Supporting Information

Base-Promoted Rearrangement of Sugar Epoxides to Unsaturated Sugars

Yuan Wang, Qin Li, Shuihong Cheng, Yanfen Wu, Dongjie Guo, Qiu-Hua Fan, Xiaofang Wang, Li-He Zhang, and Xin-Shan Ye*

The State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Road #38, Beijing, 100083, China
E-mail: xinshan@bjmu.edu.cn

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Experimental

General Procedures All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Dichloromethane (CH2Cl2), pyridine, toluene and acetonitrile (CH3CN) were distilled over calcium hydride (CaH2). Methanol and n-butanol were distilled from magnesium. DMF was stirred with CaH2 and distilled under reduced pressure. All reactions were carried out under anhydrous conditions with freshly distilled solvents, unless otherwise noted. Reactions were monitored by analytical thin-layer chromatography on silica gel 60 F254 precoated on aluminium plates (E. Merck). Spots were detected under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate. Solvents were evaporated under reduced pressure and below 40 ℃ (bath). Organic solutions of crude products were dried over anhydrous Na2SO4. Column chromatography was performed on silica gel (200–300 mesh). 1H-NMR spectra were recorded on a JEOL AL-300, Varian INOVA-500 or Advance DRX Bruker-500 spectrometers at 25 ℃. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in deuterated chloroform. 13C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl3 (δ = 77.00 ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. Elemental analysis data were recorded on a Vario EL-III elemental analyzer.

Scheme 1. Base-induced rearrangement of p-tolyl 2,3-anhydro-1-thio-β-D-allopyranoside 1 to unsaturated sugar 2

p-Tolyl 4,6-O-benzylidene-3-O-p-toluenesulfonyl-1-thio-β-D-glucopyranoside (1b). To an ice-cooled solution of p-tolyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (1a)1 (10.01 g, 26.73 mmol) in pyridine (50 mL) was added a solution of p-toluenesulfonyl chloride (10.26 g, 53.81 mmol) in CH2Cl2 (30 mL) dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 70 h. Then the reaction mixture was concentrated. The residue was dissolved in CH2Cl2 and washed with saturated NaHCO3, brine and water. The organic layer was dried, filtered, and concentrated to yield a crude oil which was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to provide compound 1b (6.07 g, 43%) as a glassy solid. The NMR data of 1b was identical to that reported previously.2

p-Tolyl 2,3-anhydro-4,6-O-benzylidene-1-thio-β-D-allopyranoside (1). To a solution of 1b (13.27 g, 25.10 mmol) in CH3OH (200 mL) was added NaOMe (30% in MeOH, 15mL, 83.30 mmol). After stirring for 1 d at room temperature, the reaction mixture was concentrated and the residue was dissolved in ethyl acetate. Then the solution was washed with brine and water. The organic layer was dried, filtered, and concentrated to yield a crude oil which was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to provide compound 1b (6.07 g, 43%) as a glassy solid. The NMR data of 1b was identical to that reported previously.2
4H), 7.34—7.37 (m, 3H), 7.18 (d, 2H, \(J = 8.0\) Hz), 5.48 (s, 1H), 5.29 (s, 1H), 4.25 (dd, 1H, \(J = 5.0, 10.0\) Hz), 3.87 (dt, 1H, \(J = 5.0, 10.0\) Hz), 3.65—3.70 (m, 3H), 3.38 (d, 1H, \(J = 4.5\) Hz), 2.38 (s, 3H); 13C NMR (75 MHz, CDCl3) \(\delta 139.09, 137.09, 134.37, 129.80, 129.19, 128.27, 126.24, 102.64, 80.01, 77.19, 68.91, 56.88, 51.55, 21.19\); MS (EI) 356 \([M]^+\); Anal. Calcd. for C20H20O4S: C, 67.39; H, 5.66. Found: C, 67.13; H, 5.65.

