ELSEVIER

Carbohydrate Research 297 (1997) 153–161

CARBOHYDRATE RESEARCH

Note

Syntheses of spacer-armed carbohydrate components of the *Mycobacterium avium* serocomplex serovar 8 [1]

János Kerékgyártó [a], Károly Ágoston [a], Gyula Batta [b], Zoltán Szurmai [a,*]

[a] *Institute of Biochemistry, L. Kossuth University, P.O. Box 55, H-4010 Debrecen, Hungary*
[b] *Research Group for Antibiotics of the Hungarian Academy of Sciences, L. Kossuth University, P.O. Box 70, H-4010 Debrecen, Hungary*

Received 23 February 1996; accepted in revised form 15 June 1996

Abstract

p-Nitrophenyl glycosides of 3-*O*-Me-β-D-Glc*p*-(1 → 3)-α-L-Rha*p*, α-L-Rha*p*-(1 → 2)-6-deoxy-α-L-Tal*p*, and 3-*O*-Me-β-D-Glc*p*-(1 → 3)-α-L-Rha*p*-(1 → 2)-6-deoxy-α-L-Tal*p* have been prepared, related to *Mycobacterium avium*. Various glycosylation methods have been used for the formation of the interglycosidic linkages. The *p*-nitrophenyl derivatives were converted into *p*-isothiocyanatophenyl glycosides, capable of forming neoglycoproteins. © 1997 Elsevier Science Ltd.

Keywords: Spacer-armed glycosides; Oligosaccharide synthesis; Mycobacterium

Over the last decade, a number of oligosaccharides related to Mycobacteria have been synthesized in our laboratory [1–5]. It is known that *Mycobacterium tuberculosis* and *M. leprae* are responsible for human tuberculosis and leprosy, respectively. Recently, there has been growing interest in the *Mycobacterium avium–M. intracellulare–M. scrofulaceum* (MAIS) serocomplex because several serovariants, as opportunistic pathogens, cause infections among people with acquired immunodeficiency syndrome (AIDS) [6]. The surface glycolipid of MAIS serovariant 8 has the following oligosaccharide component [7]: 4,6-*O*-Pyr-3-*O*-Me-β-D-Glc*p*-(1 → 3)-α-L-Rha*p*-(1 → 2)-6-deoxy-α-L-Tal*p*. This pyruvylated trisaccharide has been prepared in our laboratory by a 2 + 1 block synthesis as the *p*-trifluoroacetamidophenyl glycoside [5]. Now we describe the spacer-armed non-pyruvylated di- and trisaccharides, as *p*-isothiocyanatophenyl glycosides.

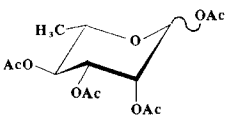
For the preparation of the 3-*O*-Me-β-D-Glc*p*-(1 → 3)-L-Rha*p* disaccharide glycoside, first suitably protected precursors were synthesized. Benzyl 4-*O*-benzyl-α-L-rhamnopyranoside (**3**) [8] and *p*-nitrophenyl 4-*O*-benzyl-α-L-rhamnopyranoside (**4**) [3] were prepared from the corresponding 2,3-*O*-isopropylidene acetals by acid hydrolysis. One compound in the well-known reaction sequence, namely, benzyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (**2**) [9], was synthesized directly from tetra-*O*-acetyl-L-rhamnose (**1**) in dry dichloromethane using boron trifluoride etherate as the promoter. It is known that **3** can be

* Corresponding author.

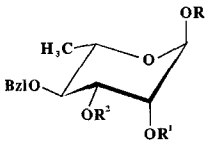
[1] Dedicated to Professor András Lipták on the occasion of his 60th birthday.

0008-6215/97/$17.00 Copyright © 1997 Elsevier Science Ltd. All rights reserved.
PII S0008-6215(96)00255-8

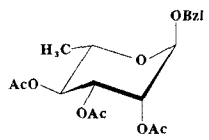
converted into the 2,4-di-*O*-benzyl derivative (**5**) by employing a phase-transfer-catalysed reaction [10] in a good yield. However, using the same conditions, compound **4** with benzyl bromide gave a mixture of the corresponding tri-*O*-benzyl, 2,4-di-*O*-benzyl (**6**), and 3,4-di-*O*-benzyl (**7**) derivatives in a molar ratio of 2:3:3 (TLC). Better selectivities were observed with a kinetically controlled benzylidenation [11] of **3** and **4**, yielding benzyl *endo*-2,3-*O*-benzylidene (**8**) and *p*-nitrophenyl *endo*-2,3-*O*-benzylidene-α-L-rhamnopyranoside (**9**), respectively. Reductive ring-opening of **8** and **9** with the lithium aluminium hydride–aluminium chloride reagent [8] at ambient temperature then resulted almost exclusively in the 2,4-di-*O*-benzyl isomers **5** and **6**, respectively. It has to be noted that in the case of **9** a prolonged reaction time of 30 min causes the reduction of the nitro group.



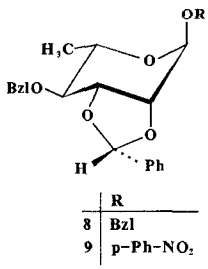
1



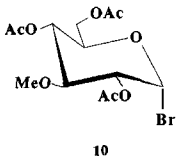
	R	R'	R²
3	Bzl	H	H
4	p-Ph-NO₂	H	H
5	Bzl	Bzl	H
6	p-Ph-NO₂	Bzl	H
7	p-Ph-NO₂	H	Bzl



2



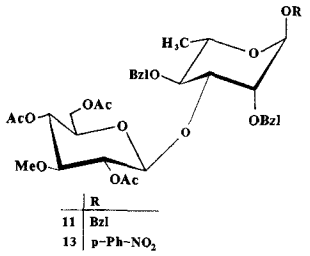
	R
8	Bzl
9	p-Ph-NO₂



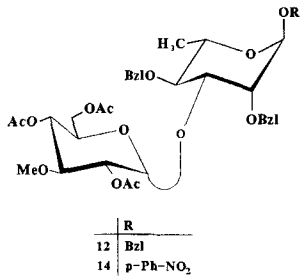
10

Glycosylation of **5** with **10** [12] under *Helferich* conditions gave a mixture of **11** and **12** in a molar ratio of 10:1, demonstrating a non-exclusive stereoselectivity. Almost the same result was observed in the case of **6**, whereby a mercuric bromide-promoted reaction [13] with **10** yielded a 5:1 mixture of **13** and **14**.

