Prearranged Glycosides, 4[◇]

Synthesis *via* Prearranged Glycosides of a Tetrasaccharide Fragment Related to the Capsular Polysaccharide of *Streptococcus pneumoniae* Type 27

Gunter Schüle and Thomas Ziegler*

Institut für Organische Chemie und Isotopenforschung, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received April 15, 1996

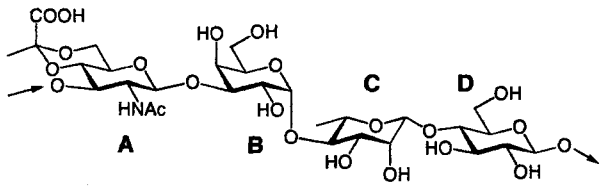
Key Words: Carbohydrates / Tetrasaccharide, bacterial / Glycosylation, intramolecular

The blockwise synthesis of the pyruvated tetrasaccharide 4,6-(*S*)-pyruvic-acetal-β-D-GlcNAc$_p$-(1→3)-α-D-Gal$_p$-(1→4)-β-L-Rha$_p$-(1→4)-β-D-Glc$_p$-O(CH$_2$)$_5$NH$_2$ (**32**), related to the repeating unit of the capsular polysaccharide of *Streptococcus pneumoniae* type 27, by coupling of the suitably protected disaccharide blocks 4,6-(*S*)-pyruvic-acetal-β-D-GlcNAc$_p$-(1→3)-α-D-Gal$_p$-trichloroacetimidate (**13**) and β-L-Rha$_p$-(1→4)-β-D-Glc$_p$-O(CH$_2$)$_5$NHZ (**29β**) is described. The latter disaccharide acceptor was prepared via prearranged glycosides by intramolecular glycosylation of a protected 5-aminopentyl β-D-glucopyranoside linked by a succinyl bridge at C-3 to C-2 of ethyl 1-thio-α-L-rhamnopyranoside. The dependence of the anomeric selectivity of the coupling on the nature of the protecting group at C-4 of the rhamnosyl moiety is studied.

Bacteria of the genus *Streptococcus pneumoniae* are the main cause of otitis media in juvenils and of pneumonia in immunocompromized individuals[1]. Since the latter infection is still one of the major causes of death in third world countries, it appears to be highly desirable to vaccinate against *S. pneumoniae*. In early attempts to obtain efficient vaccines, heat-killed cells of *S. pneumoniae*[2] were initially used and it was shown in this respect that the capsular polysaccharides of the bacteria that are present in that vaccine are responsible for the induction of a suitable immune response[3]. Thus, according to epidemiological studies[4], the currently available vaccine (Pneumovax® 23) contains 23 of the more than 85 serologically distinguishable capsular polysaccharides of *S. pneumoniae*. However, since polysaccharides are often less effective to mount and maintain an adequate antibody response[5] and since furthermore infections by pneumococcal types that are not incorporated in the vaccine cannot be prevented, several attempts were undertaken to use synthetic neoglycoconjugates related to various type of pneumococci for that purpose[6].

Recently, we synthesized a 5-aminopentyl tetrasaccharide glycoside related to the DABC sequence[6] (Figure 1) of the repeating unit of the capsular polysaccharide of *S. pneumoniae* type 27[7]. To this end, the type-27 structure appeared to be especially interesting for immunological studies due to the presence of an immunodominant pyruvated *N*-acetylglucosamine residue[7] found otherwise solely in type-4 pneumococci[8–10]. The 5-aminopentylaglycon was previously chosen as an anchor for the conjugation of the tetrasaccharide with a protein. This should result in a neoglycoprotein and increase the immunogenity of the carbohydrate epitope. For studies of the immunological properties of such neoglycoconjugates and for the evaluation of their immunogenity with respect to their use as vaccines it is, however, desirable to have all possible variations of the polysaccharide repeating unit available. Therefore, the synthesis of the ABCD sequence (Figure 1) of *S. pneumoniae* type-27 polysaccharide using the novel glycosylation protocol via prearranged glycosides[11,12] is described here. Nevertheless, this approach should also demonstrate here that the latter glycosylation strategy may be readily applied to the synthesis of complex oligosaccharides.

Figure 1. Repeating unit of the capsular polysaccharide of *Streptococcus pneumoniae* type 27



Results and Discussion

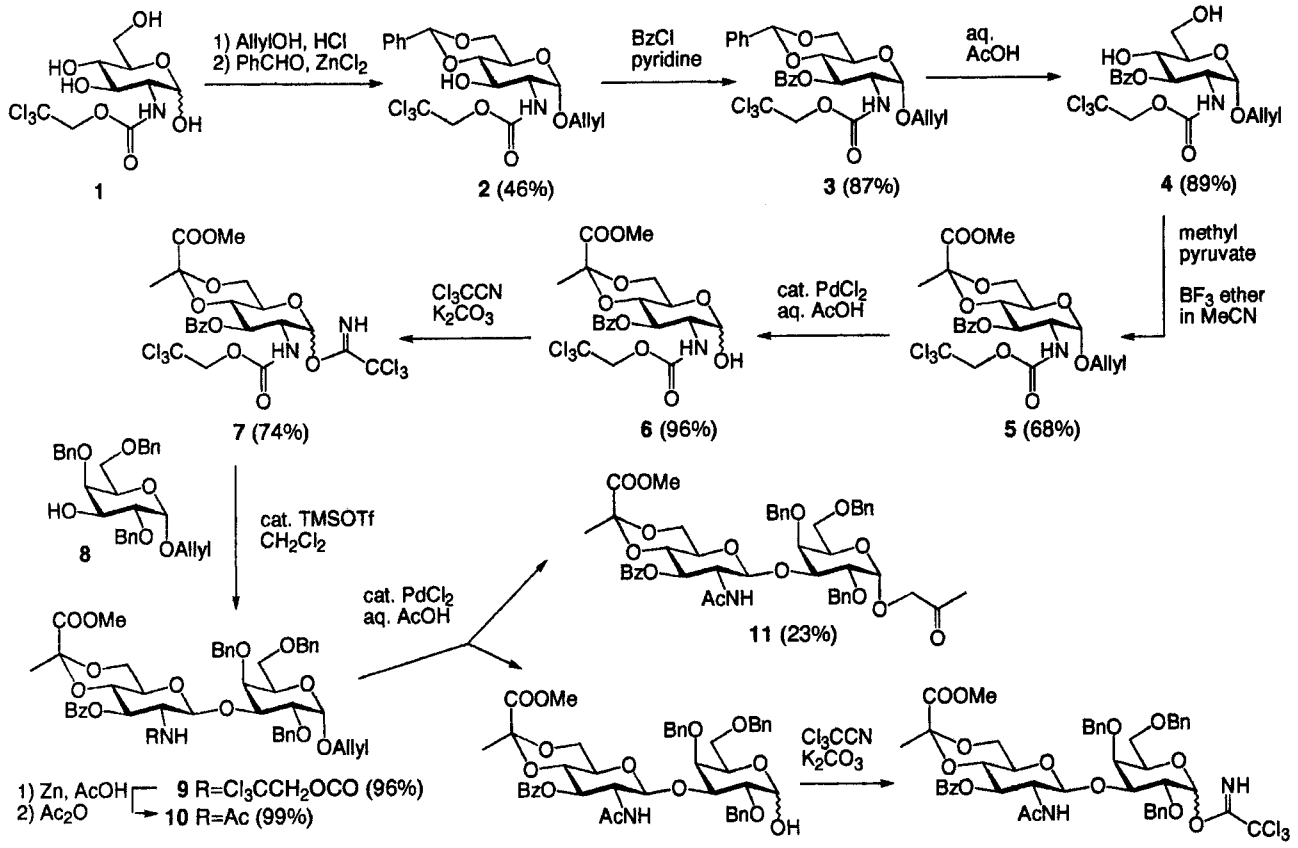
For the synthesis of the desired tetrasaccharide 5-aminopentyl glycoside of *S. pneumoniae* type 27 polysaccharide, a convergent blockwise approach via a suitably protected GlcNAc1,3Gal donor (AB part in Figure 1) and a Rha1,4Glc acceptor (CD part in Figure 1) was chosen. Thus, starting from 2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranose[13] (**1**), Fischer glycosylation with allyl alcohol followed by benzylidenation gave first the allyl glycoside **2** (46%). Next, benzoylation in 3-O afforded

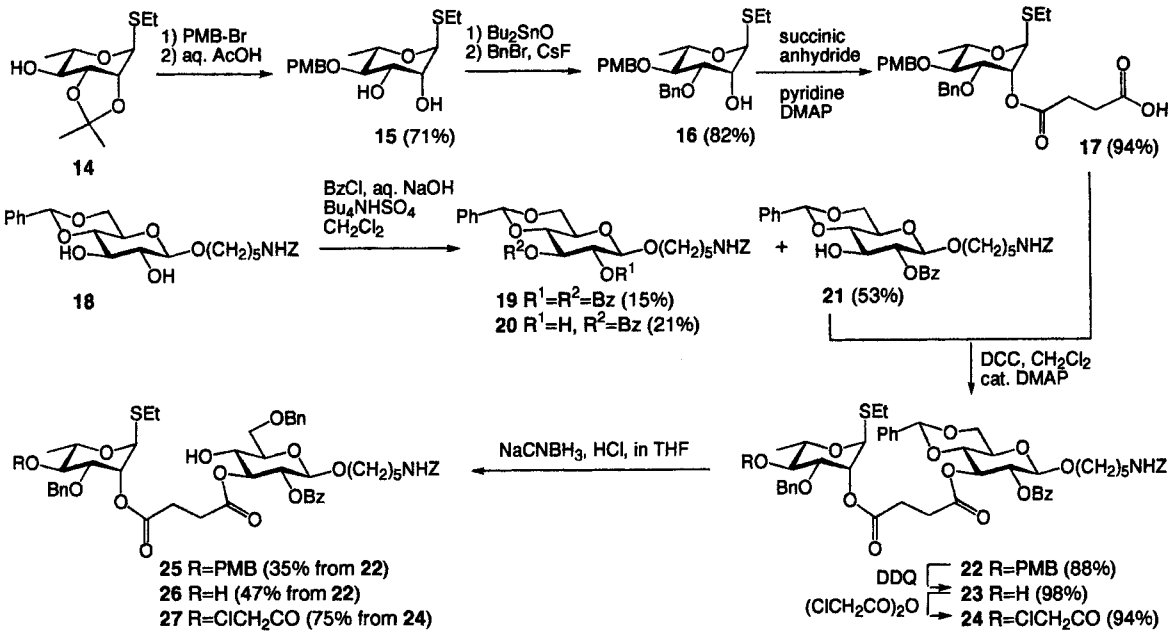
[◇] Part 3: T. Ziegler, G. Lemanski, A. Rakoczy, *Tetrahedron Lett.* **1995**, *36*, 8973–8976.

