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Stereoselective syntheses of a di-, tri-, and tetra-saccharide fragment of *Shigella dysenteriae* type 1 O-antigen using 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl chloride as a glycosyl donor *

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ABSTRACT

Methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**1**) furnished a crystalline 3-*O*-bromoacetyl derivative that was treated with the dichloromethyl methyl ether–$ZnCl_2$ reagent to give 2,4-di-*O*-benzoyl-3-*O*-bromoacetyl-α-L-rhamnopyranosyl chloride (**3**). Compounds **1** and **3** were condensed under the conditions of base-deficient, silver trifluoromethanesulfonate-mediated glycosylation to give a fully protected rhamnobioside, which on *O*-debromoacetylation afforded the disaccharide nucleophile **10**. Similar condensation of **3** with methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside, followed by *O*-debromoacetylation and condensation of the thus formed methyl *O*-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-4,6-*O*-benzylidene-3-*O*-benzoyl-α-D-galactopyranoside again with **3**, gave the trisaccharide glycoside. Subsequent *O*-debromoacetylation gave **17**, having only HO-3^3 unsubstituted. Silver perchlorate-mediated glycosylations of **1**, **10**, and **17** with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl chloride afforded, with high α stereoselectivity, protected di-, tri-, and tetra-saccharide glycosides. Subsequent hydrogenation, followed by *N*-acetylation and *O*-deacylation, afforded three oligosaccharide glycosides having nonreducing terminal 2-acetamido-2-deoxy-α-D-glucopyranosyl residues and comprising successively larger portions of the repeating unit of *Shigella dysenteriae* type 1 O-antigen.

INTRODUCTION

Lipopolysaccharides (LPSs) are cell-wall components of Gram-negative bacteria and determine their virulence[2]. *Shigella dysenteriae* type 1 (Shiga's bacillus) provokes severe forms of dysentery, especially in infants and young children. It has been pointed out that the propensity of this disease to pandemic spread, and its resistance to most clinically relevant antibiotics, make a vaccine to prevent Shiga

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dysentery a high priority[3]. We wish to study the interaction of antibodies to *S. dyseneriae* type 1 and its antigen, and explore the possibilities of developing a synthetic vaccine against this devastating disease. The O-specific side chain of *Shigella* LPS consists of a variable number of identical oligosaccharide repeating units. It extends away from the cell into the surrounding medium, and determines the immunological specificity of these organisms[4]. Based on chemical analysis of the LPS, Dmitriev et al.[5] concluded that the chemical repeating unit of the O-antigenic polysaccharide of *S. dysenteriae* type 1 is the tetrasaccharide shown below. From results of genetic and biochemical analysis, Sturm et al.[6]

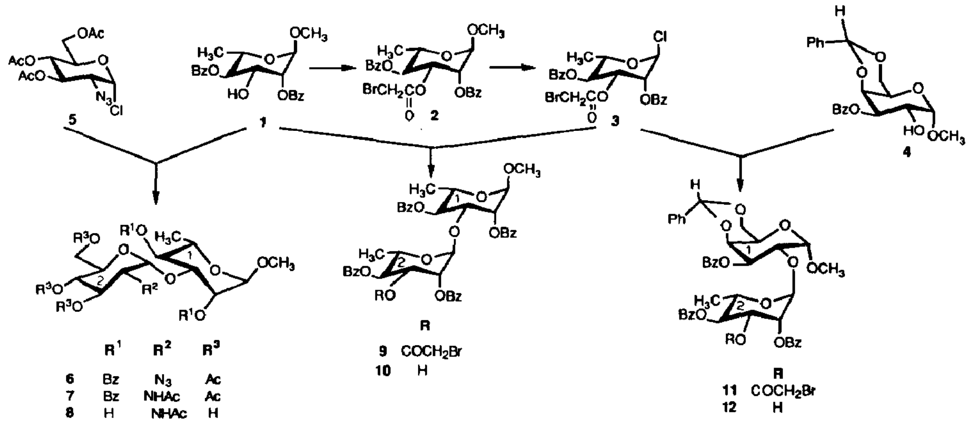
$$\rightarrow 3)\text{-}\underset{\text{A}}{\alpha\text{-L-Rha}p}\text{-}(1 \rightarrow 3)\text{-}\underset{\text{B}}{\alpha\text{-L-Rha}p}\text{-}(1 \rightarrow 2)\text{-}\underset{\text{C}}{\alpha\text{-D-Gal}p}\text{-}(1 \rightarrow 3)\text{-}\underset{\text{D}}{\alpha\text{-D-Glc}p\text{NAc}}\text{-}(1 \rightarrow$$

concluded that the sugar linked to the core is α-D-galactopyranose, and thus that the biochemical repeating unit of the O-antigen is the sequence DABC.

Our study of antigen–antibody interactions involving antibodies specific to the *Shigella* O-side chain requires a large number of ligands. The synthesis of oligosaccharides related to the sequence ABC has been reported[7]. Also, we have prepared[8,9] the methyl glycosides (α-D- or α-L-) of a large number of oligosaccharides related to the *S. dysenteriae* type 1 O-antigen. The present work describes the stepwise synthesis of three oligosaccharidic probes having the sequences DA, DAB, and DABC, respectively. Thus, these ligands all have a 2-acetamido-2-deoxy-α-D-glucopyranosyl nonreducing end-group. They were obtained as the methyl glycosides.

