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Preparation of 2,3-Anhydroallopyranosides Functionalised in the 6-Position

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Treatment of methyl 2,3-anhydro-6-bromo-6-deoxy-α-D-allopyranoside 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 α,β-unsaturated aldehydes[1] (Fig. 1) was the key reaction in our total syntheses of enantiomerically pure botryodiplodin[2] and several lignans.[3] We now report the preparation, from methyl α-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.

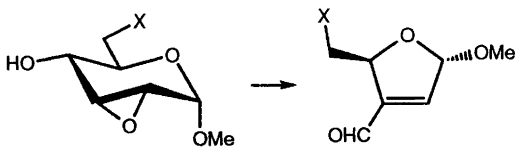

Fig. 1. Pyranosidic sugar epoxides of potential use for the preparation of furanosidic aldehydes.

Treatment of methyl α-D-glucopyranoside with benzaldehyde and zinc chloride gave crude methyl 4,6-*O*-benzylidene-α-D-glucopyranoside,[4] which was treated with *p*-toluenesulfonyl chloride in pyridine to give methyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-toluenesulfonyl-α-D-glucopyranoside[4,5] 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-α-D-allopyranoside,[5] which was treated with *N*-bromosuccinimide–barium carbonate[6] to furnish methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-allopyranoside[6] (**1**) in 98% yield. Debenzoylation of **1** (Scheme 1) gave crystalline **2** (98%; 68% overall yield from methyl α-D-glucopyranoside).

Displacement of bromide from **1** or **2**, using various base–thiol combinations[7] (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.[8] The recently published[7] 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 in high yields, since this gives directly the functionalised epoxy alcohols needed for ring-contraction to furanosidic aldehydes.[1]

Treatment of **1** with sodium phenylsulfinate[9] 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.

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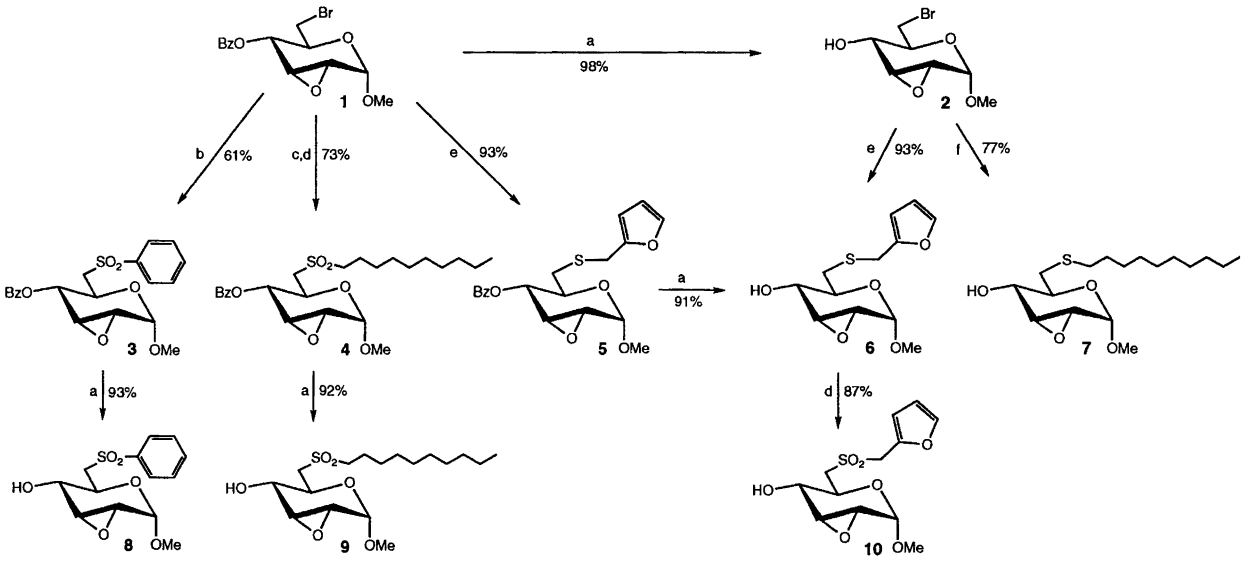

Scheme 1. (a) MeONa–MeOH, 22 °C; (b) $PhSO_2Na$–DMF, 16 h at r.t., then 30 h at 60 °C; (c) $C_{10}H_{21}SH$–Cs_2CO_3–DMF, 22 °C; (d) MCPBA–EtOAc, 22 °C; (e) 2-2-furylmethanethiol–K_2CO_3–DMF, 22 °C; (f) $C_{10}H_{21}SH$–Cs_2CO_3–CH_3CN, 22 °C.

