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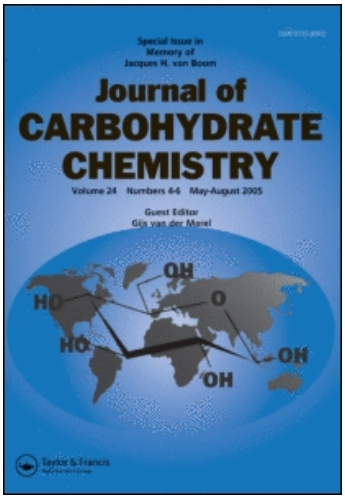

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SYNTHESES OF *O*-(2-ACETAMIDO-2-DEOXY-α-D-GALACTOPYRANOSYL)-*MYO*-INOSITOLS

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ABSTRACT

The structure of an *O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol isolated from human pregnancy urine has previously been identified as that of 1-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol. In order to ascertain the absolute configuration in the inositol part of the compound, the 1D- and 1L- isomers were synthesised. Since none of these two stereoisomers corresponded to the natural product, the corresponding 2-*O*-, the mixture of the two 1DL-4-*O*-, and 5-*O*- isomers were also synthesised. None of these gave ^{1}H NMR spectra corresponding to the natural product, the structure of which therefore remains unresolved.

INTRODUCTION

Meyer *et al.*[1] have described the isolation, from the pregnancy urine of a single donor, of a neutral inositol glycoside. Based upon ^{1}H NMR and MS, this was identified as 1-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol. Since the structural determination

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did not identify the absolute configuration in the *myo*-inositol part of the molecule, we decided to attempt to resolve this question by unambiguous synthesis.

RESULTS AND DISCUSSION

The various glycosylations were carried out on appropriately protected *myo*-inositol derivatives using 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactosyl chloride[2] as glycosyl donor and silver triflate as promoter, conditions which are known to give the α-anomer with good yield and stereoselectivity. The 1D-*myo*-inositol derivative **1a**[3] was benzoylated, and the product (**2a**) was then hydrogenolysed to give the 1L-*myo*-inositol derivative **3a** with a free 3-OH. The latter compound was then reacted with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactosyl chloride[2] (**4**) to give the glycosyl inositol derivative **5a**. The 1L-*myo*-inositol derivative **1b**[3] was similarly transformed *via* **2b** and **3b** into **5b**.

Hydrogenolysis of the two stereoisomeric glycosyl inositols **5a** and **5b**, followed by *N*-acetylation and de-*O*-acylation with sodium methoxide in methanol yielded the two stereoisomeric 1D- and 1L-1-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositols, **7a** and **7b** respectively. As seen from TABLE 1 none of these gave ^{1}H NMR spectra corresponding to those reported[1] for the natural product. Recourse was therefore taken to synthesize the remaining isomers with a 2-acetamido-2-deoxy-α-D-galactopyranosyl group attached to other positions in the *myo*-inositol residue.

Thus, 1,3,4,5,6-penta-*O*-benzyl-*myo*-inositol[3] (**8**) was glycosylated with the glycosyl chloride **4** to give **9**. This was then transformed into 2-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (**10**) as described above for the synthesis of **7a** from **5a**. Racemic 1,2,3,5,6-penta-*O*-benzoyl-*myo*-inositol[4] (**11**) was similarly glycosylated to give the mixture **12**, which then was transformed into 1DL-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (**13**). Finally, the 5-linked isomer was made, first by converting 5-*O*-benzyl-*myo*-inositol[5] (**14**) *via* **15** into 1,2,3,4,6-penta-*O*-benzoyl-*myo*-inositol (**16**) as described for the synthesis of compound **2a** above. Glycosylation of **16** gave the product **17** which was transformed into 5-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (**18**).

The identities of the various compounds are clear from their unambiguous syntheses, NMR spectra and elemental analyses. Nevertheless, as shown in TABLE 1, none of these compounds gave NMR spectra in agreement with that reported for the natural product. A sample of this unfortunately is no longer available (personal communication from Dr. C. Derappe).

