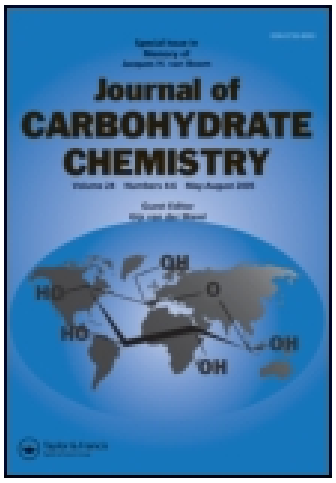

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Synthesis of p-Tolyl 4-Azido-3-O-benzyl-4,6-dideoxy-2-S-(p-tolyl)-2-thio-α-D-

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Synthesis of *p*-Tolyl 4-Azido-3-*O*-benzyl-4,6-dideoxy-2-*S*-(*p*-tolyl)-2-thio-α-D-mannopyranosyl-(1→2)-4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside

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ABSTRACT

Starting from D-galactose, the synthesis of a *p*-tolyl 4-azido-3-*O*-benzyl-4,6-dideoxy-2-*S*-(*p*-tolyl)-2-thio-α-D-mannopyranosyl-(1 → 2)-4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside has been achieved in an unconventional method involving the migration of thiotolyl with the formation of a episulfonium intermediate.

Key Words: Synthesis; 2-Thio-disaccharides; D-Viosamine; Episulfonium ion.

We were pursuing work on the synthesis of the oligosaccharide related to the O-antigen from *Escherichia coli* type O157. In this connection, we tried to synthesize a D-parosamine derivative starting from D-galactose by inversions at the 2- and 4-positions. We prepared a D-fucose derivative from D-galactose. We then attempted,[1] unsuccessfully, to invert the 2-position via oxidation with methyl sulfoxide. Another possible

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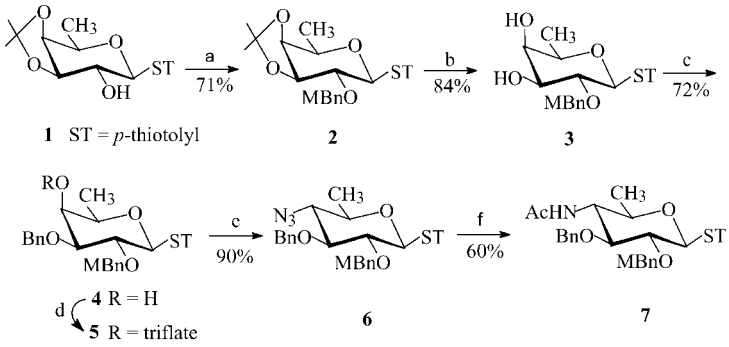
alternative strategy adopted to serve our purpose was to then invert the 4-position with an azide ion via 4-*O*-trifluoromethanesulfonate and then perform similar inversion at the 2-position. We discuss here the results obtained in this process.

p-Tolyl 3,4-*O*-isopropylidene-1-thio-*β*-D-fucopyranoside[1] (**1**) prepared as reported previously, was allowed to react with 4-methoxybenzyl chloride and NaH[2] to give the 2-*O*-(4-methoxybenzyl) compound **2** in 71% yield. The isopropylidene group of **2** was removed[3] and the resulting dihydroxy compound **3** was selectively benzylated[4] via a stannylidene derivative to give *p*-tolyl 3-*O*-benzyl-2-*O*-(4-methoxybenzyl)-1-thio-*β*-D-fucopyranoside **4**. The compound **4** having a free OH group in the 4-position was allowed to react with triflic anhydride in dichloromethane in the presence of pyridine to afford the triflate **5**, which was transformed into the 4-azido compound **6** with sodium azide[5] with inversion of configuration. Compound **6** has its characteristic peaks at δ 4.53 (H-1) and 1.36 (H-6) in its ^{1}H NMR spectrum and at δ 88.4 (C-1) in its ^{13}C NMR spectrum (Sch. 1). The presence of the N_3 group was also confirmed from the IR stretching vibration at 2113 cm^{-1}. Hydrogenation[6] of **6** with H_2/Pd–C in methanol–acetic anhydride gave 4-amino-4,6-dideoxy-D-glucose (D-viosamine derivative, **7**), with its benzyl and 4-methoxybenzyl remaining intact due to the presence of the S atom in it. Compound **7** was characterized by its NMR spectra.

