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SYNTHETIC MUCIN FRAGMENTS. METHYL 6-*O*-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)-β-D-GALACTOPYRANOSIDE, METHYL 3,4-DI-*O*-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)-β-D-GALACTOPYRANOSIDE, AND METHYL *O*-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)-(1→3)-*O*-β-D-GALACTOPYRANOSYL-(1→3)-*O*-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)-(1→3)-β-D-GALACTOPYRANOSIDE*

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ABSTRACT

Condensation of methyl 2,6-di-*O*-benzyl-β-D-galactopyranoside with 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline (**1**) in 1,2-dichloroethane, in the presence of *p*-toluenesulfonic acid, afforded a trisaccharide derivative which, on deacetylation, gave methyl 3,4-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-2,6-di-*O*-benzyl-β-D-galactopyranoside (**5**). Hydrogenolysis of the benzyl groups of **5** furnished the title trisaccharide (**6**). A similar condensation of methyl 2,3-di-*O*-benzyl-β-D-galactopyranoside with **1** produced a partially-protected disaccharide derivative, which, on *O*-deacetylation followed by hydrogenolysis, gave methyl 6-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranoside (**10**). Condensation of methyl 3-*O*-(2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside with 3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2,4,6-tri-*O*-acetyl-α-D-galactopyranosyl bromide in 1:1 benzene–nitromethane in the presence of powdered mercuric cyanide gave a fully-protected tetrasaccharide derivative, which was *O*-deacetylated and then subjected to catalytic hydrogenation to furnish methyl *O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-β-D-galactopyranosyl-(1→3)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranoside (**15**). The structures of **6**, **10**, and **15** were established by ^{13}C-n.m.r. spectroscopy.

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INTRODUCTION

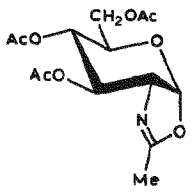
At the outset of our recently initiated program for the synthesis of some mucinous-type glycoconjugate fragments, we decided to explore the utility of the disaccharide 3-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-galactopyranose as a "building block" for the synthesis of such type of oligosaccharides. This disaccharide unit, trivially known as "lacto-*N*-biose II", forms part of the core structure, and also occurs in the side chain, attached to 2-acetamido-2-deoxy-D-galactose, that is further *O*-glycosyl-linked to protein[2]. Hence, we synthesized this sugar unit as both its methyl α-[3] and β-D-glycoside[4]. The choice of the methyl β-D-glycoside was necessitated by a desire to mimic, as closely as possible, the naturally-occurring units of the carbohydrate moiety of such glycoconjugates. All of the D-galactose residues of the inner-region of this type "megalosaccharides" are β-linked to 2-acetamido-2-deoxy-D-glucose, the last galactosyl group being β-linked to the terminal 2-acetamido-2-deoxy-galactose residue*. On the other hand, the choice of a derivative of the much less expensive methyl α-D-galactopyranoside was dictated by the fact that relatively larger quantities of the peracetylated disaccharide derivative were required for the preparation of the peracetyl glycosyl bromide which is to be used as a glycosyl donor[5].

Once this disaccharide unit (in both of its forms) was available, a variety of manipulations could be conceived. In this regard, we now describe the synthesis of the tetrasaccharide methyl *O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-β-D-galactopyranosyl-(1→3)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranoside (**15**). Additionally, we describe the syntheses of the disaccharide, methyl 6-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranoside (**10**), and of the trisaccharide, methyl 3,4-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranoside (**6**).

RESULTS AND DISCUSSION

In one of our initial attempts to prepare methyl 3-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranoside, we condensed readily accessible methyl 2,6-di-*O*-benzyl-β-D-galactopyranoside[6] (**2**) with 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline (**1**). However, instead of the β-D-(1→3)-linked disaccharide desired, the major product obtained was the di-glycosylated derivative of **2**, a result reminiscent of that previously obtained by Augé and Veyrières[7]. Interestingly, HO-3 linked to a galactopyranoside ring was immune to glycosylation by the oxazoline method when O-2 and -6 carried acetyl groups[8]. Thus, it would appear that it is a prerequisite to have certain substituents,

*For example, compare the composite structure proposed by Kabat *et al.*[2] for the water-soluble, human blood-group substances from ovarian cysts.



