ELSEVIER

Carbohydrate Research 307 (1998) 243–251

CARBOHYDRATE RESEARCH

Synthesis of some divalent *O*- and *S*-glycosides of galabiose and globotriose

Henrik C. Hansen, Göran Magnusson*

Organic Chemistry 2, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

Received 2 October 1997; accepted 20 December 1997

Abstract

Derivatives of galabiose (α-D-Gal*p*-(1→4)-D-Gal*p*) and globotriose (*a*-D-Gal*p*-(1→4)-*β*-D-Gal*p*-(1→4)-D-Glc*p*) were coupled to various 1,2- and 1,3-dihydroxymethyl- and dimercaptomethylbenzenes to give the corresponding divalent glycosides, potentially useful as inhibitors of bacterial adhesion.

Keywords: Divalent galabiosides; Divalent globotriosides, synthesis of

1. Introduction

Glycolipids containing the disaccharide moiety galabiose [Gal(α1-4)Gal] function as receptors for pathogen adhesion to cells, which constitutes the first step of an infective process [1]. The biological background to these phenomena has been summarized in several publications from this laboratory [2]. Blocking of the carbohydrate–protein recognition by receptor analogs is a potentially useful approach towards novel antibacterial agents, similar to the recent development of anti-adhesive antiviral compounds [3].

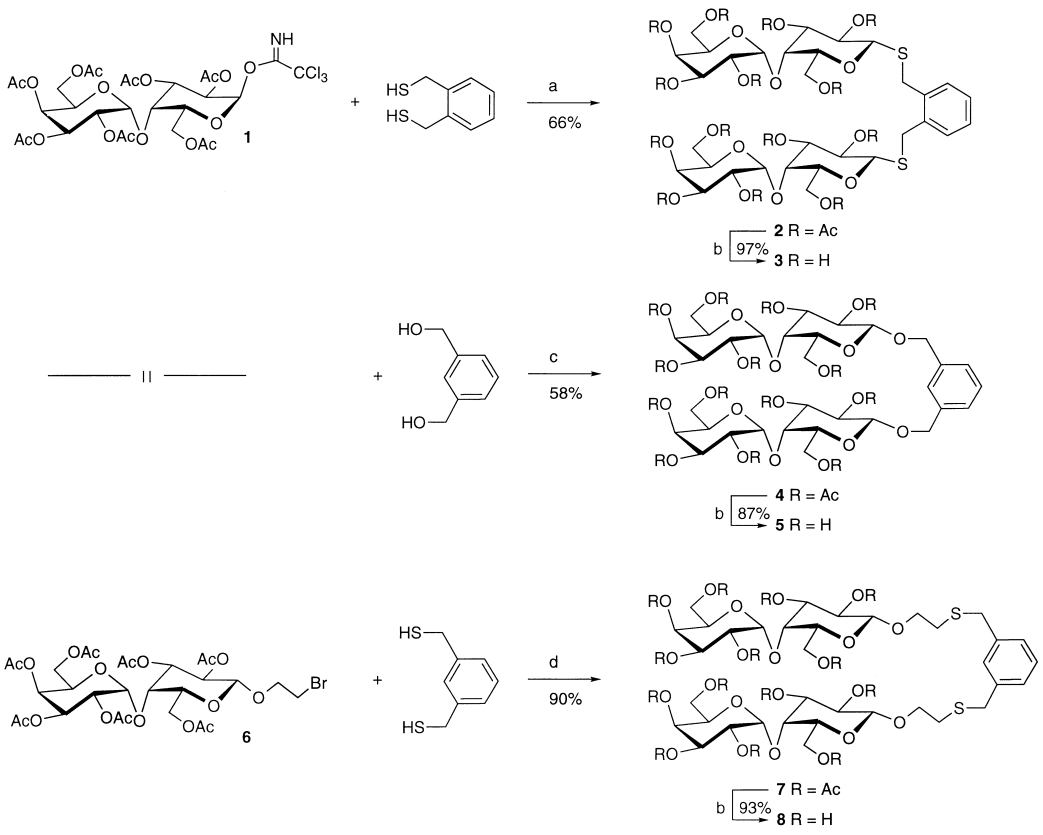
Most carbohydrate–protein interactions are rather weak and *milli*molar concentrations of an inhibitory saccharide derivative are often required for complete inhibition. Weak interactions can be compensated by the use of multivalent inhibitors, as demonstrated by several research groups [4]. We described recently that *nano*molar concentrations of glycodendrimers carrying two to four galabiosyl residues can inhibit hemagglutination between the pig pathogen *Streptococcus suis* and red blood cells [5]. The inhibitory efficiency of the glycodendrimers depends not only on the number of saccharides present in the molecule, but also on the mode of presentation of the binding epitopes. In line with an attempt to obtain additional information about the binding phenomena, we now report the synthesis of a number of novel divalent glycosides carrying the galabiose and globotriose saccharide moieties.

2. Results and discussion

A series of commercially available divalent benzene derivatives were chosen as scaffolds for the construction of the divalent glycosides. Thus, 1,2-dimercaptomethylbenzene (Scheme 1) was glycosylated with the known [5] galabiose imidate **1**

* Corresponding author. Fax: 46 46 222 8209.

0008-6215/98/$19.00
PII S0008-6215(98)00021-4



Scheme 1. (a) $BF_3{\cdot}OEt_2$, CH_2Cl_2, ~22 °C, 45 min; (b) MeONa, MeOH, ~22 °C, 6 h; (c) CF_3SO_3Ag, CH_2Cl_2, ~22 °C, 10 h; (d) Cs_2CO_3, DMF, ~22 °C, 10 h.

(2.5 equiv), using boron trifluoride etherate as promoter [6], furnishing the thiogalabioside **2** (66%). De-*O*-acetylation of **2** with methanolic sodium methoxide gave the divalent glycoside **3** (97%).

Glycosylation of 1,3-dihydroxymethylbenzene with **1** (2.8 equiv) using silver trifluoromethanesulfonate [7] as promoter, gave **4** (58%), contaminated with 3–5% of an unknown compound. De-*O*-acetylation as above gave the divalent glycoside **5** (87%) as a pure compound. Attempted glycosylation with boron trifluoride etherate as promoter was unsuccessful, leading mainly to a monoglycosylated product where the benzylic hydroxymethyl group was acetylated. Similarly, when the benzoyl-protected trichloroacetimidate analog of **1** was used instead of **1**, the product was monoglycosylated (the benzylic hydroxymethyl group was unprotected). Addition of a second portion of the imidate did not lead to a second glycosylation.

Alkylation of 1,3-dimercaptomethylbenzene with the known [8] 2-bromoethyl galabioside **6** (2.4 equiv) in the presence of cesium carbonate [9] furnished **7** (90%). De-*O*-acetylation of **7** gave the divalent glycoside **8** (93%).