  0947–3440/96/1010–1599 $ 15.00+.25/0

crystalline compound **3** (87%) that was deblocked at 4-O and 6-O by treatment with aqueous acetic acid to give the diol **4** in 89% yield. Acetalation of the latter with methyl pyruvate was performed essentially as described previously for the diastereoselective pyruvation of positions 4 and 6 in glucose derivatives[14]. Accordingly, compound **4** was treated with methyl pyruvate and $Et_2O \cdot BF_3$ in acetonitrile to give the pyruvylated derivative **5** (68%). The *S* configuration (i.e. an equatorially oriented methyl group) of the stereogenic acetal was unambiguously assigned by carbon-NMR spectroscopy which showed a significant signal at $\delta = 25.2$ for the methyl group[14,15]. Cleavage of the allyl aglycon in **5** followed by treatment of intermediate **6** (96%) with trichloroacetonitrile afforded the pyruvated donor **7** in 74% yield. The latter proved to be a superior glycosyl donor since coupling of which with allyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside[16] (**8**) gave the corresponding β-(1→3)-linked disaccharide **9** in 96% yield. For the preparation of the needed disaccharide donor, the trichloroethoxycarbonyl group in **9** was first converted in 99% yield into an acetyl group and the intermediate **10** was once again deallylated with $PdCl_2$ in aqueous acetic acid. Here the 2-oxopropyl disaccharide **11** (23%) was formed alongside the desired compound **12** (53%). Finally, the latter was converted into the disaccharide imidate **13** (95%) that was used without further purification.

The preparation of the disaccharide acceptor Rha1,4Glc required the selective construction of a difficult to establish β-L-rhamnosidic linkage. For that purpose our recently developed strategy via 2,3-succinyl-bridged glycosides which was shown to be suitable for the desired β-rhamnosylation[11,12] was applied. As a temporary protecting group for position 4 of the rhamnosyl residue the *p*-methoxybenzyl (PMB) group was chosen. First, ethyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside[17] (**14**) was converted conventionally by a two-step procedure into the diol **15** (71%) that was regioselectively benzylated at C-3 via a stannylene derivative[18] to give compound **16** (82%). Next, the succinyl spacer was introduced in 94% yield into position 2 by acylation of **16** with succinic anhydride[12]. The resulting carboxylic acid **17** was then condensed by the aid of *N,N*-dicyclohexylcarbodiimide (DCC) with the glucoside **21** to give compound **22** in 88% yield. The glucoside **21** was prepared in 53% yield from 5-(benzyloxycarbonylamino)pentyl 4,6-*O*-benzylidene-β-D-glucopyranoside[19] **18** by using Gareggs phase-transfer conditions[20]. As byproducts, compounds **19** (15%) and **20** (21%), respectively, were obtained as well. When the benzylidene acetal in **22** was reductively opened with sodium cyanoborohydride in acidic solution[21], the formation of the desired bridged disaccharide **25** (35%) was accompanied by **26** (47%) generated by acidic debenzylation of the labile PMB group.



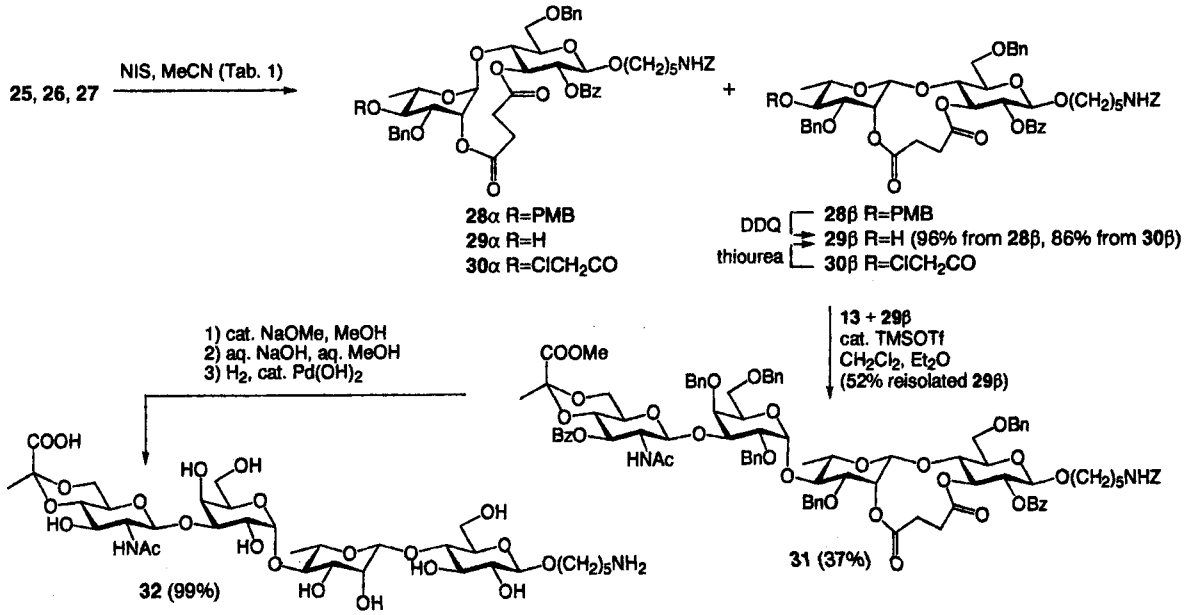


Therefore, the more stable chloroacetyl group was introduced into that position as follows. Compound **22** was selectively debenzylated with dichlorodicyanobenzoquinone (DDQ) to give first **23** (98%), chloroacetylation of which with chloroacetic anhydride afforded **24** (94%). Now the reductive opening of the benzylidene acetal proceeded smoothly and gave the desired alcohol **27** in 75% yield.

All three prearranged glycosides **25**, **26** and **27** were tested for the intramolecular glycosylation step because the influence of a distant protecting group in the donor part of succinyl-bridged glycosides could be evaluated in these cases. It is well-known from "classical" glycosylations by silver silicate-promoted Koenigs-Knorr reactions that blocking groups not directly involved in the reaction (i.e. at C-4 of a halogenose) may influence the anomeric selectivity of the coupling[22]. Indeed, when the three derivatives were treated with *N*-iodosuccinimide (NIS) in acetonitrile to give the bridged disaccharides **28**–**30**, a significant influence of the protecting group at C-4 of the donor moiety on the α/β selectivity of the ring closure reaction could be observed (Table 1). Interestingly, compound **26** bearing a free

Table 1. Intramolecular glycosylation of the prearranged glycosides **25**, **26** and **27**

Starting material	Products yield (%)				Overall yield (%)	Anomeric ratio [α:β]
25	**28α**	(7%)	**28β**	(32%)	39%	1:4.6
26	**29α**	(9%)	**29β**	(35%)	44%	1:4.1
27	**30α**	(10%)	**30β**	(55%)	65%	1:5.3



hydroxyl group at C-4 of the donor part also gave the disaccharide **29** in 44% yield. This demonstrates that the intramolecular glycosylation is favored over the intermolecular one although a large ring is formed during the condensation. Best results were obtained for the chloroacetylated compound **27**. Here, the complex β-linked disaccharide **30β**, could be isolated in 55% yield. Both disaccharides, **28β** and **30β** were finally converted into the desired acceptor block **29β** by treatment with DDQ and thiourea, respectively.

The final condensation of the disaccharide imidate **13** with the disaccharide acceptor **29β** was rather sluggish due to the pronounced instability of the imidate. The tetrasaccharide **31** could thus be isolated in poor 37% yield. However, unreacted acceptor **29β** could be reisolated in 52% yield. Sequential deblocking of **31** by first removing all acyl groups (Zemplén) followed by saponification of the methyl ester of the pyruvate acetal and hydrogenolysis afforded the 5-aminopentyl glycoside tetrasaccharide **32** in 99% yield.

We thank Dr. *P. Fischer* and *J. Rebell* for recording the NMR spectra and Dr. *J. Opitz* for performing the elemental analyses and the mass spectrometry. This work was financially supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie.*

Experimental

General Procedures: Thin-layer chromatography (TLC): precoated plastic sheets, Polygram SIL G/UV$_{254}$, 40 × 80 mm (Macherey-Nagel), appropriately adjusted mixtures of carbon tetrachloride/acetone as eluent. Spots were detected by UV light and by charring with 5% sulfuric acid in ethanol. – CC: silica gel S, Riedel-de Haën, 0.032–0.063 mm, eluent carbon tetrachloride/acetone. – Solutions in organic solvents were dried with anhydrous sodium sulfate and concentrated at <40°C, <200 Pa. – NMR spectra: Bruker AC 250 F, $CDCl_3$ solutions, internal standard TMS, 25°C. Proton signals (Table 2) were assigned by first-order analysis of the spectra. 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. Data in the first row of Table 2 refer to the first sugar residue, those in the second to forth row to the second to forth residue, respectively. Carbon signals were assigned by a comparison of the spectra and by a 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: Büchi apparatus, Model SMP-20.

Allyl 4,6-O-Benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (**2**): A solution of **1**[13] (15.8 g, 44.6 mmol) and HCl (2.1 g, 57.6 mmol) in allyl alcohol (104 ml) is stirred for 20 min at 100°C and concentrated. The residue is mixed with benzaldehyde (40 ml) and freshly molten $ZnCl_2$ (9 g, 66 mmol), and the mixture is vigorously stirred at room temp. for 12 h during which time a clear solution is obtained. The solution is poured with stirring into a mixture of H_2O (100 ml) and *n*-hexane (100 ml), and the precipitated solid is collected by filtration. The material is resuspended 3 times in *n*-hexane (100 ml) and the suspension is stirred vigorously for 0.5 h and filtered. Recrystallization of the material from EtOH affords **2** (9.9 g, 46%), m.p. 176–177°C, $[\alpha]_D$ = +57.5 (*c* = 1.4, $CHCl_3$). – ^{13}C NMR: δ = 102.0 (PhCH), 97.0 (C-1), 95.4 (CCl_3), 81.8 (C-4), 74.8 (CH_2CCl_3), 70.8 (C-3), 68.8 (OCH_2CH), 68.7 (C-6), 62.6 (C-5), 55.7 (C-2). – $C_{19}H_{22}Cl_3NO_7$ (482.7): calcd. C 47.27, H 4.59, Cl 22.03, N 2.90; found C 47.13, H 4.73, Cl 22.22, N 2.96.

