Synthesis of βDGlcNAc(1→6) and βDGal(1→4)βDGlcNAc(1→6) derivatives of the T_N (αDGalNAc) human blood group determinant

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In order to investigate the immunological properties of certain I blood group specific glycoproteins, the potential antigenic determinants βDGlcNAc(1→6)αDGalNAc and βDGal(1→4)βDGlcNAc(1→6)αDGalNAc attached as glycosides to 8-methoxycarbonyloctanol were synthesized by way of the phthalimido-chloride method.

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Dans le but d'étudier les propriétés immonulogiques de certaines glycoprotéines spécifiques du groupe sanguin I, on a synthétisé, par la méthode du chlorure de phtalimide, les déterminants antigéniques potentiels: βDGlcNAc(1→6)αDGalNAc et βDGal(1→4)-βDGlcNAc(1→6)αDGalNAc attachés en tant que glycosides au méthoxycarbonyl-8-octanol.

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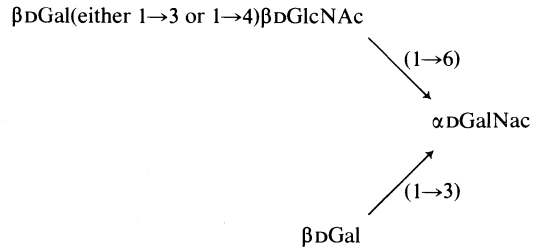
In 1968, Lloyd *et al.* (1) published a composite structure for the carbohydrate chains of A, B, H, Lewis a, and Lewis b human blood group specific glycoproteins. The structure was presented with the tetrasaccharide,



as the structural unit attached to the core protein. This unit was proposed since alkaline borohydride treatment of a Lewis a active human cyst glycoprotein had produced a substance (Lewis R_L 0.41) with composition and chemical properties consistent with the presence of either one of these units. It was to be expected that the oligosaccharide chains in the glycoprotein would be linked through *N*-acetylgalactosamine to serine and threonine units in the polypeptide portion.

It is now well established that the βDGal(1→3)-αDGalNAc disaccharide is the first disaccharide unit in the carbohydrate chains that are attached as *O*-glycosides to the core protein of the blood group active glycoproteins (2). The αDGalNAc residue is characteristic of the T_N determinant (3) and the βDGal(1→3)αDGalNAc structure is characteristic of the T determinant (4). The T determinant is also related to the M and N human blood group determinants (5). It was therefore of interest to examine in more detail the occurrence of the above-mentioned tetrasaccharide units in human blood group specific glycoproteins, by way of chemical synthesis toward structures which would be amenable to the preparation of immunochemical reagents of possible use in these regards (6).

The syntheses of the tetrasaccharide structures have not as yet been accomplished. Nevertheless, we wish to report the syntheses of the structures βDGlcNAc(1→6)αDGalNAc (**8**) and βDGal(1→4)-βDGlcNAc(1→6)αDGalNAc (**13**) attached to the potential linking arm derived from 8-methoxycarbonyloctanol since these substances proved useful to a study of the combining site of the anti-I Ma monoclonal antibody (7, 8). It was found that structure **13** binds this myeloma protein, on a molar basis, equally as well as do βDGal(1→4)βDGlcNAc(1→6)βDGalO$(CH_2)_8COOCH_3$ and βDGal-(1→4)βDGlcNAc(1→6)[βDGal(1→4)βDGlcNAc-(1→3)]βDGalO$(CH_2)_8COOCH_3$. Therefore it is possible that the antigenic determinant, which was involved in the myelomatosis and proliferation of the neoplastic monoclonal anti-I Ma producing cells, was a βDGal(1→4)βDGlcNAc(1→6)αDGal-NAc unit of the glycoprotein and not necessarily a βDGal(1→4)βDGlcNAc(1→6)βDGal unit (8). The synthesis of βDGal(1→3)αDGalNAcO$(CH_2)_8$-$COOCH_3$ (the T determinant) has been reported (9).

