Carbohydrate Research, 234 (1992) 93–106
Elsevier Science Publishers B.V., Amsterdam

Building blocks for the synthesis of glycosyl-*myo*-inositols involved in the insulin intracellular signalling process

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(Received January 6th, 1992; accepted March 28th, 1992)

ABSTRACT

Glycosylation of (±)-1-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol (**4**) with 6-*O*-acetyl-4-*O*-allyl-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranosyl trichloroacetimidate (**6**) gave the 4-*O*-(2-amino-2-deoxy-α-D-glucopyranosyl)-*myo*-inositol derivative (**9**) as a mixture of diastereoisomers which could be resolved by chromatography. Likewise α-glycosylation of **4** with 6-*O*-acetyl-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-D-glucopyranosyl trichloroacetimidate (**10**) gave the corresponding pseudotrisaccharide derivative **16** as a mixture of diastereomers which could be resolved partially by chromatography. α-Glycosylation of enantiomerically pure 2,3:5,6- (**18**) and 2,3:4,5-di-*O*-isopropylidene-1-*O*-menthoxycarbonyl-*myo*-inositol (**19**) with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidate (**20**) gave the pseudodisaccharide derivatives **21** and **22**, respectively. Likewise, α-glycosylation of **18** with **10** afforded a pseudotrisaccharide derivative (**23**).

INTRODUCTION

Insulin stimulates the phospholipase C-catalysed hydrolysis of glycosyl phosphatidylinositols in a variety of cells[1–3]. The released glycosyl-*myo*-inositol may act as an insulin mediator on the basis of insulin-dependent regulation of glycosyl phosphatidylinositol turnover[4–8], the ability of these glycosyl-*myo*-inositols to mimic some of the short-term effects of the hormone[9–13], and the selective blocking of some of the actions of insulin by anti-inositol glycan antibodies[14]. At least two structurally distinct mediators of this type have been reported[15,16]. Mato et al.[15] reported that a compound which inhibited c-AMP-dependent protein kinase contained *myo*-inositol or *chiro*-inositol, 2-amino-2-deoxyglucose, galactose, and phosphate. Larner et al.[16] obtained a compound which stimulated pyruvate dehydrogenase kinase and contained D-*chiro*-inositol, 2-amino-2-deoxygalactose, mannose, and phosphate. These compounds seem to be related to the glycosyl

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phosphatidylinositols which anchor protein, polysaccharide, or small oligosaccharides to the outer face of cellular membranes through a covalent linkage[1,17–22]. However, the complete structures of these mediators have not been elucidated.

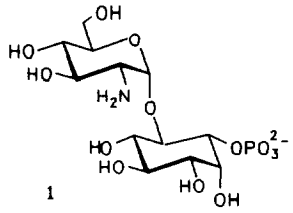
The effective preparation of building blocks for the synthesis of these inositol-containing oligosaccharides would permit the preparation, for biological investigation, of pure compounds whose structures could be varied at will. In this context, we have reported on the preparation of *myo*- and D-*chiro*-inositol derivatives to be used in the synthesis of glycosylinositols[23–26], and we now report on the synthesis of variously substituted 2-amino-2-deoxyglycosyl and lactosaminyl derivatives of *myo*-inositol. Since it has been suggested[27] that 4- (**1**) and 6-*O*-(2-amino-2-deoxy-α-D-glucopyranosyl)-*myo*-inositol (**2**) fragments could exist in the structure of the glycosyl-*myo*-inositol mediators, syntheses have been developed for each structural type. Syntheses of fragments[28,29] and of the complete glycosyl phosphatidylinositol anchor[30] of the variant surface glycoprotein of *Trypanosoma brucei*[31] and other related oligosaccharide fragments containing *myo*- or D-*chiro*-inositol have been described[32–34].