RESULTS AND DISCUSSION

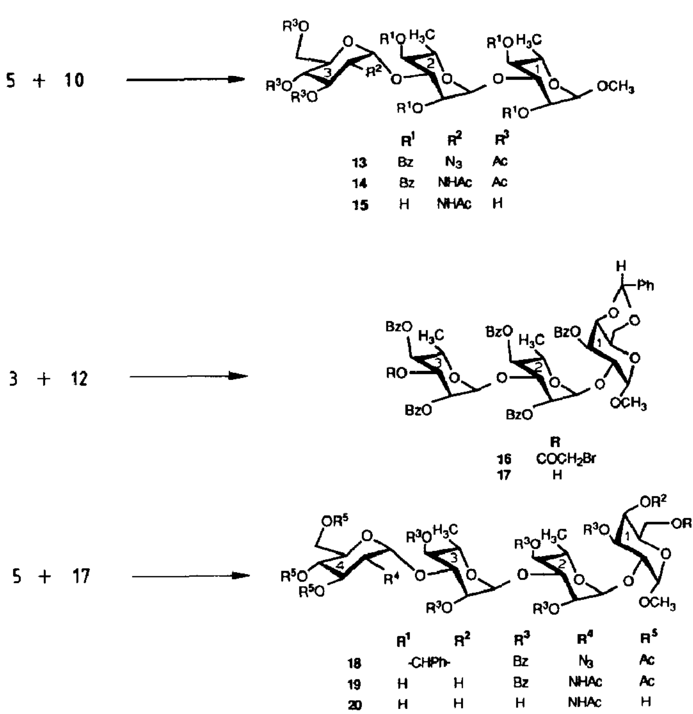
The stepwise synthesis of the target methyl α-glycosides **8**, **15**, and **20** required the construction of the α-D-glucosaminyl linkage, most effectively accomplished[10] using glycosyl donors derived from the corresponding 2-azido-2-deoxysugar. According to this strategy, advantage is taken of the nonparticipating nature of the 2-azido group during chemical glycosylation with a glycosyl halide derivative. Thus, the 2-azido-2-deoxy α-glycoside (oligosaccharide) is generated first and, at a desired stage of the overall synthesis, the 2-azido group is converted into the 2-amino or 2-acetamido function. Several new routes to 2-azido-2-deoxy derivatives of D-glucose have recently been described[1,11–14]. The glycosyl halide we used is 1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl chloride (**5**), first prepared by Paulsen et al.[15] It was previously used in connection with the synthesis of spermidines[16] but, to our knowledge, has never been applied in the synthesis of an oligosaccharide. Because of its lack of reactivity, glycosylations with **5** failed under the standard conditions[17] for coupling in the presence of silver perchlorate as promoter. However, when dichloromethane was used as the solvent, instead of ether[17] or ether–dichloromethane[8], glycosylations proceeded at a reasonable rate. The 1,2-*trans* byproducts were not isolated, preventing the direct determination of the degree of steroselectivity. However, high selectivity for the formation of the



1,2-*cis* linkage was indicated by high yields (70–80%) of the desired α-linked products. Their NMR spectra confirmed the absence of β isomers. It should be noted that these high yields were obtained using only a moderate molar excess (20–40%) of the glycosyl chloride over the acceptor nucleophile. The ^{1}H-NMR spectra of the products **6**, **13**, and **18** showed, inter alia, doublets at $\delta \sim 5$ ($J_{1,2} \sim 3.5$ Hz) confirming[18] that a 1,2-*cis* glycosidic linkage was formed. A high-field doublet of doublets, characteristic[18] of the proton in an $H–C–N_3$ group, was also present. The coupling reactions were carried out without silver carbonate[15,19], eliminating the need for carrying out the reaction in the dark. Thus, the utility of this technique in the synthesis of α-linked *N*-acetyl-D-glucosamine conjugates, employing the now readily available[1] **5** in preference to the much less accessible β-glycosyl halide[19], is clearly demonstrated.

To synthesize the methyl α-glycoside of the disaccharide DA, **5** was condensed with methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside[8] (**1**). The product (**6**) was converted into the corresponding acetamido derivative **7** by catalytic hydrogenolysis over palladium-on-charcoal in the presence of acetic acid and acetic anhydride. Subsequent deacylation gave **8**.

We have previously shown[20–22] that the *O*-bromoacetyl group can be conveniently used as a temporary blocking group in oligosaccharide synthesis. Here, we used this group to advantage in the stepwise construction of the sequence DAB. This synthesis necessitated the preparation of a suitable rhamnobioside (AB) having a free hydroxyl group at C-3², such as **10**. Thus, glycoside **1** was treated[20] with bromoacetyl bromide in the presence of 1,1,3,3-tetramethylurea, and the crystalline product (**2**) was cleaved[23] with dichloromethyl methyl ether in the presence of zinc chloride. The glycosyl chloride **3** thus obtained was condensed with **1** under base-deficient conditions with silver trifluoromethanesulfonate (silver triflate) as the promoter. The proton-coupled ^{13}C-NMR spectrum of the formed disaccharide (**9**) contained doublets for C-1² at δ 99.2 ($J_{C\text{-}1,H\text{-}1}$ 171.5 Hz) and C-1¹ at 98.4 ($J_{C\text{-}1,H\text{-}1}$ 170.8 Hz), characteristic[24] of α glycosidic linkages. Compound **9**



	R¹	R²	R³
13	Bz	N_3	Ac
14	Bz	NHAc	Ac
15	H	NHAc	H

	R
16	$COCH_2Br$
17	H

	R¹	R²	R³	R⁴	R⁵
18	-CHPh-		Bz	N_3	Ac
19	H	H	Bz	NHAc	Ac
20	H	H	H	NHAc	H

was *O*-debromoacetylated with thiourea yielding **10**, which was subsequently condensed with **5**. The resulting, fully protected trisaccharide was converted into the desired product **15** in analogy with the conversion **6** → **8**.

The starting nucleophile in the assembly of the tetrasaccharide DABC was methyl 4,6-*O*-benzylidene-3-*O*-benzoyl-α-D-galactopyranoside[25] (**4**). It was condensed with **3** to give the α-(1→2)-linked disaccharide glycoside **11**. Subsequent *O*-debromoacetylation of the latter, followed by condensation of the formed **12** with **3**, gave the trisaccharide **16**, which was converted to the trisaccharide nucleophile **17** by *O*-debromoacetylation. Finally, condensation of the glycosyl donor **5** with the glycosyl acceptor **17** afforded the tetrasaccharide **18** which, after hydrogenation, *N*-acetylation, and *O*-deacylation, afforded the target tetrasaccharide **20**. Its proton-coupled ^{13}C-NMR spectrum included four doublets showing splittings of 173.0, 170.7, 173.9, and 171.2 Hz, confirming[24] that all glycosidic linkages were α. Features in the ^{13}C-$\{^1H\}$ spectrum, as well as those in the ^1H spectrum (see Experimental) were consistent with the expected structure.