The synthesis of **8** from αDGalNAcO$(CH_2)_8$-$COOCH_3$ **1** (9) by way of the intermediates **2–7** warrants a few comments. Treatment of **2** with benzoyl chloride in pyridine was found to lead to *N*-benzoylation as well as the desired *O*-benzoylation (10). The so-called phthalimido-chloride method (11) was used to establish the β(1→6) linkage of **5**

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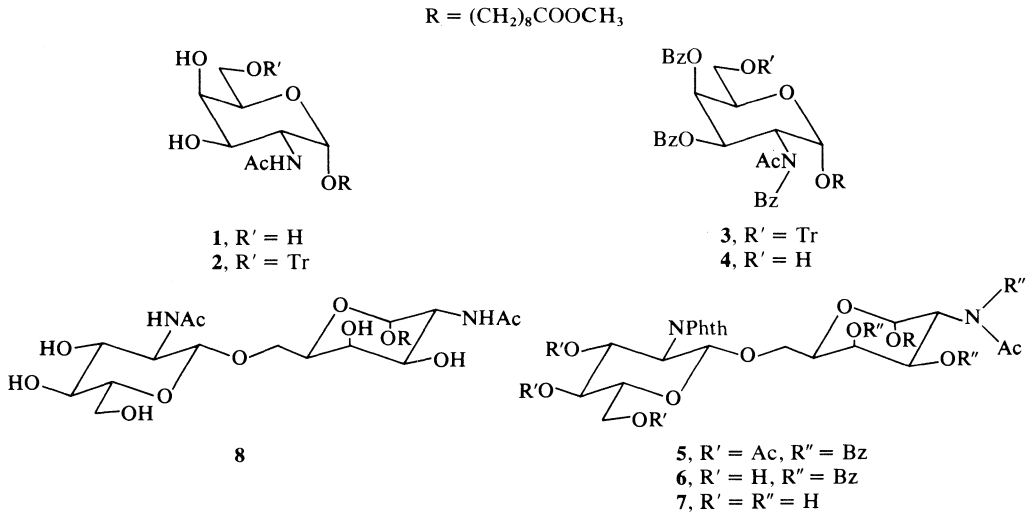


1, R′ = H
2, R′ = Tr

3, R′ = Tr
4, R′ = H

8

5, R′ = Ac, R″ = Bz
6, R′ = H, R″ = Bz
7, R′ = R″ = H

since this method has proved generally reliable for this purpose (12). Indeed, the yield was 87%. It is of interest that treatment of **5** with sodium methoxide – methanol in the cold allowed the transesterification reaction to be limited to de-*O*-acetylation. The use of magnesium methoxide (13) for this purpose therefore appears advantageous, simply because, as a less active catalyst, it allows more convenient kinetic control. It is remarkable that the treatment of **5** with sodium methoxide under conditions which removed the benzoyl groups preferentially removed the *N*-benzoyl group. Especially in view of the ^{13}C nmr data, it seems evident that the compound was an *N*-acetylbenzamido product and not an *O*-benzoyl acetamidate.