**p-Tolyl 4,6-O-benzylidene-1,2-dideoxy-1-thio-D-ribo-hex-1-enopyranoside (2).** To a solution of 1 (0.10 g, 0.28 mmol) in toluene (10 mL) and n-butanol (0.4 mL) was added tetrabutylammonium bromide (0.23 g). The mixture was stirred at room temperature for a few minutes, followed by addition of sodium hydroxide (0.35 g). The mixture was refluxed for 1 h, subsequently diluted with ethyl acetate, washed with brine and water. The organic layer was dried, filtered, and concentrated. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 6:1) to yield 2 (0.10 g, 99%) as a white solid: mp 101—102 °C; 1HNMR (500 MHz, CDCl3) \(\delta 7.47—7.49\) (m, 2H), 7.37—7.40 (m, 3H), 7.34 (d, 2H, \(J = 8.0\) Hz), 7.15 (d, 2H, \(J = 8.0\) Hz), 5.65 (s, 1H), 5.17 (d, 1H, \(J = 6.0\) Hz, H-2), 4.43 (dd, 1H, \(J = 5.0, 10.5\) Hz, H-6), 4.26—4.31 (m, 2H, H-3, H-5), 3.83—3.88 (m, 2H, H-4, H-6), 2.47 (d, 1H, \(J = 1.5\) Hz, -OH), 2.35 (s, 3H, -CH3); 13C NMR (125 MHz, CDCl3) \(\delta 153.48\) (C-1), 138.32, 136.84, 132.32, 129.97, 129.36, 128.36, 127.45, 126.16, 102.72 (C-2), 101.66, 77.40 (C-4), 68.30 (C-6), 65.72 (C-5), 61.35 (C-3), 21.14 (-CH3); MS (EI) 356 \([M]^+\); Anal. Calcd. for C20H20O4S: C, 67.39; H, 5.66. Found: C, 67.37; H, 5.86.

**Scheme 2.** Base-induced rearrangement of p-tolyl 2,3-anhydro-1-thio-β-D-mannopyranoside 3 to unsaturated sugar 4

**p-Tolyl 4,6-O-benzylidene-3-O-p-toluenesulfonyl-1-thio-β-D-glucopyranoside (1b) and p-tolyl 4,6-O-benzylidene-2-O-p-toluenesulfonyl-1-thio-β-D-glucopyranoside (3b).** To a stirred solution of 1a (1.94 g, 5.18 mmol) in dichloromethane (50 mL) at -20 °C was added freshly prepared Ag2O (1.40 g, 6.04 mmol), after 5 min, p-toluenesulfonyl chloride (1.30 g, 6.82 mmol) and KI (0.27g, 1.63 mmol) were added. The reaction mixture was stirred at room temperature for 2 h, then filtered through Celite. Evaporation of the solvent gave the residue, which was purified by column chromatography (petroleum ether/ethyl acetate, 10:1, 1% TEA) to yield inseparable 1b and 3b (2.42 g) in a total yield of 88% with the ratio of 1:2 based on 1H NMR analysis. 1H NMR of 1b and 3b: (500 MHz, CDCl3) \(\delta 7.94\) (d, 2H, \(J = 8.5\) Hz), 7.69 (d, 1H, \(J = 8.5\) Hz), 7.42—7.46
(m, 3H), 7.32—7.38 (m, 9H), 7.15 (d, 1H, J = 8.0 Hz), 7.12 (d, 2H, J = 8.0 Hz), 6.98 (d, 1H, J = 8.0 Hz), 5.52 (s, 1H), 5.33 (s, 0.5 H), 4.73 (t, 0.5 H, J = 8.5 Hz), 4.63 (d, 1H, J = 10.0 Hz), 4.58 (d, 0.5 H, J = 9.0 Hz), 4.53 (t, 1H, J = 8.5 Hz), 4.35 (dd, 1.5 H, J = 5.0, 8.0 Hz), 3.98 (dd, 1H, J = 8.5, 9.0 Hz), 3.75, 3.70 (2t, 2H, J = 10.5Hz), 3.58, 3.53 (2t, 2H, J = 9.0 Hz), 3.54, 3.53 (2t, 2H, J = 9.0 Hz), 3.41—3.48 (m, 2H), 3.14 (br, 1H), 2.76 (s, 1H), 2.45 (s, 3H), 2.35, 2.36 (2s, 5 H), 2.29 (s, 1.5H).

p-Toly 2,3-anhydro-4,6-O-benzylidene-1-thio-β-D-mannopyranoside (3). This compound was prepared as described for the preparation of 1 starting from the mixture of 1b and 3b (5.37 g, 10.2 mmol). The product was purified by column chromatography (petroleum ether/ethyl acetate, 12:1, 1% TEA) to provide 1 (0.39 g, 32%) and 3 (1.45 g, 60%) as a white crystalline solid. For compound 3: mp 196—197 °C; 1H NMR (500 MHz, CDCl3) δ 7.45—7.50 (m, 4H), 7.36—7.39 (m, 3H), 7.15 (d, 2H, J = 8.0 Hz), 5.58 (s, 1H), 5.24 (d, 1H, J = 1.0 Hz), 4.29 (dd, 1H, J = 4.5, 10.5 Hz), 3.78—3.83 (m, 2H), 3.54 (d, 1H, J = 3.5 Hz), 3.47 (dd, 1H, J = 4.5, 10.0 Hz), 2.36 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 138.30, 136.89, 132.62, 129.82, 129.68, 129.29, 128.37, 126.11, 102.39, 83.95, 74.60, 70.60, 69.25, 55.40, 52.34, 21.16; MS (ESI) 379 [M + Na]+; Anal. Calcd. for C20H20O4S: C, 67.39; H, 5.66. Found: C, 67.11; H, 5.75.