EXPERIMENTAL

General methods.—Unless stated otherwise, optical rotations were measured for solutions in $CHCl_3$, at 25°, with a Perkin–Elmer automatic polarimeter, Model 241 MC. Thin-layer chromatography (TLC) on precoated slides of Silica Gel G F254

(Analtech) was performed with solvent mixtures of appropriately adjusted polarity consisting of *A*, toluene–ethyl acetate; *B*, toluene–acetone; *C*, hexane–ethyl acetate; *D*, carbon tetrachloride–acetone; *E*, chloroform–methanol; and *F*, hexane–acetone. Detection was effected by charring with 5% H_2SO_4 in ethanol and, when applicable, with UV light. Preparative chromatography was performed by elution from columns of Silica Gel 60 (particle size 0.04–0.063 mm). For chromatography of **3**, the silica gel was dried at 140° for 16 h. NMR data were extracted from spectra measured for solutions in $CDCl_3$ or D_2O, at 25°, with a Varian XL 300 or a Varian Gemini spectrometer. Chemical shifts were measured from the resonance signals of Me_4Si and HDO ($\delta_{HDO} = 4.78$), respectively. For the ^{13}C spectra taken in D_2O the internal standard was methanol ($\delta_{MeOH} = 49.0$). Proton signal assignments were made by first-order analysis of the spectra, and were supported by homonuclear decoupling or COSY experiments. Of two magnetically nonequivalent geminal protons, the one resonating at a lower field is denoted Ha and the one at higher field Hb. Carbon signal assignments were made routinely by mutual comparison of the spectra, and by comparison with spectra of related substances[8]. Definitive ^{13}C assignments, based on HETCOR experiments, were obtained for compounds **6**, **9–12**, and **17**. The superscripts used for the notation of ring carbon atoms and protons for oligosaccharides, in the text and when reporting the NMR data (Tables I and II, and Experimental), denote the sugar residues or groups containing the designated proton or carbon atom. These are serially numbered, beginning with the residue bearing the aglycon. For example, H-1^2 refers to H-1 of the second sugar residue, and HO-3^3 refers to the hydroxyl group at position 3 of the third sugar residue. Fast-atom bombardment (FAB) mass spectra were obtained with a Jeol SX 102 spectrometer, for samples in a matrix of *m*-nitrobenzyl alcohol. Reactions requiring anhydrous conditions were performed under argon using common laboratory glassware, and reagents and solvents were handled with Hamilton Series 1000 gas-tight syringes. Unless stated otherwise, solutions in organic solvents were dried with anhydrous sodium sulfate, and concentrated at 2 kPa/40°.

Methyl 2,4-di-O-benzoyl-3-O-bromoacetyl-α-L-rhamnopyranoside (**2**).—Tetramethylurea (6 mL, 50 mmol), followed by bromoacetyl bromide (6.6 mL, 72.5 mmol), was added at 0° to a solution of methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside[8] (9.65 g, 25 mmol) in 1,2-dimethoxyethane (75 mL), and the mixture was stirred at room temperature until TLC (solvent *A*) showed that the reaction was complete (~ 3 h). After concentration of the solution the residue was partitioned between H_2O and CH_2Cl_2, and after drying, the organic phase was concentrated to dryness. Crystallization of the residue from EtOH gave pure **2** (11.67 g, 92%); mp 82–83.5°; $[\alpha]_D + 77°$ (*c* 1.8); ^{13}C-NMR ($CDCl_3$): δ 98.5 (C-1), 71.6 (C-4), 71.2 (C-3), 70.3 (C-2), 66.6 (C-5), 55.3 (OCH_3), 25.0 ($COCH_2Br$), and 17.7 (C-6); CIMS: *m/z* 524 $[M + 18]^+$.

Anal. Calcd for $C_{23}H_{23}BrO_8$: C, 54.45; H, 4.57; Br, 15.75. Found: C, 53.90; H, 4.50; Br, 15.61.

TABLE I

^{1}H-NMR data for solutions in $CDCl_3$ ^{a}

Compound	Chemical shifts (δ) and multiplicities								
	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	OCH_3	CH_3CO (CHPh)	CH_2Br (NH)
2	4.86d	5.48–5.56m ^{b}	5.64dd	5.48–5.56m ^{b}	4.10m	1.35d				3.63d
3	6.16d	5.71dd	5.91dd	5.59t	4.41m	1.39d				3.64d
6	4.87d	5.63dd	4.37dd	5.55t	4.06dt	1.36d		3.46s		
	5.20d	3.23dd	5.05t	4.80t	3.76m	3.85–3.86m ^{b}	3.85–3.86m ^{b}		1.61s, 1.92s, 2.06s	
7	4.79–4.94m ^{b}	5.54dd	4.34dd	5.49t	4.05m	1.36d		3.46s		
	5.01d	4.27dt	4.79–4.94m ^{b}	4.79–4.94m ^{b}	3.65–3.80m ^{b}	3.65–3.80m ^{b}	3.65–3.80m ^{b}		1.47s, 1.64s, 1.89s, 2.03s	(5.84d)
9	4.90d	5.49dd	4.45dd	5.56t	4.01–4.11m ^{b}	1.35d		3.46s		
	5.14–5.16m ^{b}	5.14–5.16m ^{b}	5.40dd	5.32t	4.01–4.11m ^{b}	1.16d				3.48d
10	4.89d	5.50dd	4.43dd	5.55t	3.97–4.09m	1.35d		3.46s		
	5.17d	5.01dd	3.97–4.09m	5.08t	3.97–4.09m	1.13d				
11	5.09d	4.48dd	5.55dd	4.69dd	3.85s	4.32dd	4.11dd	3.52s	(5.54s)	
	5.24d	5.42dd	5.64dd	5.48t	4.23m	1.32d				3.54d
12	5.11d	4.46dd	5.54dd	4.65 br d	3.84s	4.26–4.33m ^{b}	4.11bd	3.53s	(5.54s)	
	5.24–5.29m ^{b}	5.24–5.29m ^{b}	4.26–4.33m ^{b}	5.24–5.29m ^{b}	4.20m	1.31d				
13	4.86 br d	5.50–5.57m ^{b}	4.44dd	5.50–5.57m ^{b}	4.01–4.11m ^{b}	1.36d		3.46s		
	5.14d	5.17 br d	4.01–4.11m ^{b}	5.36t	4.01–4.11m	1.16d				
	4.66d	3.03dd	4.95t	4.73t	3.531m	3.74dd	~ 3.42dd	3.46s	1.61s, 1.88s, 2.01s	