EXPERIMENTAL

General methods. These were the same as those previously reported[5]. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C and at 100 MHz and 25 MHz respectively, using a JEOL JNM FX-100 instrument. The 2D-spectra (COSY) and the ^{1}H NMR spectra of

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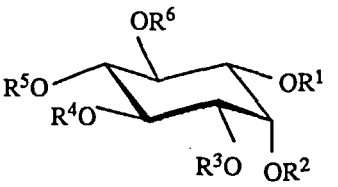
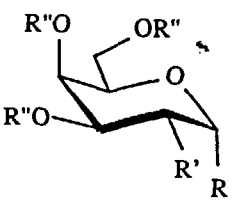


	R^1	R^2	R^3	R^4	R^5	R^6
1a	Bn	H	H	H	H	H
1b	H	H	Bn	H	H	H
2a	Bn	Bz	Bz	Bz	Bz	Bz
2b	Bz	Bz	Bn	Bz	Bz	Bz
3a	H	Bz	Bz	Bz	Bz	Bz
3b	Bz	Bz	H	Bz	Bz	Bz
5a	4a	Bz	Bz	Bz	Bz	Bz
5b	Bz	Bz	4a	Bz	Bz	Bz
6a	4b	Bz	Bz	Bz	Bz	Bz
6b	Bz	Bz	4b	Bz	Bz	Bz
7a	4c	H	H	H	H	H
7b	H	H	4c	H	H	H
8	Bn	H	Bn	Bn	Bn	Bn
9	Bn	4a	Bn	Bn	Bn	Bn
10	H	4c	H	H	H	H
11*	Bz	Bz	Bz	H	Bz	Bz
12**	Bz	Bz	Bz	4a	Bz	Bz
13**	H	H	H	4c	H	H
14	H	H	H	H	Bn	H
15	Bz	Bz	Bz	Bz	Bn	Bz
16	Bz	Bz	Bz	Bz	H	Bz
17	Bz	Bz	Bz	Bz	4a	Bz
18	H	H	H	H	4c	H

*Racemic mixture **Diastereomeric pair



	R	R'	R"
4	Cl	N_3	Ac
4a	MI	N_3	Ac
4b	MI	NHAc	Ac
4c	MI	NHAc	H

MI = *myo*-Inositol

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compounds **7a** and **7b** were recorded at 400 MHz using a JEOL GX-400 instrument, and the ^{1}H NMR spectra of compounds **10**, **13** and **18** were recorded at 270 MHz using a GSX-270 instrument.

1L-1,2,4,5,6-Penta-*O*-benzoyl-3-*O*-benzyl-*myo*-inositol (2a). Benzoyl chloride (0.50 mL, 4.3 mmol) was added dropwise to a stirred solution of 1D-1-*O*-benzyl-*myo*-inositol[3] (**1a**, 115 mg, 0.43 mmol) in pyridine (3 mL). The mixture was heated to 70 °C for 1.5 h and stirred at room temperature for 15 h. Portions of ice were added and after prolonged stirring for 30 min the solution was diluted with chloroform, washed with water, 1 M hydrochloric acid and water, dried ($MgSO_4$), filtered, concentrated and co-concentrated with toluene. The residue was purified by column chromatography (toluene-ethyl acetate, 6:1) on silica gel and crystallized from dichloromethane-diethyl ether-pentane to yield **2a** (0.28 g, 83 %), mp 209-210 °C, $[\alpha]_D$ + 18° (*c* 1.0, chloroform). ^{1}H NMR data ($CDCl_3$): δ 4.07 (dd, 1 H, H-3), 4.54 and 4.76 (each d, 2 H, CH_2Ph), 5.60 (dd, 1 H, H-1), 5.85 (dd, 1 H, H-5), 6.07 (dd, 1 H, H-4), 6.32 (dd, 1 H, H-6), 6.36 (dd, 1 H, H-2), 7.10-8.32 (m, 30 H, aromatic H). $J_{1,2}$= $J_{2,3}$ 2.9, $J_{3,4}$= $J_{5,6}$ 9.8, $J_{4,5}$ 10.0, $J_{1,6}$ 10.4, J_{CH2Ph} 12.8 Hz. ^{13}C NMR data ($CDCl_3$): δ 67.3 (C-2), 70.0 (C-6), 70.1 (C-1), 70.9 (C-5), 71.1 (C-4), 71.2 (CH_2Ph), 74.2 (C-3), 127.7-136.3 (aromatic C), 164.8, 165.2 and 165.4 (C=O).

Anal. Calcd for $C_{48}H_{38}O_{11}$: C, 72.9; H, 4.8. Found: C, 73.0; H, 4.8.

1D-1,2,4,5,6-Penta-*O*-benzoyl-3-*O*-benzyl-*myo*-inositol (2b). This compound was prepared from **1b**[3] as described for **2a** and in a comparable yield. It had mp 209-210 °C, $[\alpha]_D$ - 19° (*c* 1.0, chloroform).

Anal. Calcd for $C_{48}H_{38}O_{11}$: C, 72.9; H, 4.8. Found: C, 72.9; H, 4.7.