p-Toly 4,6-O-benzylidene-1,2-dideoxy-1-thio-D-arabino-hex-1-enopyranoside (4). This compound was synthesized from 3 (0.10 g, 0.28 mmol) as described for the preparation of 2. Purification of the crude product by column chromatography (petroleum ether/ethyl acetate, 20:1, 1% TEA) afforded 4 (0.82 g, 82%) as a white crystalline solid: mp 137—138 ℃; 1H NMR (500 MHz, CDCl3) δ 7.48—7.50 (m, 2H), 7.36—7.39 (m, 3H), 7.31—7.33 (m, 2H), 7.15 (d, 2H, J = 8.0 Hz), 5.58 (s, 1H), 5.03 (d, 1H, J = 2.0 Hz, H-2), 4.54 (d, 1H, J = 7.0 Hz, H-3), 4.34 (dd, 1H, J = 5.0, 10.5 Hz, H-6), 3.97 (dt, 1H, J = 5.0, 10.5 Hz, H-5), 3.80—3.85 (m, 2H, H-4, H-6), 2.35 (s, 3H, -CH3), 2.18 (s, 1H, -OH); 13C NMR (125 MHz, CDCl3) δ 151.06, 138.15, 136.85, 131.76, 130.00, 129.33, 128.36, 127.90, 126.21, 106.22, 101.80, 80.18, 69.80, 68.10, 67.85, 21.13; MS (ESI) 357 [M + H]+; Anal. Calcd. for C20H20O4S: C, 67.39; H, 5.66. Found: C, 67.11; H, 5.75.

Scheme 3. Base-induced rearrangement of p-tolyl 2,3-anhydro-1-thio-β-D-gulopyranoside 5 to unsaturated sugar 6

p-Toly 4,6-O-benzylidene-3-O-p-toluenesulfonyl-1-thio-β-D-galactopyranoside (5b). This compound was synthesized from 5a (2.00 g, 5.34 mmol) as described for the preparation of 1b. The product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1, 1% TEA) to provide 5b (1.78 g, 63%) as a white solid. The NMR data of the product was identical to that
reported previously.\(^2\)

**\(p\)-Tolyl 2,3-anhydro-4,6-\(O\)-benzylidene-1-thio-\(\beta\)-D-gulopyranoside (5).** To an ice-cooled solution of 5b (0.50 g, 0.94 mmol) in DMF (5 mL) was added \(t\)-BuOK (0.11 g, 0.97 mmol). The reaction mixture was stirred at room temperature for 1 h and then diluted with ethyl acetate. The solution was washed with brine and water. The organic layer was dried, filtered, and concentrated to yield a crude oil which was purified by column chromatography (petroleum ether/ethyl acetate, 10:1, 1% TEA) to provide compound 5 (0.24 g, 71%) as a white solid: mp 104—105°C; \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.61\) (d, 2H, \(J = 8.5\) Hz), 7.56 (dd, 2H, \(J = 2.0, 7.5\) Hz), 7.41—7.42 (m, 3H), 6.97 (d, 2H, \(J = 7.5\) Hz), 5.57 (s, 1H), 5.13 (s, 1H), 4.38 (d, 1H, \(J = 13.0\) Hz), 4.27 (t, 1H, \(J = 1.5\) Hz), 4.05 (dd, 1H, \(J = 1.5, 13.0\) Hz), 3.50 (d, 1H, \(J = 4.0\) Hz), 3.40 (d, 1H, \(J = 1.5\) Hz), 3.29 (t, 1H, \(J = 3.0\) Hz), 2.27 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 137.88, 137.72, 131.29, 129.80, 129.21, 128.68, 128.28, 126.32, 126.29, 125.91, 125.57, 125.26, 102.61, 101.07, 74.58, 68.97 (C-6), 67.58 (C-5), 63.61, 21.12 (-CH\(_3\)); MS (FAB) 356 [M]+; Anal. Calcd. for C\(_{20}\)H\(_{20}\)O\(_4\)S: C, 67.39; H, 5.66. Found: C, 67.50; H, 5.80.