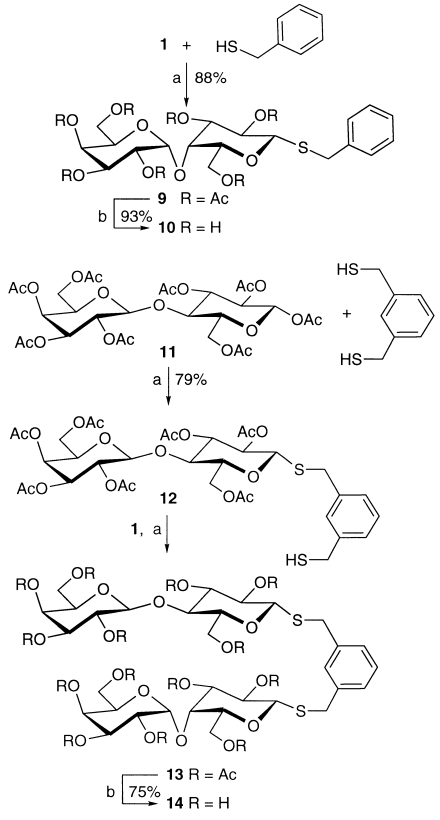
The thioglycosides **10** and **14** (Scheme 2) were designed for use as negative controls of multivalency in future biological assays, since each compound carries only one galabiosyl residue. Glycosylation of benzylthiol with the trichloroacetimidate **1** (1.7 equiv.), using boron trifluoride etherate as promoter [6], gave **9** (88%), and de-*O*-acetylation yielded the thiogalabioside **10** (93%). Boron trifluoride etherate-induced glycosylation [10] of 1,3-dimercaptomethylbenzene with the per-*O*-acetylated lactose **11** (1.1 equiv) gave the monoglycosylated compound **12** (79%). Treatment of **12** with **1** (1.2 equiv) as above furnished **13**, contaminated by 5% of an unknown compound. De-*O*-acetylation of the mixture permitted the isolation of pure **14** (57% overall yield from **12**).

The *E. coli* proteins $PapG_{J96}$ and $PapG_{AD110}$ use galabiose and globotriose, respectively, for optimal recognition [11,12], and we therefore synthesized the globotriosides **23** and **25** (Scheme 3). The known [11] 2-(trimethylsilyl)ethyl (TMSEt) globotrioside **15** was *O*-acetylated with acetic anhydride

in pyridine to yield the protected glycoside **16** (96%). Removal of the TMSEt group of **16** with trifluoroacetic acid in dichloromethane [13] gave the hemiacetal **17** [14] (90%), and **17** was transformed into the trichloroacetimidate **18** [14] (69%, α/β 10:1) by treatment [6] with trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Treatment of **18** with 2-bromoethanol and boron trifluoride etherate [6] gave the known [15] 2-bromoethyl globotrioside **19** (58%). The bromine atom of **19** was substituted by an azido group, using sodium azide in *N*,*N*-dimethylformamide, to furnish the azido compound **20** (93%). De-*O*-acetylation of **20** with methanolic sodium methoxide, followed by catalytic hydrogenation of the azido group, gave the primary amine **21** (72%).

The known [5] carboxylic acid **22** was treated with *N*-hydroxysuccinimide to give the corresponding crude NHS-ester, which was used for *N*-acylation of the amine **21** to furnish the globotriosyl amide **23** (69%). Similarly, the NHS-ester of the known [5] bis-carboxylic acid **24** acylated the amine **21** to yield the divalent glycoside **25** (69%).

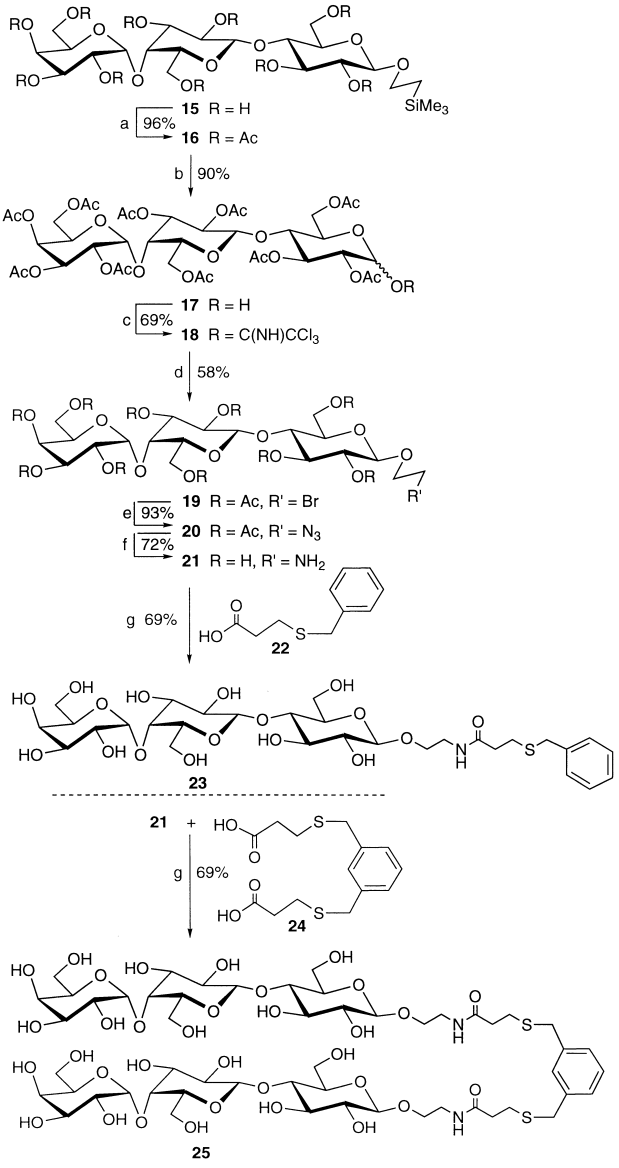
The inhibitory efficiencies of compounds **3**, **5**, **8**, **10**, **14**, **21**, **23**, and **25** against the adhesion of microbes and microbial proteins to natural glycolipids of the globo series, will be reported in due course.



Scheme 2. (a) $BF_3{\cdot}OEt_2$, CH_2Cl_2, ~22 °C, 1 h; (b) MeONa, MeOH, ~22 °C.

3. Experimental

General methods.—See previous paper [2]. Compounds **1** [5], **6** [16], **11** [17], **15** [11], **22** [5], and **24** [5] were synthesized as reported in the literature.



Scheme 3. (a) Ac_2O, pyridine, ~22 °C, 12 h; (b) CF_3COOH, CH_2Cl_2, ~22 °C, 80 min; (c) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 1 h; (d) $HOCH_2CH_2Br$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 22 °C, 40 min; (e) NaN_3, DMF, 15-crown-5, 75 °C, 24 h; (f) [i]MeONa, MeOH; [ii]H_2, Pd-C, EtOH, HCl, H_2O, ~22 °C, 2 h; (g) [i]**22**, NHS, EDC, DMF, ~22 °C, 18 h, chromatography; [ii] **21**, DMF, pyridine, 65 °C, 16 h.