Allyl 3-O-Benzoyl-4,6-O-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (**3**): Benzoyl chloride (1.8 ml, 15.6 mmol) is added with stirring at 0°C to a solution of **2** (5 g, 10.4 mmol) in pyridine (30 ml), and the mixture is stirred for 1.5 h. A few drops of H_2O are added in order to destroy excess benzoyl chloride, the mixture is diluted with CH_2Cl_2 and washed with aq. HCl and $NaHCO_3$ solution. Concentration of the solution and crystallization of the residue from EtOH furnishes **3** (5.27 g, 87%), m.p. 128°C, $[\alpha]_D$ = +34.9 (*c* = 1.0, $CHCl_3$). – ^{13}C NMR: δ = 101.5 (PhCH), 97.3 (C-1), 95.2 (CCl_3), 79.4 (C-4), 74.3 (CH_2CCl_3), 70.5 (C-3), 68.8 (OCH_2CH), 68.8 (C-6), 63.2 (C-5), 54.7 (C-2). – $C_{26}H_{26}Cl_3NO_8$ (586.9): calcd. C 53.21, H 4.47, Cl 18.12; N 2.39; found C 53.19, H 4.45, Cl 18.04, N 2.39.

Allyl 3-O-Benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (**4**): A solution of **3** (5 g, 8.5 mmol) in 90% aq. acetic acid (100 ml) is stirred at 60°C for 3 h. Concentration of the solution and chromatography (CCl_4/acetone, 3:1) of the residue affords **4** (3.78 g, 89%) as a colorless foam, $[\alpha]_D$ = +101.7 (*c* = 0.9, $CHCl_3$). – ^{13}C NMR: δ = 96.5 (C-1), 95.2 (CCl_3), 75.1 (C-4), 74.3 (CH_2CCl_3), 71.9 (C-3), 69.5 (C-5), 68.6 (OCH_2), 61.9 (C-6), 53.8 (C-2). – $C_{19}H_{22}Cl_3NO_8$ (498.7): calcd. C 45.76, H 4.45, Cl 21.33, N 2.81; found C 45.55, H 4.49,Cl 21.19, N 2.68.

Allyl 3-O-Benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)-ethylidene]-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (**5**): $Et_2O \cdot BF_3$ (0.73 ml, 5.8 mmol) is added at room temp. to a solution of **4** (1.45 g, 2.9 mmol) and methyl pyruvate (0.53 ml, 5.8 mmol) in MeCN (3 ml), and the mixture is stirred for 4.5 h. It is then neutralized by the addition of pyridine, diluted with CH_2Cl_2 and washed with aq. $NaHCO_3$ solution. Concentration of the solution and chromatography (CCl_4/acetone, 5:1) of the residue furnishes **5** (1.15 g, 68%) as a colorless foam, $[\alpha]_D$ = +94.4 (*c* = 0.9, $CHCl_3$). – ^{13}C NMR: δ = 99.4 (C_{acetal}), 97.2 (C-1), 95.2 (CCl_3), 75.4 (C-4), 74.4 (CH_2CCl_3), 70.4 (C-3), 68.8 (OCH_2), 65.4 (C-6), 62.7 (C-5), 54.6 (C-2), 52.7 ($COOCH_3$), 25.2 (CH_3). – $C_{23}H_{26}Cl_3NO_{10}$ (582.8): calcd. C 47.40, H 4.50, Cl 18.29, N 2.40; found C 47.45, H 4.49, Cl 18.38, N 2.26.

3-O-Benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)-ethylidene]-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranose (**6**): N_2 is bubbled through a suspension of **5** (0.8 g, 1.4 mmol) and $PdCl_2$ (25 mg, 0.14 mmol) in 90% aq. acetic acid (40 ml), and the mixture is stirred at 60°C for 2 d. Concentration of the suspension and chromatography (CCl_4/acetone, 5:1) of the residue affords **6** (0.71 g, 96%) as a colorless foam (mixture of α- and β anomer). – ^{13}C NMR (signals of the α anomer): δ = 99.4 (C_{acetal}), 95.2 (CCl_3), 92.8 (C-1), 75.4 (C-4), 74.3 (CH_2), 70.4 (C-3), 65.5 (C-6), 62.5 (C-5), 54.8 (C-2), 52.8 (OCH_3), 25.3 (CH_3). – $C_{20}H_{22}Cl_3NO_{10}$ (542.8): calcd. C 44.26, H 4.09, Cl 19.60, N 2.58; found C 44.03, H 4.28, Cl 19.69, N 2.47.

3-O-Benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)-ethylidene]-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl Trichloroacetimidate (**7**): K_2CO_3 (0.18 g, 1.3 mmol) is added to a solution of **6** (0.57 g, 1.1 mmol) and Cl_3CCN (0.31 ml, 3.0 mmol) in CH_2Cl_2 (10 ml), and the mixture is stirred at room temp. for 2 d. The suspension is centrifuged and decanted from the precipitated solids. Concentration of the solution and chromatography (CCl_4/acetone, 7:1) of the residue furnishes **7** (0.53 g, 74%) as a colorless foam, $[\alpha]_D$ = +70.2 (*c* = 1.0, $CHCl_3$). – ^{13}C NMR: δ = 99.6 (C_{acetal}), 95.2 (2 C, CH_2CCl_3, C-1), 90.7 (CCl_3), 74.6 (C-

4), 74.5 (CH_2CCl_3), 69.8 (C-3), 65.1 (2 C, C-5,6), 54.6 (C-2), 52.8 ($COOCH_3$), 25.1 (CH_3). – $C_{22}H_{22}Cl_6N_2O_{10}$ (687.1): calcd. C 38.46, H 3.23, Cl 30.96, N 4.08; found C 38.46, H 3.32, Cl 30.93, N 3.83.

Allyl O-{3-O-benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)-ethylidene]-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl}-(1→3)-2,4,6-tri-O-benzyl-α-D-galactopyranoside (**9**): A suspension of **7** (171.8 mg, 0.25 mmol), **8**[16] (102.2 mg, 0.21 mmol) and molecular sieves (4 Å, 2 g) in CH_2Cl_2 (14 ml) is stirred at room temp. under Ar for 1 h and then cooled to −23 °C. A solution of TMSOTf (7.5 µl, 0.042 mmol) in CH_2Cl_2 (4.5 ml) is slowly added with a syringe to this suspension, and stirring is continued for 2 h. The mixture is neutralized with pyridine, warmed to room temp. and filtered. The filtrate is washed with aq. $NaHCO_3$ solution and concentrated. Chromatography (CCl_4/acetone, 10:1) of the residue affords **9** (204 mg, 97%) as a colorless foam, $[\alpha]_D$ = +22.2 (*c* = 1.0, $CHCl_3$). – ^{13}C NMR: δ = 102.4 (C-1′), 99.4 (C_{acetal}), 95.7 (C-1), 95.4 (CCl_3), 77.6, 76.9 (C-2,3), 75.1, 73.5, 73.1 ($PhCH_2$), 74.4 (C-4′), 74.3 (CH_2CCl_3), 72.2 (C-4), 69.5, 69.3 (C-3′,5), 68.9, 68.4 (OCH_2, C-6), 65.9 (C-5′), 65.1 (C-6′), 56.9 (C-2′), 52.7 ($COOCH_3$), 25.3 (CH_3). – $C_{50}H_{54}Cl_3NO_{15}$ (1015.9): calcd. C 59.11, H 5.41, Cl 10.47, N 1.38; found C 59.19, H 5.57, Cl 10.48, N 1.35.

Allyl O-{2-Acetamido-3-O-benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-β-D-glucopyranosyl}-(1→3)-2,4,6-tri-O-benzyl-α-D-galactopyranoside (**10**): A suspension of **9** (0.58 g, 0.57 mmol) and Zn powder (2.7 g, 41.3 mmol) in acetic acid (30 ml) is stirred at room temp. for 1 h. The mixture is filtered, the filtrate is concentrated and the residual oil is dissolved in pyridine (7.4 ml). Ac_2O (3.7 ml, 39.4 mmol) is added at 0 °C to this solution, and the mixture is stirred for 1 h. Concentration of the solution and chromatography (CCl_4/acetone, 7:1) of the residue affords **10** (0.5 g, 99%) as a colorless foam, $[\alpha]_D$ = +6.6 (*c* = 0.9, $CHCl_3$). – ^{13}C NMR: δ = 103.1 (C-1′), 99.3 (C_{acetal}), 95.9 (C-1), 78.1, 77.3, 76.7 (C-2,3,4′), 75.0 (C-4), 74.9, 73.5 ($PhCH_2$), 72.7 (2 C, $PhCH_2$, C-3′), 69.5 (C-5), 69.1 (OCH_2), 68.4 (C-6), 66.1 (C-5′), 65.2 (C-6′), 54.6 (C-2′), 52.7 ($COOCH_3$), 25.2 (OCH_3), 23.0 (CH_3CO). – $C_{49}H_{55}NO_{14}$ (882.0): calcd. C 66.73, H 6.29, N 1.59; found C 66.67, H 6.37, N 1.52.

2-Oxopropyl O-{2-Acetamido-3-O-benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-β-D-glucopyranosyl}-(1→3)-2,4,6-tri-O-benzyl-α-D-galactopyranoside (**11**) *and O-{2-Acetamido-3-O-benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-β-D-glucopyranosyl}-(1→3)-2,4,6-tri-O-benzyl-D-galactopyranose* (**12**): A suspension of **10** (483 mg, 0.55 mmol) and $PdCl_2$ (25 mg, 0.14 mmol) in 90% aqueous acetic acid (60 ml) is treated at 60 °C for 4 h as described for the preparation of **6**. Chromatography (CCl_4/acetone, 5:1) affords first **11** (114.4 mg, 23%) as a colorless oil, $[\alpha]_D$ = +18.2 (*c* = 1.0, $CHCl_3$). – ^{13}C NMR: δ = 102.8 (C-1′), 99.3 (C_{acetal}), 96.7 (C-1), 77.4, 76.7, 76.4 (C-2,3,4′), 75.0 (C-4), 74.9, 73.5, 72.5 ($PhCH_2$), 72.6, 70.0 (C-3′,5), 71.2 (OCH_2), 69.1 (C-6), 66.1 (C-5′), 65.1 (C-6′), 54.5 (C-2′), 52.7 ($COOCH_3$), 26.3 ($COCH_3$), 25.2 (CH_3), 23.3 (CH_3CONH). – $C_{49}H_{55}NO_{15}$ (898.0): calcd. C 65.54, H 6.17, N 1.56; found C 65.64, H 6.19, N 1.60.
Eluted next is **12** (246.2 mg, 53%) as a colorless foam (mixture of α and β anomers). – ^{13}C NMR (significant signals of the α anomer): δ = 103.5 (C-1′), 99.3 (C_{acetal}), 91.5 (C-1), 52.8 ($COOCH_3$), 25.2 (CH_3). – $C_{46}H_{51}NO_{14}$ (841.9): calcd. C 65.63, H 6.11, N 1.66; found C 65.03, H 6.05, N 1.54.