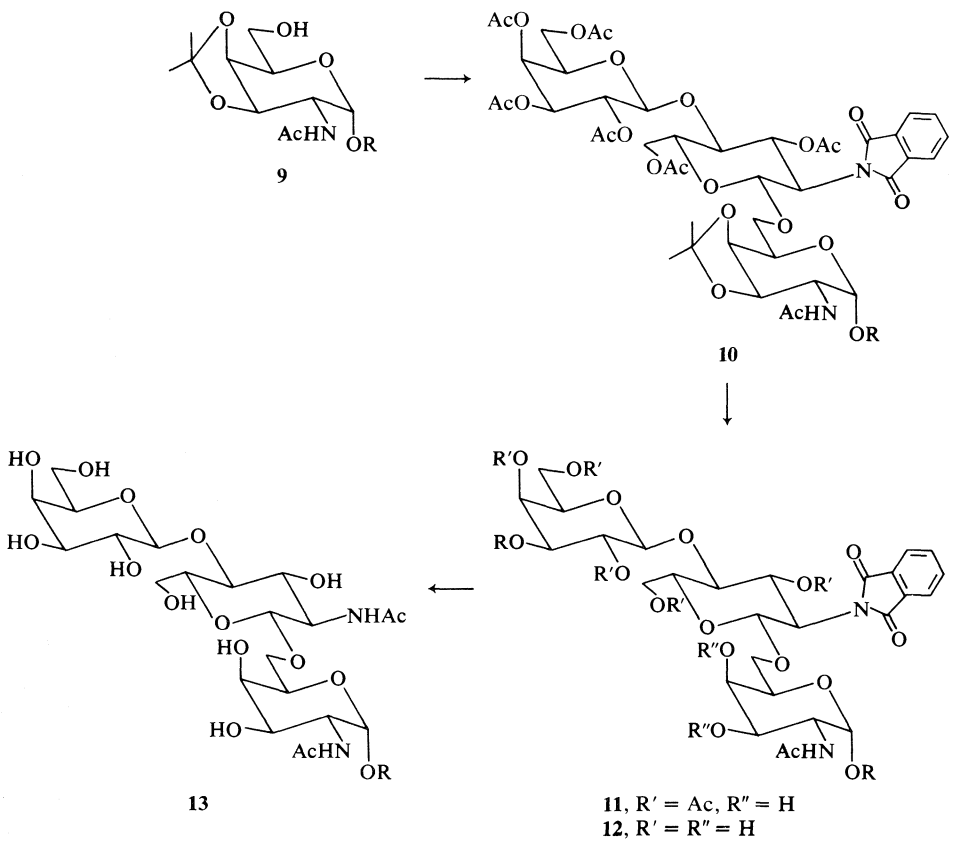
In the course of this work, we observed that the phthalimido group remained intact in the course of the deacetylation of **5** and work-up to provide **7**. Meanwhile, Bundle and Josephson (14) reported a similar experience. As was pointed out by Bundle and Josephson (14), this occurrence is a considerable convenience in the context of the need to later remove the phthalimido group without affecting the methoxycarbonyl group of the linking arm. We have now found[2] that the opening of the phthalimido group by the sodium method is strongly influenced by the configurations of the neighboring centers. Our earlier investigations (11) demonstrated the strong nonbonded interaction that exists between an equatorially oriented phthalimido group and an axial neighboring substituent. Thus it was not surprising to find that the reaction of a 2-deoxy-2-phthalimido-α-D-galactopyranosyl unit to form the *o*-methoxycarbonylbenzamido derivative was extremely rapid and quantitative. The product could quite readily be isolated. On the other hand, the reaction of a 2-deoxy-2-phthalimido-β-D-glucopyranosyl unit was relatively much slower, did not proceed quantitatively, and the products could not be isolated. In accordance with these results, the complete removal of the phthalimido group by reaction with hydrazine depends both on the ease of formation of the *o*-hydrazinocarbonylbenzamido intermediate and on how readily this reaction is reversed as compared to the formation of the amine. The method developed by Bundle and Josephson (14) which employs hydrazine at high dilution, followed by *N*-acetylation, was effective for the conversion of **7** to **8** and of **12** to **13** in acceptable yields.

Our initial attempts to prepare the 3,4-*O*-isopropylidene derivative of **1**, namely **9**, met with difficulty and it was for this reason that the preparation of **4** was undertaken. The problem arose because of the ready formation of the 4,6-*O*-isopropylidene derivative. However, it was subsequently found that extended reaction at 5°C gave the desired compound in acceptable (64%) yield. The preparation of **13** by way of the intermediates **10**, **11**, and **12** followed normal procedures for the transformations shown. The conversion of **9** to **10** using hexa-*O*-acetyl-2-deoxy-2-phthalimido-α,β-D-lactosyl chloride (15) and a slight excess of the alcohol **9** proceeded in 75% yield.

Experimental

The methods used for the isolation of products, solvent purification and removal, spectral analysis, and chromatography were in general the same as those previously reported from this laboratory (12).

[2]R. U. Lemieux and P. Hermentin, in preparation.



*8-Methoxycarbonyloctyl 2-(*N*-acetylbenzamido)-3,4-di-*O*-benzoyl-2-deoxy-α-*D*-galactopyranoside (4)*

This compound was prepared starting from 8-methoxycarbonyloctyl 2-acetamido-2-deoxy-α-D-galactopyranoside (**1**) which was prepared following the directions reported by Ratcliffe *et al.* (9). In this work, the compound was obtained after recrystallization from methanol as an anhydrous product, mp 134°C, $[\alpha]_D^{25}$ + 143.5° (*c* 1, in chloroform). Both the ^1H and ^{13}C nmr spectra were in accord with expectations.

