Prearranged Glycosides, 9[≠]

Chemical Synthesis of a Tetrasaccharide Fragment Related to the Exopolysaccharide of *Arthrobacter sp.* CE-17

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The tetrasaccharide 5-aminopentyl glycoside β-D-Man*p*-(1→4)-β-D-Glc*p*-(1→4)-α-L-Rha*p*-(1→3)-β-D-Glc*p*-1-*O*-$(CH_2)_5NH_2$(**22**) related to the exopolysaccharide of *Arthrobacter sp.* CE-17 was synthesized by coupling of the properly protected disaccharide blocks β-D-Man*p*-(1→4)-β-D-Glc*p*-1-*S*-Ph (**11**) and α-L-Rha*p*-(1→3)-β-D-Glc*p*-1-*O*-$(CH_2)_5$NHZ (**20**). Building block **11** was obtained by intramolecular β-mannosylation of a malonyl-tethered disaccharide glycoside which was prepared from phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**1**) and ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (**5**) in 5 steps. Building block **20** was obtained by coupling *N*-Z-protected 5-aminopentyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**14**) obtained from the non-benzylated counterpart **12** with ethyl 2,3-di-*O*-benzoyl-4-*O*-chloroacetyl-1-thio-α-L-rhamnopyrano- side (**18**) obtained in 3 steps from ethyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (**15**).

In 1996, the first reports appeared that soil bacteria of the genus *Arthrobacter* can cause hitherto unknown severe infections in men. In this initial case, a patient who went through eye surgery developed a severe endophthalmitis caused by *Arthrobacter*.[1][2] Several other cases of *Arthrobacter*-associated infections have previously been reported including chronic uveitis, different forms of kryptogenic polyarthritis, seronegative spondilarthropathy, meningitis and lymphadenopathy (Whipple's syndrome).[3] Thus, synthetic fragments related to the exopolysaccharides of *Arthobacter* species are likely to be interesting targets because such oligosaccharide fragments could be used for diagnostic purposes or as artificial vaccines. Furthermore, exopolysaccharides of *Arthrobacter* are of significant importance as thickeners for the food industry or as stabilizers for foams and emulsions and as a flocculant.

Of the various *Arthrobacter* exopolysaccharides[4−9] studied so far only a few structures have been determined in detail.[7−9] As part of a project toward the synthesis of pyruvated oligosaccharides[10] we were especially interested in Simusan,[9] an acidic exopolysaccharide of *Arthrobacter sp.*, strain CE-17 which exhibits an octasaccharide repeating unit that contains a 4,6-pyruvated β-D-mannopyranosyl residue (Figure 1). In particular, the synthesis of a 5-aminopentyl glycoside tetrasaccharide related to the sequence **ABCD** of Simusan (Figure 1) that contains a β-D-mannopyranosyl residue is described here.

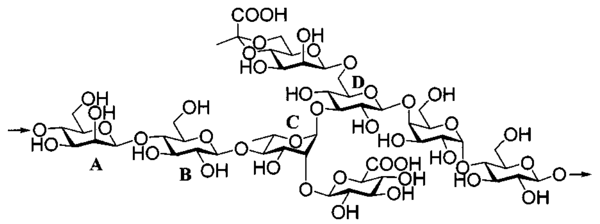

Figure 1. Repeating unit of the exopolysaccharide of *Arthrobacter sp.* CE-17

For the synthesis of the tetrasaccharide related to the sequence **ABCD** of Simusan we chose a blockwise approach. Thus, two disaccharide building blocks − β-D-Man*p*-(1→4)-D-Glc*p* as the disaccharide donor and α-L-Rha*p*-(1→3)-D-Glc*p* as the disaccharide acceptor − were needed. The donor block contains a β-D-mannosyl residue which was planned to be introduced by intramolecular glycosylation of a suitable prearranged glycoside. Recently, we developed a highly selective β-mannosylation procedure[11] which was applied to the preparation of the latter as follows. Starting from known[12] phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranose (**1**), phase-transfer catalyzed benzoylation[13] afforded dibenzoate **2** (11%), 3-*O*-benzoate **3** (16%), and the desired 2-*O*-benzoate **4** (54%). Alternative selective benzoylations of **1** gave lower yields of compound **4** (see Experimental Section for details). Next, readily available[14] ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (**5**) was esterified with *tert*-butyl malonate[15] (**6**) to give mannoside **7** (64%), the *tert*-butyl group of which was finally cleaved with trifluoroacetic acid to afford mannosyl malonate **8** in quantitative yield. The malonic acid tether in compound **8** was chosen for linking the mannose unit with glucoside **4** because previously, similarly tethered glycosides

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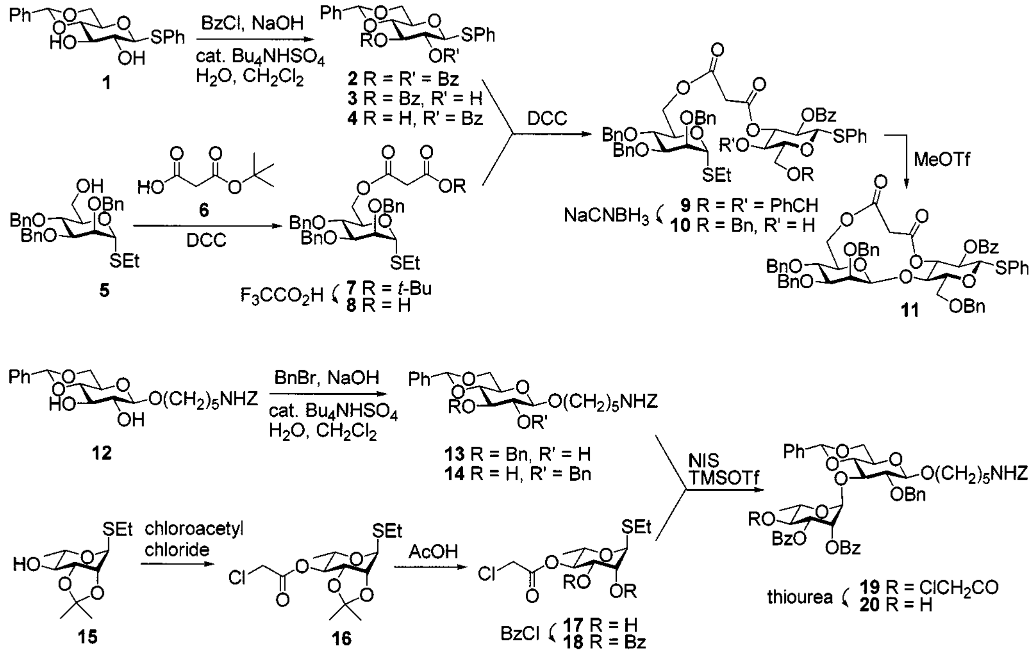
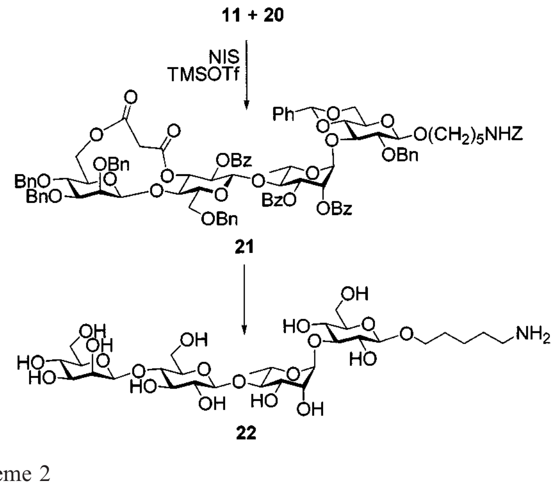