**\(p\)-Tolyl 4,6-\(O\)-benzylidene-1,2-dideoxy-1-thio-\(D\)-xylo-hex-1-enopyranoside (6).** To a solution of 5 (0.10 g, 0.28 mmol) in toluene (20 mL), DMF (2 mL) and \(n\)butanol (0.4 mL) was added tetrabutylammonium bromide (0.22 g) and the mixture was stirred at room temperature for a few minutes, followed by addition of sodium hydroxide (0.33 g). The mixture was refluxed for 0.5 h. After cooled to room temperature, the reaction mixture was diluted with ethyl acetate and washed with brine and water. The organic layer was dried, filtered, and concentrated. The resulting crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1, 1% TEA) to yield 6 (0.89 g, 89%) as a white solid: mp 75—77°C; \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.46—7.48\) (m, 2H), 7.35—7.38 (m, 5H), 7.07 (d, 2H, \(J = 8.0\) Hz), 5.59 (s, 1H), 5.26 (dd, 1H, \(J = 1.0, 5.2\) Hz, H-2), 4.42 (dd, 1H, \(J = 1.5, 12.5\) Hz, H-6), 4.05—4.09 (m, 3H, H-3, H-6, H-4), 3.97 (d, 1H, \(J = 1.5\) Hz, H-5), 2.32 (s, 3H, -CH\(_3\)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 152.95\) (C-1), 137.88, 137.72, 132.90, 129.58, 129.19, 128.24, 128.02, 126.38, 101.09, 80.16, 69.94, 69.78, 65.54, 55.19, 52.10, 21.13; MS (FAB) 357 [M]+; Anal. Calcd. for C\(_{20}\)H\(_{20}\)O\(_4\)S: C, 67.39; H, 5.66. Found: C, 67.10; H, 5.85.
Scheme 4. Base-induced rearrangement of epoxides 7 and 9 to unsaturated sugar 8 and 10

**n-Propyl 4,6-O-benzylidene-1-thio-β-D-glucopyranoside (7a).** We synthesized this compound according to the procedures in Reference 3 (the overall yield for three steps: 67%). mp 134 °C; 1H NMR (500 MHz, CDCl₃) δ 7.48—7.50 (m, 2H), 7.36—7.38 (m, 3H), 5.54 (s, 1H), 4.45 (d, 1H, J = 10.0 Hz), 4.34—4.38 (m, 1H), 3.84 (t, 1H, J = 9.0 Hz), 3.77 (t, 1H, J = 10.0 Hz), 3.58 (t, 1H, J = 9.0 Hz), 3.48—3.53 (m, 2H), 2.67—2.76 (m, 2H), 1.65—1.72 (m, 2H), 1.02 (t, 3H, J = 7.0 Hz).

**n-Propyl 4,6-O-benzylidene-3-O-p-toluenesulfonyl-1-thio-β-D-glucopyranoside (7b) and n-propyl 4,6-O-benzylidene-2-O-p-toluenesulfonyl-1-thio-β-D-glucopyranoside (9b).** These two compounds were synthesized from 7a (50.0 mg, 0.15 mmol) as described for preparation of 3b. The crude products were purified by flash column chromatography (petroleum ether/ethyl acetate, 3:1, 1% TEA) to provide inseparable 7b and 9b (64.5 mg) in a total yield of 88%. Compounds 7b and 9b are not stable enough to be identified by NMR, so they were used for the next reaction directly.

**n-Propyl 2,3-anhydro-4,6-O-benzylidene-1-thio-β-D-allopyranoside (7) and n-propyl 2,3-anhydro-4,6-O-benzylidene-1-thio-β-D-mannopyranoside (9).** These compounds were
synthesized from the mixture of 7b and 9b (64.5 mg, 0.13 mmol) as described for the preparation of 3. Purification of the crude product by column chromatography (petroleum ether/ethyl acetate, 9:1, 1% TEA) afforded inseparable 7 and 9 (26.5 mg) in a total yield of 64% as a white solid with a ratio of 1:1 based on 1H NMR spectral analysis: 1H NMR (500 MHz, CDCl_3) δ 7.52—7.54 (m, 2H), 7.40—7.43 (m, 3H), 5.60 (s, 1H), 5.18 (s, 0.5H), 5.08 (s, 0.5H), 4.26—4.34 (m, 1H), 4.11 (d, 0.5H, J = 9.0 Hz), 3.72—3.90 (m, 2.5H), 3.57 (dt, 1.5H, J = 4.5 Hz), 3.35—3.40 (m, 1H), 2.69—2.84 (m, 2H), 1.69—1.74 (m, 2H), 1.03—1.07 (m, 3H); 13C NMR (125 MHz, CDCl_3) δ 137.08, 136.99, 129.30, 129.28, 128.40, 128.36, 126.28, 126.14, 102.69, 102.38, 80.18, 78.41, 77.49, 74.76, 70.78, 69.30, 68.87, 56.85, 54.70, 52.92, 51.79, 32.92, 32.47, 23.50, 23.13, 13.51; MS (ESI) 309 [M + H]+; Anal. Calcd. for C_{16}H_{20}O_{4}S: C, 62.31; H, 6.54. Found: C, 62.24; H, 6.51.