A solution of compound **1** (670 mg, 1.71 mmol) and triphenylmethyl chloride (500 mg, 1.79 mmol) in pyridine (12 mL) was kept at 65°C for 24 h. Triphenylmethyl chloride (100 mg, 0.36 mmol) was added and the reaction was continued for a further 24 h. The reaction was monitored by tlc (benzene – ethyl acetate – methanol, 10:5:3). The solution expected to contain the trityl compound **2** was then cooled to room temperature for the addition of benzoyl chloride (1.00 g, 7.1 mmol). The resulting mixture was kept at near 23°C for 24 h prior to the addition of dichloromethane (200 mL). This solution was then processed in the usual manner to provide a yellow oil (1.98 g) which was not further purified. However, in a separate experiment, the main product was isolated by column chromatography and found on examination by ^1H nmr to contain three benzoyl groups along with one trityl group and one acetyl group. Therefore the product was assigned structure **3**.

The above-mentioned crude product was dissolved in 1% methanolic hydrogen chloride (30 mL) and the solution was kept at near 23°C for 1 h prior to neutralization with triethylamine. Solvent removal left a residue which was dissolved in dichloromethane (100 mL) for extraction with water. After drying and solvent removal, the residue was applied to a column of silica gel (40 g) for chromatographic separation using ethyl acetate – hexane (6:4). The main fraction contained a product which appeared homogeneous on examination by tlc but which resisted crystallization. The overall yield was 61% (740 mg) of a colorless foam; $[\alpha]_D^{25}$ + 133° (*c* 1.1, in chloroform). The ^{13}C nmr ($CDCl_3$) spectrum required a high state of purity and structure **4** was supported by the presence of signals for four carbonyl carbons at 165.2, 166.8, 171.6, and 173.6 ppm in addition to that for the methoxycarbonyl group at 174.3 ppm. The signal at 61.07 ppm was assigned to the CH_2OH group. The ^1H nmr confirmed the structural assignment both in terms of the relative intensities of the signals which could be unequivocally assigned and the chemical shifts of the hydrogen atoms of the pyranose ring. The occurrence of the signal for H-2 at exceptionally low field (6.18 ppm, $CDCl_3$) is noteworthy. *Anal.* calcd. for $C_{39}H_{46}O_{11}N$: C 66.45, H 6.58, N 1.99; found: C 66.58, H 6.43, N 1.81.

*8-Methoxycarbonyloctyl 2-(*N*-acetylbenzamido)-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-α-*D*-galactopyranoside (5)*

A solution of alcohol **4** (915 mg, 1.30 mmol), silver triflate (481 mg, 1.87 mmol), and *sym*-collidine (226 mg, 1.87 mmol) in nitromethane (6 mL) protected from light and moisture was cooled to −30°C. Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl chloride (**8**) (850 mg, 1.87 mmol) in nitromethane (3 mL) was added dropwise with stirring so as to maintain the temperature near −30°C. After 1 h, the stirring was continued for 2 h at −5°C. The reaction mixture was then diluted with chloroform (150 mL) and the solids were collected by filtration.

The filtrate was washed with ice-cold water (50 mL), cold 3% hydrochloric acid (50 mL), water (50 mL), and dried. Solvent removal left an oily residue (1.85 g) which was purified by chromatography on a silica gel column (60 g) which was developed with a mixture of hexane and ethyl acetate (6:4). On evaporation, the material crystallized and was recrystallized from the same solvents; mp 85–87°C, $[\alpha]_D^{25}$ + 84.7 (*c* 2.12, in chloroform) (1.27 g, 87% yield); ^{1}H nmr ($CDCl_3$) δ: 8.1–7.2 (m, 19H, phthalimido and 3 benzoyl groups), 6.06 (dd, 3.5 Hz, 11.5 Hz, 1H, H-2), 5.86 (d, 3.5 Hz, 1H, H-1), 5.74 (dd, 10.5 Hz, 9.5 Hz, 1H, H-3′), 5.56 (dd, 11.5 Hz, 3.5 Hz, 1H, H-3), 5.38 (d, 8.5 Hz, 1H, H-1), 5.14 (t, 9.5 Hz, 1H, H-4′), 4.74 (d, 3.4 Hz, 1H, H-4), 4.35–4.20 (m, 3H, H-2′, H-5, H-6″), 4.08 (dd, 3.2 Hz, 11.0 Hz, 1H, H-6), 3.83 (m, 1H, H-5′), 3.70 (s, 3H, CH_3O), 3.61 (dd, 11.0 Hz, 9.0 Hz, 1H, H-6′), 3.30–3.13 (m, 1H, —O—CH_2—$(CH_2)_7CO_2CH_3$), 2.58–2.45 (m, 1H, —OCH_2—$(CH_2)_7CO_2CH_3$), 2.33 (t, 7 Hz, 2H, CH_2—CO_2CH_3), 2.08 (s, 3H, CH_3CONH), 2.03 (s, 3H, CH_3CO), 1.86 (s, 3H, CH_3CO), 1.76 (s, 3H, CH_3CO), 1.7–1.5 (m, 2H, —CH_2—$CH_2CO_2CH_3$), 1.35–0.75 (m, 10H, CH_2—$(CH_2)_5CH_2CH_2CO_2CH_3$); ^{13}C nmr ($CDCl_3$) δ: 174.3 (1C, CO_2CH_3), 173.6, 171.6, 170.7 (3C=O), 170.1 (C=O double intensity, 2 C=O phthalimido), 169.4, 167.5, 165.0 (4 C=O), 136.0–123.6 (14C, aromatic carbons), 98.9 (C-1′), 98.3 (C-1). *Anal.* calcd. for $C_{59}H_{64}O_{20}N_2$: C 63.20, H 5.75, N 2.50; found: C 63.08, H 5.79, N 2.39.