1L-1,2,4,5,6-Penta-*O*-benzoyl-*myo*-inositol (3a). A solution of **2a** (250 mg, 0.32 mmol) in tetrahydrofuran-ethanol (1:1, 4 mL) was hydrogenolyzed by using 10 % palladium-on-carbon (150 mg) at room temperature and at 6 bar for 24 h. The mixture was filtered through Celite and concentrated. The product was purified by column chromatography (toluene-ethyl acetate, 4:1) on silica gel and crystallized from dichloromethane-diethyl ether-pentane to yield pure **3a** (165 mg, 74 %), mp 136-138 °C, $[\alpha]_D$ + 63° (*c* 1.0, chloroform). ^{1}H NMR data ($CDCl_3$): δ 3.12 (d, 1 H, OH), 4.40 (dd, 1 H, H-3), 5.68 (dd, 1 H, H-1), 5.99 (dd, 1 H, H-5), 6.00 (dd, 1 H, H-4), 6.21 (dd, 1 H, H-2), 6.30 (dd, 1 H, H-6), 7.15-8.18 (m, 25 H, aromatic H). $J_{1,2}$ = $J_{2,3}$ 3.0, $J_{3,4}$= $J_{4,5}$= $J_{5,6}$= $J_{1,6}$ 10.0, J_{OH} 8.5 Hz. ^{13}C NMR data ($CDCl_3$): δ 69.6, 70.0, 70.2, 70.7, 71.5 and 73.2 (C-1--C-6), 128.0-133.3 (11 C, aromatic C), 165.2, 165.4, 165.6 and 166.4 (C=O).

Anal. Calcd for $C_{41}H_{32}O_{11}$: C, 70.3; H, 4.6. Found: C, 69.3; H, 4.5.

1D-1,2,4,5,6-Penta-*O*-benzoyl-*myo*-inositol (3b). This compound was prepared from **2b** as described for **3a** and in a comparable yield. It had mp 136-138 °C, $[\alpha]_D$ - 65° (*c* 1.0, chloroform) (lit.[6] mp 123-125 °C, $[\alpha]_D$ - 59.5°).

Anal. Calcd for $C_{41}H_{32}O_{11}$: C, 70.3; H, 4.6. Found: C, 70.1; H, 4.6.

1D-1-*O*-(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-2,3,4,5,6-penta-*O*-benzoyl-*myo*-inositol (5a). A mixture of **3a** (150 mg, 0.215 mmol),

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TABLE 1

^{1}H-N.M.R. SPECTRA OF α-D-GALNAC-*myo*-INOSITOL GLYCOSIDES

Proton	Chemical shifts (ppm)					
	Nat.pr.	7a	7b	10	18	13
H'-1	5.46	5.11	5.08	5.23	5.26	5.22/5.24
H-2	4.24	4.24	4.20	4.09	4.05	4.28
H'-2	4.16	4.19	4.22	4.15	4.20	↑
H'-5	3.95	4.12	4.19	4.26	4.27	
H'-4	3.99	4.01	4.08	4.02	4.03	↓
H'-3	3.88	3.95	3.98	4.00	3.97	3.93
H'-6ab	3.7-3.8	3.7-3.8	3.7-3.8	3.83	3.83	3.77
H-4	n.d.	3.62	3.66	↑	↕	↑
H-6	n.d.	3.75	3.73		3.67	
H-1	3.64	3.55	3.60	↓	3.55*	↓
H-3	3.51	3.52	3.49	3.55	3.52*	3.46
H-5	3.41	3.28	3.32	3.30	3.39	3.36
AcNH	2.05	2.04	2.05	2.04	2.05	2.04

* Magnetically non-equivalent

COUPLING CONSTANTS

Residue	Coupling constants *J* (Hz)					
myo-INOSITOL	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{1,6}$
Nat. product	2.5	2.5	10.0	8.2	8.2	10.0
1DL	2.8	2.8	10.0	9.3	9.3	10.0
2	5.9	6.2	n.d.	8.8	8.8	n.d.
5	6.6	6.2	n.d.	9.2	9.2	n.d.
α-D-GALNAc	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$	$J_{6'ab}$
Nat. product	3.5	9.0	2.5	n.d.	6.0	n.d.
1DL	3.8	11.0	3.2	< 0.5	6.1	n.d.
2	4.0	11.0	3.3	< 0.5	6.2(5.9)	n.d.
5	3.7	11.0	2.9	< 0.5	6.2(6.6)	n.d.