We also synthesized compound 7 as described for the preparation of 1 (Scheme 1) from 7a (400 mg, 1.28 mmol), yielding pure 7 (50 mg, 13%) as a white solid: 1H NMR (500 MHz, CDCl_3) δ 7.50—7.52 (m, 2H), 7.35—7.39 (m, 3H), 5.58 (s, 1H), 5.15 (s, 1H), 4.25 (dd, 1H, J = 5.0, 10.0 Hz), 4.08 (dd, 1H, J = 1.0, 9.0 Hz), 3.85 (dt, 1H, J = 5.0, 10.0 Hz), 3.72 (t, 1H, J = 10.5 Hz), 3.58 (d, 1H, J = 4.5 Hz), 3.54 (d, 1H, J = 4.5 Hz), 2.67—2.78 (m, 2H), 1.65—1.73 (m, 2H), 1.03 (t, 3H, J = 7.5Hz); MS (ESI) 309 [M + H]+.

**n-Propyl 4,6-O-benzylidene-1,2-dideoxy-1-thio-D-ribo-hex-1-enopyranoside (8) and n-propyl 4,6-O-benzylidene-1,2-dideoxy-1-thio-D-arabino-hex-1-enopyranoside (10).** To a solution of the mixture of 7 and 9 (ratio 1:1) (30 mg, 0.097 mmol) in dry DMF (5 mL) was added t-BuOK (33 mg, 0.29 mmol). The reaction mixture was stirred at room temperature for 2 h and then diluted with ethyl acetate. The solution was washed with brine and water. The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 5:1, 1% TEA) to provide 8 (12.0 mg, 80%) as a colorless oil and 10 (16.1 mg, 100%) as a white crystalline solid. For compound 8: 1H NMR (300 MHz, CDCl_3) δ 7.19—7.43 (m, 5H), 5.59 (s, 1H), 5.11 (d, 1H, J = 6.0 Hz, H-2), 4.43 (dd, 1H, J = 5.4, 10.5 Hz, H-6), 4.22—4.27 (m, 2H, H-3, H-5), 3.75—3.86 (m, 2H, H-4, H-6), 2.69—2.82 (m, 1H), 2.42—2.59 (m, 2H), 1.51—1.63 (m, 2H), 0.92 (t, 3H, J = 7.5Hz, -CH3); 13C NMR (75 MHz, CDCl_3) δ 153.11, 136.87, 129.38, 128.37, 126.18, 101.67, 100.86, 77.55, 68.37, 65.35, 61.28, 33.18, 22.79, 13.26; HRMS (ESI) Calcd for C_{16}H_{21}O_{4}S [M + H]+ 309.1160, Found 309.1156. For compound 10: mp 94—95 °C; 1H NMR (300 MHz, CDCl_3) δ 7.49—7.52 (m, 2H), 7.37—7.40 (m, 3H), 5.60 (s, 1H), 5.00 (d, 1H, J = 2.1 Hz, H-2), 4.52 (d, 1H, H-3), 4.43 (dd, 1H, J = 4.8, 10.2 Hz, H-6), 3.78—4.00 (m, 3H, H-4, H-5, H-6), 2.76—2.85 (m, 1H), 2.56—2.66 (m, 1H), 2.19 (br, 1H, -OH), 1.61—1.68 (m, 2H), 1.00 (t, 3H, J = 7.2 Hz, -CH3); 13C NMR (75 MHz, CDCl_3) δ 151.11 (C-1), 136.87, 129.34, 128.38, 126.20, 103.87 (C-2), 101.82, 80.45 (C-4), 69.37 (C-5), 68.17 (C-6), 67.83 (C-3), 33.42, 22.80, 13.24; HRMS (ESI) Calcd. for C_{16}H_{21}O_{4}S [M + H]+ 309.1160. Found: 309.1156; Anal. Calcd. for C_{16}H_{20}O_{4}S: C, 62.31; H, 6.54. Found: C, 62.32; H, 6.55.