D-Viosamine has been an important constituent of many bacterial products including some *E. coli*[7] and *Streptomyces plicatus*.[8] D-Viosamine was already synthesized[9] from D-galactose in the form of its methyl glycoside in a very low yield. It may, therefore, be interesting to find an alternative procedure for its synthesis.

In an attempt to prepare the D-parosamine derivative, the 2-*O*-(4-methoxybenzyl) group of **6** was removed with 80% AcOH[10] to give the 2-hydroxy compound **8**, which was then allowed to react with trifluoromethanesulfonic anhydride (Tf_2O) in dichloromethane[4] in the presence of pyridine. The expected product was the 2-*O*-trifluoromethanesulfonate **9**. However, the actual product obtained was a highly stable crystalline disaccharide **10** (Sch. 2). The NMR spectra of this new disaccharide confirmed its structure. The peaks at δ 101.54 in the ^{13}C and at δ 5.53 in the ^{1}H NMR spectra are the signals of anomeric carbon and proton, respectively, for 1,2-diaxial substitution in **10**. Both ^{1}H and ^{13}C NMR spectra of the compound showed two signals each for $CHCH_3$, $OCH_2C_6H_5$, $SC_6H_4CH_3$



Scheme 1. (a) 4-Methoxybenzyl chloride, NaH, DMF, 0°C, 3 H; (b) 50% AcOH, 50°C, 1 hr; (c) Bu_2SnO, BnBr, Bu_4NBr, benzene, 60°C, 6 hr; (d) Tf_2O, Pyr, CH_2Cl_2, −25°C, 1 hr; (e) NaN_3, DMF, 18-Crown-6, rt, 2 hr; (f) H_2-Pd/C, MeOH, Ac_2O (20 : 1), 4 days, 60%.

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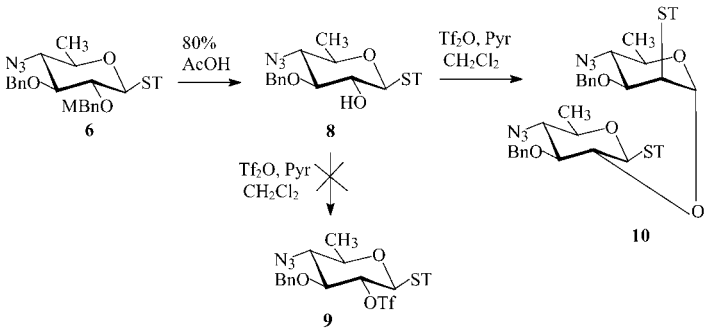


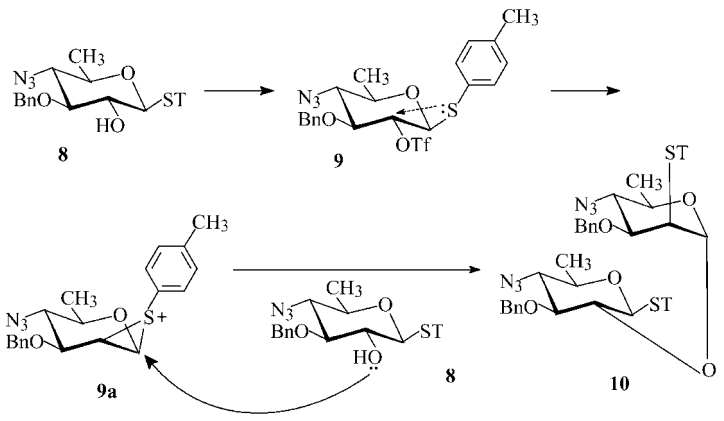
Scheme 2.

and other ring protons and carbons. The ^{13}C NMR spectrum of **10** showed 16 carbons in the region between δ 0 and 102, while only 8 carbons were expected from **9**. These data confirmed the compound to be the disaccharide **10** (Sch. 2). A probable mechanism of this transformation involving the migration of thiotolyl with the intermediate formation of a episulfonium ion **9a** has been suggested (Sch. 3). Migration of some thioglycosides under various conditions are reported previously,[11] but the simultaneous formation of a disaccharide is not reported.