*8-Methoxycarbonyloctyl 2-acetamido-2-deoxy-6-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-α-D-galactopyranoside (**8**)*

The blocked disaccharide **5** was converted to the desired hapten **8** by way of the intermediate de-*O*-acylated phthalimido compound **7**. It was noted by tlc that treatment of **5** (299 mg, 0.267 mmol) with 0.1 *M* sodium methoxide in methanol (10 mL) at 0°C led after 10 min to essentially one product. Neutralization with Amberlite IR120 (H^+) resin and solvent removal provided a product (199 mg) which appeared (^{1}H nmr) to be almost pure **6**. However, when the transesterification was performed at near 23°C for 1.5 h, this product was transformed to compound **7**. The presence of the *N*-acetyl (1.92 ppm) and the methoxycarbonyl (3.68 ppm) groups was clearly evident. The signal for the four hydrogen atoms of the phthalimido group occurred as a broad singlet at 7.83 ppm. The compound was not further purified but used directly for the formation of compound **8** by way of hydrazinolysis followed by *N*-acetylation under conditions similar to those independently developed by Bundle and Josephson (14).

Compound **7** (117.4 mg, 0.172 mmol) was dissolved in methanol (4 mL) containing 97% hydrazine (14.5 mg, 0.44 mmol) and refluxed, monitored by tlc (ethyl acetate – ethanol–water, 8:4:2). After 3 h, an additional amount of hydrazine (7 mg) in methanol (1 mL) was added and the reaction mixture was refluxed for 3 h. Then the solution was cooled to room temperature and acetic anhydride (500 mg) was added. The resulting mixture was left for 30 min and then evaporated to dryness. Ethanol (10%, 4 mL) was added, the solids were gathered by filtration and washed with a small amount of the solvent. The combined filtrates were evaporated and the residue was applied to a Bio-Gel P-2 column and eluted with 10% ethanol. The first fraction to appear in the eluate on evaporation provided an amorphous white powder (70 mg, 79% yield), $[\alpha]_D^{25}$ + 69° (*c* 1.1, water). The nmr spectra required the assigned structure and a high state of purity. Selected parameters are given: ^{1}H nmr (D_2O) δ: 4.88 (d, 3.8 Hz, H-1), 4.52 (d, 8.5 Hz, 1H, H-1′), 3.68 (s, 3H, OCH_3), 2.37 (t, 7.5 Hz, 2H, CH_2—$COOCH_3$), 2.03 (s, 3H, $NHCOCH_3$), 2.01 (s, 3H, $NHCOCH_3$); ^{13}C nmr (D_2O) δ: 177.5, 174.3, 174.0 (3 C=O), 101.4 (C-1′), 96.7 (C-1), 75.9 (C-5′), 74.0 (C-3′), 70.1 (C-4′), 69.3 (2C, C-6, C-5), 68.5 (1C, —O—CH_2—$(CH_2)_7$—), 67.8, 67.6 (C-4, C-3), 60.9 (C-6′), 55.5 (C-2′), 51.9 (OCH_3), 50.0 (C-2). *Anal.* calcd. for $C_{26}H_{46}O_{13}N_2 \cdot H_2O$: C 50.97, H 7.89, N 4.59; found: C 50.88, H 7.42, N 4.54.