Compound 8 was also prepared from pure compound 7. To a solution of 7 (20 mg, 0.065 mmol) in dry DMF (5 mL) was added t-BuOK (29.6 mg, 0.26 mmol). The reaction mixture was stirred at room temperature for 3 h and then diluted with ethyl acetate. The solution was washed with brine and water. The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 5:1, 1% TEA) to provide 8 (16.0 mg, 80%) as a colorless oil.
Scheme 5. Base-induced rearrangement of O-glycoside 11 to unsaturated sugar 12

Phenyl 4,6-O-benzylidene-3-O-p-toluenesulfonyl-β-D-glucopyranoside (11b) and phenyl 4,6-O-benzylidene-2-O-p-toluenesulfonyl-β-D-glucopyranoside (21b). These two compounds were synthesized from phenyl 4,6-O-benzylidene-β-D-glucopyranoside (11a) (50.0 mg, 0.14 mmol) as described for the preparation of 3b. The crude products were purified by column chromatography (petroleum ether/ethyl acetate, 4:1, 1% TEA) to provide inseparable 11b and 21b (61.9 mg) in a total yield of 86% with a ratio of 3:5 based on 1H NMR spectral analysis: 1H NMR (500 MHz, CDCl3) δ 7.85 (d, 2H, J = 8.5 Hz), 7.74 (d, 1H, J = 8.0 Hz), 7.47—7.49 (m, 2H), 7.27—7.40 (m, 9.6H), 7.22—7.24 (m, 2H), 7.02—7.09 (m, 4H), 6.80 (d, 2H, J = 8.0 Hz), 5.56 (s, 1H), 5.39 (s, 0.6H), 5.08 (d, 1.5H, J = 2.0 Hz, H-3), 4.80 (t, 1H, J = 9.0 Hz), 4.71 (t, 1H, J = 8.0 Hz), 4.35—4.39 (m, 1.6H), 4.07 (dt, 1H, J = 2.5, 9.0 Hz), 3.98 (dt, 1H, J = 3.0, 8.0 Hz), 3.66—3.82 (m, 3.5H), 3.52—3.58 (m, 2H), 3.09 (d, 0.6H, J = 3.0 Hz), 3.01 (d, 1H, J = 2.5 Hz), 2.41 (s, 3H), 2.32 (s, 2H).

Phenyl 4,6-O-benzylidene-2,3-anhydro-β-D-allopyranoside (11). This compound was synthesized from the mixture of 11b and 21b (56 mg, 0.11 mmol) as described for the preparation of 1. The product was purified by column chromatography (petroleum ether/ethyl acetate, 15:1, 1% TEA) to provide 11 (18 mg, 49%) as a white crystalline solid: 1H NMR (500 MHz, CDCl3) δ 7.52 (dd, 2H, J = 2.0, 8.0 Hz), 7.37—7.41 (m, 3H), 7.30—7.34 (m, 2H), 7.05—7.08 (m, 3H), 5.68 (s, 1H), 5.60 (s, 1H), 4.29 (d, 1H, J = 4.5, 10.0 Hz), 4.22 (d, 1H, J = 9.0 Hz), 3.93 (dt, 1H, J = 5.0, 10.0 Hz), 3.74 (t, 1H, J = 10.5 Hz), 3.65 (d, 1H, J = 4.0 Hz), 3.59 (d, 1H, J = 4.5Hz); 13C NMR (125 MHz, CDCl3) δ 156.46, 136.96, 129.62, 129.29, 128.35, 126.24, 122.88, 116.30, 102.73, 94.56, 77.19, 68.95, 55.13, 51.19.

Phenyl 4,6-O-benzylidene-β-D-erythro-hex-3-enopyranoside (12). Compound 12 was synthesized from 11 (50 mg, 0.15 mmol) as described for the preparation of 8 at 90°C. The resulting crude product was purified by column chromatography (petroleum ether/ethyl acetate, 7:1, 1% TEA) to yield 12 (28.5 mg, 57%) as a glassy solid: 1H NMR (500 MHz, CDCl3) δ 7.50—7.52 (m, 2H), 7.40—7.42 (m, 3H), 7.33 (t, 2H, J = 8.0 Hz), 7.06—7.08 (m, 3H), 5.61 (s, 1H), 5.54 (d, 1H, J = 2.0 Hz, H-3), 5.30 (d, 1H, J = 5.0 Hz, H-1), 4.54—4.57 (m, 2H, H-2, H-5), 4.30 (dd, 1H, J = 6.0, 10.0 Hz, H-6), 3.78 (t, 1H, J = 11.0 Hz, H-6), 2.07 (s, 1H, -OH); 13C NMR
(125 MHz, CDCl$_3$) δ 156.59, 153.58 (C-4), 136.19, 129.64, 128.45, 126.17, 122.76, 116.36, 105.42 (C-3), 103.20, 99.42 (C-1), 67.05 (C-2), 65.75 (C-5); HRMS (ESI) Calcd. for C$_{19}$H$_{19}$O$_5$ [M + H]$^+$ 327.1232. Found: 327.1231; Anal. Calcd. for C$_{19}$H$_{18}$O$_5$: C, 69.93; H, 5.56. Found: C, 69.71; H, 5.72.