14	4.86 br s	5.49–5.55m [b]	4.42dd	5.49–5.55m [b]	3.99–4.13m [b]	1.35		3.46s		
	5.09 br s	5.11 br d	3.99–4.13m [b]	5.28t	3.99–4.13m [b]	1.17d				
	4.47d	3.99–4.13m [b]	4.84t	4.70t	3.36–3.46m [b]	3.67dd	3.36–3.46m [b]		1.34s, 1.62s, 1.85s, 2.00s	(5.66d)
16	5.09–5.12m [b]	4.42–4.47m [b]	5.50–5.57m [b]	4.66 br d	3.81–3.86m [b]	4.34dd	4.09dd	3.51s	(5.54s)	
	5.26d	5.37dd	4.42–4.47m [b]	5.50–5.57m [b]	4.2m	1.34d				
	5.04d	5.09–5.12m [b]	5.32dd	5.20t	3.81–3.86m [b]	0.73d				3.45d
17	5.11d	4.39–4.47m [b]	5.49–5.57m [b]	4.67 br d	3.84 br s	4.31dd	4.10dd	3.51s	(5.54s)	
	5.26 br s	5.38 br dd	4.39–4.47m [b]	5.49–5.57m [b]	4.2m	1.33d				
	5.08 br s	4.93–5.00m [b]	4.0m	4.93–5.00m [b]	3.76m	0.73d				
18	5.11–5.29m [b]	4.40–4.47m [b]	5.49–5.55m [b]	4.65–4.74m [b]	3.76–3.84m [b]	4.32 br d	4.11 br d	3.52s	(5.54s)	
	5.11–5.29m [b]	5.39 br d	4.40–4.47m [b]	5.49–5.55m [b]	4.21m	1.34d				
	5.03d	5.11–5.29m	4.00dd	5.11–5.29m	3.76–3.84m	0.76d				
	4.65–4.74m [b]	3.02dd	4.92t	4.65–4.74m [b]	3.39–3.52m [b]	3.71dd	3.39–3.52m [b]		1.59s, 1.87s, 2.00s	
19	5.05m [b]	4.33–4.42m [b]	5.44dd	4.43–4.48m [b]	3.87–3.98m [b]	3.87–3.98m [b]	3.87–3.98m [b]	3.46s		
	5.20 br s	5.33 br s	4.33–4.42m [b]	5.50t	4.22m	1.32d				
	4.96 br s	5.05m [b]	3.87–3.98m	5.14t	3.76m	0.72d				
	4.43–4.48m	4.06dt	4.66t	4.82t	3.33–3.42m [b]	3.62dd	3.33–3.42m		1.34s, 1.60s, 1.83s, 1.99s	(5.69d)

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[a] Data in the 1st row of each entry refer to sugar residue 1; data in the 2nd and 3rd rows, if present, refer to sugar residues 2 and 3, respectively. Peak multiplicities: d, doublet; m, multiplet; s, singlet; t, triplet. [b] Overlapping signals.

TABLE II

^{1}H-NMR coupling constants [a,b]

Compound	Coupling constants (Hz)							
	$J_{1,2}$	$J_{2,3}$	$J_{2,NH}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
2	1.6	3.4		10.1	[c]	6.2		
3	1.4	3.4		10.3	9.9	6.2		
6	1.5	3.3		9.9	9.9	6.2		
	3.6	10.5		9.3	9.9	[c]	[c]	[c]
7	1.9	3.4		10.0	10.0	6.2		
	3.7	10.1	9.8	[c]	[c]	[c]	[c]	[c]
9	1.4	3.4		9.8	9.8	6.2		
	[c]	3.1		9.3	9.3	6.2		
10	1.5	3.4		9.9	9.9	6.2		
	1.4	3.4		9.8	9.8	6.3		
11	3.4	10.5		3.4	< 1.0	1.2	1.3	12.4
	1.2	3.3		10.1	9.9	6.2		
12	3.4	10.5		3.4	< 1.0	[c]	< 1.0	11.7
	[c]	[c]		[c]	[c]	6.2		
13	< 1.0	3.4		9.8	[c]	6.2		
	1.6	3.1		9.8	9.8	6.3		
	3.5	10.5		10.0	10.0	3.0	1.8	12.4
14	< 1.0	3.4		9.9	9.9	6.2		
	< 1.0	2.9		9.8	9.8	6.9		
	3.5	9.7	9.9	9.7	10.4	2.5	[c]	12.2
16	[c]	[c]		3.3	< 1.0	1.1	1.1	12.5
	1.3	3.1		[c]	[c]	6.3		
	1.4	3.3		10.0	9.7	6.2		
17	3.4	[c]		3.4	< 1.0	< 1.0	< 1.0	11.7
	1.5	3.2		[c]	9.9	6.2		
	< 1.0	3.2		9.9	9.7	6.2		
18	[c]	[c]		[c]	[c]	< 1.0	< 1.0	12.3
	[c]	[c]		[c]	9.9	6.1		
	1.4	3.2		9.8	[c]	6.2		
	3.6	10.5		9.5	[c]	2.9	[c]	12.5
19	[c]	10.4		2.7	[c]	[c]	[c]	[c]
	< 1.0	[c]		9.9	9.9	[c]		
	< 1.0	9.8		9.8	9.8	6.1		
	3.4	9.7	9.9	9.7	9.7	2.1	[c]	11.9

[a] Data in the 1st row of each entry refer to sugar residue 1; data in the 2nd and 3rd rows, if present, refer to sugar residues 2 and 3, respectively. [b] Measured in $CDCl_3$. [c] Not determined.