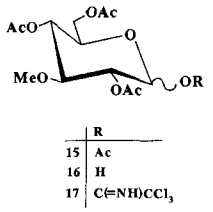
In order to get a better yield and a higher stereoselectivity in the preparation of the disaccharide derivative **11**, the imidate procedure [14] was applied. 1,2,4,6-Tetra-*O*-acetyl-3-*O*-methyl-D-glucopyranose (**15**) [12] was converted into 2,4,6-tri-*O*-acetyl-3-*O*-methyl-D-glucopyranose (**16**) using hydrazine acetate [15], and the corresponding imidate **17** was produced using trichloroacetonitrile and 1,8-diazabicyclo-[5.4.0]undec-7-ene [16]. Then, the glycosyl donor **17** was coupled with **5** in the presence of trimethylsilyl triflate (0.2 equiv) and 4 Å molecular sieves (pellets) at −40 °C. It is noteworthy that *powdered* molecular sieves removed the catalyst from the reaction mixture. The reaction was stereospecific, but a little by-product was formed with higher chromatographic mobility.



	R
11	Bzl
13	p-Ph-NO₂



	R
12	Bzl
14	p-Ph-NO₂

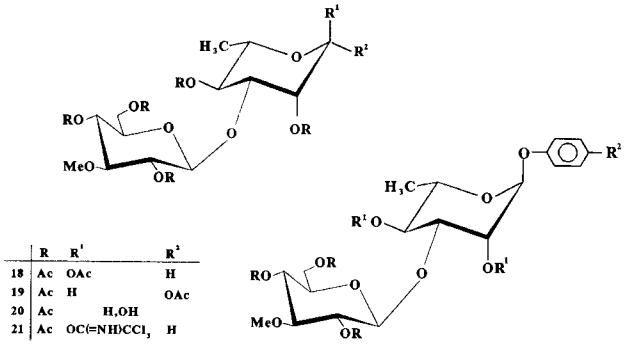


	R
15	Ac
16	H
17	C(=NH)CCl₃

The silver triflate-promoted [17] reaction of **5** with **10** gave exclusively disaccharide derivative **11** in a good yield. Hydrogenolysis (Pd–C, H_2) of **11** and conventional acetylation of the product afforded (2,4,6-tri-*O*-acetyl-3-*O*-methyl-β-D-glucopyranosyl)-(1 → 3)-1,2,4-tri-*O*-acetyl-L-rhamnopyranose as a mixture of the anomers **18** and **19**, and both compounds were isolated and characterised. Compound **18** was converted into **20** by hydrazine acetate, then the corresponding imidate **21** was formed by treatment with trichloroacetonitrile.

In order to prepare 3-*O*-Me-β-D-Glc*p*-(1 → 3)-L-Rha*p* with a *p*-isothiocyanatophenyl aglycone, compound **13** was deacylated with sodium methoxide (2.5 equiv) in methanol (→ **22**) [18]. Reduction of the nitro and benzyl groups in a one pot reaction (Pd–C, H_2, 80% ethanol) gave **23** with 10% impurity. The crude product was reacted with thiophosgene in the presence of $BaCO_3$ (→ **24**) [19], but the impurity could not be removed either by chromatography or by crystallization. Following an other route, pure **24** was prepared from **18** by reaction with *p*-nitrophenol (boron trifluoride etherate; dichloromethane, → **25**) and subsequent deacylation, yielding firstly the *p*-nitrophenyl glycoside **26**. Then, reduction of the nitro

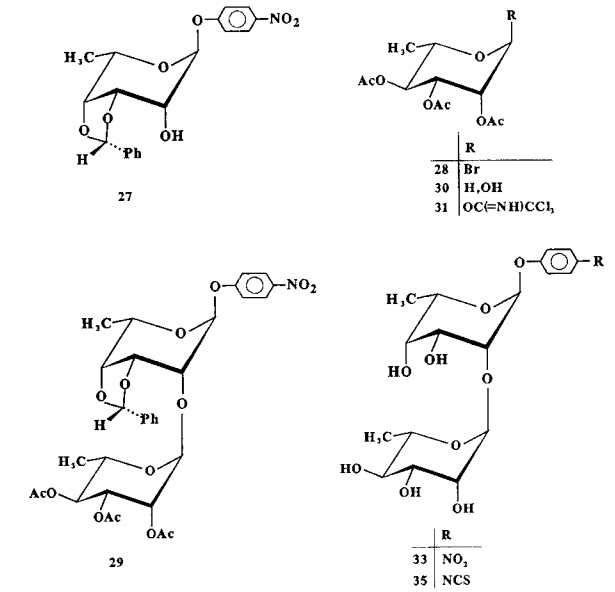
group and reaction with thiophosgene gave the spacer-armed disaccharide **24**.



	R	R'	R²
18	Ac	OAc	H
19	Ac	H	OAc
20	Ac	H,OH	
21	Ac	OC(=NH)CCl₃	H

	R	R'	R²
22	H	Bzl	NO_2
23	H	H	NH_2
24	H	H	NCS
25	Ac	Ac	NO_2
26	H	H	NO_2

The silver triflate-promoted glycosylation of *p*-nitrophenyl *endo*-3,4-*O*-benzylidene-6-deoxy-α-L-talopyranoside (**27**) with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (**28**) at −40 °C gave a complex reaction mixture. In order to prepare the disaccharide **29**, glycosyl donor **28** was converted into imidate **31** by reaction with water in the presence of silver oxide (→ **30**), followed by treatment with trichloroacetonitrile. Coupling of **27** with the rhamnosyl donor **31** at −40 °C gave **29** in an excellent yield (94%). It is noteworthy that under these conditions cleavage or isomerisation of the dioxolane-type benzylidene group have not been observed.



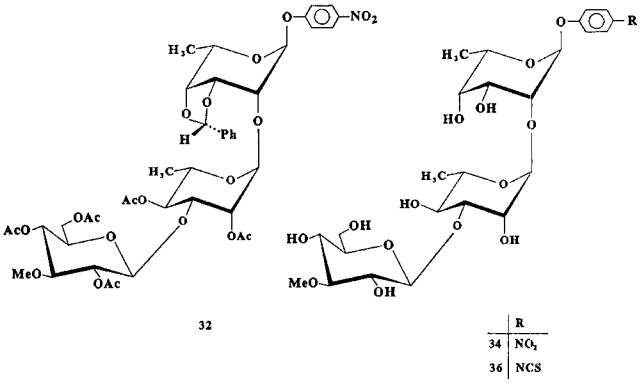
27

	R
28	Br
30	H,OH
31	OC(=NH)CCl₃

29

	R
33	NO_2
35	NCS

Reaction of **27** with the disaccharide imidate **21** yielded the fully protected trisaccharide **32** in a good yield (73%). Deprotection of disaccharide **29** and trisaccharide **32** (deacylation, then acid hydrolysis) gave the *p*-nitrophenyl glycosides **33** and **34**, respectively. The *p*-nitrophenyl group was converted into the *p*-isothiocyanatophenyl group as described for the preparation of **24**, to give the spacer-armed di- (**35**) and trisaccharides (**36**).



