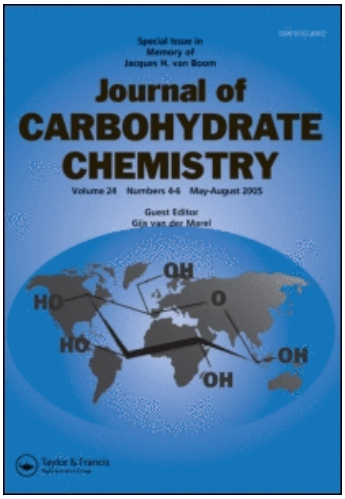


Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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

Kakali Sarkar[a]; Nirmolendu Roy[a]
[a] Department of Biological Chemistry, Indian Association for the Cultivation of Science, Kolkata, India

Online publication date: 05 March 2004

To cite this Article Sarkar, Kakali and Roy, Nirmolendu(2004) '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', Journal of Carbohydrate Chemistry, 23: 1, 41 — 47
To link to this Article: DOI: 10.1081/CAR-120030023
URL: http://dx.doi.org/10.1081/CAR-120030023

JOURNAL OF CARBOHYDRATE CHEMISTRY
Vol. 23, No. 1, pp. 41–47, 2004

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

Kakali Sarkar and Nirmolendu Roy*

Department of Biological Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India

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

*Correspondence: Nirmolendu Roy, Department of Biological Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India; Fax: +91-33-2473-2805; E-mail: nirmolendu@yahoo.com.

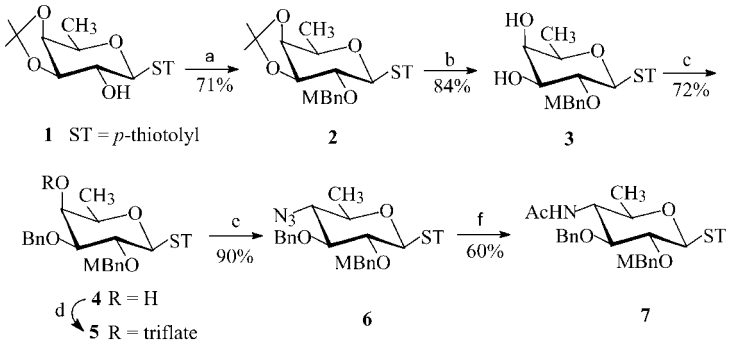
DOI: 10.1081/CAR-120030023 0732-8303 (Print); 1532-2327 (Online)

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.

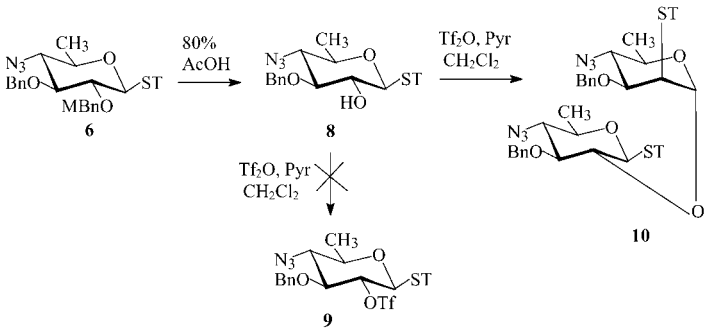
p-Tolyl 3,4-*O*-isopropylidene-1-thio-*β*-D-fucopyranoside[1] (**1**) prepared as reported previously, was allowed to react with 4-methoxybenzyl chloride and NaH[2] to give the 2-*O*-(4-methoxybenzyl) compound **2** in 71% yield. The isopropylidene group of **2** was removed[3] and the resulting dihydroxy 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%.