RESULTS AND DISCUSSION

The synthesis of the fragments **1** and **2** was envisaged from 1-*O*-substituted *myo*-inositol. We have used[25,26] a modification of the transmetallation reaction of borylated carbohydrates with tributyltinacetylacetonate[35] or dibutyltinbis(acetylacetonate)[36] for the regioselective alkylation and acylation of *myo*-inositol. Thus, *myo*-inositol gave (±)-1-*O*-benzyl-*myo*-inositol (**3**, 80%) from hexa-*O*-diethylboryl-*myo*-inositol in a one-pot procedure[26]. Isopropylidenation[37] of **3** gave (±)-1-*O*-benzyl-2,3:5,6- (**4**) and -2,3:4,5-di-*O*-isopropylidene-*myo*-inositol (**5**). It was hoped that, following glycosylation of **4** and **5**, the diastereomers could be separated, thus avoiding the need to resolve the racemates **4** and **5**.

Glycosylation by the trichloroacetimidate procedure[38,39] gave the best yields and α-stereoselectivity. 6-*O*-Acetyl-4-*O*-allyl-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranosyl trichloroacetimidate (**6**) was prepared[40] from 1,6-di-*O*-acetyl-4-*O*-allyl-2-azido-3-*O*-benzyl-2-deoxy-D-glucopyranose[41,42] (**7**), readily available[42] from 1,6-anhydro-2,3-*O*-benzylidene-β-D-mannopyranose (**8**). Reaction of **4** with **6** in dichloromethane, using trimethylsilyl triflate as the promoter, gave the 4-*O*-α-glycosylated derivative **9** (71%) as a mixture of diastereomers that could be resolved by repeated chromatography.

A similar approach involved 6-*O*-acetyl-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-D-glucopyranosyl trichloroacetimidate (**10**), prepared from **8**[42] by the following steps: mercuric salt-promoted glycosylation with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide to give 1,6-anhydro-2,3-*O*-benzylidene-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-mannopyranose (**11**, 51%), oxidative opening of the benzylidene acetal[42] using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to afford 1,6-anhydro-3-*O*-ben-



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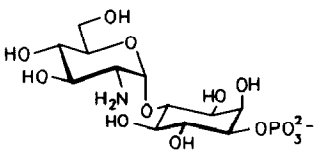

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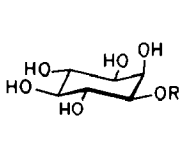

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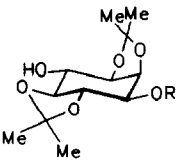

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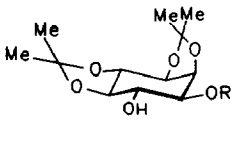
18 R = 



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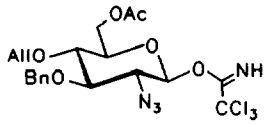
19 R = 



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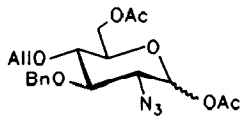

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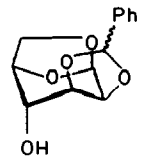

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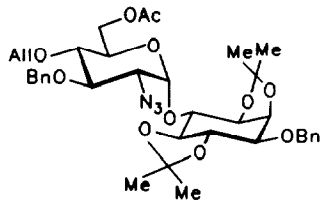

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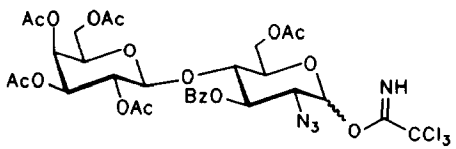
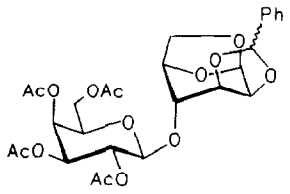


10

zoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-mannopyranose (**12**, 72%), treatment with trifluoromethanesulfonic anhydride and then with sodium azide to yield 1,6-anhydro-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranose (**13**, 92%), acetolysis of the 1,6-anhydro ring to give 1,6-di-*O*-acetyl-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-D-glucopyranose (**14**, 88%), selective deacylation[43] to give 6-*O*-acetyl-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-D-glucopyranose (**15**, 99%), and final treatment with trichloroacetonitrile and potassium carbonate[44].