O-{2-Acetamido-3-O-benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-D-glucopyranosyl}-(1→3)-2,4,6-tri-O-benzyl-D-galactopyranosyl Trichloroacetimidate (**13**): K_2CO_3 (229 mg, 1.67 mmol) is added to a solution of **12** (181 mg, 0.15 mmol) and Cl_3CCN (0.23 ml, 2.3 mmol) in CH_2Cl_2 (4 ml), and the mixture is stirred at room temp. for 3 d. The suspension is centrifuged and decanted from the precipitated solids. Concentration of the solution furnishes crude **13** (202.3 mg, 95%) as a colorless oil (1:1.8 mixture of α and β anomers), that was used without further purification in the next step. – ^{13}C NMR (significant signals): δ = 161.3 ($CNHCCl_3$), 103.2, 102.6 (C-1′), 99.3 (C_{acetal}), 98.8 (C-1β), 94.7 (C-1α), 76.3 (C-4′), 68.2 (C-6α), 68.1 (C−6β), 66.5 (C-5′), 65.1 (C-6′), 52.8 ($COOCH_3$), 25.2 (CH_3), 22.9 (CH_3CO).

Ethyl 4-O-(4-Methoxybenzyl)-1-thio-α-L-rhamnopyranoside (**15**): NaH (0.36 g, 15 mmol) is added at room temp. to a solution of **14**[17] (2.48 g, 10 mmol) in DMF (20 ml), and the mixture is stirred for 45 min. 4-Methoxybenzyl bromide (1.4 ml, 12.5 mmol) and a catalytic amount of Bu_4NBr (ca. 10 mg) are added and stirring is continued for 2.5 h. MeOH is added in order to destroy excess NaH, and the mixture is poured into H_2O. Extraction with CH_2Cl_2, washing of the extract with H_2O and concentration afford an oil that is dissolved in 70% aq. acetic acid (60 ml). The solution is stirred at 60 °C for 2 h and concentrated. Chromatography (CCl_4/acetone, 7:1) of the residue furnishes **15** (2.33 g, 71%), m.p. 72−74 °C (Et_2O/*n*-hexane), $[\alpha]_D$ = −163.9 (*c* = 1.4, $CHCl_3$). – ^{13}C NMR: δ = 83.6 (C-1), 81.6 (C-4), 74.6 ($PhCH_2$), 72.6, 71.9 (C-2,3), 67.8 (C-5), 55.3 (OCH_3), 25.0 (SCH_2), 18.0 (C-6), 14.9 (SCH_2CH_3). – $C_{16}H_{24}O_5S$ (328.4): calcd. C 58.51, H 7.37, S 9.76; found C 58.69, H 7.39, S 9.75.

Ethyl 3-O-Benzyl-4-O-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (**16**): A suspension of **15** (1.33 g, 4 mmol) and Bu_2SnO (1.17 g, 4.7 mmol) in benzene (100 ml) is refluxed for 5 h in a Soxhlet apparatus filled with molecular sieves (4 Å). The solution is concentrated and the residue is redissolved in DMF (15 ml). BnBr (0.95 ml, 8 mmol) and CsF (2.2 g, 14.4 mmol) are added and the mixture is stirred at room temp. for 5 h. The mixture is concentrated again, the residue is suspended in CH_2Cl_2 (100 ml) and the suspension is washed with aq. HCl and $NaHCO_3$ solution. Concentration of the solution and chromatography (CCl_4/acetone, 10:1) of the residue furnishes **16** (1.37 g, 82%) as a slightly yellow oil, $[\alpha]_D$ = −119.8 (*c* = 0.9, $CHCl_3$). – ^{13}C NMR: δ = 83.1 (C-1), 80.3 (C-3), 79.9 (C-4), 75.0, 72.1 ($PhCH_2$), 70.2 (C-2), 67.9 (C-5), 55.3 (OCH_3), 24.9 (SCH_2), 17.8 (C-6), 14.9 (SCH_2CH_3). – $C_{23}H_{30}O_5S$ (418.6): calcd. C 66.00, H 7.22, S 7.66; found C 65.77, H 7.20, S 7.83.

Ethyl 3-O-Benzyl-2-O-(3-carboxypropanoyl)-4-O-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (**17**): A solution of **16** (2.83 g, 6.8 mmol), succinic anhydride (5.5 g, 54.4 mmol) and a catalytic amount of DMAP (ca. 20 mg) in pyridine (55 ml) is stirred at room temp. for 2.5 d and concentrated. The residue is dissolved in CH_2Cl_2 (100 ml) and the solution is washed 3 times each with 5% aq. HCl, satd. $NaHCO_3$ solution and H_2O. Concentration of the solution and chromatography (CCl_4/acetone, gradient 5:1 → 3:1) of the residue furnishes **17** (3.31 g, 94%) as a colorless oil, $[\alpha]_D$ = −58.1 (*c* = 1.1, $CHCl_3$). – ^{13}C NMR: δ = 82.2 (C-1), 79.9 (C-3), 78.3 (C-4), 75.1, 71.7 ($ArCH_2$), 71.3 (C-2), 68.3 (C-5), 55.3 (OCH_3), 29.0, 28.9 (CH_2), 25.6 (SCH_2), 17.9 (C-6), 14.9 (SCH_2CH_3). – $C_{27}H_{34}O_8S$ (518.6): calcd. C 62.53, H 6.61, S 6.18; found C 62.31, H 6.84, S 5.97.

5-(Benzyloxycarbonylamino)pentyl 2,3-Di-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**19**) *and 5-(Benzyloxycarbonylamino)pentyl 3-O-Benzoyl-4,6-O-benzylidene-β-D-glucopyranoside* (**20**) *and 5-(Benzyloxycarbonylamino)pentyl 2-O-Benzoyl-4,6-O-benzylidene-β-D-glucopyranoside* (**21**): A mixture of **18**[19] (1.95 g, 4 mmol), BzCl (0.7 ml, 5.9 mmol) and Bu_4NHSO_4 (276 mg, 0.81 mmol) in CH_2Cl_2 (112.5 ml) and 5% aq. NaOH solution (8.75 ml) is vigorously stirred at −4 °C for 20 min. The organic phase is sep-

arated and washed with H_2O. Concentration of the solution and chromatography (CCl_4/acetone, gradient 7:1 → 5:1) of the residue affords first **19** (0.41 g, 15%), m.p. 124−126°C (acetone/*n*-hexane), $[\alpha]_D$ = +1.9 (*c* = 0.8, $CHCl_3$). − ^{13}C NMR: δ = 101.8 (PhCH), 101.4 (C-1), 78.8 (C-4), 72.5, 72.0 (C-2,3), 70.2, 66.5 (OCH_2), 68.6 (C-6), 66.6 (C-5), 40.7 ($NHCH_2$), 29.4, 28.9, 23.0 (CH_2). − $C_{40}H_{41}NO_{10}$ (695.8): calcd. C 69.05, H 5.94, N 2.01; found C 69.04, H 5.95, N 1.82.