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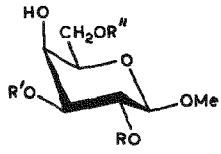
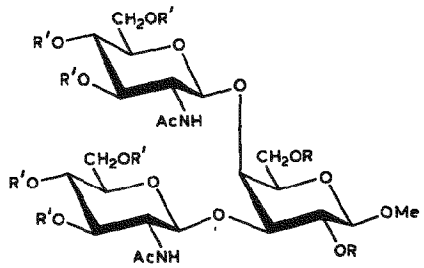


2 R = R″ = Bn, R′ = H
3 R = R′ = Bn, R″ = H

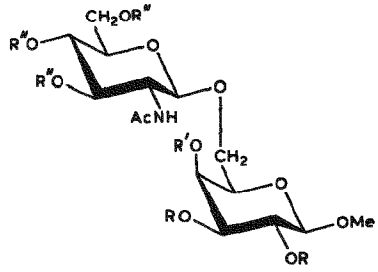
e.g., benzyl groups, at least in the immediate vicinity of the secondary hydroxyl group, to be glycosylated. However, in the absence of sufficient experimental data, it is difficult to rationalize adequately the exact nature of this type of activation. Nonetheless, it would be reasonable to assume that the presence of a benzyl group at O-6 may be necessary to enhance the reactivity of HO-4 towards oxazoline condensation. In support of this assumption, reaction of methyl 2,3-di-*O*-benzyl-β-D-galactopyranoside[9] with oxazoline **1** gave, as the major product, the β-D-(1→6)-linked disaccharide derivative (see later).

On condensation of methyl 2,6-di-*O*-benzyl-β-D-galactopyranoside (**2**) with oxazoline **1** in 1,2-dichloroethane, in the presence of *p*-toluenesulfonic acid, examination of the product mixture by t.l.c. revealed the presence of a major product, slower-migrating than **2**; small proportions of a faster-migrating product (presumably a disaccharide derivative), and of compound **2** were also revealed by t.l.c. Column-chromatographic separation and recrystallization of the major product from ethyl acetate–ether afforded compound **4**. *O*-Deacetylation of **4** in methanolic sodium methoxide gave the trisaccharide derivative **5**, the ^{13}C-n.m.r. spectrum of which was consistent with the structure assigned (see Table I). Hydrogenolysis of the benzyl groups of **5** furnished the title trisaccharide **6**, whose ^{13}C-n.m.r. spectrum was also in accord with the structure expected (see Table I).

Condensation of methyl 2,3-di-*O*-benzyl-β-D-galactopyranoside (**3**) with



4 R = Bn, R′ = Ac
5 R = Bn, R′ = H
6 R = R′ = H



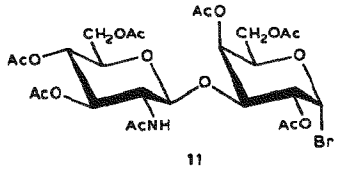
7 R = Bn, R′ = H, R″ = Ac
8 R = Bn, R′ = R″ = H
9 R = Bn, R′ = R″ = Ac
10 R = R′ = R″ = H

TABLE I

PROPOSED ^{13}C-N.M.R. CHEMICAL SHIFTS[a,b]