Acetylated Bis-thiogalabioside **2**.—To a solution of **1** (115 mg, 0.147 mmol) and 1,2-dimercaptomethylbenzene (10 mg, 0.059 mmol) in CH_2Cl_2 (2 mL) was added $BF_3{\cdot}OEt_2$ (0.037 mL, 0.294 mmol) under N_2. After 45 min at ~22 °C, sat aq $NaHCO_3$ (2 mL) and CH_2Cl_2 (15 mL) were added. The organic layer was dried and concentrated, and the residue was chromatographed (2:1 EtOAc–heptane) to give **2** (54 mg, 66%); $[\alpha]^{21}_D$ +5° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.21–7.33 (m, 4 H, Ph), 5.57 (bd, 2 H, *J* 2.3 Hz, H-4′), 5.38 (dd, 2 H, *J* 3.4, 11.0 Hz, H-3′), 5.22 (t, 2 H, *J* 10.2 Hz, H-2), 5.20 (dd, 2 H, *J* 3.6, 11.0 Hz, H-2′), 5.01 (d, 2 H, *J* 3.7 Hz, H-1′), 4.80 (dd, 2 H, *J* 2.7, 10.4 Hz, H-3), 4.49 (bt, 2 H, *J* 7.4 Hz, H-5′), 4.45 (dd, 2 H, *J* 4.4, 11.3 Hz, H-6), 4.30 (d, 2 H, *J* 9.9 Hz, H-1), 3.74 (bt, 2 H, *J* 6.4 Hz, H-5), 2.13, 2.12, 2.06, 2.03, 1.99, and 1.98 (6 s, 42 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.06, 171.0, 170.92, 170.88, 170.6, 170.2, 169.6, 135.8, 131.5, 128.1, 99.6, 83.0, 77.7, 76.2, 74.2, 69.0, 68.3, 67.8, 67.6, 67.56, 62.8, 61.0, 31.6, 21.3, 21.26, 21.2, 21.1; HRMS calcd for $C_{60}H_{78}O_{34}S_2Na$ (M + Na): 1429.3713, found: 1429.3690.

Bis-thiogalabioside **3**.—Compound **2** was dissolved in dry MeOH and a catalytic amount of MeONa was added. After 6 h, the mixture was neutralized with Duolite C436 (H^+) resin, and concentrated. The residue was chromatographed (5:5:1 CH_2Cl_2–MeOH–H_2O) to give **3** (22 mg, 97%); $[\alpha]^{22}_D$ −32° (*c* 1.8, H_2O); ^{1}H NMR (D_2O): δ 7.17–7.32 (m, 4 H, Ph), 4.82 (d, 2 H, *J* 3.9 Hz, H-1′), 4.22 (d, 2 H, *J* 9.2 Hz, H-1), 4.21 (bt, 2 H, *J* 6.1 Hz, H-5′), 4.06 (d, 2 H, *J* 13.5 Hz, PhCH_2S), 4.01 (d, 2 H, *J* 13.5 Hz, PhCH_2S), 3.92 (d, 2 H, *J* 2.6 Hz, H-4), 3.89 (d, 2 H, *J* 2.6 Hz, H-4′), 3.78 (dd, 2 H, *J* 3.2, 10.5 Hz, H-3′), 3.40–3.76 (m, 16 H, H-2,3,5,6,2′,6′); ^{13}C NMR (D_2O): δ 136.4, 131.3, 128.3, 100.7, 85.1, 79.1, 77.8, 74.1, 71.1, 70.0, 69.5, 69.3, 69.1, 60.8, 60.3, 31.5; HRMS calcd for $C_{32}H_{51}O_{20}S_2$ (M + H): 819.2415, found: 819.2405.

Acetylated Bis-galabioside **4**.—To a solution of 1,3-dihydroxymethylbenzene (5 mg, 0.036 mmol), **1** (76 mg, 0.097 mmol) and CF_3SO_3Ag (25 mg, 0.097 mmol) was added dry CH_2Cl_2 (2 mL). The mixture was stirred under N_2 at ~22 °C for 10 h. Additional CF_3SO_3Ag (25 mg, 0.097 mmol) and **1** (15 mg, 0.02 mmol) were added. After 12 h, the mixture was filtered through Celite and concentrated. The residue was chromatographed (2:1→3:1→5:1 EtOAc–heptane) to give **4** (29 mg, 58%), contaminated by 3–5% of a co-eluting compound. ^{1}H NMR ($CDCl_3$): δ 7.21–7.35 (m, 4 H, Ph), 5.59 (bd, 2 H, *J* 3.3 Hz, H-4′), 5.42 (dd, 2 H, *J* 3.3, 11.1 Hz, H-3′), 5.26 (dd, 2 H, *J* 7.8, 10.7 Hz, H-2), 5.22 (dd, 2 H, *J* 3.5, 11.1 Hz, H-2′), 5.03 (d, 2 H, *J* 3.6 Hz, H-1′), 4.93 (d, 2 H, *J* 12.4 Hz, PhCH_2O), 4.83 (dd, 2 H, *J* 2.8, 10.8 Hz, H-3), 4.64 (d, 2 H, *J* 12.4 Hz, PhCH_2O), 4.56 (m, 2 H, H-5′), 4.55 (d, 2 H, *J* 7.8 Hz, H-1), 4.49 (dd, 2 H, *J* 6.7, 11.2 Hz, H-6a), 4.05–4.24 (m, 8 H, H-6b,4,6′), 3.80 (bt, 2 H, *J* 6.8 Hz, H-5), 2.14, 2.12, 2.10, 2.08, 2.05, 2.02, and 1.99 (7 s, 42 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.1, 171.0, 170.9, 170.86, 170.6, 170.2, 169.5, 137.5, 129.1, 127.8, 127.4, 100.2, 99.8, 77.5, 73.1, 72.4, 70.8, 69.2, 69.0, 68.3, 67.8, 67.5, 62.4, 61.0, 21.3, 21.2, 21.14, 21.1, 21.06; HRMS calcd for $C_{60}H_{78}O_{36}Na$ (M + Na): 1397.4170, found: 1397.4188.

Bis-galabioside **5**.—Compound **4** (5.5 mg, 0.004 mmol) was dissolved in dry MeOH (2 mL) and a catalytic amount of MeONa was added. After 12 h, the mixture was neutralized with Duolite C436 (H^+) resin, and concentrated. The residue was chromatographed (Varian Mega Bond Elut C18; 1:0→9:1→8:2→7:3→6:4 H_2O–MeOH, 5 mL each). The purified product was chromatographed (8:5:1 CH_2Cl_2–MeOH–H_2O) to give **5** (2.7 mg, 87%); $[\alpha]^{22}_D$ +56° (*c* 0.4, H_2O); ^{1}H NMR (D_2O): δ 7.34–7.46 (m, 4 H, Ph), 4.88 (d, 2 H, *J* 11.3 Hz, PhCH_2O), 4.87 (d, 2 H, *J* 4.0 Hz, H-1′), 4.7 (2 H, PhCH_2O, disturbed by the HDO signal), 4.45 (d, 2 H, *J* 7.7 Hz, H-1), 4.28 (bt, 2 H, *J* 6.4 Hz, H-5′), 3.94 (m, 4 H, H-4,4′), 3.57–3.86 (m, 16 H, including H-3,2′,3′,6′), 3.49 (dd, 2 H, *J* 7.8, 10.0 Hz, H-2); ^{13}C NMR ($CDCl_3$): δ 137.5, 129.2, 129.0, 102.3, 100.6, 77.5, 75.5, 72.8, 71.6, 71.3, 71.2, 69.6, 69.4, 69.1, 60.9, 60.5; HRMS calcd for $C_{32}H_{50}O_{22}Na$ (M + Na): 809.2691, found: 809.2676.