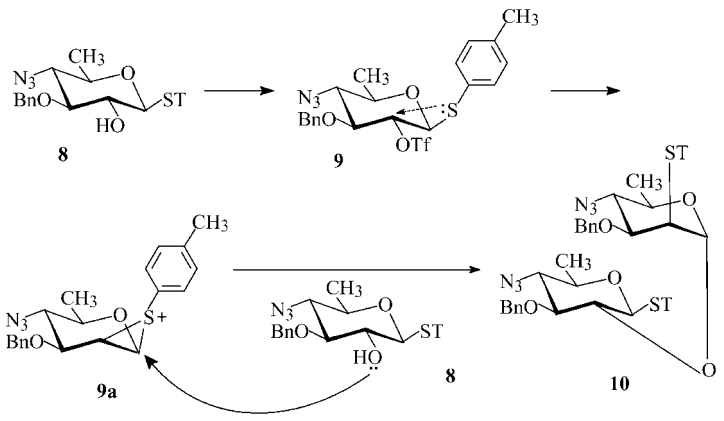
Scheme 2.

and other ring protons and carbons. The ^{13}C NMR spectrum of **10** showed 16 carbons in the region between δ0 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.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

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,

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

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,

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

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.

ACKNOWLEDGMENT

Financial support from the Council of Scientific and Industrial Research, New Delhi (Project No 01/1536/98/EMR-II) is thankfully acknowledged.

REFERENCES

1. Sarkar, K.; Roy, N. Synthesis of *p*-tolyl 3,4-*O*-isopropylidene-2-*O*-(methylthiomethyl)-β-D-fucopyranose. Ind. J. Chem. **2002**, *41B*, 639–641.
2. Pozsgay, V.; Glaudemans, C.P.J.; Robins, J.B.; Schneerson, R. Synthesis of the tetrasaccharide building block of the O-specific polysaccharide of *Shigella dysenteriae* type 1. Tetrahedron **1992**, *48*, 10249–10264.
3. Sarbajna, S.; Roy, N. Synthesis of the tetrasaccharide repeating unit of the K-antigen from *Klebsiella* type 57. Carbohydr. Res. **1998**, *306*, 401–407.
4. Augé, C.; David, S.; Veyriéres, A. Complete regioselectivity in the benzylation of a cis-diol by the stannylidene procedure. J. Chem. Soc., Chem. Commun. **1976**, 375–376.
5. Fleet, G.W.J.; Gouch, M.J.; Smith, P.W. Enantiospecific synthesis of swainsonine, (1S, 2R, 8R, 8aR)-1,2,8-trihydroxyoctahydroindolizine, from D-mannose. Tetrahedron Lett. **1984**, *25*, 1853–1856.
6. Zhang, J.; Kovac, P. Synthesis of some analogs of the methyl α-glycoside of the presumed antigenic determinant of the O-specific polysaccharide of *Vibrio cholerae* O:1 serotype Ogawa. J. Carbohydr. Chem. **1998**, *17* (3), 341–357.
7. Stevens, C.L.; Blumberg, P.; Daniher, F.A.; Strominger, J.L.; Matsuhasi, M.; Dietzler, D.N.; Suzuki, S.; Okazaki, T.; Sugimoto, K.; Okazaki, R. Synthesis of viosamine (4-amino-4,6-dideoxy-D-glucose) by double inversion at C-4 and identification with the 4-amino-4,6-dideoxyhexose from *Escherichia coli* strain B. J. Am. Chem. Soc. **1964**, *86*, 2939–2940.
8. Haskell, T.H. Amicetin, bamicetin and plicacetin. Chemical studies. J. Am. Chem. Soc. **1958**, *80*, 747–751.
9. Stevens, C.L.; Blumbergs, P.; Otterbach, D.H. Synthesis and chemistry of 4-amino-4,6-dideoxy sugars II. Glucose. J. Org. Chem. **1966**, *31*, 2822–2829.
10. Misra, A.K.; Mukherjee, I.; Mukhopadhyay, B.; Roy, N. A simple method for the removal of 4-methoxybenzyl group. Ind. J. Chem. **1999**, *38B*, 90–92.
11. Auzanneau, F.-I.; Bundle, D.R. Incidence and avoidance of stereospecific 1,2-ethylthio group migration during the synthesis of ethyl 1-thio-α-l-rhamnopyranoside 2,3-orthoester. Carbohydr. Res. **1991**, *212*, 13–24 and references cited.

Received August 21, 2003
Revised November 2, 2003
Accepted November 2, 2003

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Request Permission or Order Reprints Instantly!