Scheme 1

gave high β-selectivities for intramolecular mannosylations.[11] Furthermore, combining the phenylthio group in the glucose moiety **4** with the ethylthio group in **8** allows us to make use of the principle of armed-disarmed glycosides[16] since mannosylation (i.e. activation of the ethylthio group) is possible without affecting the phenylthio group. Thus, according to previous procedures,[17][18] compounds **4** and **8** were condensed to give first saccharide **9** (81%), the benzylidene acetal of the glucose moiety of which was subsequently opened with $NaCNBH_3$[17–19] to afford the prearranged glycoside **10** in 71% yield. As was expected from previous experiments,[11] intramolecular mannosylation of the latter with methyl trifluoromethanesulfonate (MeOTf) as the promotor proceeded smoothly to give exclusively the desired β-D-Man*p*-(1→4)-D-Glc*p* disaccharide donor block **11** in 69% yield. The β-linkage of the mannosyl moiety in **11** was evident from the NMR spectra of that compound which showed a typical[20–22] C,H-coupling constant at the anomeric center of 153.7 Hz.

The required α-L-Rha*p*-(1→3)-D-Glc*p* disaccharide acceptor was prepared conventionally from 5-benzyloxycarbonylpentyl 4,6-*O*-benzylidene-β-D-glucopyranoside[23] (**12**). First, regioselective benzylation of the latter under phase-transfer conditions[24] afforded **13** (21%) and **14** (53%). Next, a properly protected rhamnose derivative was prepared from ethyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside[25] (**15**) by chloroacetylation at the 4-position to give rhamnoside **16** (81%) followed by acidic hydrolysis of the isopropylidene group *via* **17** (88%) and rebenzoylation of the free OH-groups to give monosaccharide **18** (83%). Coupling of the latter to the 3-position of compound **14** was best performed with *N*-iodosuccinimide (NIS) in the presence of 0.5 equiv. of TMSOTf in dichloromethane. Thus, the disaccharide **19** was obtained in 79% yield and the α-linkage of the rhamnosyl group was once again proven by measuring the C,H coupling constant at the anomeric center of 174.4 Hz. Finally, the chloroacetyl group of compound **19** was removed with thiourea to afford the disaccharide acceptor **20** (87%).



Scheme 2

The coupling of disaccharide blocks **11** and **20** was somehow crucial. Several methods for the activation of thioglycosides including NIS/trifluoromethanesulfonic acid (TfOH),[26] bromine/silver trifluoromethanesulfonate (AgOTf),[27] and dimethyl (methylthio)sulfonium triflate (DMTST)[28] failed completely and resulted in products of decomposition. Only NIS/trimethylsilyl trifluoromethanesulfonate (TMSOTf)[29] gave the desired tetrasaccharide **21**. However, the reaction showed an unusual temperature dependence. At 0°C, compound **21** was obtained in poor 9% yield, whereas at −30°C or −70°C the yield of tetrasaccharide **21** could be enhanced to 32% and 64%, respectively. Final deblocking of the latter afforded the tetrasaccharide 5-aminopentyl glycoside **(22)** in 87% yield.

In summary, the efficient construction of the β-mannosyl-containing disaccharide block **11** using intramolecular glycosylation techniques in combination with the principle of armed and disarmed glycosyl donors demonstrated the usefulness of this appraoch for the construction of higher oligosaccharides. Furthermore, compound **11** can be used for the synthesis of other oligosaccharides containing this disaccharide fragment.

Experimental Section

General: Thin-layer chromatography (TLC) was performed on precoated plastic sheets, Polygram SIL G/UV_{254}, 40 × 80 mm (Macherey−Nagel) using appropriately adjusted mixtures of toluene/acetone for the developing. Spots were detected by UV light and by charring with 5% sulfuric acid in ethanol. − Column chromatography (CC) was performed by elution from columns of silica gel S (Macherey−Nagel, 0.032−0.063 mm). − Solutions in organic solvents were dried with anhydrous sodium sulfate, and concentrated at 40°C, <200 Pa. − NMR spectra were recorded for solutions in $CDCl_3$ (with TMS as an internal standard) at 25°C on a Bruker AC 250 F spectrometer. Proton signal assignments were made by first order analysis of the spectra and by H,H-cosy techniques. Of two magnetically nonequivalent geminal protons, the one resonating at lower field was designated as H_a and the one resonating at higher field was designated as H_b. Carbon signal assignments were made by C,H-correlation and by comparison of the peaks with those of related compounds. − Optical rotations were measured at 20°C with a Perkin−Elmer automatic polarimeter, Model 241. − Melting points were determined with a Büchi apparatus, Model SMP-20.