Residue or group	*Compound*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*CH_3CO*	*OCH_3*
2,6-Di-*O*-Bn-β-D-GalOMe	**5**[c]	102.77	78.53	80.14	75.46	72.95	70.29		54.47
β-D-Glc*p*NAc-(1→3)		100.54	55.68	74.42	70.75	76.82	61.13	22.88	
β-D-Glc*p*NAc-(1→4)		102.57	55.68	74.13	72.04	76.90	61.13	22.78	
β-D-Gal*p*OMe	**6**	103.80	69.20	80.74	75.12	73.35	59.81		54.93
β-D-Glc*p*NAc-(1→3)		101.48	55.50	74.49	70.57	76.53	61.00	23.10	
β-D-Glc*p*NAc-(1→4)		102.57	56.07	73.74	71.48	76.89	61.62	23.10	
β-D-Gal*p*OMe	**10**	104.78	71.68	73.74	65.04	74.79	69.74		57.97
β-D-Glc*p*NAc-(1→6)		102.42	56.51	74.50	71.00	76.87	61.74	23.08	
β-D-Gal*p*OMe	**15**	103.81	69.21	82.10	67.07	74.66	60.29		55.61
β-D-GlcNAc-(1→3) (a)		101.45	54.73	84.26	68.35	76.00	60.37	23.01	
β-D-Gal*p*-(1→3)		103.09	69.43	81.35	67.07	75.18	60.29		
β-D-Glc*p*NAc-(1→3) (b)		101.82	56.26	73.99	70.34	76.54	60.81	23.01	

[a]For solutions in $(^2H_6)Me_2SO$ with Me_4Si as the internal standard; except for **10**, where solvent was CD_3OD. [b]Carbonyl and aromatic carbon resonances are not shown. [c]Additional assignments: δ 72.95 and 72.04 ($CH_2C_6H_5$).



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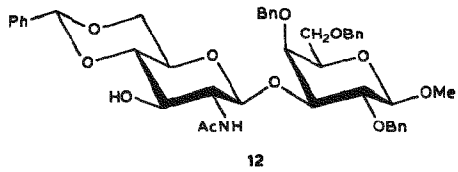

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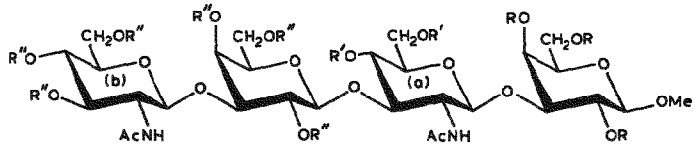

13 R = Bn; R', R' = PhCH; R'' = Ac
14 R = Bn; R', R' = PhCH; R'' = H
15 R = R' = R'' = H

oxazoline **1**, under conditions analogous to those described for **2** (to give **4**), and examination of the reaction mixture by t.l.c. revealed the presence of a major product, marginally slower-migrating than **3**. A small proportion of a slightly slower-migrating product (presumably a trisaccharide derivative) was also revealed by t.l.c. After the customary processing, followed by column-chromatographic separation, compound **7** was obtained as a crystalline solid. The ^{1}H-n.m.r. spectrum of **7** was in accord with monoglycosylation of the galactopyranosyl ring of **3**; only four acetyl-group methyl proton resonances were observed, and a broad singlet at δ 2.70 was indicative of the presence of a free hydroxyl group. In support of this, acetylation of **7** with 2:1 pyridine–acetic anhydride afforded compound **9**, the ^{1}H-n.m.r. spectrum of which was devoid of a signal at δ 2.70, but contained an additional three-proton resonance in the region of δ 2.20–1.70, confirming the introduction of another acetyl group. Systematic removal of the protecting groups of **7** afforded the title disaccharide **10**, the ^{13}C-n.m.r. spectrum of which was consistent with the structure assigned (see Table I).

Condensation of 3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2,4,6-tri-*O*-acetyl-α-D-galactopyranosyl bromide[5] (**11**) with 3-*O*-(2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside[4] (**12**) in 1:1 benzene–nitromethane, in the presence of powdered mercuric cyanide, afforded, after column-chromatographic purification, the tetrasaccharide derivative **13**. *O*-Deacetylation of **13** in methanolic sodium methoxide gave compound **14** which was in turn converted into the title tetrasaccharide **15** by catalytic hydrogenolysis of its benzylidene and benzyl groups. The identity of **15** was evident from its ^{13}C-n.m.r. spectrum (see Table I).

EXPERIMENTAL

General methods. — General and instrumental methods were the same as

those previously employed[4]. Optical rotations were recorded at ~25°. Unless otherwise indicated, the solvents used for chromatography were (v/v): (*A*) 3:1 chloroform–methanol, (*B*) 3:2:1 ethyl acetate–2-propanol–water, (*C*) 3:1 chloroform–acetone, (*D*) 6:1 chloroform–acetone, and (*E*) 3:2:2 ethyl acetate–2-propanol–water.