32

	R
34	NO_2
36	NCS

The structures of the deprotected compounds **24**, **26**, **33**, **34**, **35**, and **36** were confirmed by ^{13}C NMR spectroscopy. These compounds have been used for the preparation of the neoglycoproteins, which will be published in a separate paper.

Experimental

General.—Melting points (uncorrected) were determined on a Kofler hot-stage apparatus. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. NMR spectra were recorded with a Bruker WP-200 SY or 400 AM spectrometer for solutions in $CDCl_3$ (internal Me_4Si) or in D_2O (internal 1,4-dioxane). In the case of compound **34** COSY and HETCOR spectra were acquired at 200 MHz. A HMBC spectrum was recorded with a Bruker DRX 500 instrument to reveal long-range proton–carbon connectivities. Interglycosidic linkages were unequivocally proved by this method [20]. The reactions were monitored by TLC on Kieselgel 60 F_{254} (Merck, Darmstadt) with detection by charring with H_2SO_4. Kieselgel 60 (Merck) was used for short-column chromatography. The original procedure was used for the regioselective ring-opening reaction of **8** (→ **5**) with the $LiAlH_4$–$AlCl_3$ reagent [8] and for the preparation of compound **27** [4].

Benzyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranoside (**2**).—To a solution of 1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranose (**1**; 39.5 g, 118.9 mmol) in dry CH_2Cl_2 (100 mL) were added 4 Å molecular sieves (10 g pellets) and benzyl alcohol (20.7 mL, 200 mmol), and the mixture was stirred under Ar for 30 min. After the addition of $BF_3 \cdot Et_2O$ (24.6 mL, 200 mmol) at 0 °C, the mixture was stirred for 2 h at 0 °C, then at ambient temperature overnight. Pyridine (20 mL) was added, and the mixture was filtered through Celite, then the cake was washed with CH_2Cl_2 (2 × 50 mL). The combined filtrates were washed with aq 5% $NaHCO_3$ (2 × 50 mL) and water (3 × 50 mL), dried, and concentrated. The crystalline residue was recrystallized from EtOH to give **2** (17.48 g, 38.6%); mp 108–110 °C, lit. 110 °C [9]; $[\alpha]_D$ −75° (*c* 0.52, $CHCl_3$), lit. −73° ($CHCl_3$) [9]; ^1H NMR ($CDCl_3$): δ 7.38–7.32 (m, 5 H, Ph), 5.34 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.28 (dd, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 5.08 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.80 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.63 (dd, 2 H, PhCH_2), 3.91 (m, 1 H, $J_{5,6}$ 6.2 Hz, H-5), 2.13, 2.05, and 1.98 (3 s, each 3 H, 3 Ac), 1.21 (d, 3 H, CMe). The mother liquor was concentrated and subjected to column chromatography (99:1 → 95:5 CH_2Cl_2–EtOAc) yielding an additional amount of **2** (13.78 g, 30.5%). Overall yield: 69.1%.

*Benzyl 4-O-benzyl-*endo*-2,3-O-benzylidene-α-L-rhamnopyranoside* (**8**).—To a solution of benzyl 4-*O*-benzyl-α-L-rhamnopyranoside (**3**; 3.44 g, 10 mmol) in α,α-dimethoxytoluene (15 mL) was added *p*-toluenesulfonic acid (150 mg), and the mixture was stirred for 20 min at room temperature. Then, the mixture was diluted with CH_2Cl_2 (160 mL), washed with aq 5% $NaHCO_3$ (2 × 25 mL) and water (3 × 25 mL), dried, filtered, and concentrated. Column chromatography (hexane → 7:3 hexane–EtOAc) of the residue yielded **8** (3.42 g, 79%); mp 52–54 °C (from hexane), lit. 53–54 °C [8]; $[\alpha]_D$ −63° (*c* 1, $CHCl_3$), lit. −57° ($CHCl_3$) [8]; ^1H NMR ($CDCl_3$): δ 7.50–7.22 (m, 15 H, 3 Ph), 5.91 (s, 1 H, PhC*H*), 5.18 (s, 1 H, H-1), 4.84–4.42 (m, 5 H, 2 PhCH_2 and H-3), 4.28 (d, 1 H, H-2), 3.82 (m, 1 H, H-5), 3.27 (dd, 1 H, H-4), 1.26 (d, 3 H, CMe).

p-*Nitrophenyl 4-O-benzyl-*endo*-2,3-O-benzylidene-α-L-rhamnopyranoside* (**9**).—To a solution of *p*-nitrophenyl 4-*O*-benzyl-α-L-rhamnopyranoside [3] (**4**; 1126 mg, 3 mmol) in α,α-dimethoxytoluene (4 mL) was added *p*-toluenesulfonic acid (100 mg) and the mixture was stirred for 15 min at room temperature, then worked-up as described for **8**. Column chromatography (hexane → 7:3 hexane–EtOAc) of the residue yielded **9**, isolated as a syrup (1126 mg, 81%); $[\alpha]_D$ −133° (*c* 0.11, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.21 (d, 2 H, aromatic), 7.56–7.10 (m, 12 H, aromatic), 5.99 (s, 1 H, PhC*H*), 5.93 (s, 1 H, H-1), 4.90–4.46 (m, 4 H, PhCH_2, H-2,3), 3.78 (m, 1 H, H-5), 3.34 (dd, 1 H, H-4), 1.20 (d, 3 H, CMe). Anal. Calcd for $C_{26}H_{25}NO_7$: C, 67.37; H, 5.44. Found: C, 67.51; H, 5.40.

p-*Nitrophenyl 2,4-di-O-benzyl-* (**6**) *and* p-*nitrophenyl 3,4-di-O-benzyl-α-L-rhamnopyranoside* (**7**).—*Procedure A.*—A mixture of *p*-nitrophenyl-4-*O*-benzyl-α-L-rhamnopyranoside [3] (**4**; 751 mg, 2 mmol), CH_2Cl_2 (10 mL), aq 20% NaOH (10 mL), tetrabutylammonium bromide (0.64 g, 2 mmol), and benzyl bromide (0.29 mL, 2.4 mmol) was vigorously stirred overnight at room temperature. Then, the mixture was diluted with CH_2Cl_2 (60 mL), and the organic layer was separated and washed with water (4 × 20 mL), dried ($MgSO_4$), and concentrated. Column chromatography (98:2 CH_2Cl_2–acetone) of the residue gave **6** (257 mg, 27.6%) and **7** (240 mg, 25.8%). Compound **6** had $[\alpha]_D$ −80.6° (*c* 1.39, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.17 and 7.07 (2 d, each 2 H, aromatic), 7.43–7.22 (m, 10 H, aromatic), 5.58 (d, 1 H, $J_{1,2}$ 1 Hz, H-1), 4.95–4.63 (m, 4 H, 2 PhCH_2), 4.13 (m, 1 H, after addition of D_2O dd, $J_{2,3}$ 3.8, $J_{3,4}$ 9 Hz, H-3), 3.95 (dd, 1 H, H-2), 3.68 (m, 1 H, H-5), 3.43 (t, 1 H, H-4), 2.41 (d, 1 H, OH, disappeared after addition of D_2O), 1.29 (d, 3 H, CMe). Anal. Calcd for $C_{26}H_{27}NO_7$: C, 67.08; H, 5.85. Found: C, 67.19; H, 5.92. Compound **7** had $[\alpha]_D$ −55.9° (*c* 0.86, $CHCl_3$); Anal. Found: C, 67.26; H, 5.87.