2,4-Di-O-benzoyl-3-O-bromoacetyl-α-L-rhamnopyranosyl chloride (**3**).—Finely powdered, freshly fused zinc chloride (0.4 g) was added to a solution of the α-glycoside **2** (5.07 g, 10 mmol) in dichloromethyl methyl ether (20 mL), contained in a round-bottomed flask equipped with a dry ice condenser. The mixture was stirred at 70° (bath) with the exclusion of moisture until TLC (solvent *B*) showed that only traces of the starting material remained (~ 6 h). The solution was diluted with toluene and concentrated, and the residue was chromatographed to give pure **3** (4.44 g, 87%); $[\alpha]_D + 43°$ (*c* 1.2); ^{13}C-NMR ($CDCl_3$): δ 89.1 (C-1), 72.4, 70.8, 69.8 (2 C), 24.7 ($COCH_2Br$), and 17.3 (C-6); CIMS: m/z 530 $[M + 18]^+$.

Anal. Calcd for $C_{22}H_{20}BrClO_7$: C, 51.64; H, 3.94; Br, 15.62; Cl, 6.93. Found: C, 51.35; H, 4.10; Br. 15.69; Cl, 6.96.

Methyl O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1 → 3)-2,4-di-O-benzoyl-α-L-rhamnopyranoside (**6**).—A solution of **1** (ref. 8, 0.39 g, 1 mmol), **5** (0.49 g, 1.4 mmol), and 2,4,6-trimethylpyridine (0.186 mL, 1.4 mmol) in CH_2Cl_2 (15 mL) was added slowly at room temperature to a stirred suspension of silver perchlorate[26] (0.35 g, 1.7 mmol) in CH_2Cl_2 (15 mL). After 45 min, TLC (solvent *C*) showed almost complete conversion of starting materials into a major product. The mixture was filtered, the filtrate was washed with aq sodium thiosulfate, the organic phase was dried and concentrated, and the residue was chromatographed (solvent *A*) to give pure **6** (0.505 g, 72%); mp 134–135° (from EtOH), $[\alpha]_D + 186°$ (*c* 1.1); ^{13}C-NMR ($CDCl_3$): δ 98.8 (C-1^1), 93.7 (C-1^2), 72.2 (C-4^1), 71.6 (C-3^1), 70.2 (C-3^2), 68.0 (C-4^2), 67.4 (C-2^1,5^2), 66.4 (C-5^1), 61.3 (C-6^2), 60.5 (C-2^2), 55.3 (OCH_3), 20.7, 20.5, 20.2 (3 × $COCH_3$), and 17.6 (C-6^1); CIMS: *m/z* 717 $[M + 18]^+$.

Anal. Calcd for $C_{33}H_{37}N_3O_{14}$: C, 56.65; H, 5.33; N, 6.01. Found: C, 56.57; H, 5.33; N, 6.03.

Methyl O-(2-acetamido-2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranosyl)-(1 → 3)-2,4-di-O-benzoyl-α-L-rhamnopyranoside (**7**).—A solution of **6** (1.28 g, 1.89 mmol) and acetic anhydride (1 mL) in MeOH (100 mL) was stirred under H_2, at room temperature, with 5% Pd–C catalyst (1.3 g) for 24 h. After filtration and evaporation of the solvents, the residue was chromatographed (solvent *D*) to give **7** (1.03 g, 76%); $[\alpha]_D + 129°$ (*c* 1.1); ^{13}C-NMR ($CDCl_3$): δ 98.7 (C-1^1), 95.3 (C-1^2), 73.0 (C-4^1), 72.5 (C-3^1), 70.9 (C-3^2), 68.5 (C-4^2), 67.8 (C-5^2), 67.5 (C-2^1), 66.5 (C-5)^1, 61.2 (C-6^2), 55.3 (OCH_3), 51.2 (C-2^2), 22.3 ($NCOCH_3$), 20.6, 20.5, 20.2 (3 × $COCH_3$), and 17.6 (C-6^1); CIMS: *m/z* 716 $[M + 1]^+$.

Anal. Calcd for $C_{35}H_{41}NO_{15}$: C, 58.74; H, 5.77; N, 1.96. Found: C, 58.66; H, 5.80; N, 1.99.

Methyl O-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-(1 → 3)-α-L-rhamnopyranoside (**8**)—A solution of **7** (0.99 g, 1.4 mmol) in MeOH (100 mL) was treated with M methanolic sodium methoxide (1 mL), and the solution was kept overnight at ~ 50° (bath). After cooling to room temperature, neutralization with Amberlite IR-120 (H^+) resin, and evaporation of the solvent, the crude product was chromatographed (solvent *E*) to give pure (TLC, solvent *E*, 3:1, NMR) **8** (0.51 g, 96%) as a white, amorphous, hygroscopic solid; $[\alpha]_D + 98°$ (*c* 1.1, H_2O); CIMS: *m/z* 382 $[M + 1]^+$. Definite, diagnostically significant signals in the ^{1}H-NMR spectrum (D_2O) were at δ 4.99 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^2), 4.69 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1^1), 4.03 (br d, 1 H, H-2^1), 3.38 (s, 3 H, OCH_3), 2.03 (s, 3 H, $NCOCH_3$), and 1.31 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6^1); ^{13}C-NMR ($CDCl_3$): δ 100.8 (C-1^1), 94.4 (C-1^2), 75.5 (C-3^1), 71.9, 71.0, 70.4, 69.9, 68.6, 66.8, 60.4 (C-6^2), 54.9 (OCH_3), 53.7 (C-2^2), 22.0 ($NCOCH_3$), and 16.8 (C-6^1).