Methyl 3,4-di-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-2,6-di-O-benzyl-β-D-galactopyranoside (**4**). — A mixture of compound **2** (ref. 6; 2.85 g, 7.6 mmol), oxazoline **1** (5 g, 15.2 mmol), and *p*-toluenesulfonic acid monohydrate (95 mg) in 1,2-dichloroethane (50 mL), protected from moisture, was heated with stirring for 2 days at ~72°; additional amounts of **1** (2 g, 6.1 mmol, in 10 mL of 1,2-dichloroethane) and *p*-toluenesulfonic acid monohydrate (38 mg in 10 mL of 1,2-dichloroethane) being added after 16 h. The mixture was cooled, the acid neutralized by the addition of a few drops of pyridine, and the solvent evaporated to give a residue that was dissolved in chloroform and purified in a column of silica gel by elution with a solvent gradient consisting of 0–20% acetone in chloroform. Evaporation of the earlier fractions gave (t.l.c., solvent *C*) unchanged **2** (0.5 g), followed by a mixed fraction (0.8 g) which contained the major product in addition to some faster-migrating contaminants. Continued elution of the column and evaporation of the fractions corresponding to the major product gave **4** (2.7 g, 41.5%; based on reacted **2**). On recrystallization from dichloromethane–ether, it had m.p. 116–118°, $[\alpha]_D^{25}$ −38.8° (*c* 1.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.60–7.20 (m, 10 H, arom.), 3.52 (s, 3 H, OMe), and 2.20–1.50 (cluster of 24 H, 6 OAc and 2 NAc).

Anal. Calc. for $C_{49}H_{64}N_2O_{22}$: C, 56.96; H, 6.26; N, 2.71. Found: C, 56.67; H, 6.17; N, 2.68.

Methyl 3,4-di-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-2,6-di-O-benzyl-β-D-galactopyranoside (**5**). — Compound **4** (1.8 g) in 0.2M methanolic sodium methoxide (50 mL) was stirred for 16 h at room temperature. T.l.c. (solvent *A*) then showed the disappearance of **4** and the presence of a slower-migrating product. The base was neutralized by the addition of a few drops of glacial acetic acid, the solution evaporated to dryness, the residue dissolved in methanol, and the solution de-ionized with Amberlite IR-120 (H^+) cation-exchange resin. The resin was filtered off and washed with methanol, and the filtrate and washings were combined and evaporated to give a material (1.4 g), which was dissolved in ethanol. Addition of ether caused the precipitation of **5** (1.2 g, 88%) as an amorphous solid, $[\alpha]_D^{23}$ −5.4° (*c* 1.1, methanol); ^{1}H-n.m.r. ($CDCl_3$): δ 7.50–7.20 (m, 10 H, arom.), 3.54 (s, 3 H, OMe), and 1.59 (s, 6 H, 2 NAc).

Anal. Calc. for $C_{37}H_{52}N_2O_{16}$: C, 56.90; H, 6.73; N, 3.59. Found: C, 56.61; H, 6.76; N, 3.46.

Methyl 3,4-di-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranoside (**6**). — A solution of **5** (0.4 g) in glacial acetic acid (25 mL) was shaken under H_2 at ~345 kPa for 2 days at room temperature in the presence of 10% Pd–C (0.4 g). The suspension was filtered through a bed of Celite, the solid was

thoroughly washed with glacial acetic acid and methanol, and the filtrate and washings were combined, and evaporated under diminished pressure, to give a solid residue, which was contaminated (t.l.c., 13:6:1 chloroform–methanol–water, or solvent *B*) with some faster-migrating impurities (presumably due to incomplete debenzylation). After column-chromatographic purification on silica gel with solvent *B* as the eluant, the residue was dissolved in ethanol. Addition of ether caused the precipitation of **6** (0.27 g, 87%), amorphous; $[\alpha]_D^{23}$ −4.1° (*c* 1.0, methanol); ^{13}C-n.m.r., see Table I.