Procedure B.—To a solution of **9** (927 mg, 2 mmol) in 1:1 Et_2O–CH_2Cl_2 (10 mL) was added, with stirring, a solution of $LiAlH_4$ (114 mg, 3 mmol) and $AlCl_3$ (400 mg, 3 mmol) in Et_2O (10 mL), and stirring was continued for an additional 10 min. The mixture was diluted with CH_2Cl_2 (60 mL) and the excess reagent was decomposed with EtOAc (5 mL), and $Al(OH)_3$ was precipitated with water (5 mL). The organic layer was decanted, washed with water (2 × 15 mL), dried ($MgSO_4$), and concentrated. The residue contained **6** and **7** in a molar ratio of 9:1 (TLC). Compound **6** was isolated by column chromatography yielding 735 mg (78.9%).

Benzyl (2,4,6-tri-O-acetyl-3-O-methyl-β-D-glucopyranosyl)-(1 → 3)- (**11**) *and benzyl (2,4,6-tri-O-acetyl-3-O-methyl-α-D-glucopyranosyl)-(1 → 3)-2,4-di-O-benzyl-α-L-rhamnopyranoside* (**12**).—*Procedure A.* — A solution of **5** (869 mg, 2 mmol) and $Hg(CN)_2$ (606 mg, 2.4 mmol) in dry toluene (10 mL)

and nitromethane (10 mL) was concentrated to half its volume at atmospheric pressure. After cooling, 920 mg (2.4 mmol) of 2,4,6-tri-*O*-acetyl-3-*O*-methyl-α-D-glucopyranosyl bromide (**10**) [12] was added, and the mixture was stirred for 2 h at 50 °C, then diluted with CH_2Cl_2 (40 mL). After filtration, the filtrate was washed with aq 5% KI (2 × 10 mL) and water (2 × 10 mL), dried ($MgSO_4$), and concentrated. The products were separated by column chromatography (95:5 CH_2Cl_2–EtOAc) yielding 1017 mg (69%) of **11** and 98 mg (6.6%) of **12**. Compound **11** had $[\alpha]_D$ −57° (*c* 1.39, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.43–7.20 (m, 15 H, aromatic), 5.16–4.91 (m, 2 H, H-2′,4′), 4.87–4.51 (m, 7 H, 3 PhCH_2 and H-1), 4.40 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1′), 3.42 (s, 3 H, OMe), 2.10, 1.89, and 1.81 (3 s, each 3 H, 3 Ac), 1.27 (d, 3 H, CMe). Anal. Calcd for $C_{40}H_{48}O_{13}$: C, 65.20; H, 6.57. Found: C, 65.00; H, 6.52. Compound **12** had $[\alpha]_D$ +18° (*c* 0.53, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.43–7.20 (m, 15 H, aromatic), 5.31 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′), 5.07–4.38 (m, 9 H, 3 PhCH_2, H-1,2′,4′), 3.44 (s, 3 H, OMe), 1.99, 1.98, and 1.84 (3 s, each 3 H, 3 Ac), 1.33 (d, 3 H, CMe). Anal. Found: C, 65.39; H, 6.58.

Procedure B. — To a solution of 1,2,4,6-tetra-*O*-acetyl-3-*O*-methyl-D-glucopyranose [12] (**15**; 4.25 g, 11.73 mmol) in dry DMF (12 mL) was added hydrazine acetate [15] (1.30 g, 14.1 mmol) and the mixture was kept for 20 min at 50 °C. After cooling, the mixture was diluted with EtOAc (300 mL) and washed with aq 5% NaCl (3 × 40 mL). The combined washings were extracted with EtOAc (40 mL). The combined organic phase was washed with water (40 mL), dried, filtered, and concentrated. The obtained crude 2,4,6-tri-*O*-acetyl-3-*O*-methyl-D-glucopyranose (**16**) was dissolved in dry CH_2Cl_2 (40 mL), then trichloroacetonitrile (11.73 mL, 117 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene [16] (2.39 mL, 16 mmol) were added. The mixture was stirred for 20 min, then concentrated, and the residue was purified by column chromatography (9:1 CH_2Cl_2–EtOAc containing 0.5% Et_3N) to yield 2,4,6-tri-*O*-acetyl-3-*O*-methyl-α-D-glucopyranosyl trichloroacetimidate (**17**), isolated as a syrup (3.28 g, 60.2%). Only the pure fractions, free of UV active impurities, were collected; $[\alpha]_D$ +85.7° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.67 (s, 1 H, NH), 6.52 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.12 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.03 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.27–4.04 (m, 3 H, H-5,6a,6b), 3.82 (t, 1 H, $J_{3,4}$ 10 Hz, H-3), 3.50 (s, 3 H, OMe), 2.12 and 2.08 (2 s, 3,6 H, 3 Ac).

A solution of **5** (435 mg, 1 mmol) and **17** (558 mg, 1.2 mmol) in dry CH_2Cl_2 (8 mL), containing 4 Å molecular sieves (2 g pellets), was cooled to −40°C under Ar. Then, a solution of Me_3SiOTf (19.3 μL, 0.1 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise and the mixture was stirred for 30 min at −40 °C. After the addition of pyridine (1 mL) and CH_2Cl_2 (50 mL), the mixture was filtered through Celite, the filtrate was washed with aq 5% $NaHCO_3$ (10 mL) and water (2 × 10 mL), dried, and concentrated and co-concentrated with toluene (3 × 20 mL). The residue was purified by column chromatography (95:5 CH_2Cl_2–EtOAc) to give pure **11** (575 mg, 78%); $[\alpha]_D$ −55.5° (*c* 0.82, $CHCl_3$). A by-product with higher chromatographic mobility was also isolated (38 mg).