O

![Diagram](13a)

**Scheme 6.** Base-induced rearrangement of O-glycoside 13 to unsaturated sugar 14

**Methyl 4,6-O-benzylidene-3-O-p-toluenesulfonyl-β-D-glucopyranoside (13b).** Compound 13b was synthesized from 13a (3.28 g, 11.62 mmol) as described for the preparation of 1b. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1, 1% TEA) to provide 13b (2.31 g, 46%) as a white crystalline solid: 1H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, 2H, J = 8.5 Hz), 7.33—7.40 (m, 3H), 7.27—7.29 (m, 2H), 7.00 (d, 2H, J = 8.0 Hz), 5.36 (s, 1H), 4.73 (t, 1H, J = 9.0 Hz), 4.38 (d, 1H, J = 7.5 Hz), 4.34 (dd, 1H, J = 5.0, 10.0 Hz), 3.72 (t, 1H, J = 10.0 Hz), 3.57—3.69 (m, 6H), 3.43 (dt, 1H, J = 5.0, 9.5 Hz), 3.06 (d, 1H, J = 3.0 Hz), 2.30 (s, 3H); MS (FAB) 437 [M + H]$^+$.

**Methyl 2,3-anhydro-4,6-O-benzylidene-β-D-allopyranoside (13).** Compound 13 was synthesized from 13b (0.50 g, 1.14 mmol) as described for the preparation of 1. The product was purified by column chromatography (petroleum ether/ethyl acetate, 7:1, 1% TEA) to provide 13 (0.25 g, 83%) as a white crystalline solid: 1H NMR (500 MHz, CDCl$_3$) δ 7.50—7.52 (m, 2H), 7.35—7.40 (m, 3H), 5.58 (s, 1H), 4.91 (d, 1H, J = 0.5 Hz), 4.27 (dd, 1H, J = 2.5, 8.5 Hz), 4.08—4.10 (m, 1H), 3.70—3.77 (m, 2H), 3.52—3.55 (m, 4H), 3.34 (d, 1H, J = 4.0 Hz); MS (FAB) 265 [M + H]$^+$.

**Methyl 4,6-O-benzylidene-β-D-erythro-hex-3-enopyranoside (14).** Compound 14 was synthesized from 13 (74.1 mg, 0.28 mmol) as described for the preparation of 12 at 80°C. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1, 1% TEA) to provide 14 (47.1 mg, 64%) as a white crystalline solid: 1H NMR (500 MHz, CDCl$_3$) δ 7.50—7.52 (m, 2H), 7.39—7.41 (m, 3H), 5.58 (s, 1H), 5.38 (t, 1H, J = 2.0 Hz, H-3), 4.36—4.47 (m, 3H, H-1, H-5, H-6), 4.26—4.29 (m, 1H, H-2), 3.79 (t, 1H, J = 10.0 Hz, H-6), 3.56 (s, 3H, -OCH$_3$), 2.01 (d, 1H, J = 5.5 Hz, -OH); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 153.39 (C-4), 136.31, 129.56, 128.42, 126.17, 105.73 (C-3), 103.57 (C-1), 103.08, 69.71 (C-6), 67.59 (C-2), 65.91 (C-5), 56.92; MS (ESI) 265 [M + H]$^+$; Anal. Calcd. for C$_{14}$H$_{16}$O$_5$: C, 63.63; H, 6.10. Found: C, 63.64; H, 6.32. The spectrometric data are identical to those reported in the literature.

**5-[(4-Methylpenyl)thio]-2-furanmethanol (16).** This compound was synthesized from p-tolyl 2,3-anhydro-1-thio-β-D-ribofuranoside 15$^7$ (53.8 mg, 0.22 mmol) as described for the preparation
of 12 at 70°C. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 12:1) to provide 16 (21.2 mg, 43%) as a clear syrup.