n.d. = not determined

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3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl chloride[2] (**4**) (150 mg, 0.43 mmol) and powdered 4 A molecular sieves (0.5 g) in dichloromethane (5 mL) was stirred under nitrogen atmosphere for 30 min. The mixture was cooled to - 50 °C and silver triflate (110 mg, 0.43 mmol) was added. The temperature was raised to room temperature over a period of 2 h and after 4 h additional portions of silver triflate (55 mg) and **4** (75 mg) were added. The reaction mixture was stirred over night and then filtered through Celite and concentrated. The residue was first purified on a short column of silica gel (toluene-ethyl acetate, 4:1) and then by another column chromatography (chloroform-ethyl acetate, 6:1) to separate the α-glycosidic anomer from the β-anomer (10 %), which yielded **5a** (165 mg, 76 %) as a syrup, $[\alpha]_D$ + 76.5° (*c* 1.0, chloroform). ^{1}H NMR data ($CDCl_3$): δ 1.88, 2.03 and 2.11 (each s, 9 H, CH_3CO), 3.45 (dd, 1 H, H'-2), 4.06-4.20 (m, 2 H, H'-6ab), 4.47 (dd, 1 H, H-1), 4.48-4.64 (m, 1 H, H-5), 5.10 (dd, 1 H, H'-3), 5.17 (d, 1 H, H'-1), 5.42 (dd, 1 H,H'-4), 5.70 (dd, 1 H, H-3), 5.93 (dd, 1 H, H-5), 6.20 (dd, 1 H, H-2), 6.29 (dd, 1 H, H-6), 6.35 (dd, 1 H, H-4), 7.19-8.23 (m, 25 H, aromatic H). $J_{1,2} = J_{2,3}$ 2.7, $J_{3,4} = J_{4,5} = J_{5,6} = J_{1,6}$ 10.0, $J_{1',2'}$ 3.8, $J_{2',3'}$ 11.1, $J_{3',4'}$ 2.7, $J_{4',5'}$ 1.0 Hz. ^{13}C NMR data ($CDCl_3$): δ 20.5, 20.6, 21.4 ($\underline{C}H_3CO$), 56.9 (C'-2), 62.2 (C'-6), 67,6 (x2) and 67.8 (C-2, C'-3 and C'-4), 69.8 (x2), 70.1, 70.7 and 71.3 (C-3, C-4, C-5, C-6, and C'-5), 75.1 (C-1), 100.0 (C'-1), 127.9-133.5 (13 C, aromatic C), 164.8, 165.0, 165.1, 165.4 and 165.5 (C=O, Bz), 168.8, 169.4 and 170.4 (C=O, Ac).

Anal. Calcd for $C_{53}H_{47}O_{18}N_3$: C, 62.8; H, 4.7; N, 4.1. Found: C, 62.0; H, 4.6; N,4.2.

1L-1-*O*-(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-2,3,4,5,6-penta-*O*-benzoyl-*myo*-inositol (5b). This compound was prepared from **3b** and **4** as described for **5a** and in a comparable yield. The product was crystallized from dichloromethane-diethyl ether-pentane, mp 215-217 °C, $[\alpha]_D$ + 62° (*c* 1.0, chloroform). ^{1}H NMR data ($CDCl_3$): δ 1.90, 2.01, 2.04 (CH_3CO), 3.58 (dd, 1 H, H'-2), 3.7-3.9 (m, 3 H, H'-5 and H'-6ab), 4.47 (dd, 1 H, H-1), 4.92-5.01 (m, 2 H, H'-3, H'-4), 5.29 (dd, 1 H, H'-1), 5.68 (dd, 1 H, H-3), 5.99 (dd, 1 H, H-5), 6.25 (dd, 1 H, H-6), 6.33 (dd, 1 H, H-2), 6.34 (dd, 1 H, H-4), 7.20-8.25 (m, 25 H, aromatic H). $J_{1,2} = J_{2,3}$ 2.7, $J_{3,4} = J_{5,6}$ 10.0, $J_{4,5} = J_{1,6}$ 9.5, $J_{1',2'}$ 3.9 Hz. ^{13}C NMR data ($CDCl_3$): δ 20.5, 20.7 ($\underline{C}H_3CO$), 56.7 (C'-2), 61.1 (C'-6), 65.8, 66.7, 66.8, 67.7 (C-2, C-3, C'-3, C'-4), 69.6, 69.9, 70.5 (x2), 71.8 (C-1, C-4, C-5, C-6, C'-5), 94.3, (C'-1), 128.1-133.2 (10 C, aromatic C), 164.6, 165.1, 165.2, 165.4, 165.5 (C=O, Bz), 168.7, 169.4, 169.7 (C=O, Ac).