Anal. Calc. for $C_{23}H_{40}N_2O_{16}$: C, 45.99; H, 6.73; N, 4.66. Found: C, 45.70; H, 6.85; N, 4.90.

Methyl 6-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-2,3-di-O-benzyl-β-D-galactopyranoside (**7**). — A mixture of **3** (1.7 g, 4.6 mmol), oxazoline **1** (3.3 g, 10 mmol), and *p*-toluenesulfonic acid (76 mg) in 1,2-dichloroethane (40 mL), protected from moisture, was heated with stirring for 48 h at ~72°, additional amounts of **1** (1 g, 3 mmol) in 1,2-dichloroethane (6 mL) and *p*-toluenesulfonic acid (23 mg) in 1,2-dichloroethane (6 mL) being added after 16 h. After processing as described for **4**, t.l.c. (10:10:1, v/v, toluene–methanol–ether or solvent *C*) revealed the presence of a major product, slower-migrating than **3**; small proportions of **3** and of a slower-migrating product were also revealed in t.l.c. The crude product was purified in a column of silica gel with solvent *D* as the eluant. The first fractions to be eluted (0.5 g) were a mixture of **3** and a small proportion of the major product. On elution of the fractions corresponding to the major product, evaporation of the solvent and crystallization of the residue from dichloromethane–ether afforded **7** (1.3 g, 41%), m.p. 218–221°, $[\alpha]_D^{23}$ −8.1° (*c* 1.0, chloroform); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.40–7.00 (m, 10 H, arom.), 3.53 (s, 3 H, OMe), 2.70 (br. s, 1 H, OH), and 2.10–1.70 (cluster of s, 12 H, 3 OAc and NAc).

The last fraction to be eluted (0.7 g) was a mixture (t.l.c., solvent *C*) of **7** and a slower-migrating product (presumably a trisaccharide), but it was neither separated nor characterized.

Methyl 6-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-4-O-acetyl-2,3-di-O-benzyl-β-D-galactopyranoside (**8**). — A solution of **7** (50 mg) in 1:2 acetic anhydride–pyridine (3 mL) was kept overnight at room temperature. T.l.c. (solvent *C*) then showed the presence of one product, faster-migrating than **7**. The pyridine and acetic anhydride were evaporated under diminished pressure, the last traces being removed by co-evaporation with several added portions of toluene. The residue was crystallized from ethyl acetate–hexane to give **8** (45 mg, 86.5%), m.p. 165–168°, $[\alpha]_D^{23}$ +10.6° (*c* 1.0, chloroform); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.40–7.00 (m, 10 H, arom.), 3.50 (s, 3 H, OMe), and 2.20–1.70 (cluster of s, 15 H, 4 OAc and NAc).

Anal. Calc. for $C_{37}H_{47}NO_{15}$: C, 59.58; H, 6.36; N, 1.88. Found: C, 59.33; H, 6.50; N, 1.94.

Methyl 6-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-2,3-di-O-benzyl-β-D-

galactopyranoside (**9**). — Compound **6** (0.9 g) was stirred for 6 h at room temperature in 0.2M methanolic sodium methoxide (50 mL). Processing in the usual manner gave a solid residue which was dissolved in methanol and reprecipitated by the addition of ether to give **9** (0.65 g, 88%), amorphous, $[\alpha]_D^{23}$ +2.7° (*c* 1.0, methanol).

Anal. Calc. for $C_{29}H_{39}NO_{11}\cdot H_2O$: C, 58.47; H, 6.95; N, 2.35. Found: C, 58.19; H, 6.91; N, 2.35.

Methyl 6-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranoside (**10**). — A solution of **9** (0.5 g) in glacial acetic (25 mL) was shaken under H_2 at ~345 kPa for two days at room temperature in the presence of Pd–C (0.5 g). After the customary processing, the residue was crystallized from methanol–ethanol to give **10** (0.3 g, 88%), m.p. 256–257°, $[\alpha]_D^{23}$ −26.9° (*c* 1.1, 1:1 methanol–water); ^{13}C-n.m.r., see Table I.