Phenyl 2,3-di-*O*-Benzoyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (2), Phenyl 3-*O*-Benzoyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (3), and Phenyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (4): A) Benzoyl chloride (165 µL, 1.39 mmol) was added at −50°C to a solution of **1**[12] (0.50 g, 1.39 mmol) in pyridine (15 mL), the mixture was stirred for 48 h, poured into ice-cold water and extracted with CH_2Cl_2. The combined organic phases were subsequently washed with aqueous HCl and $NaHCO_3$ solution, dried and concentrated. Chromatography (gradient elution with toluene/acetone 55:1→35:1 v/v) afforded first **2** (116 mg, 15%), m.p. 203°C [ref.[30] 203−205°C (EtOH/ethyl acetate)]. − $[\alpha]_D^{20}$ = +42.6 (*c* = 1.1, $CHCl_3$) {ref.[30] $[\alpha]_D$ = +40 (*c* = 1.0, $CHCl_3$)}. Eluted next was **3** (295 mg, 46%), m.p. 154−156°C (EtOH). − $[\alpha]_D$ = −98.4 (*c* = 1.3, $CHCl_3$). − ^1H NMR ($CDCl_3$): δ = 5.51 (s, 1 H, PhCH), 5.50 (dd, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.76 (d, $J_{1,2}$ = 9.7 Hz, 1 H, 1-H), 4.39 (dd, $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = −10.4 Hz, 1 H, 6a-H), 3.81 (t, $J_{5,6b}$ = 9.6 Hz, 1 H, 6b-H), 3.77 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.70 (bd, $J_{2,3}$ = 8.9 Hz, 1 H, 2-H), 3.62 (dt, 1 H, 5-H), 3.04 (br. s, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 166.6 (PhCO), 101.4 (PhCH), 89.2 (C-1), 78.2 (C-4), 75.6 (C-3), 70.7 (C-5), 68.5 (2 C, C-2, C-6). − $C_{26}H_{24}O_6S$ (464.5): calcd. C 67.23, H 5.21, S 6.90; found C 67.19, H 5.26, S 6.95.

Eluted next was unchanged **1** (69 mg, 14%).

B) A mixture of **1** (0.50 g, 1.39 mmol) and di-*n*-butyltin oxide (0.36 g, 1.45 mmol) in benzene (100 mL) was heated for 24 h under reflux in a Dean-Stark apparatus, cooled to room temperature and concentrated. The residue was dissolved in benzene (50 mL), a solution of benzoyl chloride (0.18 mL, 1.53 mmol) in benzene (25 mL) was added dropwise at room temperature and the solution was stirred for 24 h. The mixture was diluted with CH_2Cl_2, filtered through a layer of Celite® and concentrated. Chromatography as described above afforded first **3** (0.38 g, 59%). Eluted next was **4** (0.15 g, 23%), which was obtained as a colorless foam. − $[\alpha]_D^{20}$ = −27.1 (*c* = 0.7, $CHCl_3$). − ^1H NMR ($CDCl_3$): δ = 5.54 (s, 1 H, PhCH), 5.15 (dd, $J_{2,3}$ = 8.8 Hz, 1 H, 2-H), 4.88 (d, $J_{1,2}$ = 10.0 Hz, 1 H, 1-H), 4.40 (dd, $J_{5,6a}$ = 4.6 Hz, $J_{6a,6b}$ = −10.5 Hz, 1 H, 6a-H), 4.03 (t, $J_{3,4}$ = 8.9 Hz, 1 H 3-H), 3.81 (t, $J_{5,6b}$ = 10.0 Hz, 1 H, 6b-H), 3.64−3.58 (m, $J_{4,5}$ = 9.3 Hz, 2 H, 4-H, 5-H), 2.85 (br. s, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 165.8 (PhCO), 101.9 (PhCH), 86.6 (C-1), 80.6 (C-4), 73.6 (C-3), 73.2 (C-2), 70.4 (C-5), 68.5 (C-6). − $C_{26}H_{24}O_6S$ (464.5): calcd. C 67.23, H 5.21, S 6.90; found C 67.17, H 5.08, S 7.04.

C) An aqueous NaOH solution (5%, 32 mL) was added with vigurous stirring −5°C to a solution of **1** (4.54 g, 12.6 mmol), Bu_4NHSO_4 (0.83 g, 2.58 mmol) and benzoyl chloride (1.97 mL, 17.02 mmol) in CH_2Cl_2 (230 mL). The mixture was stirred for 10 min, the organic layer was separated, washed with water, dried and concentrated. Chromatography as described above afforded first **2** (0.77 g, 11%), then **3** (0.96 g, 16%), and finally **4** (3.14 g, 54%).

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-(*tert*-butyloxycarbonylethanoyl)-1-thio-α-D-mannopyranoside (7): DCC (0.96 g, 4.65 mmol) was added at 0°C to a solution of **5**[14] (2.09 g, 4.23 mmol), **6**[15] (0.75 g, 4.65 mmol) and 1-hydroxy-1*H*-benzotriazole (0.69 g, 5.08 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred at room temperature for 24 h, diluted with CH_2Cl_2 and filtered through a layer of Celite®. The filtrate was subsequently washed with aqueous HCl and $NaHCO_3$ solution, dried and concentrated. Chromatography (*n*-hexane/ethyl acetate 6:1 v/v) of the residue afforded **7** (1.73 g, 64%) as a colorless foam. − $[\alpha]_D^{20}$ = +58.0 (*c* = 1.1, $CHCl_3$). − ^1H NMR ($CDCl_3$): δ = 5.33 (d, $J_{1,2}$ = 1.0 Hz, 1 H, 1-H), 4.92 (d, *J* = −10.7 Hz, 1 H, $PhCH_2$), 4.71 (d, *J* = −12.5 Hz, 1 H, $PhCH_2$), 4.65 (d, *J* = −12.5 Hz, 1 H, $PhCH_2$), 4.60−4.56 (m, 3 H, $PhCH_2$), 4.44 (dd, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = −11.8 Hz, 1 H, 6a-H), 4.36 (dd, $J_{5,6b}$ = 2.2 Hz, 1 H, 6b-H), 4.18 (ddd, 1 H, 5-H), 3.93 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.83 (2 dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 10.1 Hz, 2 H, 2-H, 3-H), 3.29 (s, 2 H, $COCH_2$), 2.66−2.47 (m, 2 H, SCH_2CH_3), 1.44 [s, 9 H, $C(CH_3)_3$], 1.23 (t, *J* = 7.4 Hz, 3 H, SCH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.9 (CO), 165.4 (CO), 82.0 ($C(CH_3)_3$), 81.9 (C-1), 80.2 (C-3), 76.2 (C-2), 75.2 ($PhCH_2$), 74.6 (C-4), 72.0 (2 C, $PhCH_2$), 70.1 (C-5), 64.3 (C-6), 42.6 ($COCH_2$), 27.9 ($C(CH_3)_3$), 25.4 (SCH_2CH_3), 14.9 (SCH_2CH_3). − $C_{36}H_{44}O_8S$ (636.8): calcd. C 67.90, H 6.96, S 5.04; found C 67.94, H 7.08, S 5.11.

