl)- $\alpha$ -D-allopyranoside (10)*. To a stirred solution of **6** (502 mg, 1.85 mmol) in EtOAc (100 ml) was added dry *m*-chloroperbenzoic acid (Fluka 55%, 1.289 g, 4.11 mmol). After 4.5 h, the solution was filtered through basic  $\text{Al}_2\text{O}_3$  (activity grade III) and concentrated. The residue was

chromatographed (heptane–EtOAc 1:3) to give **10** (490 mg, 87%), which crystallised upon standing. M.p. 94–97°C,  $[\alpha]_{\text{D}}^{23} + 87^\circ$  ( $c$  0.5,  $\text{CHCl}_3$ ). Anal.  $\text{C}_{12}\text{H}_{16}\text{O}_7\text{S}$ : C, H.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.47 (dd, 1 H,  $J$  0.9, 1.9 Hz, fur-H-5), 6.52 (d, 1 H,  $J$  3.2 Hz, fur-H-4), 6.43 (dd, 1 H,  $J$  1.9, 3.2 Hz, fur-H-3), 4.94 (d, 1 H,  $J$  3.2 Hz, H-1), 4.49, 4.39 (AB system, 2 H,  $J$  14.9 Hz,  $\text{CH}_2$ -fur), 4.24 (dt, 1 H,  $J$  2.4, 9.3 Hz, H-5), 3.81 (br t, 1 H,  $J$  9.3 Hz, H-4), 3.62 (dd, 1 H,  $J$  3.2, 4.2 Hz, H-2), 3.57 (s, 3 H, OMe), 3.51 (dd, 1 H,  $J$  1.8, 4.2 Hz, H-3), 3.45 (dd, 1 H,  $J$  1.6, 15.1 Hz, H-6), 3.21 (dd, 1 H,  $J$  9.2, 15.1 Hz, H-6), 2.15 (d, 1 H,  $J$  10.4 Hz, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  144.0, 142.4, 112.5, 111.4, 94.9, 68.1, 64.9, 56.5, 55.5, 54.3, 53.5, 53.0.

This work was supported by The Swedish Natural Science Research Council.

## References

1. (a) Sundin, A., Frejd, T. and Magnusson, G. *J. Org. Chem.* 51 (1986) 3927; (b) Rehnberg, N. and Magnusson, G. *J. Org. Chem.* 55 (1990) 5467.
2. Rehnberg, N. and Magnusson, G. *Acta Chem. Scand.* 44 (1990) 377.
3. Rehnberg, N. and Magnusson, G. *J. Org. Chem.* 55 (1990) 4340.
4. Miller, V., Yang, D., Weigel, T., Han, O. and Hung, W. *J. Org. Chem.* 54 (1989) 4175.
5. Szeja, W. *Carbohydr. Res.* 183 (1988) 135.
6. Hanessian, S. *Org. Synth. Coll. Vol.* 65, 243.
7. Khurana, J. and Sahoo, P. *Synth. Commun.* 22 (1992) 1691.
8. Jeanloz, R., Prins, D. A. and Reichstein, T. *Helv. Chim. Acta* 29 (1946) 371.
9. Julia, M. and Arnould, D. *Bull. Soc. Chim. Fr.* (1973) 743.

Received December 13, 1993.