Table 2. ^1H-NMR spectra (δ values) in $CDCl_3$

No.	1-H ($J_{1,2}$)	2-H ($J_{2,3}$)	3-H ($J_{3,4}$)	4-H ($J_{4,5}$)	5-H ($J_{5,6a}$)	6a-H ($J_{6a,6b}$)	6b-H ($J_{5,6b}$)	substituents
2	4.92d (3.0)	3.70-4.05m	3.70-4.05m (8.9)	3.57t (8.9)	3.70-4.05m (5.1)	4.27dd (-9.6)	3.70-4.05m	5.98-5.82m (C*H*=CH_2), 5.55s (PhCH), 5.35-5.10m (CH=CH_2, NH), 4.82d, 4.68d (CH_2CCl_3, *J* = -12.0 Hz), 4.25-4.16m, 4.04-3.70m (OCH_2), 2.71d (OH, *J* = 2.3 Hz)
3	4.98d (3.7)	4.28dt (10.2)	5.67dd (9.7)	3.87t (9.4)	4.09-3.98m (4.7)	4.33dd (-10.1)	3.91-3.78m	6.00-5.84m (C*H*=CH_2), 5.55s (PhCH), 5.41d (NH, *J* = 10.1 Hz), 5.39-5.24m (CH=CH_2), 4.68d, 4.47d (CH_2CCl_3, *J* = -12.0 Hz), 4.25-4.21m 4.09-3.98m (OCH_2)
4	4.95d (3.6)	4.17dt (10.7)	5.38dd (9.0)	3.97-3.76m	3.97-3.76m	3.97-3.76m (-9.8)	3.79dd (3.5)	5.99-5.82m (C*H*=CH_2), 5.46d (NH, *J* = 10.1 Hz), 5.40-5.24m (CH=CH_2), 4.69d, 4.46d (CH_2CCl_3, *J* = -12.0 Hz), 4.27-4.18m, 4.07-3.98m (OCH_2), 3.34d, 2.38br.d (OH)
5	4.92d (3.6)	4.17dt (10.0)	5.51t (10.0)	3.70t (10.2)	3.83-3.65m	4.22-3.93m (-10.0)	3.88dd (4.7)	5.99-5.83m (C*H*=CH_2), 5.40d (NH, *J* = 10.1 Hz), 5.37-5.24m (CH=CH_2), 4.66d, 4.48d (CH_2CCl_3, *J* = -12.0 Hz), 4.22-3.92m (OCH_2), 3.83s ($COOCH_3$), 1.49s (CH_3)
6[a]	5.34d (3.5)	4.31-4.05m (10.0)	5.58t (10.0)	3.70t (9.9)	4.31-4.05m	4.31-4.05m (-10.0)	3.75t (10.4)	5.82d (NH, *J* = 10.0 Hz), 4.69d, 4.45d (CH_2CCl_3), 3.83s ($COOCH_3$), 1.49s (CH_3)
7	6.40d (3.7)	4.37ddd (10.5)	5.59dd (9.5)	3.70t (9.5)	3.94-3.77m (4.7)	4.13dd (-10.2)	3.99dd (4.7)	8.78s (C=NH), 5.40d (CONH, *J* = 9.3 Hz), 4.60s (CH_2CCl_3), 3.86s ($COOCH_3$), 1.51s (CH_3)
9	4.76d (3.5)	3.98dd (10.2)	4.20-3.85m	3.55-3.42m	3.55-3.43m	4.20-3.85m	3.55m-3.42	5.96-5.80m (C*H*=CH_2), 5.30-5.15m (CH=CH_2), 5.09d (NH, *J* = 10.1 Hz), 4.61-4.54m (CH_2CCl_3), 4.93d, 4.67d, 4.50d, 4.48d, 4.40d, 4.20-
	4.90d (8.8)	4.20-3.85m (9.6)	5.22t (9.6)	3.72t (9.6)	3.77-3.68m	4.20-3.85m	4.20-3.85m	3.85m ($PhCH_2$), 4.20-3.85m (OCH_2-CH=CH_2), 3.82s ($COOCH_3$), 1.49s (CH_3)
10	4.79d (3.6)	3.96dd (10.2)	4.12dd (3.0)	3.92br.d (<1.0)	3.97-3.91m	3.52-3.46m (-10.0)	3.48dd (5.2)	5.93-5.85m (C*H*=CH_2), 5.29-5.16m (CH=CH_2), 5.33d (NH, *J* = 9.8 Hz), 4.93d, 4.51d ($PhCH_2$, *J* = -11.4 Hz), 4.61s ($PhCH_2$), 4.47d, 4.40d
	4.89d (8.4)	4.34dt (9.9)	5.23t (9.9)	3.72t (9.7)	3.52-3.46m	4.15-4.10m (-10.5)	3.74t (10.5)	($PhCH_2$, *J* = -11.8 Hz), 4.15-4.10m, 3.97-3.91m (OCH_2-CH=CH_2), 3.83s ($COOCH_3$), 1.62s (CH_3CON), 1.49s (CH_3)
11	4.93d (3.5)	3.99dd (10.3)	4.18dd (2.9)	3.91br.d (<1.0)	4.03-3.93m	3.54-3.41m	3.54-3.41m	5.25-5.16m (NH), 4.94-4.84m ($PhCH_2$), 4.62d (2H, $PhCH_2$, *J* = -12.1 Hz), 4.49d (2H, $PhCH_2$, *J* = -11.4 Hz), 4.47d, 4.38d ($PhCH_2$, *J* = -11.5
	4.91d (7.7)	4.35dt (9.5)	5.20t (9.5)	3.71t (9.5)	3.54-3.41m (5.0)	4.13dd (-10.5)	3.73t (10.5)	Hz), 4.17s (OCH_2CO), 3.82s ($COOCH_3$), 2.10s (CH_3CO), 1.59s (CH_3CON), 1.49s (CH_3)
12[a]	5.24br.s	4.18-3.31m (10.2)	3.97dd (3.3)	3.92br.d (<1.0)	4.18-3.31m (6.5)	3.53dd (-9.4)	3.46dd (5.8)	5.82d (NH, *J* = 9.7 Hz), 4.87br.s, 4.65br.s (4H, $PhCH_2$), 4.50d (2H, $PhCH_2$, *J* = -11.5 Hz), 4.47d, 4.37d ($PhCH_2$, *J* = -11.8 Hz), 3.82s
	4.51d (8.5)	4.18-4.04m (10.0)	5.28t (10.0)	3.71t (9.5)	4.18-3.31m (4.9)	4.07dd (-10.5)	4.18-3.31m	($COOCH_3$), 1.59s (CH_3CON), 1.48s (CH_3)
15	5.23d (1.3)	4.00dt (3.5)	3.85ddd (9.3)	3.36t (9.4)	4.08dq (6.2)	1.34d		4.69d, 4.62d ($PhCH_2$, *J* = -11.1 Hz), 3.80s (OCH_3), 2.72d (OH, *J* = 3. Hz), 2.43d (OH, *J* = 4.9 Hz), 2.68-2.48m (SCH_2), 1.28t (SCH_2CH_3, *J* 7.4 Hz)
16	5.28d (0.9)	4.06dd (3.3)	3.79dd (9.1)	3.46t (9.3)	4.11-4.01m (6.2)	1.29d		4.80d, 4.57d ($PhCH_2$, *J* = -10.5 Hz), 4.68s ($PhCH_2$), 3.80s (OCH_3), 2.66d (OH, *J* = 1.8 Hz), 2.64-2.46m (SCH_2), 1.27t (SCH_2CH_3, *J* = 7.4 Hz)
17	5.17d (1.5)	5.44dd (3.3)	3.85dd (9.3)	3.41t (9.3)	4.05dq (6.2)	1.29d		4.81d, 4.53d ($PhCH_2$, *J* = -10.5 Hz), 4.65d, 4.50d ($PhCH_2$, *J* = -11.3 Hz), 3.80s (OCH_3), 2.77-2.48m (CH_2), 1.26t (SCH_2CH_3, *J* = 7.4 Hz)
19	4.76d (7.8)	5.46dd (9.5)	5.78t (9.6)	3.95-3.84m (9.5)	3.69dt (4.9)	4.43dd (-10.5)	3.95-3.84m (9.6)	5.53s (PhCH), 5.08 ($PhCH_2$), 4.06br.s (NH), 3.55-3.45m (OCH_2), 3.20br.d (NCH_2), 1.56-1.18m (CH_2)
20	4.52d (7.7)	3.72dd (9.2)	5.48t (9.4)	3.87-3.75m (9.4)	3.92dt (4.9)	4.38dd (-10.5)	3.87-3.75m (9.4)	5.51s (PhCH), 5.07 ($PhCH_2$), 4.85br.t (NH), 3.65-3.52m (OCH_2), 3.4 3.14m (NCH_2), 1.31-1.25m (CH_2)
21	4.63br.d (7.9)	5.18dd (9.1)	3.65t (9.3)	4.03br.t (9.2)	3.92-3.77m (4.9)	4.37dd (-10.5)	3.82t (10.2)	5.54s (PhCH), 5.06 ($PhCH_2$), 4.63br.d (NH), 3.55-3.42m (OCH_2), 2.93-2.14m (NCH_2), 1.57-1.17m (CH_2)
22	4.68d (7.9)	5.29dd (9.6)	5.56t (9.7)	3.84t (10.3)	3.59dt (5.0)	4.40dd (-10.6)	3.93-3.74m (9.7)	5.51s (PhCH), 5.07s ($PhCH_2OCO$), 4.76d, 4.48d ($PhCH_2$, *J* = -10.4 Hz), 4.57br.t (NH), 4.45d, 4.35d ($PhCH_2$, *J* = -11.2 Hz), 3.93-3.74m
	5.14d (1.1)	5.29dd (3.3)	3.76dd (9.3)	3.36t (9.4)	4.03dq (6.2)	1.28d		(OCH_2), 3.79s (OCH_3), 2.96-2.89m (NCH_2), 3.69-3.35m (CH_2), 1.24 (SCH_2CH_3, *J* = 7.4 Hz), 1.54-1.15m (CH_2)
23	4.68d (7.8)	5.28dd (9.5)	5.54t (9.5)	3.77t (9.5)	3.59dt (4.9)	4.38dd (-10.4)	3.92-3.73m (9.4)	5.51s (PhCH), 5.07s ($PhCH_2OCO$), 4.44d, 4.21d ($PhCH_2$, *J* = -11.1 Hz), 4.57br.t (NH), 3.92-3.73m, 3.63-3.41m (OCH_2), 2.78br.s (OH),
	5.18d (1.0)	5.28dd (3.0)	3.56dd (9.3)	3.48br.t (9.3)	4.00dq (6.2)	1.29d		1.27t (SCH_2CH_3, *J* = 7.4 Hz), 1.51-1.05m (CH_2)
24	4.68d (7.8)	5.28dd (9.3)	5.55t (9.5)	3.78t (9.5)	3.59dt (5.0)	4.39dd (-10.4)	3.51-3.42m (10.4)	5.53s (PhCH), 5.07s ($PhCH_2OCO$), 4.57br.t (NH), 4.42d, 4.18d ($PhCH_2$, *J* = -12.0 Hz), 3.94-3.74m, 3.51-3.42m (OCH_2), 3.88s, 3.86s
	5.21d (1.3)	5.29dd (3.3)	3.69dd (9.7)	4.97t (9.7)	4.10dq (6.2)	1.18d		(CH_2Cl), 2.93br.q (NCH_2), 2.70-2.40m (CH_2), 1.27t (SCH_2CH_3, *J* = 7.4 Hz), 1.65-1,16m (CH_2)
25	4.54d (7.6)	5.20dd (9.7)	5.29t (9.7)	3.90-3.71m	3.90-3.71m	3.90-3.71m	3.90-3.71m	5.07s ($PhCH_2OCO$), 4.78d ($PhCH_2$, *J* = -10.4 Hz), 4.59-4.41m ($PhCH_2$, NH), 3.63-3.42m (OCH_2), 3.79s (OCH_3), 2.94-2.88m
	5.12d (1.5)	5.35dd (3.2)	3.90-3.71m (9.4)	3.36t (9.4)	4.04dq (6.2)	1.29d		(NCH_2), 2.78-2.41m (CH_2), 1.25t (SCH_2CH_3, *J* = 7.4 Hz), 1.64-1.21r (CH_2)
26	4.47d (7.4)	5.18-5.06m	5.18-5.06m (9.3)	3.50dt (9.3)	3.91-3.81m (3.3)	3.78dd (-11.0)	3.71dd (5.0)	5.07s ($PhCH_2OCO$), 4.65-4.55m ($PhCH_2$, NH), 4.31d ($PhCH_2$, *J* = -11.0 Hz), 3.44-3.32m (OCH_2), 3.40br.d (OH), 2.76br.d (OH),
	5.15d (1.5)	5.36dd (3.0)	3.64dd (9.4)	3.91-3.81m (9.3)	4.01dq (6.2)	1.30d		2.91br.q (NCH_2), 2.73-2.16m (CH_2), 1.27t (SCH_2CH_3, *J* = 7.4 Hz), 1.50-1.19m (CH_2)
27	4.57d (7.6)	5.18dd (9.3)	5.28t (9.8)	3.65-3.57m	3.93-3.75m (5.0)	3.84dd (-10.5)	3.93-3.75m	5.07s ($PhCH_2OCO$), 4.62-4.53m ($PhCH_2$, NH), 4.51d, 4.26d ($PhCH_2$ = -12.2 Hz), 3.93-3.75m, 3.50-3.40m (OCH_2), 3.87s, 3.83s (CH_2Cl),
	5.18d (1.6)	5.36dd (3.2)	3.70dd (9.8)	4.97t (9.8)	4.11dq (6.2)	1.18d		2.92br.q (NCH_2), 2.82-2.35m (CH_2), 1.27t (SCH_2CH_3, *J* = 7.4 Hz), 1.69-1,16m (CH_2)
28α	4.54d (7.9)	5.16dd (9.5)	5.52t (10.2)	4.05t (10.5)	3.82-3.77m (1.5)	3.93dd (-10.6)	3.76-3.70m	5.10s ($PhCH_2OCO$), 4.65d ($PhCH_2$, *J* = -12.4 Hz), 4.58-4.50m ($PhCH_2$, NH), 4.36d, 4.19d ($PhCH_2$, *J* = -11.4 Hz), 3.90-3.84m, 3.43
	5.07br.s (<1.0)	5.07br.s (<1.0)	3.82-3.77m (<1.0)	3.23br.d (9.8)	3.76-3.70m (6.4)	1.10d		br.q (OCH_2), 3.81s (OCH_3), 2.94-2.89m ($NHCH_2$), 2.74-2.46m, 1.94-1.16m (CH_2)