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-(hydroxycarbonylethanoyl)-1-thio-α-D-mannopyranoside (8): Trifluoroacetic acid (5.3 mL, 51.8 mmol) was added at room temperature to a solution of **7** (1.65 g, 2.59 mmol) in CH_2Cl_2 (80 mL), the mixture was stirred for 3 h and concentrated. Coevaporation of toluene (3 times) afforded crude **8** (2.58 g, 100%) which was used without further purification in the next step.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-4,6-*O*-benzylidene-1-phenylthio-β-D-glucopyranos-3-yloxy)carbonylethanoyl]-1-thio-α-D-mannopyranoside (9): DCC (0.47 g, 2.28 mmol) was added at room temperature to a solution of **4** (1.04 g, 2.24 mmol), crude **8** (1.19 g, 2.05 mmol) and a catalytic amount of DMAP (ca. 20 mg) in CH_2Cl_2 (30 mL), and the mixture was stirred for 24 h. Workup as described for the preparation of **7** and chromatography (toluene/ethyl acetate 22:1 v/v) afforded **9** (1.86 g, 81%) as a colorless foam.

− $[\alpha]_D^{20}$ = +36.8 (*c* = 1.1, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 5.54 (t, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 5.49 (s, 1 H, PhCH), 5.28 (dd, $J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 5.27 (s, 1 H, 1′-H), 4.93 (d, $J_{1,2}$ = 10.0 Hz, 1 H, 1-H), 4.85 (d, *J* = −10.9 Hz, 1 H, $PhCH_2$), 4.68 (d, *J* = −12.1 Hz, 1 H, $PhCH_2$), 4.62 (d,, *J* = −12.3 Hz 1 H, $PhCH_2$), 4.54 (s, 2 H, $PhCH_2$), 4.49 (d, *J* = −10.9 Hz, 1 H, $PhCH_2$), 4.41 (dd, $J_{5,6a}$ = 4.7 Hz, $J_{6a,6b}$ = −10.4 Hz, 1 H, 6a-H), 4.25−4.20 (m, 2 H, 6a′-H, 6b′-H), 4.10−4.04 (m, 1 H, 5′-H), 3.83−3.76 (m, $J_{5,6b}$ = 9.6 Hz, 4 H, 2′-H, 3′-H, 4′-H, 6b-H), 3.75 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.63 (dt, 1 H, 5-H), 3.27 (s, 2 H, $COCH_2$), 2.60−2.43 (m, 2 H, SCH_2CH_3), 1.19 (t, *J* = 7.4 Hz, 3 H, SCH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 165.4 (CO), 165.3 (CO), 165.2 (CO), 101.4 (PhCH), 87.0 (C-1), 81.8 (C-1′), 80.2 (C-3′), 78.0 (C-4), 76.1, 74.6 (C-2′,4′), 75.0 ($PhCH_2$), 73.6 (C-3), 72.0 (2 C, $PhCH_2$), 70.8 (2 C, C-2, C-5), 70.0 (C-5′), 68.4 (C-6), 64.4 (C-6′), 40.8 ($COCH_2$), 25.3 (SCH_2CH_3), 14.9 (SCH_2CH_3). − $C_{58}H_{58}O_{13}S_2$ (1027.2): calcd. C 67.82, H 5.69, S 6.24; found C 67.77, H 5.73, S 6.22.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-6-*O*-benzyl-1-phenylthio-β-D-glucopyranos-3-yloxy)carbonylethanoyl]-1-thio-α-D-mannopyranoside (10): A solution of HCl in THF was added portionwise at room temperature to a suspension of **9** (1.60 g, 1.51 mmol), $NaCNBH_3$ (1.19 g, 18.9 mmol) and 3 Å molecular sieves (ca. 1.0 g) in THF (50 mL) until the evolution of gas ceased. The mixture was diluted with CH_2Cl_2 and filtered through a layer of Celite®. The filtrate was washed with an aqueous $NaHCO_3$ solution, dried and concentrated. Chromatography (toluene/ethyl acetate 8:1 v/v) afforded **10** (1.10 g, 71%) as a colorless foam. − $[\alpha]_D^{20}$ = +42.5 (*c* = 1.6, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 5.30 (s, 1 H, 1′-H), 5.30−5.25 (m, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 5.13 (t, $J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 4.89 (d, *J* = −11.0 Hz, 1 H, $PhCH_2$), 4.81 (d, $J_{1,2}$ = 9.9 Hz, 1 H, 1-H), 4.68 (d, *J* = −12.3 Hz, 1 H, $PhCH_2$), 4.55 (br. s, 5 H, $PhCH_2$), 4.53 (d, *J* = −11.3 Hz, 1 H, $PhCH_2$), 4.37−4.27 (m, 2 H, 6a′-H, 6b′-H), 4.15−4.10 (m, 1 H, 5′-H), 3.92 (t, $J_{4',5'}$ = 9.2 Hz, 1 H, 4′-H), 3.84 (m, 3 H, 2′-H, 3′-H, 6a-H), 3.73−3.66 (m, 2 H, 6b-H, OH), 3.61 (bm, 2 H, 4-H, 5-H), 3.35 (d, *J* = −16.1 Hz, 1 H, $COCH_2$), 3.20 (d, *J* = −16.1 Hz, 1 H, $COCH_2$), 2.59−2.46 (m, 2 H, SCH_2CH_3), 1.20 (t, *J* = 7.4 Hz, 3 H, SCH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.9 (PhCO), 165.6 ($COCH_2$), 165.2 ($COCH_2$), 85.9 (C-1), 81.9 (C-1′), 80.0 (C-3′), 79.4 (C-5), 78.2 (C-3), 76.2 (C-2′), 75.1 ($PhCH_2$), 74.0 (C-4′), 73.5 ($PhCH_2$), 72.0 ($PhCH_2$), 71.9 ($PhCH_2$), 70.2 (C-2), 69.8 (C-5′), 69.4 (C-6), 68.9 (C-4), 64.6 (C-6′), 41.3 ($COCH_2$), 25.5 (SCH_2CH_3), 14.9 (SCH_2CH_3). − $C_{58}H_{60}O_{13}S_2$ (1029.2): calcd. C 67.69, H 5.88, S 6.23; found C 67.57, H 5.88, S 6.21.