Procedure C. — To a stirred solution of **5** (435 mg, 1 mmol) and **10** (460 mg, 1.2 mmol) in dry CH_2Cl_2 (8 mL) was added 4 Å powdered molecular sieves (1 g), and the mixture was stirred under Ar for 15 min. A solution of silver triflate [17] (308 mg, 1.2 mmol) in 8 mL dry toluene was added to the mixture over a period of 5 min at −50 °C. Stirring was continued for an additional hour while the temperature was raised to −40 °C. The mixture was neutralized with pyridine, diluted with CH_2Cl_2 (100 mL), and filtered through Celite. The filtrate was washed with aq 10% sodium thiosulfate (2 × 20 mL) and water (2 × 20 mL), dried, and evaporated. The product was purified by column chromatography giving pure **11** (659 mg, 89.4%); $[\alpha]_D$ −54.4° (*c* 0.40, $CHCl_3$).

p-*Nitrophenyl (2,4,6-tri*-O-*acetyl-3*-O-*methyl-β*-D-*glucopyranosyl)-(1 → 3)-* (**13**) *and* p-*nitrophenyl (2,4,6-tri*-O-*acetyl-3*-O-*methyl-α*-D-*glucopyranosyl)-(1 → 3)-2,4-di*-O-*benzyl-α*-L-*rhamnopyranoside* (**14**). —A mixture of **6** (400 mg, 0.859 mmol), dry CH_2Cl_2 (10 mL), 2,4,6-tri-*O*-acetyl-3-*O*-methyl-α-D-glucopyranosyl bromide (**10**) [12] (395 mg, 1.03 mmol), and 4 Å powdered molecular sieves (1 g), was stirred under Ar for 15 min. Then, $HgBr_2$ (371 mg, 1.03 mmol) was added [13] and stirring was continued for 2 days at room temperature. The mixture was diluted with CH_2Cl_2 (100 mL), filtered, and the filtrate was washed with aq 5% KI (2 × 15 mL), dried ($MgSO_4$), and concentrated. Column chromatography (95:5 CH_2Cl_2–EtOAc) of the residue gave amorphous **13** (292 mg, 44.3%); $[\alpha]_D$ −79° (*c* 0.47, $CHCl_3$); NMR data ($CDCl_3$): ^1H (400 MHz), δ 8.15 and 7.03 (2 d, each 2 H, aromatic), 7.44–7.25 (m, 10 H, aromatic), 5.43 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 5.12 (dd, 1 H, H-2′), 5.03 (t, 1 H, H-4′), 4.86 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.90–4.54 (m, 4 H, 2 PhCH_2), 4.19–4.05 (m, 4 H,

H-2,3,6a',6b'), 3.65–3.60 (m, 3 H, H-4,5,5'), 3.48 (t, 1 H, H-3'), 3.41 (s, 3 H, OMe), 2.11, 1.95, and 1.91 (3 s, each 3 H, 3 Ac), 1.20 (d, 3 H, CMe); ^{13}C (100.6 MHz), δ 101.93 (C-1'), 96.62 (C-1), 58.91 (OMe). Anal. Calcd for $C_{39}H_{45}NO_{15}$: C, 61.01; H, 5.91. Found: C, 60.82; H, 5.97.

Further elution gave **14** (92 mg, 13.9%); mp 176–177 °C (from cyclohexane–EtOH); $[\alpha]_D$ −6° (*c* 0.60, $CHCl_3$); NMR data ($CDCl_3$): ^{1}H (400 MHz), δ 8.17 and 7.07 (2 d, each 2 H, aromatic), 7.41–7.27 (m, 10 H, aromatic), 5.49 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1), 5.38 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1'), 5.02 (dd, 1 H, H-4'), 4.86 (dd, 1 H, H-2'), 4.92–4.58 (m, 4 H, 2 PhCH_2), 4.21 (dd, 1 H, H-3), 4.13 (m, 1 H, H-5'), 4.00–3.92 (m, 3 H, H-2,6a',6b'), 3.77–3.69 (m, 3 H, H-3',4,5), 3.44 (s, 3 H, OMe), 2.02, 1.96, and 1.90 (3 s, each 3 H, 3 Ac), 1.30 (d, 3 H, CMe); ^{13}C (100.6 MHz), δ 96.16 (C-1), 92.41 (C-1'), 60.17 (OMe). A mixture of **13** and **14** (125 mg, 18.9%) was also isolated.

*(2,4,6-Tri-*O*-acetyl-3-*O*-methyl-β-*D*-glucopyranosyl)-(1 → 3)-1,2,4-tri-*O*-acetyl-α-* (**18**) *and β-*L*-rhamnopyranose* (**19**).—Compound **11** (1 g) was hydrogenated over Pd–C (100 mg) in 10:1 EtOH–HOAc (33 mL) for 2 days. After filtration, the filtrate was concentrated and co-concentrated with toluene (3 × 15 mL). The residue was conventionally acetylated in 1:1 pyridine–Ac_2O (30 mL), and the product was purified by column chromatography (7:3 CH_2Cl_2–EtOAc) to yield **18** (0.57 g, 71%) and **19** (64 mg, 8%). Compound **18** had mp 185–187 °C (from EtOH); $[\alpha]_D$ −36.5° (*c* 0.72, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.99 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 5.17 (dd, 1 H, $J_{2,3}$ 3.8 Hz, H-2), 5.11 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.05 (t, 1 H, $J_{4',5'}$ 9.8 Hz, H-4'), 4.93 (dd, 1 H, $J_{2',3'}$ 9.8 Hz, H-2'), 4.55 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 4.15 (d, 2 H, H-6a',6b'), 4.06 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 3.81 (m, 1 H, H-5), 3.57 (m, 1 H, H-5'), 3.44 (t, 1 H, $J_{3',4'}$ 9.8 Hz, H-3'), 3.37 (s, 3 H, OMe), 2.13, 2.12, 2.10, and 2.09 (4 s, 6,3,3,6 H, 6 Ac), 1.19 (d, 3 H, CMe). Anal. Calcd for $C_{25}H_{36}O_{16}$: C, 50.67, H, 6.12. Found: C, 50.50; H, 6.11. Compound **19** had mp 178–180°C (from EtOH); $[\alpha]_D$ +4.3° (*c* 0.28, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.72 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 5.44 (dd, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 5.08–4.94 (m, 2 H, H-4,4'), 4.88 (dd, 1 H, $J_{2',3'}$ 9.7 Hz, H-2'), 4.48 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.11 (d, 2 H, H-6a',6b'), 3.79 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 3.60–3.44 (m, 2 H, H-5,5'), 3.39 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3'), 3.33 (s, 3 H, OMe), 2.12, 2.08, 2.06, 2.05, 2.04, and 2.03 (6 s, each 3 H, 6 Ac), 1.22 (d, 3 H, CMe). Anal. Found: C, 50.52; H, 6.15.