This compound was also synthesized from p-toly 2,3-anhydro-1-thio-D-lyxofuranoside 17[8] (88.5 mg, 0.37 mmol) as described for the preparation of 12 at 70°C. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 12:1) to provide 16 (37.8 mg, 46%) as a clear syrup. 

1H NMR (500 MHz, CDCl3) δ 7.13 (d, 2H, \( J = 8.5 \) Hz), 7.07 (d, 2H, \( J = 8.0 \) Hz), 6.65 (d, 1H, \( J = 3.0 \) Hz), 6.33 (d, 1H, \( J = 3.5 \) Hz), 4.57 (s, 2H), 2.29 (s, 3H), 1.92 (s, 1H); 13C NMR (125 MHz, CDCl3) δ 157.82, 143.80, 136.64, 132.10, 129.84, 128.40, 119.71, 109.61, 57.67, 20.95; MS (EI) 220 [M]+; Anal. Calcd. for C12H14O3S: C, 65.43; H, 5.49. Found: C, 65.30; H, 5.52.

Methyl 2,3-anhydro-4,6-O-benzylidene-β-D-mannopyranoside (18). 5b, 5c, 9 Compound 18 was synthesized from methyl 4,6-O-benzylidene-2-O-p-toluenesulfonyl-β-D-glucopyranoside[2] (0.5 g, 1.14 mmol) as described for the preparation of 1 at 60°C. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 9:1, 1% TEA) to provide 18 (0.25 g, 83%) as a white crystalline solid: 1H NMR (500 MHz, CDCl3 δ 7.49 – 7.51 (m, 2H), 7.37 – 7.39 (m, 3H), 5.57 (s, 1H), 4.96 (d, 1H, \( J = 1.0 \) Hz), 4.29 (dd, 1H, \( J = 4.5, 10.5 \) Hz), 3.81 (t, 1H, \( J = 10.5 \) Hz), 3.75 (d, 1H, \( J = 3.5 \) Hz), 3.35 (dt, 1H, \( J = 1.0, J = 5.0 \) Hz), 3.27 (d, 1H, \( J = 4.0 \) Hz); 13C NMR (125 MHz, CDCl3) δ 136.90, 129.23, 128.32, 126.07, 102.36, 99.62, 74.53, 69.18, 68.32, 57.29, 54.97, 50.63.

Methyl 2,3-anhydro-4,6-O-benzylidene-α-D-mannopyranoside (19). 10, 5b Compound 19 was synthesized from methyl 4,6-O-benzylidene-2-O-p-toluenesulfonyl-α-D-glucopyranoside[2] (0.11 g, 0.24 mmol) as described for the preparation of 1. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 15:1, 1% TEA) to provide 19 (47.1 mg, 73%) as a white crystalline solid: 1H NMR (500 MHz, CDCl3 δ 7.50 (dd, 2H, \( J = 2.5, 8.0 \) Hz), 7.37 – 7.41 (m, 3H), 5.57 (s, 1H), 4.90 (s, 1H), 4.26 (m, 1H), 3.67 – 3.76 (m, 3H), 3.47 – 3.48 (m, 4H), 3.17 (d, 1H, \( J = 3.5 \) Hz); 13C NMR (125 MHz, CDCl3) δ 137.02, 129.27, 128.37, 126.07, 102.36, 99.62, 74.86, 69.40, 61.65, 55.76, 53.82, 50.54; MS (FAB) 265 [M + H]+.

Scheme 7. Synthesis of 2,3-anhydro β-D-gulopyranoside 20

Methyl 4,6-O-benzylidene-3-O-p-toluenesulfonyl-β-D-galactopyranoside (20b). Compound 20b was synthesized from 20a (6.14 g, 21.75 mmol) as described for the preparation of 1b. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 2:1, 1% TEA) to provide 20b (6.61g, 70%) as a white solid. The NMR data of the product are identical to those reported previously. 2

Methyl 2,3-anhydro-4,6-O-benzylidene-β-D-gulopyranoside (20). 11 Compound 20 was
synthesized from 20b (2.77 g, 6.35 mmol) as described for the preparation of 5. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 7:1, 1% TEA) to provide 20 (0.95 g, 57%) as a white crystalline solid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.52—7.54 (m, 2H), 7.34—7.39 (m, 3H), 5.58 (s, 1H), 4.82 (s, 1H), 4.30—4.35 (m, 2H), 4.08 (dd, 1H, $J = 2.5, 13.0$ Hz), 3.60 (s, 3H), 3.45 (br, 1H), 3.29 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.58, 129.15, 128.26, 126.29, 101.19, 98.21, 70.46, 69.73, 62.08, 56.12, 53.75, 51.75.

References
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