Acetylated Bis-galabioside **7**.—To a mixture of compound **6** (209.5 mg, 0.28 mmol), 1,3-mercaptomethylbenzene (0.018 mL, 0.118 mmol), and dry DMF (3 mL), was added Cs_2CO_3 (103 mg, 0.316 mmol). The mixture was stirred at ~22 °C for 10 h under N_2, and H_2O (10 mL) and CH_2Cl_2 (30 mL) were added. The organic layer was dried and concentrated and the residue was chromatographed (1:1 EtOAc–heptane) to give **7** (158 mg, 90%); $[\alpha]^{21}_D$ +41° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.16–7.30 (m, 4 H, Ph), 5.55 (bd, 2 H, *J* 2.3 Hz, H-4′), 5.37 (dd, 2 H, *J* 3.3, 11.0 Hz, H-3′), 5.19 (dd, 2 H, *J* 3.8, 11.0 Hz, H-2′), 5.17 (dd, 2 H, *J* 8.0, 11.1 Hz, H-2), 4.99 (d, 2 H, *J* 3.6 Hz, H-1′),

4.80 (dd, 2 H, *J* 2.6, 10.8 Hz, H-3), 4.51 (bt, 2 H, *J* 7.0 Hz, H-5′), 4.47 (d, 2 H, *J* 7.8 Hz, H-1), 4.43 (dd, 2 H, *J* 6.8, 11.3 Hz, H-6a), 4.04–4.20 (m, 8 H, including H-4,6b,6′), 3.94–4.04 (m, 2 H, OCH_2CH_2S), 3.78 (bt, 2 H, *J* 6.4 Hz, H-5), 3.73 (s, 4 H, $PhCH_2$), 3.56-3.66 (m, 2 H, OCH_2CH_2S), 2.57–2.72 (m, 4 H, OCH_2CH_2S), 2.12, 2.09, 2.07, 2.04, 2.02, and 1.98 (6 s, 42 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.1, 171.0, 170.9, 170.85, 170.6, 170.2, 169.6, 139.1, 129.7, 129.1, 128.1, 101.6, 99.8, 73.1, 72.4, 69.6, 69.0, 68.3, 67.8, 67.5, 62.4, 60.9, 36.9, 31.2, 21.4, 21.2, 21.14, 21.09, 21.06; HRMS calcd for $C_{64}H_{86}O_{36}S_2Na$ (M + Na): 1517.4238, found: 1517.4243.

Bis-galabioside **8**.—Compound **7** (100 mg, 0.067 mmol) was dissolved in dry MeOH and a catalytic amount of 0.5 M MeONa was added. After 10 h, the mixture was neutralized with Duolite C436 (H^+) resin and concentrated. The residue was chromatographed (10:5:1 CH_2Cl_2–MeOH–H_2O) to give **8** (56 mg, 93%); $[\alpha]^{21}_D$ +72° (*c* 0.7, D_2O); ^1H NMR (D_2O): δ 7.15–7.29 (m, 4 H, Ph), 4.84 (d, 2 H, *J* 3.9 Hz, H-1′), 4.26 (d, 2 H, *J* 7.8 Hz, H-1), 4.23 (bt, 2 H, *J* 6.7 Hz, H-5′), 3.88–3.92 (m, 4 H, H-4,4′), 3.52–3.87 (m, 24 H, including H-3,5,2′,3′ and OCH_2CH_2S), 3.41 (dd, 2 H, *J* 7.7, 10.2 Hz, H-2), 2.60 (dt, 4 H, *J* 0.9, 6.8 Hz, OCH_2CH_2S); ^{13}C NMR (D_2O): δ 139.4, 129.8, 129.5, 128.2, 103.4, 100.6, 77.4, 75.3, 72.7, 71.23, 71.15, 69.5, 69.3, 69.2, 69.1, 60.9, 60.3, 35.5, 30.6; HRMS calcd for $C_{36}H_{58}O_{22}S_2Na$ (M + Na): 929.2759, found: 929.2763.

Benzyl (2,3,4,6-tetra-O-*acetyl*-α-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl-1-thio*-β-D-*galactopyranoside* (**9**).—To a mixture of **1** (50 mg, 0.064 mmol), benzylthiol (0.007 mL, 0.06 mmol), and CH_2Cl_2 (2 mL), was added $BF_3{\cdot}OEt_2$ (0.008 mL, 0.064 mmol) under N_2. After 1 h at ~22 °C, sat aq $NaHCO_3$ (10 mL) and CH_2Cl_2 (20 mL) were added. The organic layer was dried and concentrated, and the residue was chromatographed (2:1 EtOAc–heptane) to give **9** (38 mg, 88%); $[\alpha]^{21}_D$ +36° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.30–7.37 (m, 5 H, Ph), 5.58 (bd, 1 H, *J* 3.3 Hz, H-4′), 5.40 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3′), 5.29 (t, 1 H, *J* 10.1 Hz, H-2), 5.22 (dd, 1 H, *J* 3.7, 11.1 Hz, H-2′), 5.03 (d, 1 H, *J* 3.7 Hz, H-1′), 4.82 (dd, 1 H, *J* 2.7, 10.3 Hz, H-3), 4.50 (bt, 1 H, *J* 6.5 Hz, H-5′), 4.45 (dd, 1 H, *J* 7.1, 11.4 Hz, H-6a), 4.31 (d, 1 H, *J* 9.9 Hz, H-1), 4.06–4.20 (m, 4 H, H-4,6b,6′), 3.98 (d, 1 H, *J* 12.9 Hz, $PhCH_2$), 3.87 (d, 1 H, *J* 12.9 Hz, $PhCH_2$), 3.74 (bt, 1 H, *J* 6.5 Hz, H-5), 2.14, 2.12, 2.11, 2.08, 2.05, 2.02, and 2.00 (7 s, 21 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.03, 171.0, 170.9, 170.6, 170.2, 169.7, 137.5, 129.5, 129.0, 127.7, 99.5, 82.8, 77.7, 76.3, 74.3, 68.9, 68.3, 67.8, 67.6, 67.5, 62.8, 61.0, 34.0, 21.4, 21.2, 21.16, 21.1, 21.07; HRMS calcd for $C_{33}H_{42}O_{17}SNa$ (M + Na): 765.2040, found: 765.2040.

*Benzyl (*α-D-*galactopyranosyl)-(1→4)-1-thio*-β-D-*galactopyranoside* (**10**).—Compound **9** (45 mg, 0.06 mmol) was dissolved in dry MeOH (3 mL) and a catalytic amount of 0.5 M MeONa was added. After 10 h, the mixture was neutralized with Duolite C436 (H^+) resin and concentrated. The residue was chromatographed (10:5:1 CH_2Cl_2–MeOH–H_2O) to give **10** (25 mg, 93%); $[\alpha]^{22}_D$ +7° (*c* 0.3, H_2O); ^1H NMR (D_2O): δ 7.17–7.35 (m, 5 H, Ph), 4.80 (d, 1 H, *J* 3.4 Hz, H-1′), 4.19 (d, 1 H, *J* 7.7 Hz, H-1), 4.14–4.25 (m, 1 H, H-5′); ^{13}C NMR (D_2O): δ 138.4, 129.1, 127.7, 100.7, 84.9, 79.2, 77.9, 74.1, 71.1, 70.06, 69.5, 69.3, 69.1, 60.8, 60.4, 34.2; HRMS calcd for $C_{19}H_{28}O_{10}SNa$ (M + Na): 471.1301, found: 471.1316.