EXPERIMENTAL

General

All reactions were monitored by TLC on silica gel G (E. Merck, India). Column chromatography was performed on 100–200 mesh silica gel (SRL, India). All solvents were distilled and/or dried before use and all evaporations were conducted below 50°C under reduced pressure unless stated otherwise. Optical rotations were measured with a



Scheme 3.

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Perkin Elmer model 241 MC polarimeter. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 Spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard unless otherwise mentioned. Melting points were determined on a paraffin oil bath and are uncorrected. The FAB-MS machine used is a JEOL SX 102/DA-6000 MASS Spectrometer using Argon/Xenon (6 kV, 10 mA) as the FAB Gas and *m*-nitrobenzyl alcohol as matrix, the accelerating voltage being 10 kV.

p-Tolyl 3,4-*O*-Isopropylidene-2-*O*-(4-Methoxybenzyl)-1-Thio-β-D-fucopyranoside (2)

To a solution of *p*-tolyl 3,4-*O*-isopropylidene-1-thio-*β*-D-fucopyranoside (**1**) (4.88 g, 15.7 mmol) and NaH (0.56 g, 23.4 mmol) in DMF (15 mL) at 0°C, 4-methoxy benzyl-chloride (2.7 mL, 18.7 mmol) was added drop-wise with stirring. After 3 hr, the reaction was quenched by slow addition of MeOH (2 mL). The reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3 × 75 mL). The combined organic extract was washed with water (3 × 100 mL), dried (Na_2SO_4), and concentrated to a syrup, which on column chromatography with 3 : 1 toluene–EtOAc gave **2** (4.8 g, 70.9%); $[\alpha]_D^{25}$ +14.1 (*c* 0.95, $CHCl_3$). ^{1}H NMR δ 7.45–6.85 (8H, aromatic protons), 4.75, 4.61 (2 d, 2H, $J = 11.1$ Hz, $CH_2C_6H_4OMe$), 4.51 (d, 1H, $J_{1,2} = 9.6$ Hz, H-1), 4.20 (dd, 1H, H-4), 4.03 (dd, 1H, $J_{2,3} = 5.7$ Hz, $J_{3,4} = 1.3$ Hz, H-3), 3.80 (s, 3H, $CH_2C_6H_4OCH_3$), 3.77 (m, 1H, H-5), 3.47 (dd, 1H, $J_{1,2} = 9.6$ Hz, $J_{2,3} = 6.3$ Hz, H-2), 2.33 (s, 3H, $CH_3C_6H_4S$), 1.42, 1.36 [2 s, 6H, $C(CH_3)_2$], 1.38 (d, 3H, $J = 6.6$ Hz, H-6). Anal. Calcd for $C_{24}H_{30}O_5S$: C, 66.95; H, 7.02. Found: C, 66.68; H, 7.24.

p-Tolyl 2-*O*-(4-Methoxybenzyl)-1-Thio-β-D-fucopyranoside (3)

A solution of **2** (2.5 g, 5.8 mmol) in 50% AcOH (100 mL) was stirred at 50°C for 1 hr when TLC showed complete removal of the isopropylidene group. The reaction mixture was concentrated and co-evaporated with toluene to remove traces of acetic acid. Column chromatography with 1 : 1 toluene–EtOAc gave **3** (1.9 g, 83.8%); $[\alpha]_D^{25}$ + 13.6 (*c* 1.4, $CHCl_3$). ^{1}H NMR δ 7.49–6.85 (8H, aromatic protons), 4.90, 4.61 (2 d, $J = 10.8$ Hz, CH_2Ph), 4.52 (d, 1H, $J = 9.6$ Hz, H-1), 3.81 (s, 3H, $PhOCH_3$), 3.72 (m, 1H, H-4), 3.62 (m, 1H, H-3), 3.59 (m, 1H, H-4), 3.49 (t, 1H, $J = 9.3$ Hz, H-2), 2.34 (s, 3H, $C_6H_5CH_3$) 1.34 (d, 3H, $J_{5,6} = 6.6$ Hz, H-6). Anal. Calcd for $C_{21}H_{26}O_5S$: C, 64.59; H, 6.71. Found: C, 64.54; H, 6.82.