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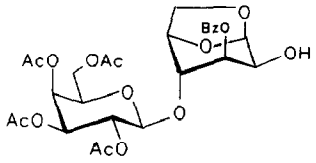

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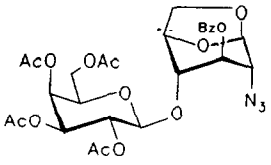

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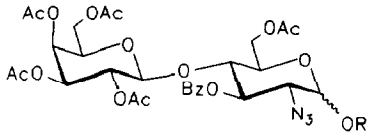

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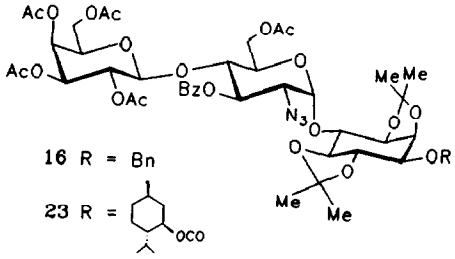
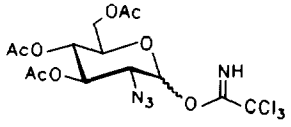
15 R = H



16 R = Bn

23 R =



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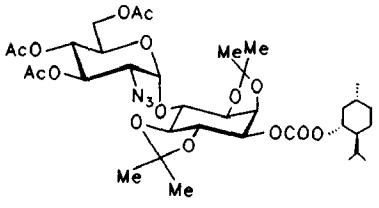

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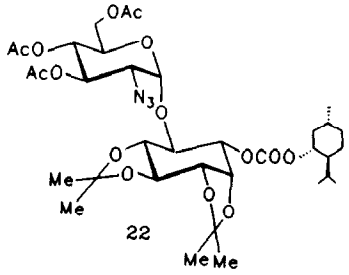
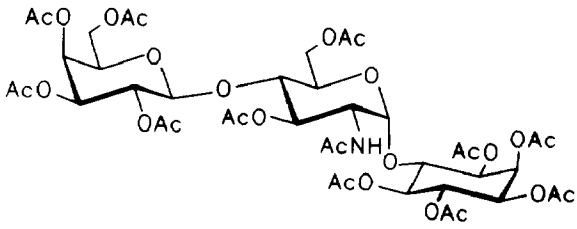


22

Trimethylsilyl triflate-promoted reaction of **4** with **10** gave the 4-*O*-α-glycosylated derivative **16** (80%) as a mixture of diastereomers which was resolved partially by chromatography. The diastereomer having the higher R_F value was obtained pure, and its configuration was established unequivocally by application in sequence of *O*-deacylation, azide reduction, acetylation, hydrogenolysis of the



24

benzyl group, and acetylation, which gave **24** identical with the product obtained from the enantiomerically pure *myo*-inositol derivative (see below). As with **9**, the preparation of **16** was tedious, laborious, and of limited practical use.

Therefore, the mixture of enantiomers of 1-*O*-substituted *myo*-inositol was resolved prior to glycosylation. Regioselective mono-*O*-acylation of hexa-*O*-diethylboryl-*myo*-inositol, using the boron-tin transmetallation procedure[26], can be performed with a chiral electrophile. Thus, the pure diastereomer 1-*O*-menthoxycarbonyl-*myo*-inositol (**17**) could be obtained in 30% overall yield[26]. Isopropylidenation[26] of **17** gave the 2,3:5,6- (**18**) and the 2,3:4,5-diacetal (**19**). Glycosylation of **18** with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidate (**20**), prepared by diazo transfer from trifluoromethanesulfonyl azide to 2-amino-2-deoxy-D-glucose[45], gave 1-*O*-menthoxycarbonyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-*myo*-inositol (**21**, 88%). Likewise, glycosylation of **19** with **20** afforded 2,3:4,5-di-*O*-isopropylidene-1-*O*-menthoxycarbonyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-*myo*-inositol (**22**, 51%). In the latter reaction, the formation of **21** was detected (TLC and ^{1}H NMR spectroscopy). In an attempt to improve the yield, **20** was added progressively to **19**, but partial isomerisation of **19** occurred and **21** and **22** were obtained in yields of 45 and 39%, respectively.