(3-Mercaptomethyl)benzyl (2,3,4,6-tetra-O-*acetyl*--β-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl-1-thio*-β-D-*glucopyranoside* (**12**).—To a mixture of octaacetyl-*β*-lactose **11** [17] (87 mg, 0.128 mmol), 1,3-mercaptomethylbenzene (0.018 mL, 0.118 mmol), and CH_2Cl_2 (2 mL), was added $BF_3{\cdot}OEt_2$ (0.074 mL, 0.587 mmol) under N_2. After 1 h at ~22 °C, sat aq $NaHCO_3$ (2 mL) and CH_2Cl_2 (10 mL) were added. The organic layer was dried and concentrated, and the residue was chromatographed (1:1 EtOAc–heptane) to give **12** (73 mg, 79%); $[\alpha]^{21}_D$ −43° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.14–7.30 (m, 4 H, Ph), 5.34 (d, 1 H, *J* 3.2 Hz, H-4′), 5.13 (t, 1 H, *J* 9.9 Hz, H-3), 5.09 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2′), 4.97 (t, 1 H, *J* 9.9 Hz, H-2), 4.95 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3′), 4.49 (m, 1 H, H-6a), 4.47 (d, 1 H, *J* 7.7 Hz, H-1′), 4.26 (d, 1 H, *J* 10.1 Hz, H-1), 4.03–4.16 (m, 3 H, H-6b,6′), 3.89 (d, 1 H, *J* 12.8 Hz, $PhCH_2SC$), 3.86 (bt, 1 H, *J* 6.7 Hz, H-5′), 3.74–3.82 (m, 2 H, H-4 and $PhCH_2SC$), 3.73 (d, 2 H, *J* 7.6 Hz, $PhCH_2SH$), 3.54 (ddd, 1 H, *J* 1.6, 5.4, 9.9 Hz, H-5), 2.15, 2.14, 2.05, 2.03, 2.01, and 1.96 (6 s, 21 H, Ac), 1.78 (t, 1 H, *J* 7.6 Hz, SH); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.6, 170.5, 170.11, 170.10, 169.5, 142.0, 137.7, 129.4, 129.2, 128.2, 127.6, 101.5, 82.0, 77.0, 76.7, 74.2, 71.4, 71.1, 70.6, 69.5, 67.0, 62.7, 61.2, 34.1, 29.2, 21.4, 21.2, 21.14, 21.1, 20.9; HRMS calcd for $C_{34}H_{44}O_{17}S_2Na$ (M + Na): 811.1918, found: 811.1918.

Acetylated thiolactosyl-thiogalabiosyl dimer (**13**).—To a mixture of compound **12** (40 mg, 0.051 mmol), compound **1** (47.5 mg, 0.061 mmol), and CH_2Cl_2 (2 mL), was added $BF_3{\cdot}OEt_2$ (0.015 mL, 0.12 mmol) under N_2. After 1 h at ~22 °C, sat aq $NaHCO_3$ (2 mL) and CH_2Cl_2 (15 mL) were added. The organic layer was dried and concentrated, and the residue was chromatographed (2:1 EtOAc–heptane) to give **13** contaminated with 5% of an unknown compound (54 mg). An analytical sample of **13** was obtained by rechromatography of crude **13**; $[\alpha]^{21}_D$ −14° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.15–7.30 (m, 4 H, Ph), 5.58 (bd, 1 H, *J* 3.2 Hz, H-4′$_{gala}$), 5.40 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3′$_{gala}$), 5.36 (bd, 1 H, *J* 3.3 Hz, H-4′$_{lac}$), 5.30 (t, 1 H, *J* 10.1 Hz, H-2$_{gala}$), 5.22 (dd, 1 H, *J* 3.6, 11.1 Hz, H-2′$_{gala}$), 5.16 (t, 1 H, *J* 9.2 Hz, H-3$_{lac}$), 5.11 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2′$_{lac}$), 5.03 (d, 1 H, *J* 3.5 Hz, H-1′$_{gala}$), 4.98 (t, 1 H, *J* 9.9 Hz, H-2$_{lac}$), 4.97 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3′$_{lac}$), 4.85 (dd, 1 H, *J* 2.7, 10.4 Hz, H-3$_{gala}$), 4.51 (m, 1 H, H-5′$_{gala}$), 4.49 (d, 1 H, *J* 7.9 Hz, H-1′$_{lac}$), 4.45 (dd, 1 H, *J* 7.0, 11.4 Hz, H-6a$_{lac}$), 4.35 (d, 1 H, *J* 10.1 Hz, H-1$_{lac}$), 4.34 (d, 1 H, *J* 9.8 Hz, H-1$_{gala}$), 4.05–4.20 (m, 7 H, including H-4$_{gala}$, H-6b$_{lac}$), 3.75–4.00 (m, 7 H, including H-4$_{lac}$), 3.58 (m, 1 H, H-5$_{lac}$), 2.165, 2.160, 2.15, 2.13, 2.12, 2.09, 2.07, 2.065, 2.05, 2.045, 2.035, 2.030, 2.00, and 1.98 (14 s, 42 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.9, 170.8, 170.6, 170.2, 169.5, 138.0, 137.7, 130.1, 129.2, 128.7, 128.4, 101.6, 99.6, 82.9, 82.4, 76.7, 76.3, 74.2, 71.4, 71.1, 70.6, 69.5, 68.9, 68.3, 67.7, 67.6, 67.5, 67.0, 62.6, 61.2, 61.0, 34.1, 33.7, 21.4, 21.2, 21.1, 20.9; HRMS calcd for $C_{60}H_{78}O_{34}S_2Na$ (M + Na): 1429.3714, found: 1429.3721.

Thiolactosyl-thiogalabiosyl dimer **14**.—Crude **13** (42 mg) was dissolved in MeOH and MeONa (0.5 M) was added. After 6 h, the mixture was neutralized with Duolite C436 (H^+) resin and concentrated. The residue was chromatographed (Varian Mega Bond Elut Column C18; 9:1→8:2→7:3→6:4→5:5 H_2O–MeOH, 5 mL each) to give pure **14** (18.4 mg, 57% overall yield from **12**); $[\alpha]^{21}_D$ −77° (*c* 1.3, H_2O); ^{1}H NMR (D_2O): δ 7.16–7.30 (m, 4 H, Ph), 4.80 (d, 1 H, *J* 3.9 Hz, H-1′$_{gala}$), 4.31 (d, 1 H, *J* 7.8 Hz, H-1′$_{lac}$), 4.21 (bt, 1 H, *J* 6.6 Hz, H-5′$_{gala}$), 4.15 (d, 1 H, *J* 9.9 Hz, H-1$_{lac}$), 4.12 (bd, 1 H, *J* 9.6 Hz, H-1$_{gala}$), 3.86–3.94 (m, 4 H), 3.30–3.84 (m, 22 H), 3.27 (dd, 1 H, *J* 9.0, 9.9 Hz, H-2$_{lac}$); ^{13}C NMR (D_2O): δ 138.7, 138.6, 130.1, 129.4, 128.4, 103.2, 100.7, 84.4, 83.8, 79.2, 78.9, 78.5, 77.9, 76.1, 75.7, 74.1, 72.9, 72.3, 71.3, 71.1, 70.1, 69.5, 69.3, 69.1, 68.9, 61.4, 60.8, 60.6, 60.5, 33.7, 33.6; HRMS calcd for $C_{32}H_{50}O_{20}S_2Na$ (M + Na): 841.2235, found: 841.2260.