Anal. Calcd for $C_{53}H_{47}O_{18}N_3$: C, 62.8; H, 4.7; N, 4.1. Found: C, 62.1; H, 4.5; N, 4.2.

1D-1-*O*-(2-Acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (7a). Compound **5a** (160 mg, 0.16 mmol) in methanol-ethyl acetate (4:1, 5 mL) was hydrogenated by using 10 % palladium-on-carbon (100 mg) at 6 bar for 30 h. The mixture was filtered through Celite and concentrated. The residue in a mixture of pyridine (1 mL) and acetic anhydride (1 mL) was stirred at 100 °C for half an hour. Concentration gave a homogenous product **6a**, which was purified by column chromatography (toluene-ethyl acetate, 1:2) on silica gel. The purified product (**6a**) in methanol (10 mL) was treated with methanolic sodium methoxide (1 mL, 1 %) until complete reaction was visualized by TLC (toluene-ethyl acetate, 1:2, and/or

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ethyl acetate-acetic acid-methanol-water, 12:3:3:2). The solution was neutralized with Dowex 50 (H^+) resin, filtered and concentrated to a crystalline product, which was recrystallized from water-ethanol to yield pure **7a** (45 mg, 75 %), mp 233-235 °C (decomp.), $[\alpha]_D$ + 127° (*c* 0.4, water). ^1H NMR data (D_2O, acetone as reference, δ 2.225): δ 2.04 (CH_3CONH), 3.25 (dd, 1 H, H-5), 3.52 (dd, 1 H, H-3), 3.55 (dd, 1 H, H-1), 3.62 (dd, 1 H, H-4), 3.75 (dd, 1 H, H-6), 3.74-3.81 (m, 2 H, H'-6ab), 3.95 (dd, 1 H, H'-3), 4.01 (dd, 1 H, H'-4), 4.12 (m, 1 H, H'-5), 4.19 (dd, 1 H, H'-2), 4.24 (dd, 1 H, H-2), 5.11 (d, 1 H, 1). See also Table 1. ^{13}C NMR data (D_2O, 1,4-dioxan as reference, δ 67.4): δ 23.0 (CH_3CONH), 51.0 (C'-2), 62.2 (C'-6), 68.8, 69.5 (C'-3, C'-4), 71.9, 72.4, 72.5, 72.8, 73.0 (C-2, C-3, C-4, C-6, C'-5), 75.2 (C-5), 80.5 (C-1), 100.4 (C'-1), 175.0 (CH_3CONH).

Anal. Calcd for $C_{14}H_{25}O_{11}N \cdot 2\,H_2O$: C, 40.1; H, 7.0; N, 3.3. Found: C, 40.2; H, 7.0; N, 3.0.

1L-1-*O*-(2-Acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (7b). This compound was prepared from **5b** as described for **7a** and in a comparable yield. It had mp 255 °C (decomp.), $[\alpha]_D$ + 182° (*c* 0.4, water). ^1H NMR data (D_2O, acetone as reference δ 2.225): δ 2.05 (s, 3 H, CH_3CONH), 3.32 (dd, 1 H, H-5), 3.49 (dd, 1 H, H-3), 3.60 (dd, 1 H, H-1), 3.66 (dd, 1 H, H-4), 3.73 (dd, 1 H, H-6), 3.70-3.78 (m, 2 H, H'-6ab), 3.98-4.08 (m, 2 H, H'-3, H'-4), 4.19 (m, 1 H, H'-5), 4.20 (dd, 1 H, H-2), 4.22 (dd, 1 H, H'-2), 5.08 (d, 1 H, H'-1). See also Table 1. ^{13}C NMR data (D_2O, 1,4-dioxan as reference, δ 67.4): δ 23.0 (CH_3CONH), 50.6 (C'-2), 61.8 (C'-6), 68.4, 68.9, 69.2 (C-2, C'-3, C'-4), 71.8, 71.9 (x2) (C-3, C-6, C'-5), 72.9 (C-4), 74.9 (C-5), 76.0 (C-1), 94.7 (C'-1), 175.2 (CH_3CONH).

Anal. Calcd for $C_{14}H_{25}O_{11}N$: C, 43.9; H, 6.6; N, 3.7. Found: C, 43.1; H, 6.6; N, 3.4.