*(2,4,6-Tri-*O*-acetyl-3-*O*-methyl-β-*D*-glucopyranosyl)-(1 → 3)-2,4-di-*O*-acetyl-α-*L*-rhamnopyranosyl trichloroacetimidate* (**21**).—Compound **18** (450 mg, 0.76 mmol) was converted into imidate **21**, via **20**, as described for the preparation of **17** from **15**. Yield: 314 mg (59.5%); mp 149–156°C; $[\alpha]_D$ −33° (*c* 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.74 (bs, 1 H, NH), 6.20 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.35 (dd, 1 H, H-2), 5.21–4.91 (m, 3 H, H-4,2',4'), 4.56 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.19–4.07 (m, 3 H, H-3,6a',6b'), 3.95 (m, 1 H, H-5), 3.58 (m, 1 H, H-5'), 3.44 (t, 1 H, H-3'), 3.37 (s, 3 H, OMe), 2.16, 2.14, 2.12, 2.10, and 2.09 (5 s, each 3 H, 5 Ac), 1.22 (d, 3 H, CMe). This compound was used for the next step without further purification.

*p-Nitrophenyl (3-*O*-methyl-β-*D*-glucopyranosyl)-(1 → 3)-2,4-di-*O*-benzyl-α-*L*-rhamnopyranoside* (**22**).—To a solution of **13** (307 mg, 0.4 mmol) in dry MeOH (50 mL) was added NaOMe (54 mg, 1 mmol), and the mixture was kept for 3 days at ambient temperature. The solution was neutralized with Amberlite IR 120 (H^+) resin, filtered, and concentrated. Column chromatography (8:2 CH_2Cl_2–acetone) of the residue gave glassy **22** (160 mg, 62.3%); $[\alpha]_D$ −103° (*c* 0.43, MeOH); ^{1}H NMR ($CDCl_3$): δ 8.19 (d, 2 H, aromatics), 7.42–7.23 (m, 10 H, aromatics), 7.08 (d, 2 H, aromatics), 4.85–4.43 (m, 5 H, H-1 and 2 PhCH_2), 4.37 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1'), 3.53 (s, 3 H, OMe), 2.68 (bs, 1 H, OH), 1.70 (bs, 2 H, 2 OH), 1.23 (d, 3 H, CMe). Anal. Calcd for $C_{33}H_{39}NO_{12}$: C, 61.77; H, 6.13. Found: C, 61.92; H, 6.10.

*Attempted preparation of p-isothiocyanatophenyl (3-*O*-methyl-β-*D*-glucopyranosyl)-(1 → 3)-α-*L*-rhamnopyranoside* (**24**).—Compound **22** (64 mg, 0.1 mmol) was hydrogenated over Pd–C (120 mg) in aq 80% EtOH (15 mL) and the reaction was monitored by TLC. Conversion of the nitro group into an amino group was rather quick (9:1 CH_2Cl_2–MeOH), but the removal of the benzyl groups was not completed within days (8:2 CH_2Cl_2–MeOH). After 4 days, the catalyst was filtered out, the pH of the filtrate was adjusted to 8 with $BaCO_3$ and maintained at 8 by adding $BaCO_3$ whilst thiophosgene (0.2 mL) was added, and the mixture was stirred for 1 h at room temperature. Filtration and concentration yielded a slightly coloured syrup, which was purified by column chromatography (95:5 CH_2Cl_2–MeOH) to give an impure material (37 mg) which could not be purified either by repeated chromatography or by crystallization (from EtOH or EtOAc–MeOH).

*p-Nitrophenyl (2,4,6-tri-*O*-acetyl-3-*O*-methyl-β-*D*-glucopyranosyl)-(1 → 3)-2,4-di-*O*-acetyl-α-*L*-rhamnopyranoside* (**25**).—To a stirred mixture of **18** (148 mg, 250 μmol), *p*-nitrophenol (52 mg, 375 μmol), 4

Å molecular sieves (1 g pellets), and dry CH_2Cl_2 (5 mL) under Ar was added $BF_3 \cdot Et_2O$ (31 μL, 250 μmol). After 24 h an additional amount of $BF_3 \cdot Et_2O$ (31 μL) was added, and stirring was continued for an additional day. Pyridine (1 mL) and CH_2Cl_2 (30 mL) were added, the mixture was filtered through Celite, and the filtrate was washed with aq 5% $NaHCO_3$ (2 × 10 mL) and water (3 × 10 mL), dried, and concentrated. The residue was purified by column chromatography to yield pure **25** (69 mg, 41%); $[\alpha]_D$ −71.6° (*c* 0.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.22–7.14 (2 d, 4 H, aromatics), 5.58 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 5.34 (dd, 1 H, H-2), 5.22–4.91 (m, 3 H, H-4,2′,4′), 4.61 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1′), 4.28–4.10 (m, 3 H, H-3,6a′,6b′), 3.87–3.57 (m, 2 H, H-5,5′), 3.48 (t, 1 H, H-3′), 3.38 (s, 3 H, OMe), 2.18, 2.13, 2.11, 2.09, and 2.08 (5 s, each 3 H, 5 Ac), 1.18 (d, 3 H, CMe). Anal. Calcd for $C_{29}H_{37}NO_{17}$: C, 51.86; H, 5.55. Found: C, 52.04; H, 5.60.

p-*Nitrophenyl (3-*O*-methyl-β-*D*-glucopyranosyl)-(1 → 3)-α-*L*-rhamnopyranoside* (**26**).—Compound **25** (67 mg, 0.1 mmol) was deacetylated as described for the preparation of **22** from **13**. The product was purified by column chromatography (9:1 CH_2Cl_2–MeOH) yielding **26**, isolated as a foam (30 mg, 65%); $[\alpha]_D$ −119° (*c* 0.52, MeOH); ^{13}C NMR (D_2O): δ 161.80 and 143.32 (aromatic-q), 127.01 and 117.72 (aromatic), 104.80 (C-1′), 98.81 (C-1), 86.14 (C-3′), 80.93 (C-3), 61.49 (C-6′), 60.63 (OMe), 17.72 (C-6). Anal. Calcd for $C_{19}H_{27}NO_{12}$: C, 49.45; H, 5.90. Found: C, 49.67; H, 5.93.

p-*Nitrophenyl* endo-*3,4-*O*-benzylidene-6-deoxy-α-*L*-talopyranoside* (**27**).—This compound was prepared as described earlier [4]. The product was crystallized from hexane–EtOAc to give pure **27**; mp 89–90 °C; $[\alpha]_D$ −106.8° (*c* 1.1, $CHCl_3$), lit. −106° ($CHCl_3$) [4].

p-*Nitrophenyl (2,3,4-tri-*O*-acetyl-α-*L*-rhamnopyranosyl)-(1 → 2)-*endo*-3,4-*O*-benzylidene-6-deoxy-α-*L*-talopyranoside* (**29**).—A mixture of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (**28**; 353 mg, 1 mmol), 'old' Ag_2O (463 mg, 2 mmol), CH_2Cl_2 (2 mL) and water (0.1 mL) was stirred for 1 h at room temperature, then diluted with CH_2Cl_2 (20 mL), and filtered through Celite. The filtrate was washed with aq 10% $Na_2S_2O_3$ (5 mL) and water (3 × 5 mL), dried, and concentrated. The residue was converted into imidate **31** as described for **17**. Column chromatography (9:1 CH_2Cl_2–EtOAc, containing 0.5% Et_3N) gave **31** (276 mg, 63%); $[\alpha]_D$ −38.3° (*c* 1.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.74 (bs, 1 H, NH), 6.20 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 5.46 (dd, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 5.37 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.17 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.09 (m, 1 H, H-5), 2.19, 2.08, and 2.01 (3 s, each 3 H, 3 Ac), 1.28 (d, 3 H, CMe).