Phenyl *O*-(2,3,4-Tri-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-1-thio-β-D-glucopyranoside 3,6′-Malonate (11): MeOTf (0.37 mL, 3.40 mmol) was added at room temperature under argon to a mixture of **10** (0.70 g, 0.68 mmol) and 4 Å molecular sieves (1.76 g) in acetonitrile (30 mL). The mixture was stirred for 6 h, diluted with CH_2Cl_2 and filtered. The filtrate was washed with water, dried and concentrated. Chromatography (toluene/acetone 40:1 v/v) of the residue afforded **11** (0.45 g, 69%) as a colorless foam. − $[\alpha]_D^{20}$ = −4.2 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 5.31 (t, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 5.15 (t, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 4.86 (d, *J* = −11.3 Hz, 1 H, $PhCH_2$), 4.82 (d, $J_{1,2}$ = 10.1 Hz, 1 H, 1-H), 4.74 (d, *J* = −11.8 Hz, 1 H, $PhCH_2$), 4.70 (d, *J* = −12.5 Hz, 1 H, $PhCH_2$), 4.56−4.50 (m, $J_{6a',6b'}$ = −11.1 Hz, 1 H, 6a′-H), 4.50 (s, 3 H, $PhCH_2$), 4.47 (d, *J* = −11.8 Hz, 1 H, $PhCH_2$), 4.36 (d, *J* = −12.1 Hz, 1 H, $PhCH_2$), 4.29 (s, 1 H, 1′-H), 4.03 (dd, $J_{5',6b'}$ = 8.4 Hz, 1 H, 6b′-H), 3.97 (t, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.74 (t, $J_{4',5'}$ = 9.2 Hz, 1 H, 4′-H), 3.60 (bd, $J_{2',3'}$ = 2.9 Hz, $J_{5,6a}$ = 10.0 Hz, $J_{6a,6b}$ = −11.0 Hz, 3 H, 2′-H, 5′-H, 6a-H), 3.53 (bt, $J_{5,6b}$ = 3.7 Hz, 1 H, 5-H), 3.44 (dd, 1 H, 6b-H), 3.38 (dd, $J_{3',4'}$ = 8.8 Hz, 3′-H), 3.17 (bd, 2 H, $COCH_2$). − ^{13}C NMR ($CDCl_3$): δ = 165.6, 165.2, 164.5 (CO), 103.5 (C-1′, $J_{C-1',1'-H}$ = 153.7 Hz), 85.5 (C-1, $J_{C-1,1-H}$ = 157.0 Hz), 82.2 (C-3′), 78.9 (C-5), 78.6 (C-4), 76.7 (2 C, C-3, C-4′), 74.8 ($PhCH_2$), 74.4 (C-2′), 73.7, 73.5, 72.0 ($PhCH_2$), 71.2 (C-2), 70.4 (C-5′), 68.4 (C-6), 64.2 (C-6′), 42.7 ($COCH_2$). − $C_{56}H_{54}O_{13}S$ (967.1): calcd. C 69.55, H 5.63, S 3.32; found C 69.26, H 5.41, S 3.26.

5-Benzyloxycarbonylaminopentyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (13) and 5-Benzyloxycarbonylaminopentyl 2-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (14): Aqueous 5% NaOH solution (7.95 mL) was added with vigurous stirring at room temperature to a solution of **12**[23] (2.79 g, 5.72 mmol), BnBr (1.19 mL, 10.02 mmol) and Bu_4NHSO_4 (0.38 g, 1.13 mmol) in CH_2Cl_2 (50 mL) and the mixture was refluxed for 72 h. The mixture was diluted with CH_2Cl_2, washed with water, dried and concentrated. Chromatography (gradient elution with toluene/acetone 15:1→10:1 v/v) of the residue afforded first **14** (1.82 g, 53%), m.p. 112−113°C (EtOH). − $[\alpha]_D^{20}$ = −19.3 (*c* = 1.6, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 5.49 (s, 1 H, PhCH), 5.07 (s, 2 H, $PhCH_2OCO$), 4.92 (d, *J* = −11.5 Hz, 1 H, $PhCH_2$), 4.73 (bd, *J* = −11.5 Hz, 2 H, $PhCH_2$, NH), 4.48 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.32 (dd, $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = −10.4 Hz, 1 H, 6a-H), 3.93−3.87 (m, 1 H, OCH_2), 3.85−3.79 (m, $J_{3,4}$ = 9.1 Hz, $J_{3,OH}$ = 2.1 Hz, 1 H, 3-H), 3.75 (t, $J_{5,6b}$ = 10.2 Hz, 1 H, 6b-H), 3.58−3.53 (m, 1 H, OCH_2), 3.52 (t, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.43−3.37 (m, $J_{5,6a}$ = 4.9 Hz, 1 H, 5-H), 3.33 (dd, $J_{2,3}$ = 8.8 Hz, 1 H, 2-H), 3.17−3.11 (m, 2 H, CH_2), 2.59 (d, 1 H, OH), 1.66−1.33 (m, 6 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 156.3 (OCONH), 103.7 (C-1), 101.7 (PhCH), 81.8 (C-2), 80.4 (C-4), 74.7 ($PhCH_2$), 73.1 (C-3), 70.1 (OCH_2), 68.7 (C-6), 66.5 ($PhCH_2OCO$), 66.0 (C-5), 40.8 (CH_2NH), 29.6, 29.3, 23.2 (CH_2). − $C_{33}H_{39}NO_8$ (577.7): calcd. C 68.61, H 6.81, N 2.43; found C 68.58, H 6.79, N 2.37.

Eluted next was **13** (0.68 g, 21%), m.p. 119−120°C (EtOH). − $[\alpha]_D^{20}$ = −26.0 (*c* = 1.8, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 5.54 (s, 1 H, PhCH), 5.09 (s, 2 H, $PhCH_2OCO$), 4.95 (d, *J* = −11.7 Hz, 1 H, $PhCH_2$), 4.85 (br. s, 1 H, NH), 4.80 (d, *J* = −11.8 Hz, 1 H, $PhCH_2$), 4.37 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.33 (dd, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = −10.4 Hz, 1 H, 6a-H), 3.92−3.84 (m, 1 H, OCH_2), 3.78 (t, $J_{5,6b}$ = 10.3 Hz, 1 H, 6b-H), 3.72−3.66 (m, 1 H, 4-H), 3.65 (t, $J_{3,4}$ = 8.7 Hz, 1 H, 3-H), 3.58−3.48 (m, 2 H, 2-H, OCH_2), 3.46−3.88 (m, 1 H, 5-H), 3.19−3.15 (m, 2 H, CH_2), 2.70 (br. s, 1 H, OH), 1.69−1.36 (m, 6 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 156.4 (OCONH), 103.3 (C-1), 101.2 (PhCH), 81.3 (C-3), 80.3 (C-4), 74.5 ($PhCH_2$), 74.3 (C-2), 68.7 (C-6), 66.6 ($PhCH_2OCO$), 66.4 (C-5), 40.8 (CH_2NH), 29.5, 20.9, 23.0 (CH_2). − $C_{33}H_{39}NO_8$ (577.7): calcd. C 68.61, H 6.81, N 2.43; found C 68.52, H 6.84, N 2.36.