2-*O*-(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-1,3,4,5,6-penta-*O*-benzyl-*myo*-inositol (9). A mixture of 1,3,4,5,6-penta-*O*-benzyl-*myo*-inositol[3] (**8**, 250 mg, 0.4 mmol), **4** (280 mg, 0.8 mmol) and powdered 4 A molecular sieves (1.4 g) in dry dichloromethane (8 mL) was stirred under nitrogen atmosphere for 30 min. The reaction mixture was cooled to -50 °C and silver triflate (200 mg, 0.8 mmol) was added. The temperature was allowed to attain room temperature over a period of 2 h. After 4 and after 20 h additional portions of silver triflate (50 mg) were added and the reaction mixture was stirred another 24 h and then filtered through Celite and concentrated. The crude product was purified by silica gel column chromatography (toluene:ethyl acetate, 6:1) to yield **9** (117 mg, 31 %) as a syrup, $[\alpha]_D$ + 76.9° (*c* 0.66, chloroform). ^1H NMR data ($CDCl_3$): δ 1.86, 2.08, 2.11 (s, 9 H, CH_3CO), 3.23-4.31 (m, 10 H, H-2 - H-6, H-1, H'-2, H'-5, H-6'ab), 4.68, 4.87, 4.91 (s, 10 H, CH_2Ph), 5.30 (dd, 1 H, H'-3), 5.42 (dd, 1 H, H'-4), 5.63 (d, 1 H, H'-1), 7.26-7.31 (m, 25 H, aromatic H). ^{13}C NMR data ($CDCl_3$): δ 20.5, 20.7 (CH_3CO), 58.0 (C'-2), 60.7 (C'-6), 65.7, 67.2, 68.3 (C'-3 - C'-5), 72.3, 72.7, 73.2, 78.3, 80.6, 81.1, 83.4 (CH_2Ph, C-1 - C-6), 97.0 (C'-1), 125.0-128,7 (aromatic C), 137.5, 137.6, 138.2 (ipso C), 169.4, 169.7 (C=O).

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Anal. Calcd for $C_{53}H_{57}O_{13}N_3$: C, 67.4, H, 6.1, N, 4.5. Found: C, 67.4, H, 6.1, N, 4.6.

2-*O*-(2-Acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (10). Compound **9** (100 mg, 0.106 mmol) was dissolved in methanol-ethyl acetate (2 mL, 4:1) and hydrogenated by using 10 % palladium-on-carbon (70 mg) at atmospheric pressure for 36 h. The mixture was filtered through Celite and concentrated. The residue in pyridine (3mL) was treated with acetic acid anhydride (3 mL) and heated at 100 °C for half an hour. The mixture was concentrated and co-distilled several times with toluene and then purified by column chromatography on silica gel (EtOAc). The product was de-*O*-acetylated by using sodium methoxide in methanol. When the reaction was complete, the solution was neutralized with Dowex 50(H^+) cation exchange resin, filtered and concentrated. Recrystallization from water-ethanol gave **10** (28 mg, 69 %), mp 237-238 °C, $[\alpha]_D$ + 126° (c 0.4, water). ^{1}H NMR data (D_2O, acetone as reference, δ 2.225): δ 2.05 (s, 3 H, CH_3CONH), 3.30 (dd, 1 H, H-5), 3.53-3.83 (m, 6 H, H-1, H-3, H-4, H-6, H'-6ab), 4.00 (dd, 1 H, H'-3), 4.02 (d, 1 H, H'-4), 4.09 (dd, 1 H, H-2), 4.15 (dd, 1 H, H'-2), 4.26 (dd, 1 H, H'-5), 5.23 (d, 1 H, H'-1). $J_{1,2}$ 5.9, $J_{2,3}$ 6.2, $J_{4,5}$= $J_{5,6}$ 8.8, $J_{1',2'}$ 4.03, $J_{2',3'}$ 11.0, $J_{3',4'}$ 3.3, $J_{4',5'}$ < 0.5, $J_{5',6'}$ 6.2 (5.9). ^{13}C NMR data (D_2O, 1,4-dioxane as reference, δ 67.4): δ 23.0 (CH_3CO), 51.3 (C'-2), 61.7 (C'-6), 68.2, 69.2, 71.4, 71.8, 72.2, 73.4, 73.5, 75.3 (C-1, C-3 - 6, C'-3 - 5), 81.0 (C-2), 99.4(C'-1), 175.2 (CH_3CONH).

Anal. Calcd for $C_{14}H_{25}O_{11}N \cdot H_2O$: C, 41.9, H, 6.8, N, 3.5. Found: C, 42.2, H, 6.4, N, 3.5.

Synthesis of **10** was also performed using 1,3,4,5,6-penta-*O*-acetyl-*myo*-inositol[7] as aglycone. The yield in the glycosylation reaction was however not improved (30 %).