Table 2 *(Continued)*

No.	1-H ($J_{1,2}$)	2-H ($J_{2,3}$)	3-H ($J_{3,4}$)	4-H ($J_{4,5}$)	5-H ($J_{5,6a}$)	6a-H ($J_{6a,6b}$)	6b-H ($J_{5,6b}$)	substituents
28β	4.54d (7.9)	5.18dd (9.8)	5.37t (9.7)	3.88t (9.5)	3.87m (5.9)	3.80dd (-9.5)	3.59br.d (<1.0)	5.07s ($PhCH_2OCO$), 4.78d, 4.73d ($PhCH_2$, J = -11.1 Hz), 4.60m (NH
	4.65d (1.3)	5.48br.d (3.3)	3.40dd (8.6)	3.26t (8.7)	3.19dq (6.1)	1.29d		4.71d, 4.46d ($PhCH_2$, J = -12.0 Hz), 4.43d ($PhCH_2$, J = -10.7 Hz), 4.32d ($PhCH_2$, J = -11.0 Hz), 3.81s (OCH_3), 3.43-3.39m, 2.94-2.87m (OCH_2, $NHCH_2$), 2.76-2.51m, 1.54-1.28m (CH_2)
29α	4.58d (7.7)	5.17dd (9.4)	5.48t (10.0)	4.06t (10.3)	3.94br.d (9.9)	3.88-3.73m	3.88-3.73m	5.06s ($PhCH_2OCO$), 4.68-4.53m ($PhCH_2$, NH), 3.46-3.42m (OCH_2), 2.92br.q ($NHCH_2$), 2.69-2.48m, 1.51-1.12m (CH_2)
	5.08s (0)	5.09d (3.0)	3.88-3.73m (<1.0)	3.60br.d (8.9)	3.88-3.73m (6.0)	1.29d		
29β	4.54d (7.9)	5.19dd (9.8)	5.36t (9.6)	3.89t (9.6)	3.59br.d	3.91-3.79m	3.91-3.79m	5.07s ($PhCH_2OCO$), 4.82d, 4.22d ($PhCH_2$, J = -10.9 Hz), 4.59br.s (NH), 4.78d, 4.43d ($PhCH_2$, J = -11.8 Hz), 3.43br.q (OCH_2), 2.95-2.89m ($NHCH_2$), 2.68-2.48m, 1.53-1.15m (CH_2), 2.23s (OH)
	4.58d (0)	5.48d (3.2)	3.10dd (9.4)	3.34t (9.3)	3.04dq (6.2)	1.29d		
30α	4.75-4.56m (7.7)	5.14dd (10.2)	5.48t (10.2)	4.05t (10.2)	3.95-3.86m (<1.0)	3.94d (-9.3)	3.76-3.71m	5.07s ($PhCH_2OCO$), 4.71d ($PhCH_2$, J = -12.8 Hz), 4.65d ($PhCH_2$, J = -12.4 Hz), 4.75-4.56m (NH), 4.58d, 4.57d ($PhCH_2$, J = -12.1 Hz), 4.0
	4.75-4.56m	5.18-5.14m	3.76-3.71m (7.7)	4.90dd (3.0)	3.76-3.71m (6.5)	1.23d		(CH_2Cl), 3.95-3.68m, 3.46-3.42m (OCH_2), 2.93br.q (NCH_2), 2.64-2.45m, 1.57-1.22m (CH_2)
30β	4.55d (7.8)	5.18dd (9.8)	5.38t (9.5)	3.93-3.79m	3.93-3.79m	3.93-3.79m (-9.5)	3.58br.d (<1.0)	5.07s ($PhCH_2OCO$), 4.78d, 4.45d ($PhCH_2$, J = -12.0 Hz), 4.71d, 4.33
	4.58d (1.4)	5.43d (3.5)	3.35dd (8.8)	4.84t (8.7)	3.10dq (6.3)	1.19d		($PhCH_2$, J = -12.2 Hz), 4.62-4.53m (NH), 3.93s, 3.92s (CH_2Cl), 3.93-3.79m, 3.49-3.38m (OCH_2), 2.93br.q (NCH_2), 2.66-2.50m, 1.54-1.13
31	4.77-4.25m (8.0)	5.16dd (9.9)	5.40t (9.9)	4.02t (10.2)	3.96-3.68m	3.96-3.68m	3.65-3.38m	(CH_2) 5.39-5.03m (NHCO), 5.07s ($PhCH_2OCO$), 4.72-4.25m ($PhCH_2$,
	4.77-4.25m (0)	5.29d (2.9)	3.75dd (9.0)	3.61t (9.1)	3.33dq (6.1)	1.34d		$NHCH_2$), 3.83s ($COOCH_3$), 3.96-3.68m, 3.65-3.38m (OCH_2), 2.92br (NCH_2), 2.62-2.30m, 1.81-1.12m (CH_2), 1.54s (CH_3CO), 1.50s (CH_3
	4.87d (3.5)	4.08-3.98m (10.5)	3.93dd (3.3)	3.96-3.68m	3.96-3.68m	3.65-3.38m (-9.4)	3.41dd (6.4)	
	4.94-4.86m	4.08-3.98m (9.9)	5.24t (9.9)	3.73t (9.4)	3.65-3.38m	4.17dd (-10.9)	3.96-3.68m	

[a] Signals of the α anomer.

Eluted next is **21** (1.24 g, 53%), m.p. 142°C (EtOH), $[\alpha]_D$ = −36.7 (c = 1.0, $CHCl_3$). − ^{13}C NMR: δ = 101.9 (PhCH), 101.6 (C-1), 80.9 (C-4), 74.8 (C-3), 72.3 (C-2), 70.1, 68.6 (OCH_2), 66.5 (C-6), 66.3 (C-5), 40.8 ($NHCH_2$), 29.4, 28.9, 23.0 (CH_2). − $C_{33}H_{37}NO_9$ (591.7): calcd. C 66.99, H 6.30, N 2.37; found C 66.91, H 6.32, N 2.18.

Eluted next is **20** (0.5 g, 21%), m.p. 142°C (EtOH), $[\alpha]_D$ = −73.4 (c = 0.9, $CHCl_3$). − ^{13}C NMR: δ = 103.7 (PhCH), 101.4 (C-1), 78.6 (C-4), 74.4 (C-2), 73.6 (C-3), 70.3, 68.7 (OCH_2), 66.6 (C-6), 66.5 (C-5), 40.8 ($NHCH_2$), 29.5, 28.9, 23.1 (CH_2). − $C_{33}H_{37}NO_9$ (591.7): calcd. C 66.99, H 6.30, N 2.37; found C 67.12, H 6.34, N 2.31.

Ethyl 2-O-{[2-O-Benzoyl-4,6-O-benzylidene-1-O-(5-benzyloxycarbonylaminopentyl)-β-D-glucopyranos-3-yloxy]carbonylpropanoyl}-3-O-benzyl-4-O-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (**22**): A mixture of **17** (640 mg, 1.23 mmol), **21** (803.6 mg, 1.36 mmol), DCC (281 mg, 1.36 mmol), and DMAP (15 mg, 0.123 mmol) in CH_2Cl_2 (12 ml) is stirred at room temp. for 26 h. The precipitated dicyclohexylurea is filtered off and the filtrate is washed with H_2O and 5% aq. acetic acid. Concentration of the solution and chromatography (CCl_4/acetone, 8:1) of the residue furnishes **22** (1.18 g, 88%) as a colorless foam, $[\alpha]_D$ = −37.4 (c = 0.9, $CHCl_3$). − ^{13}C NMR: δ = 101.8 (C-1), 101.4 ($PhCH_2$), 82.2 (C-1′), 79.8, 79.4, 78.3 (C-3′,4,4′), 75.0, 71.5 ($PhCH_2$), 72.5, 71.7, 70.9 (C-2,3,2′), 70.2, 66.8 (CH_2O), 68.6 (C-6), 68.2 (C-5′), 66.5 (C-5), 55.3 (OCH_3), 40.7 (NCH_2), 25.5 (SCH_2), 17.6 (C-6′), 15.0 (SCH_2CH_3). − $C_{60}H_{69}NO_{16}S$ (1092.3): calcd. C 65.98, H 6.37, N 1.28, S 2.94; found C 65.98, H 6.32, N 1.11, S 2.96.

Ethyl 2-O-{[2-O-Benzoyl-4,6-O-benzylidene-1-O-(5-benzyloxycarbonylaminopentyl)-β-D-glucopyranos-3-yloxy]carbonylpropanoyl}-3-O-benzyl-1-thio-α-L-rhamnopyranoside (**23**): A mixture of **22** (1.04 g, 0.96 mmol) and DDQ (0.24 g, 1.05 mmol) in CH_2Cl_2 (18 ml) and H_2O (1 ml) is stirred at room temp. for 16 h and washed with aq. $NaHCO_3$ solution. Concentration of the solution and chromatography (CCl_4/acetone, 6:1) of the residue furnishes **23** (0.91 g, 98%) as a colorless foam, $[\alpha]_D$ = −23.0 (c = 0.78, $CHCl_3$). − ^{13}C NMR: δ = 101.8 ($PhCH_2$), 101.4 (C-1), 82.4 (C-1′), 78.4, 77.9 (C-3′,4), 72.5 (C-3), 71.9, 71.8, 70.0 (C-2,2′,4′), 71.2 ($PhCH_2$), 70.2, 66.5 (OCH_2), 68.6 (C-6), 68.5 (C-5′), 66.5 (C-5), 40.8 (NCH_2), 25.6 (SCH_2), 17.6 (C-6′), 14.9 (SCH_2CH_3). − $C_{52}H_{61}NO_{15}S$ (972.1): calcd. C 64.25, H 6.32, N 1.44, S 3.30; found C 64.32, H 6.38, N 1.29, S 3.34.