Methyl O-(2,4,di-O-benzoyl-3-O-bromoacetyl-α-L-rhamnopyranosyl)-(1 → 3)-2,4-di-O-benzoyl-α-L-rhamnopyranoside (**9**).—A solution of **1** (1.69 g, 4.4 mmol), **3** (2.75 g, 5.3 mmol), and 2,4,6-trimethylpyridine (0.5 mL, 3.94 mmol) in CH_2Cl_2 (20 mL) was added dropwise at 22° to a stirred suspension of silver triflate (1.352 g, 5.3 mmol) in CH_2Cl_2 (20 mL). When TLC (solvent *B*) showed complete conversion of the starting materials (~ 1 h) the reaction mixture was worked up as described for the preparation of **6**, and chromatography gave **9** (2.28 g, 60%, white foam); $[\alpha]_D + 112°$ (*c* 1.7); ^{13}C-NMR ($CDCl_3$): δ 99.2 (C-1^2, $J_{C,H}$ 171.5 Hz), 98.4 (C-1^1, $J_{C,H}$ 170.8 Hz), 76.0 (C-3^1), 73.3 (C-4^1), 72.2 (C-2^1), 71.3 (C-4^2), 70.5 (C-3^2), 70.2 (C-2^2), 67.5 (C-5^2), 66.6 (C-5^1), 55.2 (OCH_3), 24.9 ($COCH_2Br$), 17.7 (C-6^1), and 17.3 (C-6^2); CIMS: *m/z* 878 $[M + 18]^+$.

Anal. Calcd for $C_{43}H_{41}BrO_{14}$: C, 59.94; H, 4.80; Br, 9.27. Found: C, 59.79; H, 4.83; Br, 9.37.

Methyl O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-2,4-di-O-benzoyl-α-L-rhamnopyranoside (**10**).—A solution of thiourea (0.66 g, 8.6 mmol) in MeOH (10 mL) was added to a solution of **9** (1.86 g, 2.16 mmol) in 1 : 1 MeOH–CH_2Cl_2 (20 mL). The mixture was kept at room temperature until TLC (solvent *A*) showed that the reaction was complete (~ 30 min), and concentrated. A solution of the residue in CH_2Cl_2 was successively washed with 10% HCl, a mixture of satd aq $NaHCO_3$ and NaCl, and H_2O, dried, and concentrated. Chromatography gave **10** (1.57 g, ~ 100%); $[\alpha]_D + 108°$ (*c* 1.4); ^{13}C-NMR ($CDCl_3$): δ 99.3 (C-1^2), 98.4 (C-1^1), 76.4 (C-3^1), 75.2 (C-4^2), 73.2 (C-4^1), 73.0 (C-2^2), 72.4 (C-2^1), 68.5 (C-5^2), 67.0 (C-3^2), 66.6 (C-5^1), 55.2 (OCH_3), 17.7 (C-6^1), and 17.3 (C-6^2); CIMS: *m/z* 758 $[M + 18]^+$.

Anal. Calcd for $C_{41}H_{40}O_{13}$:C, 66.48; H, 5.44. Found: C, 66.38; H, 5.45.

Methyl O-(2,4-di-O-benzoyl-3-O-bromoacetyl-α-L-rhamnopyranosyl)-(1 → 2)-4,6-O-benzylidene-3-O-benzoyl-α-D-galactopyranoside (**11**).—A solution of methyl 4,6-*O*-benzylidene-3-*O*-benzoyl-α-D-galactopyranoside[25] (0.38 g, 1 mmol), **3** (0.51 g, 1 mmol), and 2,4,6-trimethylpyridine (0.12 mL, 0.9 mmol) in CH_2Cl_2 (5 mL) was treated with silver triflate (0.31 g, 1.2 mmol) as described for the preparation of **9**. After workup, as described above, crystallization from EtOH gave 0.65 g (75%) of **11**; mp 160–162°; $[\alpha]_D + 144°$ (*c* 1.8); ^{13}C-NMR ($CDCl_3$): δ 100.7 (*C*H-benzylic), 99.9 (C-1^1), 99.6 (C-1^2), 75.2 (C-2^1), 74.3 (C-4^1), 71.7 (C-4^2), 70.8 (C-3^2), 70.7 (C-3^1), 70.4 (C-2^2), 69.2 (C-6^1), 67.3 (C-5^2), 62.3 (C-5^1), 55.6 (OCH_3), 24.9 ($COCH_3$), and 17.7 (C-6^2); CIMS: *m/z* 878 $[M + 18]^+$.

Anal. Calc. for $C_{43}H_{41}BrO_{14}$: C, 59.94; H, 4.80; Br, 9.27. Found: C, 59.86; H, 4.83; Br, 9.34.

Methyl O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-4,6-O-benzylidene-3-O-benzoyl-α-D-galactopyranoside (**12**).—To a solution of **11** (4.4 g, 5.1 mmol) in 1 : 1 MeOH–CH_2Cl_2 (70 mL) was added thiourea (1.55 g, 20.4 mmol) and 2,4,6-trimethylpyridine (0.62 g, 5.1 mmol) in MeOH (35 mL), and the mixture was stirred at room temperature until TLC (solvent *A*) showed that the reaction was complete (~ 30 min). The mixture was processed as described for the preparation of **10**, and chromatography of the crude product gave **12** (3.7 g, ~ 100%); $[\alpha]_D + 124°$ (*c* 1.0); ^{13}C–NMR ($CDCl_3$): δ 100.6 (*C*H-benzylic), 99.8 (C-1^1), 99.6 (C-1^2), 75.3, 73.1

(C-2^2, 4^2), 75.2 (C-2^1), 74.3 (C-4^1), 70.3 (C-3^1), 69.1 (C-6^1), 68.5 (C-3^2), 66.8 (C-5^2), 62.1 (C-5^1), 55.5 (OCH_3), and 17.7 (C-6^2); CIMS: m/z 758 $[M+18]^+$.

Anal. Calcd for $C_{41}H_{40}O_{13}$: C, 66.48; H, 5.44. Found: C, 66.33; H, 5.47.