Glycosylation of **18** with **10** gave the optically pure pseudotrisaccharide derivative **23** (47%), which was converted, by the sequence of reactions applied above to **16**, into **24** ($[\alpha]_D$ +35°).

The above results indicate that glycosylation of the diacetals of enantiomerically pure 1-*O*-menthoxycarbonyl-*myo*-inositol (**17**) with trichloroacetimidates of 2-azido-2-deoxy sugars constitutes a convenient route to fragments of glycosyl-*myo*-inositols involved in insulin action, and its application for the synthesis of biologically active oligosaccharides containing *myo*-inositol 1-phosphate is being investigated.

EXPERIMENTAL

General methods.—Meltings points were determined on a Kofler hot-stage apparatus and are uncorrected. TLC was performed on Silica Gel GF_{254} (Merck)

with detection by charring with H_2SO_4 or phosphomolybdic acid. Column chromatography was performed on silica gel (70–230 mesh, Merck). The ^1H and ^{13}C NMR spectra were recorded with a Varian XL-300 or Bruker AM-200 spectrometer. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter.

(±)-4-O-(6-O-Acetyl-4-O-allyl-2-azido-3-O-benzyl-2-deoxy-α-D-glucopyranosyl)-1-O-benzyl-2,3:5,6-di-O-isopropylidene-myo-inositol (**9**).—To a solution of (±)-1-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol[37] (**4**; 0.110 g, 0.314 mmol) and 6-*O*-acetyl-4-*O*-allyl-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranosyl trichloroacetimidate[40] (**6**; 0.208 g, 0.398 mmol) in dry CH_2Cl_2 (10 mL) at −30° under Ar was added dropwise a solution of trimethylsilyl triflate (0.005 mL, 0.025 mmol) in dry CH_2Cl_2 (0.06 mL). After a further 1 h, $NaHCO_3$ and then satd aq $NaHCO_3$ (20 mL) and CH_2Cl_2 (50 mL) were added. The aqueous phase was washed with CH_2Cl_2 (2 × 50 mL), and the combined organic phases were washed with water (100 mL) and brine (100 mL), dried (Na_2SO_4), and concentrated. Column chromatography (3:1 hexane–EtOAc) of the residue (0.360 g) gave **9**, isolated as a syrup (0.159 g, 71%). Repeated preparative TLC (4:1 hexane–EtOAc) gave the pure faster-moving diastereomer as a syrup which had $[\alpha]_D$ +125° (*c* 0.85, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 7.40–7.28 (m, 10 H, 2 Ph), 5.90–5.79 (m, 1 H, CH_2=C*H*CH_2), 5.35 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1'), 5.26–5.12 (m, 2 H, CH_2=CHCH_2), 4.82 (ABq, 2 H, CH_2Ph), 4.81 (ABq, 2 H, CH_2Ph), 4.36 (dd, 1 H, $J_{5',6'a}$ 3, $J_{6'a,6'b}$ 12.3 Hz, H-6'a), 4.31–3.88 (m, 8 H, H-3,4,6,3',5',6'b, and CH_2=CHCH_2), 4.27 (t, 1 H, $J_{1,2} = J_{2,3}$ = 4.4 Hz, H-2), 3.44 (t, 1 H, $J_{3',4'} = J_{4',5'}$ = 9.2 Hz, H-4'), 3.36 (dd, 1 H, *J* 10.6 and 9.5 Hz, H-5), 3.27 (dd, 1 H, $J_{2',3'}$ 10.3 Hz, H-2'), 2.06 (s, 3 H, Ac), 1.51, 1.43, 1.30 (3 s, 12 H, 2 CMe_2); ^{13}C (50 MHz), δ 170.7, 137.90, 137.8, 134.3, 128.5, 128.4, 128.1, 127.9, 117.5, 112.6, 110.0, 96.3, 79.7, 79.3, 78.7, 77.6, 77.2, 76.0, 75.4, 74.1, 74.0, 71.9, 68.7, 63.0, 62.6, 28.2, 27.0, 26.9, 25.8, 20.8.