p-Tolyl 3-*O*-Benzyl-2-*O*-(4-Methoxybenzyl)-1-Thio-β-D-fucopyranoside (4)

To a solution of compound **3** (2.6 g, 6.7 mmol) in benzene (73 mL), Bu_2SnO (1.84 g, 7.4 mmol) was added and the mixture was refluxed for 20 hr with azeotropic removal of water when a clear solution was obtained. The solution was cooled, and benzyl bromide (0.96 mL, 8.1 mmol) and Bu_4NBr (2.59 g, 8.0 mmol) were added and stirring was continued at 60°C. The reaction was complete in 6 hr (TLC). The mixture was then concentrated, MeOH (20 mL) was added and the contents were kept at −10°C for 2 hr,

then filtered and concentrated. Column chromatography with 3 : 1 toluene–EtOAc gave **4** (2.3 g, 71.8%); $[\alpha]_D^{25}$ +22.5 (*c* 0.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.49–6.86 (13 H, aromatic protons), 4.77, 4.67 (2 d, 4H, $J = 9.96$ Hz, $CH_2C_6H_5$, $CH_2C_6H_4OCH_3$), 4.51 (d, 1H, $J_{1,2} = 9.5$ Hz, H-1), 3.81 (s, 3H, $CH_2C_6H_4OCH_3$), 3.64 (t, 1H, $J = 9.36$ Hz, H-2), 3.55 (m, 2H, H-3, H-5), 2.32 (s, 3H, $CH_3C_6H_4S$), 1.35 (d, 3H, $J = 6.39$ Hz, H-6). ^{13}C NMR δ 159.35–113.8 (aromatic carbons), 87.86 (H-1), 82.96, 76.57, 75.35, 74.16, 72.16, 69.46 (ring carbons), 55.31 (OCH_3) 21.13 ($SC_6H_4CH_3$), 16.75 (C-6). Anal. Calcd for $C_{28}H_{32}O_5S$: C, 69.97; H, 6.67. Found: C, 69.55; H, 6.78.

p-Tolyl 4-Azido-3-*O*-benzyl-4,6-dideoxy-2-*O*-(4-Methoxybenzyl)-1-Thio-β-D-glucopyranoside (6)