Ethyl 2-O-{[2-O-Benzoyl-4,6-O-benzylidene-1-O-(5-benzyloxycarbonylaminopentyl)-β-D-glucopyranos-3-yloxy]carbonylpropanoyl}-3-O-benzyl-4-O-chloroacetyl-1-thio-α-L-rhamnopyranoside (**24**): A solution of **23** (1.58 g, 1.63 mmol) and chloroacetic anhydride (0.34 g, 2 mmol) in pyridine (12 ml) is stirred at 0°C for 1 h. The mixture is poured into H_2O and extracted several times with CH_2Cl_2. The combined organic extracts are washed with aq. HCl and $NaHCO_3$ solution and concentrated. Chromatography (CCl_4/acetone, 7:1) of the residue affords **24** (1.6 g, 94%) as a colorless foam, $[\alpha]_D$ = −25.3 (c = 0.7, $CHCl_3$). − ^{13}C NMR: δ = 101.8 (C-1), 101.4 (PhCH), 82.3 (C-1′), 78.5 (C-3′), 74.7, 74.5 (C-4,4′), 72.5, 71.7 (C-2′,3), 71.2 ($PhCH_2$), 70.3 (C-2), 70.2, 66.5 (OCH_2), 68.6 (2 C, C-5′,6), 66.6 (C-5), 40.8, 40.6 (NCH_2, $ClCH_2$), 25.7 (SCH_2), 17.4 (C-6′), 14.9 (SCH_2CH_3). − $C_{54}H_{62}ClNO_{16}S$ (1048.6): calcd. C 61.85, H 5.96, Cl 3.38, N 1.34, S 3.01; found C 61.82, H 5.98, Cl 3.49, N 1.27, S 2.88.

Ethyl 2-O-{[2-O-Benzoyl-6-O-benzyl-1-O-(5-benzyloxycarbonylaminopentyl)-β-D-glucopyranos-3-yloxy]carbonylpropanoyl}-3-O-benzyl-4-O-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (**25**) *and Ethyl 2-O-{[2-O-Benzoyl-6-O-benzyl-1-O-(5-benzyloxycarbonylaminopentyl)-β-D-glucopyranos-3-yloxy]carbonylpropanoyl}-3-O-benzyl-1-thio-α-L-rhamnopyranoside* (**26**): HCl in Et_2O is added at room temp. to a suspension of **22** (1.1 g, 1.01 mmol), $NaCNBH_3$ (0.8 g, 12.7 mmol) and molecular sieves (3 Å, 1 g) in THF (15 ml) until the evolution of H_2 has ceased. The mixture is stirred for additional 5 min., diluted with CH_2Cl_2 and filtered. The filtrate is washed with H_2O and aq. $NaHCO_3$ solution and concentrated. Chromatography (CCl_4/acetone, 5:1) of the residue affords first **25** (0.38 g, 35%) as a colorless foam, $[\alpha]_D$ = −27.9 (c = 0.7, $CHCl_3$). − ^{13}C NMR: δ = 101.1 (C-1), 82.2 (C-1′), 79.8, 78.2 (C-3′,4′), 76.0

(C-3), 75.0, 73.7, 71.7 ($ArCH_2$), 74.5 (C-4), 71.6, 71.4 (C-2',5), 70.3 (C-2), 69.8 (C-6), 68.3 (C-5'), 69.8, 66.5 (OCH_2), 55.3 (OCH_3), 40.8 (NCH_2), 25.6 (SCH_2), 17.8 (C-6'), 14.9 (SCH_2CH_3). – $C_{60}H_{71}NO_{16}S$ (1094.3): calcd. C 65.86, H 6.54, N 1.28, S 2.93; found C 65.71, H 6.53, N 1.14, S 2.94.

Eluted next is **26** (0.46 g, 47%) as a colorless foam, $[\alpha]_D = -28.7$ ($c = 1.0$, $CHCl_3$). – ^{13}C NMR: δ = 101.0 (C-1), 82.2 (C-1'), 78.3 (C-3'), 75.8, 75.0 (C-3,4), 73.7 ($PhCH_2$), 71.8 (2 C, C-4', $PhCH_2$), 71.5 (C-2'), 70.4 (C-2), 69.7, 66.5 (OCH_2), 69.6, 68.7 (C-5,5'), 69.4 (C-6), 40.8 (NCH_2), 25.7 (SCH_2), 17.7 (C-6'), 14.9 (SCH_2CH_3). – $C_{52}H_{63}NO_{15}S$ (974.1): calcd. C 64.12, H 6.52, N 1.44, S 3.29; found C 63.96, H 6.52, N 1.42, S 3.35.

Ethyl 2-O-{[2-O-Benzoyl-6-O-benzyl-1-O-(5-benzyloxycarbonylaminopentyl)-β-D-glucopyranos-3-yloxy]carbonylpropanoyl}-3-O-benzyl-4-O-chloroacetyl-1-thio-α-L-rhamnopyranoside (**27**): Compound **24** (1.6 g, 1.52 mmol) in THF (34 ml) is treated with $NaCNBH_3$ (1.19 g, 19 mmol) and HCl in Et_2O as described for the preparation of compounds **25** and **26**. Chromatography (CCl_4/acetone, 5:1) furnishes **27** (1.19 g, 75%) as a colorless oil, $[\alpha]_D = -25.3$ ($c = 0.7$, $CHCl_3$). – ^{13}C NMR: δ = 101.1 (C-1), 82.2 (C-1'), 76.1 (C-3'), 74.9 (C-4), 74.4 (2 C, C-3,4'), 73.7, 71.2 ($PhCH_2$), 71.7, 70.5, 70.0 (C-2,2',5), 69.9, 66.5 (OCH_2), 69.7 (C-6), 66.7 (C-5'), 40.8, 40.6 (NCH_2, $ClCH_2$), 25.7 (SCH_2), 17.3 (C-6'), 14.9 (SCH_2CH_3). – $C_{54}H_{64}ClNO_{16}S$ (1050.6): calcd. C 61.74, H 6.14, Cl 3.37, N 1.33, S 3.05; found C 61.65, H 6.09, Cl 3.54, N 1.30, S 3.06.

5-(Benzyloxycarbonylamino)pentyl O-[3-O-Benzyl-4-O-(4-methoxybenzyl)-α/β-L-rhamnopyranosyl]-(1→4)-2-O-benzoyl-6-O-benzyl-β-D-glucopyranoside-3,2'-succinate (**28**): *N*-Iodosuccinimide (NIS, 259 mg, 1.15 mmol) is added under Ar at 0°C to a stirred mixture of **25** (251.5 mg, 0.23 mmol) and molecular sieves (3 Å, 0.5 g) in MeCN (3.5 ml), and the mixture is stirred for 21 h. It is then diluted with CH_2Cl_2 and filtered through a layer of Celite. The filtrate is washed with aq. $Na_2S_2O_3$ solution and H_2O and concentrated. Chromatography (CCl_4/acetone, 6:1) of the residue gives first **28α** (17 mg, 7%) as a colorless oil, $[\alpha]_D = -51.0$ ($c = 0.7$, $CHCl_3$). – ^{13}C NMR: δ = 100.9 (C-1), 92.8 (C-1'), 81.3 (C-4'), 75.3 (C-3), 74.2 (C-3'), 73.5, 72.7, 71.0 ($ArCH_2$), 73.3, 72.8, 72.3 (C-2,2',4), 70.1 (C-5), 79.7 (2 C, $PhCH_2O$, C-5'), 68.9 (C-6), 66.5 (OCH_2), 55.3 (OCH_3), 40.8 (NCH_2), 18.9 (C-6'). – $C_{58}H_{65}NO_{16}$ (1031.4): FAB MS 1032.1 (MH^+).

Eluted next is **28β** (75.3 mg, 32%) as a slightly yellow oil, $[\alpha]_D = +16.5$ ($c = 1.0$, $CHCl_3$). – ^{13}C NMR: δ = 101.4 (C-1), 97.5 (C-1'), 79.4, 78.8 (C-3',4'), 74.9 (C-3), 74.6, 73.6, 72.1 ($ArCH_2$), 73.4 (C-4), 72.3, 72.0 (C-2,2'), 71.3 (C-5), 69.7, 66.6 (OCH_2), 68.2 (C-6), 66.5 (C-5'), 55.3 (OCH_3), 40.8 (NCH_2), 18.2 (C-6'). – $C_{58}H_{65}NO_{16}$ (1031.4): FAB MS 1032.6 (MH^+).

5-(Benzyloxycarbonylamino)pentyl O-(3-O-Benzyl-α/β-L-rhamnopyranosyl)-(1→4)-2-O-benzoyl-6-O-benzyl-β-D-glucopyranoside-3,2'-succinate (**29**): A) Treatment of **26** (222 mg, 0.23 mmol) with NIS (257 mg, 1.15 mmol) in MeCN (10 ml) as described for the preparation of **28** and chromatography (CCl_4/acetone, 4.5:1) affords first **29α** (18 mg, 9%) as a slightly yellow oil, $[\alpha]_D = -25.9$ ($c = 1.4$, $CHCl_3$). – ^{13}C NMR: δ = 100.9 (C-1), 92.0 (C-1'), 79.0 (C-3'), 74.5 (C-3), 73.5, 73.1 ($PhCH_2$), 72.9, 72.6 (C-2,5'), 70.9 (4 C, C-2',3,3',5), 69.7, 66.5 (OCH_2), 68.8 (C-6), 40.8 (NCH_2), 18.0 (C-6'). – $C_{50}H_{57}NO_{15}$ (912.0): FAB MS 912.6 (MH^+).

Eluted next is **29β** (74 mg, 35%) as a colorless foam, $[\alpha]_D = +24.9$ ($c = 0.4$, $CHCl_3$). – ^{13}C NMR: δ = 101.4 (C-1), 97.2 (C-1'), 79.4 (C-3'), 74.8 (C-5), 73.2 (C-3), 72.8, 72.0 (C-2,5'), 71.7, 70.8 ($PhCH_2$), 70.7, 70.1 (C-4,4'), 69.8, 66.5 (OCH_2), 68.8 (C-6), 65.3 (C-2'), 40.8 (NCH_2), 17.7 (C-6'). – $C_{50}H_{57}NO_{15}$ (912.0): calcd. C 65.85, H 6.30, N 1.54; found C 65.76, H 6.34, N 1.41.