Anal. Calcd for $C_{37}H_{47}N_3O_{11}$: C, 62.61; H, 6.67; N, 5.72. Found: C, 62.51; H, 6.47; N, 5.60.

The slower-moving diastereomer, isolated as a syrup, had $[\alpha]_D$ +37° (*c* 0.98, $CHCl_3$). ^1H NMR data (300 MHz, C_6D_6): δ 7.48–7.10 (m, 10 H, 2 Ph), 5.88–5.77 (m, 1 H, CH_2=C*H*CH_2), 5.69 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), 5.23–5.00 (m, 2 H, CH_2=CHCH_2), 4.87–4.67 (ABq, 4 H, 2 CH_2Ph), 4.66–4.00 (m, 10 H, H-2,3,6, H-4 or H-3', H-4',5',6'a,6'b, and CH_2=CHCH_2), 3.53 (dd, 1 H, $J_{1,2}$ 3.9, $J_{1,6}$ 10.1 Hz, H-1), 3.45 (dd, 1 H, *J* 8.9 and 9.9 Hz, H-4 or H-3'), 3.48 (dd, 1 H, *J* 10.9 and 9.4 Hz, H-5), 3.23 (dd, $J_{2',3'}$ 10.3 Hz, H-2'), 1.80 (s, 3 H, Ac), 1.50, 1.39, 1.38, 1.26 (4 s, each 3 H, 2 CMe_2).

Anal. Found: C, 62.90; H, 6.52; N, 5.77.

1,6-Anhydro-2,3-O-benzylidene-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-mannopyranose (**11**).—To a mixture of **8**[42] (0.850 g, 3.4 mmol), mercuric bromide (1.2 g, 3.4 mmol), mercuric cyanide (0.85 g, 3.4 mmol), and 4A molecular sieves (2 g) in dry benzene (30 mL) was added 2,3,4,6,-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (3.35 g, 8.1 mmol) with stirring under Ar. The reaction was

continued at 60° for 24 h, and the mixture was then filtered through Celite, diluted with CH_2Cl_2 (300 mL), washed with aq KI (200 mL), aq $NaHCO_3$ (150 mL), water (150 mL), and brine (150 mL), dried (Na_2SO_4), and concentrated. Column chromatography (3.5:1 hexane–acetone) of the residue gave **11** (1.0 g, 51%) as a 1:1 *exo–endo* mixture, $[\alpha]_D$ −23° (*c* 0.3, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 7.68–7.35 (m, 10 H, 2 Ph), 6.29 (s, 1 H, C*H*Ph *exo*), 5.74 (s, 1 H, C*H*Ph *endo*), 5.51 (t, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.48 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1), 5.41 and 5.39 (2 dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 1.1 Hz, H-4′), 5.26 and 5.23 (2 dd, 1 H, $J_{1',2'}$ 8.1, $J_{2',3'}$ 10.5 Hz, H-2′), 5.05 and 5.03 (2 dd, 1 H, H-3′), 4.69 and 4.66 (2 d, 1 H, H-1′), 4.57 (m, 2 H, 2 H-5′), 4.37 (m, 2 H, H-3), 4.26–4.06 (m, 9 H, 2 H-2,5,6′a,6′b and H-6*endo*), 4.01 (dd, 1 H, $J_{5,6endo}$ 1.5, $J_{6endo,6exo}$ 7.5 Hz, H-6*endo*), 3.96–3.88 (m, 2 H, 2 H-4), 3.84 (dd, 1 H, $J_{5,6exo}$ 6.2 $J_{6endo,6exo}$ 7.4 Hz, H-6*exo*), 3.83 (dd, 1 H, $J_{5,6exo}$ 6.2, $J_{6endo,6exo}$ 7.4 Hz, H-6*exo*), 2.17, 2.15, 2.09, 2.07, 2.03, 2.00, 1.99, 1.97 (8 s, each 3 H, Ac); ^{13}C (50 MHz), δ 170.12, 170.04, 169.33, 139.74, 136.09, 129.75, 129.08, 128.38, 128.33, 127.49, 125.92, 104.92, 104.33, 100.48, 100.29, 99.87, 99.03, 76.67, 76.52, 76.34, 74.37, 73.30, 73.06, 72.85, 71.37, 70.99, 70.65, 68.64, 68.59, 68.31, 67.18, 67.11, 66.89, 64.81, 64.22, 61.22, 20.67, 20.54, 20.47.