*2-(Trimethylsilyl)ethyl (2,3,4,6-tetra-*O*-acetyl-*α*-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-*β*-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*β*-*D*-glucopyranoside* (**16**).—The TMSEt globotrioside **15** [11] (34 mg, 0.056 mmol) was dissolved in pyridine (6 mL) and Ac_2O (6 mL). The mixture was stirred at ~22 °C for 12 h, toluene (30 mL) was added, and the mixture was concentrated. The residue was chromatographed (1:1 EtOAc–heptane) to give **16** (55 mg, 96%); $[\alpha]^{21}_D$ +40° (*c* 2.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.60 (bd, 1 H, *J* 2.2 Hz, H-4″), 5.40 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3″), 5.21 (t, 1 H, *J* 9.2 Hz, H-3), 5.19 (dd, 1 H, *J* 3.6, 11.1 Hz, H-2″), 5.11 (dd, 1 H, *J* 7.7, 10.8 Hz, H-2′), 4.99 (d, 1 H, *J* 3.6 Hz, H-1″), 4.88 (dd, 1 H, *J* 7.9, 9.4 Hz, H-2), 4.74 (dd, 1 H, *J* 2.6, 10.8, H-3′), 4.52 (d, 1 H, *J* 7.7 Hz, H-1′), 4.50 (d, 1 H, *J* 7.9 Hz, H-1), 4.41–4.53 (m, 3 H, H-5″,6a,6′a), 4.07–4.21 (m, 4 H, H-6b,6′b, 6″), 4.02 (d, 1 H, *J* 2.1 Hz, H-4′), 3.95 (dt, 1 H, *J* 5.8, 10.0 Hz, CH_2CH_2O), 3.73–3.85 (m, 2 H, H-4,5′), 3.61–3,67 (m, 1 H, H-5), 3.57 (dt, 1 H, *J* 6.9, 9.9 Hz, CH_2CH_2O), 2.14, 2.12, 2.09, 2.08, 2.075, 2.070, 2.065, 2.06, 2.04, and 1.99 (10 s, 30 H, Ac), 0.79–1.01 (m, 2 H, CH_2SiMe_3), 0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 171.1, 170.9, 170.5, 170.2, 170.0, 169.3, 101.6, 100.4, 100.1, 77.4, 73.8, 73.3, 72.9, 72.3, 72.2, 69.4, 69.3, 68.3, 67.9, 67.6, 67.5, 62.8, 61.7, 60.7, 21.4, 21.3, 21.2, 21.15, 21.1, 21.0, 20.9, 18.3, −1.0; HRMS calcd for $C_{43}H_{64}O_{26}SiNa$ (M + Na): 1047.3353, found: 1047.3344.

*(2,3,4,6-Tetra-*O*-acetyl-*α*-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-*β*-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*β*-*D*-glucopyranose* (**17**) [14].—To a solution of compound **16** (250 mg, 0.24 mmol) in CH_2Cl_2 (1.2 mL) was added CF_3COOH (2.4 mL, 0.031 mmol), and the mixture was stirred at ~22 °C under N_2. After 80 min, *n*-propyl acetate (10 mL) and toluene (10 mL) were added, and the mixture was concentrated and co-concentrated twice with toluene. The residue was chromatographed (3:1 EtOAc–heptane) to give the hemiacetal **17** (204 mg, 90%); HRMS calcd for $C_{38}H_{52}O_{26}Na$ (M + Na): 947.2645, found: 947.2652.

*(2,3,4,6-Tetra-*O*-acetyl-*α*-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-*β*-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*α*-*D*-glucopyranosyl trichloroacetimidate* (**18**) [14].—Compound **17** (204 mg, 0.22 mmol) was dissolved in a mixture of

dry CH_2Cl_2 (3.4 mL) and dry Cl_3CCN (0.85 mL, 8.4 mmol). The mixture was cooled to 0 °C under N_2, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.051 mL, 0.34 mmol) was added. The mixture was stirred at 0 °C for 1 h, then washed with cold H_2O, dried, and concentrated. The residue was chromatographed (2:1 EtOAc–heptane) to give **18** (163 mg, 69%) as an α/β mixture (10:1). ^{1}H NMR for **18**α ($CDCl_3$): δ 8.66 (s, 1 H, =NH), 6.49 (d, 1 H, *J* 3.8 Hz, H-1), 5.60 (bs, 1 H, H-4″), 5.57 (t, 1 H, *J* 9.5 Hz, H-3), 5.41 (dd, 1 H, *J* 3.4, 11.1 Hz, H-3″), 5.19 (dd, 1 H, *J* 3.5, 10.9 Hz, H-2″), 5.13 (dd, 1 H, *J* 7.8, 10.8 Hz, H-2′), 5.08 (dd, 1 H, *J* 3.8, 10.2 Hz, H-2), 5.00 (d, 1 H, *J* 3.5 Hz, H-1″), 4.75 (dd, 1 H, *J* 2.4, 10.8 Hz, H-3′), 4.55 (d, 1 H, *J* 7.8 Hz, H-1′), 4.42–4.55 (m, 3 H, H-5″,6′a,6a), 4.07–4.22 (m, 5 H, H-6″,6′b,5,6b), 4.03 (d, 1 H, *J* 2.2 Hz, H-4′), 3.88 (t, 1 H, *J* 9.4 Hz, H-4), 3.78 (t, 1 H, *J* 6.7 Hz, H-5′), 2.14, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.02, and 1.99 (10 s, 30 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.1, 170.9, 170.7, 170.54, 170.5, 169.9, 169.7, 169.2, 161.5, 101.7, 100.0, 93.4, 76.4, 73.4, 72.3, 71.4, 70.4, 70.2, 69.5, 69.4, 68.3, 67.6, 67.5, 62.1, 61.8, 60.7, 21.4, 21.2, 21.15, 21.1, 21.0, 20.9; HRMS calcd for $C_{40}H_{52}O_{26}Cl_3NNa$ (M + Na): 1090.1741, found: 1090.1757. ^{1}H NMR for **18**β ($CDCl_3$): δ 5.89 (d, 1 H, *J* 7.7 Hz, H-1), the remaining signals were obscured by the signals of the main component **18**α.

2-Bromoethyl (2,3,4,6-tetra-O-*acetyl*-α-D-*galacto-pyranosyl)-(1→4)-(2,3,6-tri*-O-*acetyl*-β-D-*galacto-pyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl*-β-D-*glucopyr-anoside* (**19**) [15].—A mixture of compound **18** (139 mg, 0.13 mmol), 2-bromoethanol (0.015 mL, 0.21 mmol), and CH_2Cl_2 (3.5 mL) was cooled to 0 °C, and $BF_3{\cdot}OEt_2$ (0.016 mL, 0.13 mmol) was added. The mixture was stirred at ~22 °C under N_2. After 40 min, sat aq $NaHCO_3$ (2 mL) and CH_2Cl_2 (10 mL) were added. The organic layer was isolated, dried, and concentrated. The residue was chromatographed (3:1 EtOAc–heptane) to give **19** (78 mg, 58%); $[\alpha]^{22}_D$ +45° (*c* 1.0, $CHCl_3$), lit +45° [15]; ^{1}H NMR ($CDCl_3$): δ 5.59 (bd, 1 H, *J* 3.2 Hz, H-4″), 5.39 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3″), 5.21 (t, 1 H, *J* 9.1 Hz, H-3), 5.18 (dd, 1 H, *J* 3.6, 11.0 Hz, H-2″), 5.11 (dd, 1 H, *J* 7.8, 10.9 Hz, H-2′), 4.99 (d, 1 H, *J* 3.6 Hz, H-1″), 4.92 (dd, 1 H, *J* 7.9, 9.4 Hz, H-2), 4.74 (dd, 1 H, *J* 2.6, 10.8 Hz, H-3′), 4.55 (d, 1 H, *J* 7.9 Hz, H-1), 4.52 (d, 1 H, *J* 7.8 Hz, H-1′), 4.44–4.52 (m, 2 H, H-5″,6a), 4.43 (dd, 1 H, *J* 6.2, 11.1 Hz, H-6′a), 4.06–4.20 (m, 5 H, H-6′b,6b,6″ and OCH_2CH_2Br), 4.01 (bd, 1 H, *J* 2.4 Hz, H-4′), 3.73–3.86 (m, 3 H, H-4,5′ and OCH_2CH_2Br), 3.64 (ddd, 1 H, *J* 1.9, 5.0, 9.8 Hz, H-5′), 3.39–3.49 (m, 2 H, CH_2Br), 2.13, 2.12, 2.08, 2.065, 2.060, 2.055, 2.05, 2.045, and 1.98 (9 s, 30 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.1, 170.9, 170.86, 170.8, 170.5, 170.2, 170.0, 169.95, 169.3, 101.5, 101.2, 100.1, 77.3, 76.8, 73.3, 73.2, 73.1, 72.3, 71.9, 70.2, 69.4, 69.3, 68.3, 67.6, 67.5, 62.5, 61.8, 60.7, 30.2, 21.34, 21.26, 21.2, 21.12, 21.1, 21.05, 21.0, 20.9; HRMS calcd for $C_{40}H_{55}O_{26}BrNa$ (M + Na): 1053.2063, found: 1053.2089.