*8-Methoxycarbonyloctyl 2-acetamido-2-deoxy-3,4-O-isopropylidene-α-D-galactopyranoside (**9**)*

A solution of compound **1** (9) (1.61 g, 4.12 mmol) in *N,N*-dimethylformamide (50 mL) containing *p*-toluenesulphonic acid (0.1 g, 0.75 mmol) and 2,2′-dimethoxypropane (7 g, 67.30 mmol) was kept at 5°C for 28 h. The reaction mixture was neutralized with triethylamine, evaporated under vacuum, and the residue (2.21 g) was chromatographed on a silica gel column (100 g) eluting with ethyl acetate – hexane (7:3) to provide compound **9** (1.14 g, 64% yield after one recrystallization from the same solvents); mp 64°C, $[\alpha]_D^{25}$ + 109.5° (*c* 2.37, in chloroform); ^{1}H nmr ($CDCl_3$) δ: 5.87 (d, 8.5 Hz, 1H, NH), 4.77 (d, 3.5 Hz, 1H, H-1), 4.4–3.2 (m, 8H), 3.65 (s, 3H, OCH_3), 2.9–2.7 (m, 1H, O*H*), 2.30 (t, 7 Hz, 2H, $CH_2CO_2CH_3$), 2.02 (s, 3H, NAC), 1.55 (s, 3H, CH_3), 1.8–1.2 (m, 15H, $(CH_2)_6CH_2CO_2CH_3$ and CH_3); ^{13}C nmr ($CDCl_3$) δ: 174.36 (CO_2CH_3), 170.29 ($NHCOCH_3$), 109.85 (isopropylidene $(CH_3)_2C$), 97.73 (C-1), 74.67, 73.47, 68.22, 67.86 (3 ring carbons and $OCH_2(CH_2)_7CO_2CH_3$), 62.61 (C-6), 51.44 (C-2), 50.81 (OCH_3), 34.02, 29.99, 29.33, 29.14, 28.29, 28.05, 26.83, 26.65, 26.03, 24.88, 23.36 ($(CH_2)_7CO_2CH_3$ and 3 CH_3). *Anal.* calcd. for $C_{21}H_{37}O_8N$: C 58.45, H 8.64, N 3.25; found: C 58.33, H 8.65, N 3.10.

*8-Methoxycarbonyloctyl 2-acetamido-2-deoxy-6-O-[3,6-di-O-acetyl-4-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-3,4-O-isopropylidene-α-D-galactopyranoside (**10**)*

A solution of alcohol **9** (575.8 mg, 1.10 mmol), silver triflate (283.3 mg, 1.10 mmol), and *sym*-collidine (133 mg, 1.10 mmol) in nitromethane (protected from light and moisture) (3 mL) was cooled to −30°C. Hexa-*O*-acetyl-2-deoxy-2-phthalimido-D-lactosyl chloride (15) (745.6 mg, 1.00 mmol) in nitromethane (4 mL) was added dropwise. The resulting solution was stirred at −20°C for 2 h and then at room temperature for 4 h. The solution was diluted with chloroform (100 mL) and the solids were filtered and washed with chloroform. The combined filtrates were washed with cold water (30 mL), a cold aqueous hydrochloric acid solution (10%, 30 mL), cold water (30 mL), an aqueous cold sodium bicarbonate solution (30 mL), and water (30 mL), dried, and evaporated under vacuum. The residue was dissolved in a mixture of ethyl acetate – hexane (1:1) and passed through a short alumina column yielding compound **10** (856 mg, 75% yield from **9**); mp 102–105°C, $[\alpha]_D^{25}$ = +57.3° (*c* 1.77, in chloroform); ^{1}H nmr ($CDCl_3$) δ: 7.95–7.6 (m, 4H, phthaloyl), 5.76 (dd, 8 Hz, 10 Hz, H-3′), 3.66 (s, 3H, OCH_3), 2.33 (t, 7 Hz, 2H, $CH_2CO_2CH_3$), 2.14, 2.12, 2.06, 2.04, 1.94, 1.93, 1.90 (6 *O*-acetyls, 1 *N*-acetyl), 1.47, 1.14 (each s, 3H, —CH_3); ^{13}C nmr ($CDCl_3$) δ: 174.25 (CO_2CH_3), 170.41 ($NHCOCH_3$), 170.17, 170.06, 169.87, 169.69, 169.09 (CH_3CO), 134.26, 131.76, 128.41, 123.49 (aromatic), 109.80 (isopropylidene $(CH_3)_2C$), 101.4 (C-1″), 98.96 (C-1′), 97.27 (C-1), 79.31, 77.17, 76.99, 75.05, 74.74, 72.85, 71.10, 70.73, 70.37, 69.28, 67.45, 66.70, 66.59, 62.28, 60.81, 55.13 (C-2′), 51.32 (CH_3O), 50.51 (C-2), 34.03, 29.14, 27.89, 26.48, 25.99, 24.89, 23.32, 20.87, 20.58 ($(CH_3)_2C$). *Anal.* calcd. for $C_{53}H_{72}O_{25}N_2$: C 55.98, H 6.38, N 2.46; found: C 55.47, H 6.38, N 2.33.