Ethyl 4-*O*-Chloroacetyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (16): Chloroacetyl chloride (4.7 mL, 59.3 mmol) was added dropwise at 0°C to a solution of **15**[25] (9.2 g, 37.1 mmol) and pyridine (4.0 mL, 49.6 mmol) in CH_2Cl_2 (180 mL). The mixture was stirred for 16 h at room temperature and poured into water. The organic layer was separated, washed with aqueous HCl and $NaHCO_3$ solution, dried and concentrated. Crystallisation of the residue from acetone afforded **16** (9.74 g, 81%), m.p. 122°C. − $[\alpha]_D^{20}$ = −43.1 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 5.56 (s, 1 H, 1-H), 4.96 (dd, $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 4.22−4.19 (m, 1 H, 2-H), 4.18−4.12 (m, $J_{3,4}$ = 7.5 Hz, $J_{5,6}$ = 6.3 Hz, 2 H, 3-H, 5-H), 4.11 (2 s, 2 H, $ClCH_2CO$), 2.74−2.49 (m, 2 H, SCH_2CH_3), 1.57 [s, 3 H, $C(CH_3)_2$], 1.34 [s, 3 H, $C(CH_3)_2$], 1.31 (t, *J* = 7.5 Hz, 3 H, SCH_2CH_3), 1.19 (d, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 166.6 ($ClCH_2CO$), 110.0 [$C(CH_3)_2$], 79.4 (C-1), 76.9, 76.8 (C-2,4), 75.2

(C-3), 64.2 (C-5), 27.7 [C(CH_3)$_2$], 26.4 [C(CH_3)$_2$], 24.5 (SCH_2CH_3), 16.9 (C-6), 14.6 (SCH$_2$$CH_3$). − $C_{13}H_{21}ClO_5S$ (324.8): calcd C 48.07, H 6.52, Cl 10.92, S 9.87; found C 48.05, H 6.56, Cl 10.94, S 9.79.

Ethyl 4-*O*-Chloroacetyl-1-thio-α-L-rhamnopyranoside (17): Acetic acid (150 mL) was added to a solution of **16** (8.39 g, 25.82 mmol) in a small amount of CH_2Cl_2. The mixture was stirred for 7 h at 60°C, cooled to room temperature and concentrated. Crystallisation of the residue from *n*-hexane/acetone afforded **17** (6.47 g, 88%), m.p. 137−139°C. − $[\alpha]_D^{20} = -89.5$ (c = 0.7, $CHCl_3$). − ^{1}H NMR ([D$_6$]acetone): δ = 5.25 (d, $J_{1,2}$ = 1.0 Hz, 1 H, 1-H), 4.99 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.49 (d, $J_{2,OH}$ = 4.1 Hz, 1 H, OH), 4.34 (d, J = −15.0 Hz, 1 H, ClCH$_2$CO), 4.26 (d, J = −15.0 Hz, 1 H, ClCH$_2$CO), 4.16 (d, $J_{3,OH}$ = 7.0 Hz, 1 H, OH), 4.13−4.03 (m, $J_{5,6}$ = 6.3 Hz, 1 H, 5-H), 3.97 (dt, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 3.78 (ddd, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 2.70−2.52 (m, 2 H, SCH_2CH$_3$), 1.25 (t, J = 7.4 Hz, 3 H, SCH$_2$CH_3), 1.14 (d, 1 H, 6-H). − ^{13}C NMR ([D$_6$]acetone): δ = 167.8 (ClCH$_2$$C$O), 85.4 (C-1), 77.3 (C-4), 73.4 (C-2), 70.5 (C-3), 67.0 (C-5), 41.7 (SCH$_2$CH$_3$), 17.6 (C-6), 15.3 (SCH$_2$$CH_3$). − $C_{10}H_{17}ClO_5S$ (284.8): calcd C 42.18, H 6.02, Cl 12.45, S 11.26; found C 42.33, H 5.99, Cl 12.97, S 11.16.

Ethyl 2,3-Di-*O*-benzoyl-4-*O*-chloroacetyl-1-thio-α-L-rhamnopyranoside (18): A mixture of BzCl (11.7 mL, 100.6 mmol) and pyridine (8.0 mL, 98.59 mmol) was slowly dropped at 0°C into a solution of **17** (5.73 g, 20.12 mmol) in acetonitrile (80 mL). The mixture was stirred for 2 h at room temperature, poured into water and extracted with CH_2Cl_2. The combined extracts were washed with aqueous HCl and $NaHCO_3$ solution, dried and concentrated. Chromatography (*n*-hexane/ethyl acetate 12:1 v/v) of the residue and crystallisation from *n*-hexane/diethyl ether afforded **18** (8.23 g, 83%), m.p. 73−75°C. − $[\alpha]_D^{20} = +31.9$ (c = 1.5, $CHCl_3$). − ^{1}H NMR (CDCl$_3$): δ = 5.73 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 5.61 (dd, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 5.49 (t, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 5.45 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.48−4.41 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5-H), 4.01 (d, J = −14.5 Hz, 1 H, ClCH$_2$CO), 3.94 (d, J = −14.5 Hz, 1 H, ClCH$_2$CO), 2.78−2.64 (m, 2 H, SCH_2CH$_3$), 1.35 (t, J = 7.4 Hz, 3 H, SCH$_2$CH_3), 1.35 (d, 1 H, 6-H). − ^{13}C NMR (CDCl$_3$): δ = 166.7 (ClCH$_2$$C$O), 165.4 (PhCO), 165.3 (PhCO), 82.0 (C-1), 73.4 (C-4), 72.5 (C-2), 70.2 (C-3), 66.7 (C-5), 40.5 (ClCH$_2$CO), 25.6 (SCH$_2$CH$_3$), 17.4 (C-6), 14.9 (SCH$_2$$CH_3$). − $C_{24}H_{25}ClO_7S$ (493.0): calcd C 58.47, H 5.11, S 6.50; found C 58.49, H 5.03, S 6.56.