2-Azidoethyl (2,3,4,6-tetra-O-*acetyl*-α-D-*galacto-pyranosyl)-(1→4)-(2,3,6-tri*-O-*acetyl*-β-D-*galacto-pyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl*-β-D-*glucopyr-anoside* (**20**).—To a solution of compound **19** (75 mg, 0.073 mmol) in DMF (3 mL) were added NaN_3 (15 mg, 0.23 mmol) and 15-crown-5 (0.015 mL, 0.073 mmol), and the mixture was stirred at 75 °C. After 24 h, the mixture was cooled to ~22 °C and H_2O (5 mL) and Et_2O (20 mL) were added. The organic layer was isolated, dried, and concentrated. The residue was chromatographed (2:1 EtOAc–heptane) to give **20** (67 mg, 93%); $[\alpha]^{22}_D$ +35° (*c* 1.2 , $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.58 (bd, 1 H, *J* 3.4 Hz, H-4″), 5.39 (dd, 1 H, *J* 3.4, 11.0 Hz, H-3″), 5.21 (t, 1 H, *J* 9.1 Hz, H-3), 5.18 (dd, 1 H, *J* 3.6, 11.0 Hz, H-2″), 5.11 (dd, 1 H, *J* 7.7, 10.8 Hz, H-2′), 4.99 (d, 1 H, *J* 3.6 Hz, H-1″), 4.92 (dd, 1 H, *J* 7.8, 9.3 Hz, H-2), 4.74 (dd, 1 H, *J* 2.5, 10.8 Hz, H-3′), 4.57 (d, 1 H, *J* 7.8 Hz, H-1), 4.53 (d, 1 H, *J* 7.6 Hz, H-1′), 4.45–4.54 (m, 2 H, H-5″,6a), 4.43 (dd, 1 H, *J* 6.3, 11.1 Hz, H-6′a), 4.06–4.20 (m, 4 H, H-6″,6′b,6b), 4.01 (bd, 1 H, *J* 2.3 Hz, H-4′), 3.98 (ddd, 1 H, *J* 3.6, 5.0, 8.6 Hz, OCH_2CH_2N$_3$), 3.82 (t, 1 H, *J* 9.6 Hz, H-4), 3.76 (dt, 1 H, *J* 6.9 Hz, H-5′), 3.61–3.73 (m, 2 H, H-5 and OCH_2CH_2N$_3$), 3.47 (ddd, 1 H, *J* 3.4, 8.2, 13.3 Hz, CH$_2$CH_2N$_3$), 3.27 (ddd, 1 H, *J* 3.4, 4.8, 13.3 Hz, CH$_2$CH_2N$_3$), 2.13, 2.11, 2.08, 2.075, 2.065, 2.06, 2.05, 2.04, and 1.98 (9 s, 30 H, Ac); ^{13}C NMR ($CDCl_3$): δ 171.1, 170.9, 170.86, 170.8, 170.5, 170.2, 170.1, 170.0, 169.3, 101.5, 100.8, 100.1, 77.3, 76.8, 73.6, 73.2, 73.1, 72.3, 72.0, 69.4, 69.3, 69.1, 68.3, 67.6, 67.5, 62.4, 61.7, 60.7, 50.9, 21.3, 21.25, 21.13, 21.1, 21.04, 21.0, 20.9; HRMS calcd for $C_{40}H_{55}O_{26}N_3Na$ (M + Na): 1016.2971, found: 1016.2980.

*2-Aminoethyl (*α-D-*galactopyranosyl)-(1→4)-(*β-D-*galactopyranosyl)-(1→4)-*β-D-*glucopyranoside* (**21**).—Compound **20** (65 mg, 0.065 mmol) was dissolved in MeOH and a catalytic amount of MeONa (0.5 M) was added. After 12 h, the mixture was neutralized with Duolite C436 (H^+) resin and

concentrated. The residue was dissolved in a mixture of EtOH (7 mL) and 0.1 M aq HCl (0.65 mL, 0.065 mmol), and hydrogenated (H_2, 10% Pd-C, 1 atm) for 2 h. The mixture was filtered through Celite, passed through a column packed with Duolite A147 (OH^-) resin and concentrated. The residue was chromatographed (Varian Mega Bond Elut Column C18; 9:1→8:2→7:3 H_2O–MeOH, 6 mL each) to give **21** (25.8 mg, 72%); $[\alpha]^{22}_D$ +51° (*c* 1.0, H_2O); ^{1}H NMR (D_2O): δ 4.86 (d, 1 H, *J* 3.9 Hz, H-1″), 4.39–4.44 (2 d, 2 H, *J* 7.8, 8.0 Hz, H-1′,1), 4.26 (bt, 1 H, *J* 6.6 Hz, H-5″), 3.95 (bd, 1 H, *J* 3.2 Hz, H-4′), 3.94 (bd, 1 H, *J* 3.3 Hz, H-4″), 3.20–3.28 (m, 1 H, H-2), 3.10–3.20 and 2.77–2.90 (multiplets, 2 H, CH_2NH_2/$CH_2NH_3^+$); ^{13}C NMR (D_2O): δ 103.7, 102.5, 100.7, 79.1, 77.8, 75.8, 75.2, 74.8, 73.3, 72.6, 71.3, 71.2, 70.4, 69.5, 69.4, 69.0, 60.9, 60.8, 60.4; HRMS calcd for $C_{20}H_{38}O_{16}N$ (M + H): 548.2191, found: 548.2197.

2-(5-Phenyl-4-thiapentanoylamido)ethyl (α-D-galactopyranosyl)-(1→4)-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (**23**).—Treatment of compound **22** with *N*-hydroxysuccinimide (NHS) furnished the corresponding NHS-ester, as described [5]. The NHS-ester (6 mg, 0.02 mmol) and compound **21** (10 mg, 0.018 mmol) were dissolved in 1:1 DMF-pyridine (1 mL), and the mixture was stirred at 60 °C. After 10 h, the mixture was cooled to ~22 °C and concentrated, and the residue was chromatographed (Varian Mega Bond Elut C18; 9:1→8:2→7:3→6:4→5:5→4:6 H_2O–MeOH, 5 mL each) to give **23** (9 mg, 69%); $[\alpha]_D^{23}$ +45° (*c* 0.6, H_2O); ^{1}H NMR (D_2O): δ 7.16–7.29 (m, 5 H, Ph), 4.80 (d, 1 H, *J* 3.9 Hz, H-1″), 4.34 (d, 2 H, *J* 7.9 Hz, H-1′,1), 4.20 (bt, 1 H, *J* 6.7 Hz, H-5″), 2.59 (t, 2 H, *J* 6.9 Hz, SCH_2CH_2CO), 2.38 (t, 2 H, *J* 6.9 Hz, SCH_2CH_2CO); ^{13}C NMR (D_2O): δ 175.0, 138.7, 129.3, 129.2, 127.7, 103.6, 102.5, 100.7, 79.0, 77.7, 75.8, 75.1, 74.7, 73.2, 72.5, 71.2, 69.4, 69.2, 68.8, 60.8, 60.7, 60.3, 39.7, 35.7, 35.5, 27.0; HRMS calcd for $C_{30}H_{48}O_{17}NS$ (M + H): 726.2642, found: 726.2637.