1DL-4-*O*-(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-1,2,3,5,6--penta-*O*-benzoyl-*myo*-inositol (12). This compound was prepared from racemic 1,2,3,5,6-penta-*O*-benzoyl-*myo*-inositol[4] (**11**) and compound **4** as described for **5a** in a yield of 72 %. ^{1}H NMR data ($CDCl_3$): δ 1.80, 1.92, 1.97 (s, 9 H, CH_3CO), 3.30-4.09 (m, 4 H, H'-2, H'-5, H'-6ab), 4.73 (dd, 1 H, H-4), 5.14 (m, 2 H, H'-3, H'-4), 5.28 (d, 1 H, H'-1), 5.79, 5.85 (2 dd, 2 H, H-1, H-3), 5.99 (dd, 1 H, H-5), 6.24, 6.31 (2 dd, 2 H, H-6, H-2), 7.14-8.17 (m, aromatic H). ^{13}C NMR data ($CDCl_3$): δ 20.2, 20.4, 20.4 (CH_3CO), 57.2 (C'-2), 60.3 (C'-6), 66.7, 68.1, 69.2, 69.3, 70.3, 71.6, 72.4 (C'-3 - 5, C-1 - 3, C-5 - 6), 76.5 (C-4), 98.7, 98.9 (C'-1, diastereomers), 128-133.5 (aromatic carbons), 164.4-169.5 (C=O).

Anal. Calcd for $C_{53}H_{47}O_{18}N_3$: C, 62.8, H, 4.7, N, 4.1. Found: C, 63.0, H, 4.7, N, 4.3.

1DL-4-*O*-(2-Acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (13). Compound **12** (320 mg, 0.32 mmol) in methanol:ethyl acetate (2:1, 12 mL) was hydrogenated by using 10 % palladium-on-carbon (200 mg) at atmospheric pressure for 40 h. The mixture was filtered through Celite and concentrated. The product was *N*-acetylated and deprotected as described for compound **7a**. The product was purified by column chromatography on Biogel P-2 and then recrystallized from water-ethanol to yield **13** (60 mg, 49 %), $[\alpha]_D$ + 119° (*c* 1.2, water, diastereomeric mixture). ^{1}H NMR data (D_2O, acetone as reference, δ 2.225): δ 2.04 (s, 3 H, CH_3CONH), 3.35-3.76 (m, 7 H, H-1, H-3 - 6, H'-6ab), 3.92-4.07 (m, 3 H, H-2,

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H'-3, H'-4), 4.16-4.32 (m, 2 H, H'-2, H'-5), 5.22/5.24 (d, 1 H, H'-1, diastereomers). ^{13}C NMR data (D_2O, 1,4-dioxan as reference, δ 67.4): δ 23.2 ($\underline{C}H_3CO$), 51.1 (C'-2), 61.7, 61.9 (C'-6, diastereomers), 68.7, 69.2, 69.3, 70.9, 71.8, 72.1, 72.6, 73.2, 73.5, 74.0, 75.3 (C'-3 - 5, C-1 - 3, C-5, C-6, diastereomers), 81.3, 81.7 (C-4, diastereomers), 99.0 (C'-1), 175.2 ($CH_3\underline{C}ONH$).

Anal. Calcd for $C_{14}H_{25}O_{11}N \cdot H_2O$: C, 41.9, H, 6.8, N, 3.5. Found: C, 42.2, H, 6.5, N, 3.5.

1,2,3,4,6-Penta-*O*-benzoyl-5-*O*-benzyl-*myo*-inositol (15). Compound **15** was synthesized from 5-*O*-benzyl-*myo*-inositol[5] (**14**) as described for compound **2a** in a yield of 87 %, mp 270-271 °C. ^1H NMR data ($CDCl_3$): δ 4.18 (dd, 1 H, H-5), 4.64 (s, 2 H, CH_2Ph), 5.71 (dd, 2 H, H-1, H-3), 6.24 (dd, 1 H, H-2), 6.28 (dd, 2 H, H-4, H-6), 6.98-8.15 (m, 30 H, aromatic H). ^{13}C NMR data ($CDCl_3$): δ 69.0 (C-2), 69.6, 71.7, 75.2 (C-1, C-3 - 6, CH_2Ph), 127.6-133.3 (aromatic C), 136.3 (ipso C), 164.9 (C=O).

Anal. Calcd for $C_{48}H_{38}O_{11}$: C, 72.9, H, 4.8. Found: C, 72.7, H, 4.8.