5-Benzyloxycarbonylaminopentyl *O*-(2,3-Di-*O*-benzoyl-4-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (19): A mixture of **14** (0.98 g, 1.70 mmol), **18** (1.01 g, 2.04 mmol) and 4 Å molecular sieves (ca. 1.0 g) in CH_2Cl_2 (25 mL) was cooled under argon to 0°C and stirred for 10 min. NIS (0.46 g, 2.04 mmol) and TMSOTf (184 µL, 1.02 mmol) were successively added, the mixture was stirred for 20 min, neutralized by the addition of triethylamine and filtered through a layer of Celite®. The filtrate was washed with aqueous $Na_2S_2O_3$ solution, dried and concentrated. Chromatography (toluene/acetone 17:1 v/v) of the residue afforded **19** (1.35 g, 79%) as a colorless foam. − $[\alpha]_D^{20} = +38.4$ (c = 1.2, $CHCl_3$). − ^{1}H NMR (CDCl$_3$): δ = 5.71 (dd, $J_{2',3'}$ = 3.5 Hz, 1 H, 2′-H), 5.64 (dd, $J_{3',4'}$ = 10.0 Hz, 1 H, 3′-H), 5.55 (s, 1 H, PhCH), 5.35 (d, $J_{1',2'}$ = 1.3 Hz, 1 H, 1′-H), 5.27 (t, $J_{4',5'}$ = 10.0 Hz, 1 H, 4′-H), 5.08 (br. s, 2 H, PhCH$_2$OCO), 4.89 (d, J = −10.7 Hz, 1 H, PhCH$_2$), 4.73 (bd, 2 H, PhCH$_2$, NH), 4.49 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.42−4.32 (m, $J_{5',6'}$ = 6.2 Hz, 2 H, 5′-H, 6a-H), 3.96 (t, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.90−3.88 (m, 1 H, OCH$_2$), 3.84−3.77 (m, 2 H, 6b-H), 3.83 (d, J = −14.5 Hz, 1 H, ClCH$_2$CO), 3.78 (d, J = −14.5 Hz, 1 H, ClCH$_2$CO), 3.64 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.60−3.50 (m, 2 H, OCH$_2$, 2-H), 3.48−3.40 (m, 1 H, 5-H), 3.19−3.12 (m, 2 H, CH$_2$), 1.68−1.64 (m, 2 H, CH$_2$), 1.54−1.37 (m, 4 H, CH$_2$), 0.86 (d, 1 H, 6′-H). − ^{13}C NMR (CDCl$_3$): δ = 166.6, 165.6, 165.2 (CO), 156.4 (OCONH), 104.2 (C-1), 101.9 (PhCH), 97.9 (C-1′, $J_{C-1',1'-H}$ = 174.4 Hz), 82.7 (C-2), 79.1 (C-4), 76.4 (C-3), 75.2 (PhCH$_2$), 73.3 (C-4′), 70.4 (C-2′), 70.2 (OCH$_2$), 70.0 (C-3′), 68.8 (C-6), 66.6 (PhCH$_2$OCO), 66.4 (C-5), 65.8 (C-5′), 40.9 (CH$_2$NH), 40.4 (ClCH$_2$CO), 29.7 (CH$_2$), 29.4 (CH$_2$), 23.3 (CH$_2$), 16.8 (C-6′). − $C_{55}H_{58}ClNO_{15}$ (1008.5): calcd C 65.50, H 5.80, N 1.39; found C 65.41, H 5.93, N 1.30.

5-Benzyloxycarbonylaminopentyl *O*-(2,3-Di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (20): A solution of **19** (0.60 g, 0.6 mmol) and thiourea (0.2 g, 2.63 mmol) in a mixture of MeOH (17 mL) and CH_2Cl_2 (6 mL) was stirred at room temperature for 3 d and concentrated. The residue was dissolved in CH_2Cl_2, washed with water, dried and concentrated. Chromatography (toluene/acetone 12:1 v/v) of the residue afforded **20** (0.48 g, 87%) as a colorless foam. − $[\alpha]_D^{20}$ = +17.4 (c = 1.0, $CHCl_3$). − ^{1}H NMR (CDCl$_3$): δ = 5.67 (dd, $J_{2',3'}$ = 3.4 Hz 1 H, 2′-H), 5.56 (s, 1 H, PhCH), 5.50 (dd, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 5.33 (d, $J_{1',2'}$ = 1.4 Hz, 1 H, 1′-H), 5.07 (s, 2 H, PhCH$_2$OCO), 4.89 (d, J = −10.7 Hz, 1 H, PhCH$_2$), 4.73 (bd, 2 H, PhCH$_2$, NH), 4.49 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.36 (dd, $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = −10.3 Hz, 1 H, 6a-H), 4.21−4.16 (m, $J_{5',6'}$ = 6.1 Hz, 1 H, 5′-H), 3.97 (t, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.95−3.88 (m, 1 H, OCH$_2$), 3.80 (t, $J_{5,6b}$ = 9.6 Hz, 1 H, 6b-H), 3.75 (dt, $J_{4',5'}$ = 9.7 Hz, $J_{4',OH}$ = 5.5 Hz, 1 H, 4′-H), 3.63 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.57−3.50 (m, 2 H, OCH$_2$, 2-H), 3.44 (dt, 1 H, 5-H), 3.16−3.11 (m, 2 H, CH$_2$), 2.13 (d, 1 H, OH), 1.68−1.62 (m, 2 H, CH$_2$), 1.53−1.36 (m, 4 H, CH$_2$), 1.02 (d, 1 H, 6′-H). − ^{13}C NMR (CDCl$_3$): δ = 167.0, 165.2 (CO), 156.3 (OCONH), 104.1 (C-1, $J_{C-1-H-1}$ = 158.1 Hz), 101.6 (PhCH), 98.1 (C-1′, $J_{C-1'-H-1'}$ = 175.0 Hz), 82.8 (C-2), 79.1 (C-4), 76.6 (C-3), 75.1 (PhCH$_2$), 73.3 (C-3′), 71.9 (C-4′), 70.1 (OCH$_2$), 70.7 (C-2′), 68.7 (C-6), 68.5 (C-5′), 66.6 (PhCH$_2$OCO), 66.4 (C-5), 40.9 (CH$_2$NH), 29.6 (CH$_2$), 29.3 (CH$_2$), 23.2 (CH$_2$), 17.0 (C-6′). − $C_{53}H_{57}NO_{14}$ (932.0): calcd C 68.30, H 6.16, N 1.50; found C 68.12, H 6.31, N 1.39.