Bis-globotrioside **25**.—Treatment of compound **24** with *N*-hydroxysuccinimide (NHS) furnished the corresponding NHS-ester, as described [5]. A solution of compound **21** (18 mg, 0.032 mmol) in freshly distilled DMF (3 mL) was added to a solution of the crude NHS-ester (4 mg, 0.0079 mmol) in pyridine (1 mL), and the mixture was stirred at 65 °C. After 16 h, the mixture was concentrated, and the residue was chromatographed (Varian Mega Bond Elut C18; 1:0→9:1→8:2→7:3→6:4→5:5 H_2O–MeOH, 6 mL each). The product was chromatographed on SiO_2 (5:5:1 CH_2Cl_2–MeOH–H_2O→1:1 MeOH–H_2O) to give **25** (7.5 mg, 69%); $[\alpha]^{23}_D$ +48° (*c* 0.75, H_2O); ^{1}H NMR (D_2O): δ 7.18–7.33 (4 H, Ph), 4.86 (d, 2 H, *J* 3.8 Hz, H-1″), 4.41 and 4.40 (2 d, each 1 H, *J* 7.7 and 8.0 Hz, H-1′,1), 4.26 (bt, 2 H, *J* 6.3 Hz, H-5″), 3.92–3.97 (m, 4 H, H-4″,4′), 3.23 (bdd, 2 H, *J* 8.0, 9.2 Hz, H-2′ or H-2), 2.64 (t, 4 H, *J* 6.9 Hz, SCH_2CH_2CO), 2.43 (t, 4 H, *J* 6.9 Hz, SCH_2CH_2CO); ^{13}C NMR (D_2O): δ 175.0, 139.3, 129.7, 129.6, 128.1, 103.7, 102.6, 100.7, 79.1, 77.8, 75.8, 75.2, 74.7, 73.3, 72.6, 71.3, 71.2, 69.5, 69.4, 69.0, 68.9, 60.9, 60.8, 60.5, 39.8, 35.8, 35.4, 27.0; HRMS calcd for $C_{54}H_{88}O_{34}N_2S_2Na$ (M + Na): 1395.4558, found: 1395.4541.

Acknowledgements

This work was supported by grants from the Swedish Natural Science Research Council and the National Institutes of Health (NIH, USA).

References

[1] D. Mirelman, *Microbial Lectins and Agglutinins*, Wiley Interscience, New York, 1986; D. Zopf and S. Roth, *Lancet*, 347 (1996) 1017–1021.

[2] H.C. Hansen and G. Magnusson, *Carbohydr. Res.*, 307 (1998) 233–242; J. Kihlberg and G. Magnusson, *Pure Appl. Chem.*, 68 (1996) 2119–2128.

[3] M. von Itzstein, W.-Y. Wu, G.B. Kok, M.S. Pegg, J.C. Dyason, B. Jin, T.V. Phan, M.L. Smythe, H.F. White, S.W. Oliver, P.M. Colman, J.N. Varghese, D.M. Ryan, J.M. Woods, R.C. Bethell, V.J. Hotham, J.M. Cameron, and C.R. Penn, *Nature*, 363 (1993) 418–423.

[4] R.T. Lee and Y.C. Lee, Enhanced Biochemical affinities of multivariant neoglycoconjugates, in Y.C. Lee and R.T. Lee (Eds.), *Neoglycoconjugates: Preparation and Applications*, Academic Press, San Diego, 1994, pp 23–50; R. Roy, *Trends Glycosci. Glycotechnol.*, 8 (1996) 79–99; D. Zanini and R. Roy, *J. Org. Chem.*, 61 (1996) 7348–7354; G.D. Armstrong, E. Fodor, and R. Vanmaele, *J. Infect. Dis.*, 164 (1991) 1160–1167; L.D. Heerze, M.A. Kelm, J.A. Talbot, and G.D. Armstrong, *J. Infect. Dis.*, 169 (1994) 1291–1296; G.D. Armstrong, P.C. Rowe, P. Goodyer, E. Orrbine, T.P. Klassen, G. Wells, A. MacKenzie, H. Lior, C. Blanchard, F. Auclair, B. Thompson, D.J. Rafter, and P.N. McLaine, *J. Infect. Dis.*, 171 (1995) 1042–1045.

[5] H.C. Hansen, S. Haataja, J. Finne, and G. Magnusson, *J. Am. Chem. Soc.*, 119 (1997) 6974–6979.

[6] R.R. Schmidt and W. Kinzy, *Adv. Carbohydr. Chem. Biochem.*, 50 (1994) 21–123.
[7] S.P. Douglas, D.M. Whitfield, and J.J. Krepinsky, *J. Carbohydr. Chem.*, 12 (1993) 131–136.
[8] J. Dahmén, T. Frejd, G. Magnusson, and G. Noori, *Carbohydr. Res.*, 111 (1982) C1–C4.
[9] J. Buter and R.M. Kellogg, *J. Org. Chem.*, 46 (1981) 4481–4485.
[10] R.J. Ferrier and R.H. Furneaux, *Methods Carbohydr. Chem.*, 8 (1980) 251–253; G. Magnusson, G. Noori, J. Dahmén, T. Frejd, and T. Lave, *Acta Chem. Scand.*, B35 (1981) 213–216.
[11] J. Kihlberg, S.J. Hultgren, S. Normark, and G. Magnusson, *J. Am. Chem. Soc.*, 111 (1989) 6364–6368.
[12] R. Striker, U. Nilsson, A. Stonecipher, G. Magnusson, and S.J. Hultgren, *Mol. Microbiol.*, 16 (1995) 1021–1029; U. Nilsson, R.T. Striker, S.J. Hultgren, and G. Magnusson, *Bioorg. Med. Chem.*, 4 (1996) 1809–1817.
[13] K. Jansson, S. Ahlfors, T. Frejd, J. Kihlberg, G. Magnusson, J. Dahmén, G. Noori, and K. Stenvall, *J. Org. Chem.*, 53 (1988) 5629–5647.
[14] K. Koike, M. Sugimoto, S. Sato, Y. Ito, Y. Nakahara, and T. Ogawa, *Carbohydr. Res.*, 163 (1987) 189–208.
[15] J. Dahmén, T. Frejd, G. Magnusson, G. Noori, and A.-S. Carlström, *Carbohydr. Res.*, 127 (1984) 15–25.
[16] J. Dahmén, T. Frejd, G. Grönberg, T. Lave, G. Magnusson, and G. Noori, *Carbohydr. Res.*, 116 (1983) 303–307.
[17] C.S. Hudson and J.M. Johnson, *J. Am. Chem. Soc.*, 37 (1915) 1270–1275.