A solution of *p*-nitrophenyl *endo*-3,4-*O*-benzylidene-6-deoxy-α-L-talopyranoside (**27**) (93.3 mg, 250 μmol) and 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl trichloroacetimidate (**31**; 163 mg, 375 μmol) in dry CH_2Cl_2 (4 mL), containing 4 Å molecular sieves (0.5 g pellets), was cooled to −40 °C under Ar. A solution of Me_3SiOTf (9.7 μL, 50 nmol) in dry CH_2Cl_2 (1 mL) was added dropwise and the mixture was stirred for 20 min at −40 °C. After the addition of pyridine (0.5 mL) and CH_2Cl_2 (30 mL), the mixture was filtered through Celite, the filtrate was washed with aq 5% $NaHCO_3$ (5 mL) and water (3 × 5 mL), dried, and concentrated and co-concentrated with toluene (3 × 10 mL). The product was purified by column chromatography (95:5 CH_2Cl_2–EtOAc) to give **29** (152 mg, 94.2%); $[\alpha]_D$ −91.5° (*c* 1.18, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.24 and 7.14 (2 d, 4 H, aromatics), 7.67–7.40 (m, 5 H, Ph), 5.82 (s, 1 H, PhC*H*), 5.73 (d, 1 H, $J_{1,2}$ 6.4 Hz, H-1), 5.30 (dd, 1 H, H-2′), 5.19 (dd, 1 H, $J_{2',3'}$ 3.5, $J_{3',4'}$ 10 Hz, H-3′), 5.06 (t, 1 H, H-4′), 5.06 (bs, 1 H, H-1′), 4.71 (dd, 1 H, $J_{2,3}$ 2.8, $J_{3,4}$ 8.2 Hz, H-3), 2.17, 1.99, and 1.93 (3 s, each 3 H, 3 Ac), 1.29 and 1.21 (2 d, each 3 H, 2 CMe). Anal. Calcd for $C_{31}H_{35}NO_{14}$: C, 57.67; H, 5.46. Found: C, 57.91; H, 5.50.

p-*Nitrophenyl (2,4,6-tri-*O*-acetyl-3-*O*-methyl-β-*D*-glucopyranosyl)-(1 → 3)-(2,4-di-*O*-acetyl-α-*L*-rhamnopyranosyl)-(1 → 2)-*endo*-3,4-*O*-benzylidene-6-deoxy-α-*L*-talopyranoside* (**32**).—Compound **27** (101 mg, 0.27 mmol) was reacted with imidate **21** (209 mg, 0.3 mmol) as described for **29**. Column chromatography of the crude product yielded amorphous **32** (178 mg, 72.8%); $[\alpha]_D$ −86.8° (*c* 0.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.24 and 7.14 (2 d, 4 H, aromatic), 7.67–7.40 (m, 5 H, aromatic), 5.81 (s, 1 H, PhC*H*), 5.67 (d, 1 H, $J_{1,2}$ 6 Hz, H-1), 5.22 (dd, 1 H, H-2′), 5.12–4.65 (m, 4 H, H-1′,4′,2″,4″), 4.39 (d, 1 H, $J_{1'',2''}$ 7.8 Hz, H-1″), 3.48 (m, 1 H, H-5″), 3.34 (t, 1 H, H-3″), 3.32 (s, 3 H, OMe), 2.10, 2.04, 2.02, and 1.82 (4 s, 3,6,3,3 H, 5 Ac), 1.28 and 1.17 (2 d, each 3 H, 2 CMe). Anal. Calcd for $C_{42}H_{51}NO_{21}$: C, 55.69; H, 5.68. Found: C, 55.81; H, 5.73.

p-*Nitrophenyl* α-*L*-rhamnopyranosyl-(1 → 2)-6-deoxy-α-*L*-talopyranoside* (**33**).—To a solution of **29** (129 mg, 0.2 mmol) in dry MeOH (4 mL) was added a catalytic amount of NaOMe. The mixture was kept at room temperature overnight, then neutralized with HOAc, and concentrated. The residue was dissolved in aq 60% HOAc (4 mL) and the solution was kept

Table 1
NMR data for trisaccharide **34** in D_2O (δ in ppm, J in Hz)

Sugar unit	Atom No.	δ, ^{13}C	δ, ^{1}H	J, ^{1}H
6-deoxy-Tal	1	97.86	5.70	$J_{1,2}$ 1.2
	2	76.94	4.05	$J_{2,3}$ 3.6
	3	66.28	4.16	$J_{3,4}$ 3.7
	4	71.87	3.67	$J_{4,5}$ 1.1
	5	69.16	3.99	$J_{5,6}$ 6.6
	6	16.06	1.10	
Rha	1	103.17	4.98	$J_{1',2'}$ 1.8
	2	70.36	4.27	$J_{2',3'}$ 3.3
	3	80.23	3.92	$J_{3',4'}$ 9.7
	4	71.70	3.55	$J_{4',5'}$ 9.7
	5	70.00	3.78	$J_{5',6'}$ 6.1
	6	17.49	1.20	
Glc	1	104.24	4.65	$J_{1'',2''}$ 8.1
	2	73.46	3.34	$J_{2'',3''}$ 9.5
	3	85.86	3.20	$J_{3'',4''}$ 9.5
	4	69.51	3.44	$J_{4'',5''}$ 9.5
	5	76.32	3.38	$J_{5'',6a''}$ 2.3
				$J_{5'',6b''}$ 5.3
	6	61.09	3.81 (a)	
			3.65 (b)	
	Aromatic (q)	161.50		
		143.00		
	Aromatic	126.77	8.08	
		117.29	7.09	

for 20 min at 70 °C. After concentration and co-concentration with toluene (3 × 5 mL), the product was purified by column chromatography (75:25 CH_2Cl_2–MeOH) to give amorphous **33** (58 mg, 67%); $[\alpha]_D$ −64° (*c* 0.73, MeOH); ^{13}C NMR (D_2O): δ 103.83 (C-1′), 98.39 (C-1), 77.57 (C-2), 17.75 (C-6′), 16.38 (C-6). Anal. Calcd for $C_{18}H_{25}NO_{11}$: C, 50.11; H, 5.84. Found: C, 50.50; H, 5.86.