Anal. Calcd for $C_{27}H_{32}O_{14}$: C, 55.86; H, 5.52. Found: C, 55.57; H, 5.74.

*1,6-Anhydro-3-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-mannopyranose* (**12**).—To a solution of **11** (2.06 g, 3.55 mmol) in 8:1 CH_2Cl_2–water (9 mL) was added a suspension of DDQ (2.45 g, 10.92 mmol) in CH_2Cl_2 (8 mL) in the dark, at room temperature, and under Ar. The mixture was stirred for 3 days. Dichloromethane (200 mL) was added, and the organic layer was washed with aq $NaHCO_3$ (150 mL), water (150 mL), and brine (150 mL), dried (Na_2SO_4), and concentrated. Column chromatography (2:1 hexane–acetone) of the residue gave **12** (1.51 g, 71%), mp 189–191° (from EtOH–hexane), $[\alpha]_D$ −50.9° (*c* 0.95, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 8.07–7.44 (m, 5 H, Ph), 5.70 (dq, 1 H, *J* 1.7, 3.1, and 5.6 Hz, H-3), 5.48 (bs, 1 H, H-1), 5.42 (dd, 1 H, $J_{3',4'}$ 3.5, $J_{4',5'}$ 1.1 Hz, H-4′), 5.29 (dd, 1 H, $J_{2',3'}$ 10.5, $J_{1',2'}$ 7.9 Hz, H-2′), 5.07 (dd, 1 H, H-3′), 4.79 (d, 1 H, H-1′), 4.51 (m, 1 H, H-5), 4.22 (dd, 1 H, $J_{5',6'a}$ 7.2, $J_{6'a,6'b}$ 11.4 Hz, H-6′a), 4.19 (dd, 1 H, $J_{5',6'b}$ 5.9 Hz, H-6′b), 4.10 (dd, 1 H, $J_{5,6endo}$ 0.6, $J_{6endo,6exo}$ 7.8 Hz, H-6*endo*), 4.05 (m, 1 H, H-5′), 3.97 (m, 1 H, H-2), 3.87 (t, 1 H, H-4), 3.87 (dd, 1 H, $J_{5,6exo}$ 5.7, $J_{6endo,6exo}$ 7.9 Hz, H-6*exo*), 2.29 (d, 1 H, OH), 2.14, 2.02, 1.98, 1.96 (4 s, each 3 H, Ac); ^{13}C (50 MHz), δ 170.4, 170.2, 170.0, 169.2, 165.5, 133.7, 129.6, 129.1, 128.7, 78.5, 73.8, 71.2, 70.8, 70.4, 66.9, 67.0, 65.8, 64.9, 61.3, 20.7, 20.6, 20.5.

Anal. Calcd for $C_{27}H_{32}O_{15}$: C, 54.36; H, 5.37. Found: C, 54.18; H, 5.50.

*1,6-Anhydro-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyransoyl)-β-*D*-glucopyranose* (**13**).—A solution of triflic anhydride (0.75 mL, 4.45 mmol) in dry CH_2Cl_2 (3 mL) was added at −10° under Ar to a stirred solution of pyridine (0.41 mL, 5.19 mmol) in dry CH_2Cl_2 (14 mL). After 10 min, a solution of **12** (1.33 g, 2.23 mmol) in CH_2Cl_2 (4 mL) was added and stirring under Ar was continued for 2 h at 0°. Aqueous $NaHCO_3$ and CH_2Cl_2 were added, the aqueous layer was washed with CH_2Cl_2, and the combined organic layers were washed with