Anal. Calc. for $C_{15}H_{27}NO_{11}\cdot H_2O$: C, 44.32; H, 6.96; N, 3.45. Found: C, 44.38; H, 6.95; N, 3.24.

Methyl O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-(1→3)-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranoside (**13**). — A stirred solution of methyl 3-*O*-(2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside[4] (**12**; 2 g, 2.7 mmol) in 1:1 benzene–nitromethane (180 mL) was boiled until ~60 mL of the solvent had distilled off. The temperature was then adjusted to ~55°, powdered $Hg(CN)_2$ (0.8 g, 3.2 mmol) and a solution of 3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2,4,6-tri-*O*-acetyl-α-D-galactopyranosyl bromide[5] (**11**; 2.1 g, 3 mmol) in 1:1 benzene–nitromethane (20 mL) were added, stirring was continued for 16 h at ~55°, more portions of $Hg(CN)_2$ (0.4 g, 1.6 mmol) and bromide **11** (1.0 g, 1.4 mmol) in 1:1 benzene–nitromethane (10 mL) were added, and stirring was continued for 5 h at 55°. After processing in the usual manner, t.l.c. (2:1, v/v, chloroform–acetone) showed the presence of a major product, slower-migrating than **12**; a small proportion of **12**, together with some slower-migrating contaminants (presumably due to the decomposition of **11**) were also revealed in t.l.c. The crude mixture was applied to a column of silica gel and eluted first with solvent *D* to give unreacted **12** (0.5 g). On elution with solvent *C*, evaporation of the fractions corresponding to the major product afforded a solid residue which was dissolved in a small volume of dichloromethane. Addition of ether–hexane caused the precipitation of **13** (1.1 g, 41%; based on reacted **12**) as an amorphous white solid, $[\alpha]_D^{23}$ −1.2° (*c* 0.6, chloroform).

Anal. Calc. for $C_{69}H_{84}N_2O_{27}$: C, 60.34; H, 6.16; N, 2.04. Found: C, 60.25; H, 6.25; N, 1.87.

Methyl O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-O-β-D-galactopyranosyl-(1→3)-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranoside (**14**). — A suspension of **13** (1.48 g) in 0.5M methanolic sodium methoxide (80 mL) was stirred at room temperature. The solid gradually dissolved, and, within 0.5 h, crystallization ensued. The mixture

was stirred for 24 h at room temperature, the base neutralized by the addition of a few drops of glacial acetic, and the solid material filtered off and thoroughly washed with cold ethanol. On crystallization from aqueous ethanol, it afforded **14** (1.02 g, 85%), m.p. 164–166°, $[\alpha]_D^{23}$ −34.1° (*c* 0.7, dimethyl sulfoxide).

Anal. Calc. for $C_{57}H_{72}N_2O_{21}\cdot H_2O$: C, 58.24; H, 6.70; N, 2.38. Found: C, 58.44; H, 6.52; N, 2.87.

Methyl O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1→3)*-O-*β-*D-*galacto-pyranosyl-(1→3)*-O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1→3)-β-*D-*galacto-pyranoside* (**15**). — A mixture of **14** (0.7 g) and 10% Pd–C (0.7 g) in glacial acetic acid (30 mL) and ethanol (15 mL) was shaken under H_2 at ~345 kPa for 3 days at room temperature. The suspension was filtered through a bed of Celite, the solid was thoroughly washed with 1:1 (v/v) methanol–water, and the filtrate and washings were combined and evaporated under diminished pressure to give a solid residue which showed in t.l.c. (solvent *E*) some faster-migrating impurities (presumably due to incomplete hydrogenolysis). The crude product was applied to a column of silica gel and eluted with solvent *E*. On evaporation of the fraction corresponding to the product, the resulting solid residue was dissolved in a small volume of water. Addition of ethanol caused the precipitation of **15** (0.36 g, 75%), amorphous, $[\alpha]_D^{23}$ +1.2° (*c* 0.5, water); ^{13}C-n.m.r., see Table I.

Anal. Calc. for $C_{29}H_{50}N_2O_{21}$: C, 43.60; H, 6.80; N, 3.50. Found: C, 43.68; H, 7.16; N, 3.37.

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