To a solution of **4** (3 g, 6.2 mmol) in dry dichloromethane (50 mL) containing pyridine (1.6 mL) at −25°C was added Tf_2O (1.99 mL, 11.8 mmol) under nitrogen. The mixture was then allowed to reach room temperature. After 1 hr, TLC (9 : 1 toluene–EtOAc) indicated a single faster moving spot. The reaction mixture was then diluted with dichloromethane (50 mL) and washed successively with cold water (2 × 75 mL), cold saturated $NaHCO_3$ solution (2 × 75 mL), and cold water (2 × 75 mL); dried (Na_2SO_4) and filtered. The solution was concentrated to give compound **5** (3.84 g). A solution of **5** (3.84 g, 5.75 mmol) in DMF (62 mL) containing sodium azide (1.04 g, 16.0 mmol) and 18-crown-6 (54 mg, 0.20 mmol) was stirred for 2 hr at room temperature. The mixture was then extracted with ethyl ether (2 × 75 mL), and the extract was washed with saturated $NaHCO_3$ (2 × 100 mL) and water (2 × 100 mL), dried (Na_2SO_4) and concentrated. Column chromatography with 15 : 1 toluene–EtOAc gave pure **6** (2.85 g, 90%); $[\alpha]_D^{25}$ +34.4 (*c* 0.7, $CHCl_3$). ^{1}H NMR δ 7.45–6.86 (13 H, aromatic protons), 4.89, 4.82 (2 d, 2H, $J = 10.8$ Hz, $CH_2C_6H_4OCH_3$), 4.82, 4.65 (2 d, 2H, $J = 9.9$ Hz, $CH_2C_6H_5$), 4.53 (d, 1H, $J = 9.34$ Hz, H-1), 3.79 (s, 3H, OCH_3) 3.47 (m, 2H, H-2, H-3), 3.19 (m, 2H, H-4, H-5), 2.34 (s, 3H, $CH_3C_6H_4S$), 1.36 (d, 3H, $J = 5.7$ Hz, H-6). ^{13}C NMR δ 159.87–114.32 (aromatic carbons) 88.36 (C-1), 85.37, 81.09, 76.48, 75.51, 75.19, 68.18 (ring carbons), 55.85 (OCH_3), 21.58 ($SC_6H_4CH_3$); 19.19 (C-6). I.R. (thin film) 1346 cm^{-1} (weak), 2113 cm^{-1} (strong) [N_3]. Anal. Calcd for $C_{28}H_{31}O_4SN_3$: C, 66.51; H, 6.18; N, 8.31. Found: C, 66.48; H, 6.50; N, 8.69.

p-Tolyl 4-Acetamido-3-*O*-benzyl-4,6-dideoxy-2-*O*-(4-Methoxybenzyl)-1-Thio-β-D-glucopyranoside (7)

A solution of **6** (100 mg, 0.2 mmol) in methanol (4 mL) containing Ac_2O (0.2 mL) was stirred under H_2 in the presence of 10% Pd–C for 4 days. The mixture was filtered and the filtrate was concentrated to a syrup. Column chromatography then gave pure **7** (62 mg, 60%); $[\alpha]_D^{25}$ −18.4 (*c* 0.7, MeOH). ^{1}H NMR δ 7.47–6.86 (m, 13H, aromatic protons), 4.93 (d, 1H, $J = 8.4$ Hz, N*H*), 4.85, 4.64 (2 d, 2H, $J = 10.9$ Hz, $CH_2C_6H_5$), 4.85, 4.61 (2 d, 2H, $J = 12.1$ Hz, 4.56 (d, 1H, $J_{1,2} = 9.2$ Hz, H-1), 3.80 (s, 3H, $C_6H_4OCH_3$), 3.61 (t, 1H, $J = 9.3$ Hz, H-2), 3.52 (m, 2H, H-3, H-4), 3.42 (m, 1H, H-5), 2.34 (s, 3H, $C_6H_4OCH_3$), 1.78 (s, 3H, $NHCOCH_3$), 1.24 (d, 3H, $J_{5,6}$ 6.15 Hz, H-6). ^{13}C NMR δ 169.05 ($COCH_3$), 158.39–112.84 (aromatic carbons), 86.65 (C-1), 81.32, 80.06, 74.31, 73.90,

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73.53, 55.27 (C-4), 54.28 (OCH_3), 22.45 ($NHCOCH_3$), 20.11 ($SC_6H_4CH_3$), 17.22 (C-6). Anal. Calcd for $C_{30}H_{35}O_5SN$: C, 69.07; H, 6.75; N, 2.68. Found: C, 68.9; H, 6.8; N, 2.56.

p-Tolyl 4-Azido-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside (8)