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 epoxide 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 α-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 α,β-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 $CDCl_3$ as the solvent and $CHCl_3$ as an internal standard (δ 7.26 from Me_4Si). Optical rotations were measured with a Perkin-Elmer 141 polarimeter. For TLC analysis Merck SiO_2 60 F_{254} precoated aluminium sheets were used and the spots were visualised with UV light, I_2 in SiO_2, or by charring with 5% anisaldehyde in sulfuric acid and ethanol. Liquid chromatography was performed on Matrex SiO_2 60 (35–70 μm) silica gel.

*Methyl 2,3-anhydro-6-bromo-6-deoxy-α-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_2 (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, $[\alpha]_D^{23}$ + 127° (*c* 1.4, $CHCl_3$). Anal. $C_7H_{11}BrO_4$: C,H. ^1H NMR (C_6D_6): δ 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). ^{13}C NMR ($CDCl_3$): δ 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-α-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 × 25 ml), then dried (Na_2SO_4), filtered, and concentrated and the residue was chromatographed (heptane–EtOAc 2:1) to give **3** (217 mg, 61%) as an oil; $[\alpha]_D^{23}$ + 170° (*c* 4.8, $CDCl_3$). ^1H NMR ($CDCl_3$): δ 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). ^{13}C NMR ($CDCl_3$): δ 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-α-D-allopyranoside (**4**).* To a stirred solution of **1** (259 mg, 0.75 mmol) in DMF (7.5 ml) was added decanethiol (230 µl, 1.57 mmol) and Cs_2CO_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 × 20 ml). The extract was dried (Na_2SO_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 Al_2O_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; $[\alpha]_D^{23}$ +140° (*c* 1.9; $CDCl_3$). Anal. $C_{24}H_{36}O_7S$: C,H. ^{1}H NMR ($CDCl_3$): δ 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, $SO_2CH_2CH_2$), 1.82 (m, 2 H, $SO_2CH_2CH_2$), 1.40–1.20 [m, 14 H, $(CH_2)_7$], 0.88 (dd, 3 H, *J* 6.5, 7.5 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 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-α-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 K_2CO_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 × 20 ml). The extract was dried (Na_2SO_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%). $[\alpha]_D^{23}$ +194° (*c* 1.1, $CHCl_3$); Anal. $C_{19}H_{20}O_6S$: C,H. ^{1}H NMR ($CDCl_3$): δ 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, CH_2-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}C NMR ($CDCl_3$): δ 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-α-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 K_2CO_3 (1.31 g, 9.41 mmol). After 15 h, the mixture was poured into water (170 ml) and the mixture was extracted with CH_2Cl_2 (5 × 35 ml). The organic extract was dried (Na_2SO_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, $[\alpha]_D^{23}$ +124° (*c* 0.8, $CHCl_3$). Anal. $C_{12}H_{16}O_5S$: C,H. ^{1}H NMR ($CDCl_3$): δ 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, CH_2-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}C NMR ($CDCl_3$): δ 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-α-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, 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-α-D-allopyranoside (**7**).* To a stirred solution of **2** (244 mg, 1.0 mmol) in dry CH_3CN (56 ml) was added decanethiol (0.255 ml, 1.2 mmol) and Cs_2CO_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; $[\alpha]_D^{23}$ +105° (*c* 3.2, $CDCl_3$). Anal. $C_{17}H_{32}O_4S$: C,H. ^{1}H NMR ($CDCl_3$): δ 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, $SO_2CH_2CH_2$), 1.98 (d, 1 H, *J* 9.5 Hz, OH), 1.58 (quintet, 2 H, *J* 7.3 Hz, $SO_2CH_2CH_2$), 1.40–1.20 [m, 14 H, $(CH_2)_7$], 0.88 (t, 3 H, *J* 6.8 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 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-α-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 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; $[\alpha]_D^{23}$ +123° (*c* 0.5, $CDCl_3$); Anal. $C_{13}H_{16}O_6S$: C,H. ^{1}H NMR ($CDCl_3$): δ 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}C NMR ($CDCl_3$): δ 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-α-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, 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, $[\alpha]_D^{23}$ +83° (*c* 2.6, $CDCl_3$). Anal. $C_{17}H_{32}O_6S$: C,H. ^{1}H NMR ($CDCl_3$): δ 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, $SO_2CH_2CH_2$), 2.60 (br d, 1 H, *J* 7.4 Hz, OH), 1.82 (m, 2 H, $SO_2CH_2CH_2$), 1.40–1.20 [m, 14 H, $(CH_2)_7$], 0.87 (t, 3 H, *J* 7.0 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 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)-α-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 Al_2O_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, $[\alpha]_D^{23}$ +87° (*c* 0.5, $CHCl_3$). Anal. $C_{12}H_{16}O_7S$: C,H. ^{1}H NMR ($CDCl_3$): δ 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, 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}C NMR ($CDCl_3$): δ 144.0, 142.4, 112.5, 111.4, 94.9, 68.1, 64.9, 56.5, 55.5, 54.3, 53.5, 53.0.

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