*8-Methoxycarbonyloctyl 2-acetamido-6-O-[2-acetamido-4-O-(β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranosyl]-α-D-galactopyranoside (**13**)*

Compound **10** (177 mg, 0.1556 mmol) was dissolved in a 10% solution of 99% trifluoroacetic acid in dichloromethane (7 mL) and left at room temperature for 1 h. The solution was diluted with dichloromethane (50 mL), washed with ice-cold water

(25 mL), cold aqueous sodium bicarbonate solution (25 mL), and cold water (25 mL), dried, and evaporated to provide a crude compound **11** (136 mg, 70% yield) which was characterized by ^{1}H nmr. Without purification, the product was treated with 0.1 *N* sodium methoxide in methanol (5 mL) for 5 min. The solution was then neutralized with Amberlite IR-120 (H^+) resin and evaporated to provide compound **12** (103 mg, 94% yield). The material appeared essentially pure; ^{1}H nmr ($CDCl_3$) δ: 7.82 (s, 4H, phthalimido), 5.68 (dd, 8 Hz, 10 Hz, H-3′), 3.64 (s, 3H, OCH_3), 2.32 (t, 7 Hz, 2H, CH_2—CO_2CH_3), 1.90 (s, 3H, *N*-acetyl), 1.8–1.2 (m, 12H, $(CH_2)_6CH_2CO_2CH_3$).

Crude compound **12** (94.2 mg) was dissolved in methanol (5 mL) containing 97% hydrazine (14.5 mg) and the solution was brought to reflux. The course of the reaction could be monitored by tlc (ethyl acetate – ethanol–water, 8:4:2). After 2 H, an additional amount of hydrazine was added (10.8 mg in 1.5 mL of methanol) and the reaction mixture was refluxed for a further 2 h. The solution was cooled to room temperature, acetic anhydride (500 mg) was added, and the mixture was left at room temperature for 20 min. Solvent removal left a solid residue which was extracted with 10% ethanol in water. The combined filtrates were evaporated for application to a Biogel P-2 column and elution with 10% ethanol in water. The major fraction was freeze-dried to a powder (75 mg, 89% yield), $[\alpha]_D^{25}$ + 129° (*c* 2.7, in water); ^{1}H nmr (D_2O, HOD, 400 mHz) δ: 4.96 (d, 3.8 Hz, H-1), 4.75 (d, 8.3 Hz, H-1′), 4.72 (d, 8.3 Hz, H-1″), 4.37 (dd, 10.8 Hz, H-2), 2.63 (t, 7 Hz, 2H, $CH_2CO_2CH_3$), 2.29, 2.26 (2s, 6H, *N*-acetyls); ^{13}C nmr (D_2O, dioxane) δ: 177.2, 174.1, 173.8 ($COOCH_3$, 2 *N*—$COCH_3$), 102.9 (C-1″), 101.3 (C-1′), 96.7 (C-1), 78.83, 75.29 (C-5″), 74.74, 72.58, 72.47 (C-3″), 70.94 (C-2″), 69.26, 68.52 (C-4″), 67.70, 67.56, 66.5, 60.9 (C-6″), 60.2, 54.97 (C-2′), 51.94, 49.99 (C-2, OCH_3), 33.63, 28.32, 28.25, 28.19, 25.24, 24.27, 22.22, 21.95.

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