A solution of compound **6** (1 g, 1.98 mmol) in 80% AcOH (20 mL) was stirred at 80°C for 10 hr. The solvents were removed under reduced pressure. Co-evaporation with toluene removed the traces of AcOH. The product was crystallized from ether–petroleum ether (60–80°C) to afford compound **8** (540 mg, 70.7%); m.p. 78°C; $[\alpha]_D^{25}$ −18.4 (*c* 1.2, $CHCl_3$). ^{1}H NMR δ 7.43–7.1 (9H, aromatic protons), 4.93, 4.83 (2 d, 4H, $J = 10.8$ Hz, 2 $CH_2C_6H_4$), 3.42 (m, 2H, H-2, H-3), 3.25 (m, 1H, H-4), 3.09 (m, 1H, H-5), 2.34 (s, 3H, $C_6H_4CH_3$), 1.36 (d, 3H, $J = 6.3$ Hz, H-6). ^{13}C NMR δ 139.1, 138.2, 134.1, 130.2, 128.9, 128.7, 128.4, 127.7 (aromatic protons), 88.74 (C-1), 84.22, 75.54, 75.5, 73.2, 67.6 (C-4), 21.59 ($C_6H_4CH_3$), 19.20 (C-6). I.R. 2117 cm^{-1} (sharp) [N_3]. Anal. Calcd for $C_{20}H_{23}O_3N_3S$: C, 62.3; H, 6.01; N, 10.9. Found: C, 62.5; H, 5.89; N, 10.6.

p-Tolyl 4-Azido-3-*O*-benzyl-4,6-dideoxy-2-*S*-(*p*-Tolyl)-2-Thio-α-D-mannopyranosyl-(1 → 2)-4-Azido-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside (10)

To a solution of pyridine (0.12 mL) in dichloromethane (0.4 mL) at −25°C under N_2, a solution of Tf_2O (0.057 mL, 0.34 mmol) in 0.2 ml CH_2Cl_2 was added with stirring. A solution of **8** (112 mg, 0.29 mmol) in CH_2Cl_2 (3.7 mL) was then slowly added to it. The stirring was continued for 30 min after which the mixture was allowed to attain 25°C. After 1 hr, the solution was diluted with CH_2Cl_2 (25 mL) and washed with water (2 × 25 mL), dried (Na_2SO4) and concentrated to give a product **10** (89.7 mg, 82%), which crystallized from hot ethanol; m.p. 62–64°C; $[\alpha]_D^{25}$ −56.7°C (c 0.74, $CHCl_3$). ^{1}H NMR δ 7.44–7.00 (12 H, aromatic protons), 5.53 (s, 1H, H-1^{II}), 4.81, 4.68 (2d, 2H, $J = 10.5$ Hz, $CH_2C_6H_4$), 4.61, 4.51 (2d, 2H, $J = 11.4$ Hz, $CH_2C_6H_4$), 4.35 (d, 1H, $J_{1,2} = 9.6$ Hz, H-1^{I}), 4.07 (dd, 1H, $J_{1,2} = 9.6$ Hz, $J_{2,3} = 4.5$, H-2^{I}), 3.87 (dd, 1H, $J_{1,2} = 1.2$ Hz, $J_{2,3} = 4.5$ Hz, H-2^{II}), 3.75 (m, 1H, H-3^{I}), 3.52 (t, 1H, $J = 9.4$ Hz, H-3^{II}), 3.47 (t, 1H, $J = 9.9$ Hz, H-4^{I}), 3.30 (t, 1H, $J = 9$ Hz, H-4^{II}), 3.22, 3.14 (2m, 2H, H-5^{I}, H-5^{II}), 2.35, 2.25 (2s, 6H, 2 $C_6H_5CH_3$), 1.36 (d, 3H, $J = 6$ Hz, H-6^{II}), 1.02 (d, 3H, $J = 6.3$ Hz, H-6^{I}). ^{13}C NMR δ 138.5–128.2 (aromatic carbons), 101.54 (C-1^{II}), 88.48 (C-1^{I}), 83.93, 78.0, 76.9, 75.84, 75.39, 71.32, 68.84, 68.56, 65.05 (C-4^{I}), 53.52 (C-4^{II}), 21.55, 21.50 (2 $CH_3C_6H_4S$), 19.05, 18.78 (C-6^{I}, C-6^{II}). Anal. Calcd for $C_{40}H_{44}N_6S_2O_5$: C, 63.81; H, 5.89; N, 11.16. Found C, 63.62; H, 5.97; N, 10.98. FAB-MS: Calcd for $C_{40}H_{44}N_6S_2O_5$: [M + 1] 753.96. Found: 754.

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