Methyl O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-2,4-di-O-benzoyl-α-L-rhamnopyranoside (**13**).—A solution of **10** (1.48 g, 2 mmol), **5** (0.98 g, 2.8 mmol), and 2,4,6-trimethylpyridine (0.37 mL, 2.8 mmol) in CH_2Cl_2 (10 mL) was added at 0° to a suspension of silver perchlorate (0.7 g, 3.4 mmol) in CH_2Cl_2 (30 mL), and the mixture was stirred until TLC (solvent *A*) showed complete conversion of the starting materials (~ 1 h). One major product was formed. Workup as described for the preparation of **6** and chromatography (solvent *C*) gave **13** (1.74 g, 82%); $[\alpha]_D + 177°$ (c 0.95); ^{13}C-NMR ($CDCl_3$): δ 99.3 (C-1^2), 98.5 (C-1^1), 93.9 (C-1^3), 76.1 (C-3^1), 73.3 (C-4^1), 72.0, 71.9, 71.8 (C-2^2, 3^2, 4^2), 70.3 (C-3^3), 67.8, 67.6, 67.3, 67.2 (C-2^1, 5^2, 4^3, 5^3), 66.6 (C-5^1), 60.9 (C-6^3), 60.4 (C-2^3), 55.3 (OCH_3), 20.6, 20.5, 20.2 (3 × OCOCH_3), 17.7 (C-6^1), and 17.4 (C-6^2); CIMS: m/z 1071 $[M+18]^+$.

Anal. Calcd for $C_{53}H_{55}N_3O_{20}$: C, 60.40; H, 5.26; N, 3.99. Found: C, 60.37; H, 5.30; N, 3.97.

Methyl O-(2-acetamido-2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-2,4-di-O-benzoyl-α-L-rhamnopyranoside (**14**).—A solution of **13** (1.71 g, 1.62 mmol) in MeOH (100 mL) was hydrogenated in the presence of acetic anhydride (1 mL), as described for the preparation of **7**. After processing as for **7** and chromatography (solvent *B*), amorphous **14** (1.2 g, 70%) showed $[\alpha]_D + 157°$ (c 1.2); ^{13}C-NMR ($CDCl_3$): δ 99.2 (C-1^2), 98.5 (C-1^1), 95.7 (C-1^3), 76.1 (C-3^1), 73.3, 73.1 (C-4^1, 4^2), 72.2, 72.0 (C-2^2, 3^2), 71.0 (C-3^3), 68.7 (C-4^3), 67.7, 67.4, 67.2 (C-2^1, 5^2, 5^3), 66.5 (C-5^1), 60.9 (C-6^3), 55.3 (OCH_3), 50.9 (C-2^3), 22.2 (NCOCH_3), 20.5, 20.2 (1 C, 2 C, 3 × COCH_3), 17.7 (C-6^1), and 17.4 (C-6^2); CIMS: m/z 1070 $[M+1]^+$.

Anal. Calc. for $C_{55}H_{59}NO_{21}$: C, 61.73; H, 5.56; N, 1.31. Found: C, 61.80; H, 5.58; N, 1.29.

Methyl O-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranoside (**15**).—Deprotection of **14** (1 g, 0.93 mmol), as described for the preparation of compound **8**, and chromatography (solvent *E*) gave pure (TLC, solvent *E*, 2:1; NMR) **15** (0.38 g, 77%) as a white, amorphous, hygroscopic solid, $[\alpha]_D + 38°$ (c 1, H_2O). Definite, diagnostically significant signals in the ^{1}H-NMR spectrum (D_2O) were at δ 5.03 (br d, 2 H, overlapping H-1^2,1^3), 4.65 (br s, H-1^1), 3.38 (s, 3 H, OCH_3), 2.03 (s, 3 H, NCOCH_3), 1.29, 1.28 (2 d, J 6.2 and J 6.1 Hz, H-6^1, 6^2); ^{13}C-NMR (D_2O): δ 102.1 (C-1^2), 100.9 (C-1^1), 94.4 (C-1^3), 78.1 (C-3^1), 75.5 (C-3^2), 72.0, 71.5, 71.0, 70.4, 69.9 (2 C), 69.2, 68.7, 67.0, 60.5 (C-6^3), 54.9 (OCH^3), 53.7 (C-2^3), 22.0 (NCOCH_3), 16.8, and 16.7 (C-6^1, 6^2); CIMS: m/z 528 $[M+1]^+$.

Methyl O-(2,4-di-O-benzoyl-3-O-bromoacetyl-α-L-rhamnopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-4,6-O-benzylidene-3-O-benzoyl-α-D-galactopyranoside (**16**).—A solution of **3** (1.18 g, 2.3 mmol), **12** (1.48 g, 2 mmol), and 2,4,6-trimethylpyridine (0.24 mL, 1.8 mmol) in CH_2Cl_2 (15 mL) was allowed to react with silver triflate (0.62 g, 2.4 mmol) as described for the preparation of **9**. The mixture was worked up as for **9** and chromatographed (solvent *C*) to give **16**, and also some unchanged **12**. Yield, 1.67 g (70%, or 92% based on the amount of nucleophile consumed); $[\alpha]_D$ + 129° (*c* 1.1); ^{13}C-NMR ($CDCl_3$): δ 100.7 (*C*H-benzylic), 99.8 (C-1^1), 99.7 (C-1^2), 99.0 (C-1^3), 75.8 (C-3^2), 75.5 (C-2^1), 74.4 (C-4^1), 73.1 (C-4^2), 72.2 (C-2^2), 71.2 (C-4^3), 70.4 (C-3^3), 70.3 (C-3^1), 70.1 (C-2^3), 69.2 (C-6^1), 67.4 (C-5^2), 67.2 (C-5^3), 62.2 (C-5^1), 55.5 (O*C*H_3), 24.9 (CO*C*H_2Br), 17.8 (C-6^2), and 16.8 (C-6^3); CIMS: *m/z* 1234 $[M + 18]^+$.

Anal. Calcd for $C_{63}H_{59}BrO_{20}$: C, 62.22; H, 4.89; Br, 6.57. Found: C, 62.65; H, 5.09; Br, 6.65.