B) Treatment of **28β** (43 mg, 0.04 mmol) with DDQ (10.5 mg, 0.05 mmol) in CH_2Cl_2 (9 ml) and H_2O (0.5 ml) as described for the preparation of **23** affords **29β** (36.5 mg, 96%).

C) A solution of **30β** (237.5 mg, 0.24 mmol, see below) and thiourea (42 mg, 0.55 mmol) in MeOH (10 ml) is stirred at room temp. for 13 d and concentrated. The residue is redissolved in CH_2Cl_2, the solution washed with H_2O and concentrated again. Chromatography (CCl_4/acetone, 5:1) of the residue furnishes **29β** (187.7 mg, 86%).

5-(Benzyloxycarbonylamino)pentyl O-(3-O-Benzyl-4-O-chloroacetyl-α/β-L-rhamnopyranosyl)-(1→4)-2-O-benzoyl-6-O-benzyl-β-D-glucopyranoside-3,2'-succinate (**30**): Treatment of **27** (802.3 mg, 0.76 mmol) with NIS (860 mg, 3.82 mmol) in MeCN (11 ml) as described for the preparation of **28** and chromatography (CCl_4/acetone, 6:1) affords first **30α** (77.8 mg, 10%) as a colorless foam, $[\alpha]_D = -29.9$ ($c = 0.8$, $CHCl_3$). – ^{13}C NMR: δ = 100.9 (C-1), 91.7 (C-1'), 75.5 (2 C, C-3,3'), 75.4 (C-4), 74.3, 72.6 ($PhCH_2$), 73.4, 73.0 (C-2,4'), 72.6 (C-2'), 71.6 (C-5), 69.6, 66.5 (OCH_2), 68.8 (C-5'), 68.7 (C-6), 40.8, 40.7 (NCH_2, $ClCH_2$), 18.1 (C-6'). – $C_{52}H_{58}ClNO_{16}$ (988.5): calcd. C 63.19, H 5.91, N 1.42; found C 63.47, H 6.37, N 1.55; FAB MS 989.5 (MH^+).

Eluted next is **30β** (415.2 mg, 55%) as a colorless foam, $[\alpha]_D = -22.3$ ($c = 0.7$, $CHCl_3$). – ^{13}C NMR: δ = 101.4 (C-1), 97.5 (C-1'), 75.4 (C-3'), 74.8 (C-4'), 73.9, 71.6 ($PhCH_2$), 73.6, 73.4 (C-2,3), 72.0, 71.8 (C-4,5'), 70.6 (C-5), 69.8, 66.5 (OCH_2), 68.0 (C-6), 65.8 (C-2'), 40.8, 40.6 (NCH_2, $ClCH_2$), 17.8 (C-6'). – $C_{52}H_{58}ClNO_{16}$ (988.5): calcd. C 63.19, H 5.91, Cl 3.59, N 1.42; found C 63.09, H 6.04, Cl 3.47, N 1.43.

5-(Benzyloxycarbonylamino)pentyl O-{2-Acetamido-3-O-benzoyl-2-deoxy-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-β-D-glucopyranosyl}-(1→3)-(2,4,6-tri-O-benzyl-α-D-galactopyranosyl)-(1→4)-(3-O-benzyl-β-L-rhamnopyranosyl)-(1→4)-2-O-benzoyl-6-O-benzyl-β-D-glucopyranoside-3,2'-succinate (**31**): TMSOTf (14 µl, 0.08 mmol) is added at 0°C under Ar to a stirred mixture of crude **13** (228.6 mg, 0.23 mmol), **29β** (140 mg, 0.15 mmol) and crushed molecular sieves (3 Å, 1.5 g) in CH_2Cl_2 (1.5 ml) and Et_2O (9 ml). The mixture is stirred for 3 h, neutralized by the addition of pyridine and filtered. The filtrate is washed with aq. $NaHCO_3$ solution and concentrated. Chromatography (CCl_4/acetone, 5:1) of the residue affords first **31** (98.6 mg, 37%) as a colorless foam, $[\alpha]_D = +24.5$ ($c = 0.42$, $CHCl_3$). – ^{13}C NMR: δ = 103.1 (C-1‴), 101.0 (C-1), 99.3 (C_{acetal}), 98.9 (C-1″), 97.6 (C-1'), 78.0, 77.7, 77.6 (C-3',3″,5'), 76.9, 76.8, 76.5 (C-2″,4',4‴), 75.7, 75.1, 74.9 (C-4,4″,5), 74.8, 73.5, 73.2, 72.9, 72.2 ($PhCH_2$), 73.8 (C-3), 72.5 (C-3‴), 71.9 (C-2), 70.0 (C-5″), 69.6, 66.4 (OCH_2), 69.4, 68.4 (C-6,6″), 67.2 (C-2'), 66.1 (C-5‴), 65.1 (C-6‴), 54.5 (C-2‴), 52.7 ($COOCH_3$), 40.7 (NCH_2), 30.8, 30.6, 29.3, 28.8, 23.0 (CH_2), 25.2 (CH_3), 22.9 (CH_3CONH), 19.4 (C-6'). – $C_{96}H_{100}N_2O_{28}$ (1735.9): calcd. C 66.42, H 6.15, N 1.61; found C 66.29, H 6.26, N 1.75.

Eluted next is unconsumed **29β** (72.6 mg, 52%).

5-Aminopentyl O-{2-Acetamido-3-O-benzoyl-2-deoxy-4,6-O-[(S)-1-carboxyethylidene]-β-D-glucopyranosyl}-(1→3)-(α-D-galactopyranosyl)-(1→4)-(β-L-rhamnopyranosyl)-(1→4)-β-D-glucopyranoside (**32**): A solution of **31** (69 mg, 39.8 µmol) and a catalytic amount of NaOMe in MeOH (4 ml) is stirred at room temp. for 23 h. The solution is neutralized by addition of ion exchange resin (Lewatit, H^+ form) and filtered. The filtrate is concentrated and the residue is redissolved in MeOH (4 ml). Aq. NaOH solution (1 N, 0.35 ml) is added, the solution is stirred for 3 d, neutralized with ion exchange resin (Lewatit, H^+ form) and filtered. The filtrate is mixed with $Pd(OH)_2$ (10% on charcoal, ca. 20 mg) and stirred at room temp. under H_2 for 6 d. Filtration of the mixture, concen-

tration of the filtrate, chromatography of the residue with H_2O on Bio Gel P2 and lyophilization of carbohydrate-containing fractions affords **32** (33.5 mg, 99%) as a colorless foamy material, $[\alpha]_D$ = +61.8 (*c* = 1.0, H_2O). – ^{13}C NMR (D_2O): δ = 103.6 (C-1‴), 102.5 (C-1), 101.5 (C_{acetal}), 100.9, 100.3 (C-1′,1″), 81.0 (C-3″), 79.1 (C-3′), 76.9 (C-4‴), 76.7 (C-5), 75.9 (C-4′), 74.9 (C-3‴), 73.5 (C-2), 72.0 (C-2′), 71.8 (2 C, C-5′,5″), 71.3 (C-4), 71.2 (OCH_2), 70.4 (C-3), 69.9, 69.3 (C-2″,4″), 66.1 (C-5″), 64.6 (C-6‴), 61.1, 60.7 (C-6,6″), 56.6 (C-2‴), 39.7 (NCH_2), 28.5, 26.8, 22.4 (CH_2), 25.0 (CH_3), 22.5 (*C*H_3CONH), 17.3 (C-6′). – $C_{34}H_{58}N_2O_{22}$ (846.8): FAB MS (neg.) 845.1 ($M - H^+$).

[1] S. J. Cryz in *Immunotherapy and Vaccines* (Ed.: S. J. Cryz), VCH, Weinheim, **1991**, p. 21–24.
[2] R. Austrian, *Trans. Am. Clin. Climatol. Assoc.* **1977**, *89*, 141–161.
[3] C. M. McLeod, M. R. Kraus, *J. Exp. Med.* **1974**, *86*, 493–453.
[4] J. B. Robbins, R. Austrian, C.-J. Lee, S. C. Rastogi, G. Schiffman, J. Henry, P. H. Mäkelä, C. V. Broome, R. R. Facklam, R. H. Tiesjema, J. C. Parl, *J. Infec. Dis.* **1983**, *148*, 1136–1140.
[5] J. A. Leech, A. Gervais, F. L. Ruben, *Can. Med. Assoc. J.* **1987**, *136*, 361–365.
[6] G. Schüle, T. Ziegler, *Tetrahedron* **1996**, *52*, 2925–2936, and references cited therein.
[7] L. G. Bennett, C. T. Bishop, *Can. J. Chem.* **1977**, *55*, 8–16.
[8] J. D. Higginbotham, M. Heidelberger, *Carbohydr. Res.* **1973**, *27*, 297–302.
[9] J. Y. Lew, M. Heidelberger, *Carbohydr. Res.* **1976**, *52*, 255–258.
[10] P.-E. Jansson, B. Lindberg, U. Lindquist, *Carbohydr. Res.* **1981**, *95*, 73–80.
[11] T. Ziegler, R. Lau, *Tetrahedron Lett.* **1995**, *36*, 1417–1420.
[12] R. Lau, G. Schüle, U. Schwaneberg, T. Ziegler, *Liebigs Ann.* **1995**, 1745–1754.
[13] M. Imoto, H. Yoshimura, T. Shimamoto, N. Sakaguchi, T. Shiba, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2205–2214.
[14] T. Ziegler, *Tetrahedron Lett.* **1994**, *35*, 6857–6860.
[15] P. J. Garegg, P.-E. Jansson, B. Lindberg, F. Lindh, J. Lönngren, I. Kvarnström, W. Nimmich, *Carbohydr. Res.* **1980**, *78*, 127–132.
[16] M. A. Nashed, L. Anderson, *Carbohydr. Res.* **1976**, *51*, 65–72.
[17] A. M. P. van Steijn, M. Jetten, J. P. Kamerling, J. F. G. Vliegenthart, *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 374–383.
[18] N. Nagashima, M. Ohno, *Chem. Lett.* **1987**, 141–144.
[19] E. Eckhardt, T. Ziegler, *Carbohydr. Res.* **1994**, *264*, 263–269.
[20] P. J. Garegg, I. Kvarnström, A. Niklasson, G. Niklasson, S. C. T. Svensson, *J. Carbohydr. Chem.* **1993**, *12*, 933–953.
[21] P. Garegg, H. Hultberg, *Carbohydr. Res.* **1981**, *93*, C10–C11.
[22] C. A. A. van Boeckel, T. Beetz, S. F. van Aelst, *Tetrahedron* **1984**, *40*, 4097–4107.

[96105]