1,2,3,4,6-Penta-*O*-benzoyl-*myo*-inositol (16). Compound **15** (239 mg, 0.31 mmol) was dissolved in tetrahydrofuran-ethanol (5:1, 3 mL) and hydrogenolyzed by using 10 % palladium-on-carbon (40 mg) at atmospheric pressure and room temperature for 28 h. The reaction mixture was filtered through Celite and concentrated. The product was crystallized from dichloromethane-light petroleum (40-60 °C) to yield **16** (158 mg, 75 %), mp 246-248 °C. ^1H NMR data ($CDCl_3$): δ 2.95 (d, 1 H, OH), 4.27 (m, 1 H, H-5), 5.75 (dd, 2 H, H-1, H-3), 6.10 (dd, 2 H, H-4, H-6), 6.26 (dd, 1 H, H-2), 7.25-8.15 (m, 25 H, aromatic H). ^{13}C NMR data ($CDCl_3$): δ 69.2 (C-1 - 3), 72.1 (C-5), 72.8 (C-4, C-6), 128.1-133.4 (aromatic C), 164.9-166.0 (C=O).

Anal. Calcd for $C_{41}H_{32}O_{11}$: C, 70.3, H, 4.6. Found: C, 69.8, H, 4.5.

5-*O*-(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-1,2,3,4,6-penta-*O*-benzoyl-*myo*-inositol (17). This compound was prepared from **16** and **4** as described for **5a** in a yield of 74 %, $[\alpha]_D$ + 74.1° (*c* 0.9, chloroform). ^1H NMR data ($CDCl_3$): δ 1.80, 1.95, 1.98 (s, 9 H, CH_3CO), 3.32-4.16 (m, 4 H, H'-2, H'-5, H'-6ab), 4.48 (dd, 1 H, H-5), 5.20-5.32 (m, 3 H, H'-1, H'-3, H'-4), 5.72 (dd, 2 H, H-1, H-3), 6.30 (m, 3 H, H-2, H-4, H-6), 7.22-8.16 (m, 25 H, aromatic H). ^{13}C NMR data ($CDCl_3$): δ 20.5 ($\underline{C}H_3CO$), 57.3 (C'-2), 59.9 (C'-6), 66.5, 66.8, 68.3, 68.7, 69.4, 69.7, 70.8, 71.4, 77.8 (C-1 - 6, C'-3 - 5), 99.2 (C'-1), 128.1-133.4 (aromatic C), 164.9-169.5 (C=O).

Anal. Calcd for $C_{53}H_{47}O_{18}N_3$: C, 62.8, H, 4.7, N, 4.1. Found: C, 62.1, H, 4.6, N, 4.1.

5-*O*-(2-Acetamido-2-deoxy-α-D-galactopyranosyl)-*myo*-inositol (18). This compound was prepared from **17** as described for **10** in a comparable yield. Compound **18** had mp 226-227 °C, $[\alpha]_D$ + 124.3° (*c* 0.34, water). ^1H NMR data (D_2O, acetone as reference, δ 2.225): δ 2.05 (s, 3 H, $CH_3\underline{C}ONH$) 3.39 (dd, 1 H, H-5), 3.50-3.58 (m, 2 H, H-1, H-3), 3.67-3.83 (m, 4 H, H-4, H-6, H'-6ab), 3.96 (dd, 1 H, H'-3), 4.03 (dd, 1H, H'-4), 4.05 (dd, 1 H, H-2), 4.20 (dd, 1 H, H'-2), 4.27 (dd, 1 H, H'-5), 5.26 (d, 1 H, H'-1). $J_{1,2}$ 6.6, $J_{2,3}$ 6.2, $J_{4,5}$ = $J_{5,6}$ 9.2, $J_{1',2'}$ 3.7, $J_{2',3'}$ 11.0, $J_{3',4'}$ 2.9, $J_{4',5'}$ < 0.5, $J_{5',6'}$ 6.2 (6.6). ^{13}C NMR data (D_2O,

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1,4-dioxan as reference, δ 67.4): δ 23.0 ($\underline{C}H_3CONH$), 51.0 (C'-2), 61.7 (C'-6), 68.5, 69.2, 71.7, 71.8, 72.0, 72.2, 72.7, 73.6 (C'-3 - 5, C-1 - 4, C-6), 82.8 (C-5), 98.9 (C'-1), 175.1 ($CH_3\underline{C}ONH$).

Anal. Calcd for $C_{14}H_{25}O_{11}N \cdot H_2O$: C, 41.9, H, 6.8, N, 3.5. Found: C, 42.2, H, 6.4, N, 3.5.

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