p-*Nitrophenyl (3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-6-deoxy-α-L-talopyranoside* (**34**).—To a solution of **32** (90.6 mg, 0.1 mmol) in dry MeOH (5 mL) was added NaOMe (8.1 mg, 0.15 mmol). The mixture was kept for 2 days at room temperature, then neutralized with Amberlite IR 120 (H^+) resin, filtered, and concentrated. The residue was dissolved in aq 60% HOAc (8 mL), and the solution was stirred for 20 min at 70 °C, then concentrated and co-concentrated with toluene (3 × 10 mL). The product was purified by column chromatography (9:1 CH_2Cl_2–MeOH) to give **34**, isolated as a foam (49 mg, 69%); $[\alpha]_D$ −103° (*c* 0.96, MeOH). For ^{1}H and ^{13}C NMR data, see Table 1. Anal. Calcd for $C_{25}H_{37}NO_{16}$: C, 49.42; H, 6.14. Found: C, 49.76; H, 6.09.

p-*Isothiocyanatophenyl (3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-α-L-rhamnopyranoside* (**24**).—Compound **26** (23.1 mg, 50 μmol) was hydrogenated over Pd–C (8 mg) in aq 80% EtOH (4 mL) for 2 h, then the catalyst was filtered out. The pH of the filtrate was adjusted to 8 with $BaCO_3$ and maintained at 8 by adding $BaCO_3$ whilst thiophosgene (80 μL) was added, and the mixture was stirred for 1 h at room temperature. Filtration and concentration yielded a slightly coloured syrup. Column chromatography (9:1 CH_2Cl_2–MeOH) of the crude product gave **24** (15 mg, 63%); $[\alpha]_D$ −72.8° (*c* 0.75, MeOH); ^{13}C NMR (D_2O): δ 128.07 (aromatic), 118.44 (aromatic), 104.48 (C-1′), 94.64 (C-1), 86.06 (C-3′), 61.54 (C-6′), 60.49 (OMe), 17.97 (C-6). FABMS(+): Calcd for $C_{20}H_{27}NO_{10}S$ (473.49). Found: 473 $[M]^+$.

p-*Isothiocyanatophenyl α-L-rhamnopyranosyl-(1 → 2)-6-deoxy-α-L-talopyranoside* (**35**).—Compound **33** (21.6 mg, 50 μmol) was converted into **35** as described for **24**. Column chromatography (9:1 CH_2Cl_2–MeOH) of the product yielded pure **35** (14.5 mg, 65%); $[\alpha]_D$ −90.9° (*c* 0.8, MeOH); ^{13}C NMR (1:1 D_2O–Me_2SO-d_6): δ 104.33 (C-1′), 99.07 (C-1), 78.34 (C-2), 18.41 (C-6′), 17.10 (C-6). FABMS(+): Calcd for $C_{19}H_{25}NO_9S$ (443.46). Found: 467 [M + 1 + Na]$^+$.

p-*Isothiocyanatophenyl (3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-6-deoxy-α-L-talopyranoside* (**36**).—Compound **34** (30.4 mg, 50 μmol) was converted into **36** as described for **24**. Column chromatography (85:15 CH_2Cl_2–MeOH) of the product gave pure **36** (18.2 mg, 59%); $[\alpha]_D$ −85.7° (*c* 1.89, MeOH); ^{13}C NMR (D_2O): δ 103.52 (C-1″), 102.73 (C-1′), 97.48 (C-1), 60.35 (C-6″), 59.79 (OMe), 17.23 (C-6′), 15.84 (C-6). FABMS(+): Calcd for $C_{26}H_{37}NO_{14}S$ (619.63). Found: 644 [M + 1 + Na]$^+$.

Acknowledgements

We thank the National Research Foundation (OTKA F 4066 to J.K.; OTKA 1694 to Z.Sz.; OTKA T014982 to Gy.B.) for financial support.

References

[1] Z. Szurmai, J. Kerékgyártó, J. Harangi, and A. Lipták, *Carbohydr. Res.*, 164 (1987) 313–325.
[2] A. Lipták, J. Kerékgyártó, Z. Szurmai, and H. Duddeck, *Carbohydr. Res.*, 175 (1988) 241–248.

[3] A. Borbás and A. Lipták, *Carbohydr. Res.*, 241 (1993) 99–116.
[4] J. Kerékgyártó, Z. Szurmai, and A. Lipták, *Carbohydr. Res.*, 245 (1993) 65–80.
[5] I. Bajza, J. Kerékgyártó, J. Hajkó, L. Szilágyi, and A. Lipták, *Carbohydr. Res.*, 253 (1994) 111–120.
[6] A. Lipták, A. Borbás, and I. Bajza, *Med. Res. Rev.*, 14 (1994) 307–352.
[7] P.J. Brennan, G.O. Aspinall, and J.E. Nam Shin, *J. Biol. Chem.*, 256 (1981) 6817–6822.
[8] A. Lipták, P. Fügedi, and P. Nánási, *Carbohydr. Res.*, 65 (1978) 209–217.
[9] J.S. Brimacombe, M.C. Cook, and L.C.N. Tucker, *J. Chem. Soc.*, (1965) 2292–2294.
[10] V. Pozsgay, *Carbohydr. Res.*, 69 (1979) 284–286.
[11] J. Kerékgyártó and A. Lipták, *Carbohydr. Res.*, 248 (1993) 361–364.
[12] T. Fujiwara, S.W. Hunter, and P.J. Brennan, *Carbohydr. Res.*, 148 (1986) 287–298.
[13] J.-C. Jacquinet, D. Duchet, M.-L. Milat, and P. Sinaÿ, *J. Chem. Soc., Perkin Trans. I*, (1981) 326–330.
[14] R.R. Schmidt and J. Michel, *Angew. Chem.*, 92 (1980) 763–764.
[15] G. Excoffier, D. Gagnaire, and J.-P. Utille, *Carbohydr. Res.*, 39 (1975) 368–373.
[16] S. Sato, Y. Ito, T. Nukada, Y. Nakahara, and T. Ogawa, *Carbohydr. Res.*, 167 (1989) 197–210.
[17] F.J. Kronzer and C. Schuerch, *Carbohydr. Res.*, 27 (1973) 379–390; S. Hanessian and J. Banoub, *Carbohydr. Res.*, 53 (1977) C13–C16.
[18] Z. Szurmai, A. Lipták, and G. Snatzke, *Carbohydr. Res.*, 200 (1990) 201–208.
[19] P.J. Garegg and B. Gotthammar, *Carbohydr. Res.*, 58 (1977) 345–352.
[20] Gy. Batta and A. Lipták, *J. Chem. Soc., Chem. Commun.*, (1985) 368–370.