5-Benzyloxycarbonylaminopentyl *O*-(2,3,4-Tri-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside 3′′,6′′′-Malonate (21): Treatment of a mixture of **11** (120 mg, 0.12 mmol), **20** (116 mg, 0.12 mmol) and 3 Å molecular sieves (ca. 0.2 g) in CH_2Cl_2 (5 mL) under argon at −70°C with NIS (28.0 mg, 0.12 mmol) and TMSOTf (11 µL, 62 µmol) for 6 h and workup as described for the preparation of **19** followed by chromatography (toluene/acetone 20:1 v/v) afforded **21** (141 mg, 64%) as a colorless foam. − $[\alpha]_D^{20}$ = +36.1 (c = 0.8, $CHCl_3$). − ^{1}H NMR (CDCl$_3$): δ = 5.65 (dd, $J_{2',3'}$ = 3.5 Hz, 1 H, 2′-H), 5.52 (s, 1 H, PhCH), 5.45 (dd, $J_{3',4'}$ = 9.8 Hz, 1 H, 3′-H), 5.22 (d, $J_{1',2'}$ = 1.3 Hz, 1 H, 1′-H), 5.14 (dd, $J_{2'',3''}$ = 9.5 Hz, 1 H, 2″-H), 5.06 (t, s, $J_{3'',4''}$ = 9.3 Hz, 1 H, 2 H, 3″-H, PhCH$_2$OCO), 4.72 (s, 1 H, NH), 4.71 (d, $J_{1'',2''}$ = 7.8 Hz, 1 H, 1″-H), 4.86 (d, J = −11.4 Hz, 1 H, PhCH$_2$), 4.83 (d, J = −10.7 Hz, 1 H, PhCH$_2$), 4.79 (d, J = −12.5 Hz, 1 H, PhCH$_2$), 4.70 (d, J = −12.6 Hz, 1 H, PhCH$_2$), 4.62 (d, J = −10.6 Hz, 1 H, PhCH$_2$), 4.56 (d, J = −10.9 Hz, 1 H, PhCH$_2$), 4.54 (d, J = −10.9 Hz, 1 H, PhCH$_2$), 4.52 (s, 1 H, PhCH$_2$), 4.50 (dd, $J_{6a''',6b'''}$ = −11.4 Hz, 1 H, 6a′′′-H), 4.48 (d, J = −12.4 Hz, 1 H, PhCH$_2$), 4.44 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.39 (d, J = −12.3 Hz, 1 H, PhCH$_2$), 4.37−4.32 (m, $J_{6a,6b}$ = −10.5 Hz, 2 H, 6a-H, 1′′′-H), 4.27−4.22 (m, $J_{5',6'}$ = 6.2 Hz, 1 H, 5′-H), 4.05 (dd, 1 H, 6b′′′-H), 4.01 (t, $J_{4'',5''}$ = 9.3 Hz, 1 H, 4″-H), 3.91−3.87 (m, 1 H, OCH$_2$), 3.87 (t, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.82 (t, $J_{4',5'}$ = 9.8 Hz, 1 H, 4′-H), 3.78 (t, $J_{5,6b}$ = 10.5 Hz, 1 H, 6b-H), 3.74 (t, $J_{4''',5'''}$ = 9.4 Hz, 1 H, 4'''-H), 3.67 (bd, $J_{2''',3'''}$ = 3.2 Hz, 1 H, 2'''-H), 3.62 (t, $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.61−3.57 (m, $J_{5''',6a'''}$ = 7.5 Hz, $J_{5''',6b'''}$ = 8.1 Hz, 1 H, 5'''-H), 3.55−3.49 (m, 3 H, 6a''-H, 6b''-H, OCH_2), 3.47−3.35 (m, 4 H, 2-H, 3'''-H, 5-H, 5''-H), 3.14−3.11 (m, 2 H, $CONHCH_2$), 3.12 (d, J = −12.2 Hz, 1 H, $COCH_2$), 3.07 (d, J = −12.2 Hz, 1 H, $COCH_2$), 1.66−1.35 (m, 6 H, CH_2), 0.90 (d, 1 H, 6'-H). − ^{13}C NMR ($CDCl_3$): δ = 165.6 ($COCH_2$), 165.1, 165.0 (1 C, 2 C, PhCO), 164.4 ($COCH_2$), 156.3 (OCONH), 104.1 (C-1, $J_{C-1-H-1}$ = 160.2 Hz), 103.5 (C-1''', $J_{C-1''',H-1'''}$ = 154.1 Hz), 101.5 (PhCH), 100.5 (C-1'', $J_{C-1'',H-1''}$ = 162.1 Hz), 98.3 (C-1', $J_{C-1',H-1'}$ = 174.8 Hz), 82.6 (C-2), 82.0 (C-3'''), 78.8 (C-4), 78.5 (C-4''), 77.0 (C-3), 76.6 (2 C, C-4', C-4'''), 75.6 (C-3''), 75.1 ($PhCH_2$), 74.9 ($PhCH_2$), 74.6 (C-2'''), 74.5 (C-5''), 73.6, 73.5 ($PhCH_2$), 72.6 (C-3'), 72.4 (C-2''), 72.0 ($PhCH_2$), 70.5 (C-5'''), 70.4 (C-2'), 70.1 (OCH_2), 68.6 (C-6), 68.4 (C-6''), 66.7 (C-5'), 66.5 (2 C, C-5, $PhCH_2OCO$), 64.1 (C-6'''), 42.8 ($COCH_2$), 40.8 (CH_2NH), 30.0, 29.3, 23.2 (CH_2), 17.2 (C-6'). − $C_{103}H_{105}NO_{27}$ (1789.0): calcd C 69.15, H 5.92, N 0.78; found C 69.09, H 6.07, N 0.69.

5-Aminopentyl *O*-(β-D-Mannopyranosyl)-(1→4)-(β-D-glucopyranosyl)-(1→4)-(α-L-rhamnopyranosyl)-(1→3)-β-D-glucopyranoside (22): A solution of **21** (60 mg, 33 μmol) and a catalytic amount of NaOMe in methanol (4 mL) was stirred at room temperature for 30 h, neutralized with ion exchange resin (Dowex 1X8, H^+ form) and concentrated. The residue was dissolved in methanol/acetic acid (1:1 v/v, 10 mL), a catalytic amount of $Pd(OH)_2$ on charcoal was added, the suspension was hydrogenized (1013 hPa H_2) at room temperature for 6 d, filtered and concentrated. Chromatography of the residue with water on Biogel P2 and lyophilisation of the carbohydrate-containing fractions afforded **22** (21 mg, 87%) as a colorless foam. − $[\alpha]_D^{20}$ = +73.4 (c = 1.1, H_2O). − ^{13}C NMR (D_2O): δ = 104.2 (C-1''), 102.5 (C-1), 102.1 (C-1'), 101.3 (C-1'''), 83.3 (C-3), 82.3 (C-4'), 79.2 (C-4''), 77.2 (C-5), 75.1 (C-2), 75.0 (C-5''), 74.8 (C-3''), 73.9 (C-2''), 72.5 (C-3'''), 72.2 (C-5'''), 71.6, 71.4, 71.3 (C-2',3',2'''), 71.2 (OCH_2), 70.7 (C-4'''), 69.7 (C-4), 69.1 (C-5'), 62.0 (C-6), 61.3, 61.1 (C-6'',6'''), 39.8 (NCH_2), 28.4, 26.6, 22.2 (CH_2), 17.9 (C-6'). − $C_{29}H_{53}NO_{20}$ (735.7): FAB MS (pos.); m/z: 737 (M + H^+).

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