Methyl O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-4,6-O-benzylidene-3-O-benzoyl-α-D-galactopyranoside (**17**).—Compound **16** (1.31 g, 1.1 mmol) was *O*-debromoacetylated with thiourea (0.33 g, 4.3 mmol) in the presence 2,4,6-trimethylpyridine (0.14 mL, 1.1 mmol), as described for the preparation of **12**. Chromatography of the crude product (solvent *B*) gave **17** (1.03 g, 87%); $[\alpha]_D$ + 124° (*c* 0.9); ^{13}C-NMR ($CDCl_3$): δ 100.7 (*C*H-benzylic), 99.8 (C-1^1), 99.6 (C-1^2), 99.1 (C-1^3), 75.9 (C-3^2), 75.8 (C-2^1), 75.1 (C-4^3), 74.4 (C-4^1), 73.0 (C-4^2), 72.8 (C-2^3) 72.4 (C-2^2), 70.3 (C-3^1), 69.2 (C-6^1), 68.4 (C-3^3), 67.4 (C-5^2), 66.8 (C-5^3), 62.2 (C-5^1), 55.5 (O*C*H_3), 17.8 (C-6^2), and 16.9 (C-6^3); CIMS: *m/z* 1112 $[M + 18]^+$.

Anal. Calcd for $C_{61}H_{58}O_{19}$: C, 66.90; H, 5.34. Found: C, 66.71; H, 5.29.

Methyl O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-4,6-O-benzylidene-3-O-benzoyl-α-D-galactopyranoside (**18**).—A solution of **17** (1.87 g, 1.7 mmol), **5** (0.83 g, 2.4 mmol), and 2,4,6-trimethylpyridine (0.32 mL, 2.4 mmol) in CH_2Cl_2 (10 mL) was treated with silver perchlorate (0.6 g, 2.9 mmol) as described for the preparation of **13**. After workup as for **13** and chromatography (solvent *F*) the amorphous **18** (1.72 g, 72%) showed $[\alpha]_D$ + 191° (*c* 1.1); ^{13}C-NMR ($CDCl_3$): δ 100.7 (*C*H-benzylic), 99.8 (2 C, C-1^1, 1^2), 99.1 (C-1^3), 93.8 (C-1^4), 75.9 (C-3^2), 75.5 (C-2^1), 74.4, 73.1, 72.1, 71.8, 71.6, 70.3 (2 C), 69.2 (C-6^1), 67.7, 67.4, 67.2, 62.2 (C-5^1), 60.9 (C-4^4), 60.4 (C-2^4), 55.5 (O*C*H_3), 20.5, 20.4, 20.2 (3 × CO*C*H_3), 17.8 (C-6^2), and 16.7 (C-6^3); CIMS: *m/z* 1430 $[M + H]^+$.

Anal. Calcd for $C_{73}H_{73}N_3O_{26}$: C, 62.26; H, 5.23; N, 2.99. Found: C, 62.49; H, 5.32; N, 2.96.

Methyl O-(2-acetamido-2-deoxy-3,4,6-tri-O-acetyl-α-D-glucopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-O-(2,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-3-O-benzoyl-α-D-galactopyranoside (**19**).—A solution of **18** (1.65 g, 1.17 mmol) and acetic anhydride (1 mL) in MeOH (100 mL) was stirred in a H_2 atmosphere with 5% Pd–C catalyst (1.65 g) for 24 h. TLC (solvent *B*) showed complete conversion of **18** into two products, both showing lower mobility than the starting material. Acetic acid (20 mL) was added, and hydrogenation was continued for another 24 h, when TLC showed that the faster moving product was almost fully converted into the slower moving one. After processing as described for the preparation of **8**, and concentration and coevaporation with toluene to remove acetic acid, chromatography of the residue gave **19** (0.78 g, 50%); $[\alpha]_D$ + 169° (*c* 1.4); ^{13}C-NMR ($CDCl_3$): δ 100.0 (C-1^1), 99.4 (C-1^2), 99.0 (C-1^3), 95.7 (C-1^4), 76.4 (C-3^2), 75.7 (C-2^1), 73.1, 73.0, 72.2 (2 C), 72.0, 70.1, 69.7, 68.9, 68.5, 67.6, 67.3, 67.2 (2 C), 63.2 (C-6^1), 60.9 (C-6^4), 55.3 (OCH_3), 50.9 (C-2^4), 22.1 ($NCOCH_3$), 20.5 (2 C), 20.2 (3 × $COCH_3$), 17.8 (C-6^2), and 16.8 (C-6^3); CIMS: *m/z* 1336 $[M + 1]^+$.

Anal. Calcd for $C_{68}H_{73}NO_{27}$: C, 61.12; H, 5.51; N, 1.05. Found: C, 61.21; H, 5.51; N, 1.04.

Methyl O-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 2)-α-D-galactopyranoside (**20**).— Deprotection of **19** (0.57 g, 0.43 mmol) as described for the preparation of compound **8**, and chromatography (solvent *E*) of the crude product, gave pure (TLC, solvent *E*, 1.5 : 1; NMR) **20** (0.19 g, 65%) as a white, amorphous, hygroscopic solid; $[\alpha]_D$ + 75° (*c* 1, H_2O). Definite, diagnostically significant signals in the ^{1}H-NMR spectrum (D_2O) were at δ 5.04 (br d, 2 H overlapping, H-1^3, 1^4), 4.91 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1^1), 4.89 (br s, 1 H, H-1^2), 4.18, 4.13 (2 br s, 2 H, H-2^2, 2^3), 3.42 (s, 3 H, OCH_3), 2.03 (s, 3 H, $NCOCH_3$), 1.30 (d, 6 H, $J_{5,6}$ 6.1 Hz, H-6^2, 6^3); ^{13}C-NMR (D_2O): δ 102.9, 102.4 (2 C_2 $^1J_{C,H}$ 173.0 and 170.7 Hz, resp., C-1^2, 1^3), 99.1 ($^1J_{C,H}$ 173.9 Hz, C-1^1), 94.6 ($^1J_{C,H}$ 170.7 Hz, C-1^4), 78.8 (C-3^2), 77.6 (C-2^1), 75.6 (C-3^3), 72.1, 71.4, 71.2, 70.9, 70.6, 70.0 (2 C), 69.6 (2 C), 69.5, 68.7, 67.1, 61.5 (C-6^1), 60.6 (C-6^4), 55.1 (OCH_3), 53.9 (C-2^4), 22.2 ($NCOCH_3$), 17.1, and 17.0 (C-6^2, 6^3); CIMS: *m/z* 690 $[M + 1]^+$.

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