water and brine, dried (Na_2SO_4), and concentrated. To a solution of the residue in *N,N*-dimethylformamide (60 mL) was added sodium azide (1.44 g, 22.2 mmol), and the mixture was stirred at room temperature for 18 h, then concentrated. A solution of the residue in CH_2Cl_2 was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography (2.5:1 → 1.5:1 hexane–EtOAc) of the residue gave **13** (1.28 g, 92%), mp 130–132° (from hexane–EtOAc), $[\alpha]_D$ −1.2° (*c* 0.65, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 8.05–7.43 (m, 5 H, Ph), 5.52 (bs, 1 H, H-1), 5.49 (m, 1 H, H-3), 5.40 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 1.1 Hz, H-4′), 5.31 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10.4 Hz, H-2′), 5.07 (dd, 1 H, H-3′), 4.88 (d, 1 H, H-1′), 4.67 (m, 1 H, H-5), 4.19 (m, 2 H, 2 H-6′), 4.15 (dd, 1 H, $J_{5,6endo}$ 0.9, $J_{6endo,6exo}$ 7.7 Hz, H-6*endo*), 4.02 (m, 1 H, H-5′), 3.88 (dd, 1 H, $J_{5,6exo}$ 6.0, $J_{6endo,6exo}$ 7.7 Hz, H-6*exo*), 3.80 (bs, 1 H, H-4), 3.40 (bs, 1 H, H-2), 2.06, 2.00, 1.99, 1.55 (4 s, each 3 H, 4 Ac); ^{13}C (50 MHz), δ 171.3, 170.1, 170.0, 169.1, 165.0, 133.7, 129.7, 129.1, 128.6, 100.6, 100.1, 75.4, 73.7, 71.2, 71.0, 70.4, 68.8, 67.0, 65.0, 61.4, 58.7, 20.5.

Anal. Calcd for $C_{27}H_{31}N_3O_{14}$: C, 52.17; H, 5.03; N, 6.76. Found: C, 51.98; H, 4.82; N, 6.49.

*1,6-Di-*O*-acetyl-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-α,β-*D*-glucopyranose* (**14**).—To a solution of **13** (1.20 g, 1.93 mmol) in acetic anhydride (42 mL) was added trifluoroacetic acid (2.1 mL, 27.40 mmol), and the mixture was stirred at room temperature for 5 days. 1:1 Toluene–EtOAc was added and the mixture was concentrated. Column chromatography (2:1 hexane–acetone) of the residue gave **14** (1.23 g, 88%) as a 3:2 α,β-mixture, $[\alpha]_D$ +45° (*c* 1.2, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 8.14–7.45 (m, 5 H, Ph), 6.28 (d, 0.6 H, $J_{1,2}$ 3.7 Hz, H-1α), 5.70 (dd, 0.6 H, $J_{2,3}$ 9.0, $J_{3,4}$ 10.6 Hz, H-3), 5.57 (d, 0.4 H, $J_{1,2}$ 8.5 Hz, H-1β), 5.34 (dd, 0.4 H, $J_{2,3}$ 9.0, $J_{3,4}$ 10.3 Hz, H-3), 5.13 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 0.9 Hz, H-4′), 5.05 (dd, 0.6 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.2 Hz, H-2′), 5.01 (dd, 0.4 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.3 Hz, H-2′), 4.84 (dd, 0.6 H, H-3′), 4.83 (dd, 0.4 H, H-3′), 4.45 (d, 0.6 H, H-1′), 4.43 (d, 0.4 H, H-1′), 4.47–4.38 (m, 2 H, 2 H-6a), 4.12 (dd, 0.8 H, $J_{5,6b}$ 4.9, $J_{6a,6b}$ 12.2 Hz, H-6b), 4.11 (dd, 1.2 H, $J_{5,6b}$ 4.4, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.04 (ddd, 0.6 H, $J_{4,5}$ 11.7, $J_{5,6a}$ 1.9 Hz, H-5), 3.92 (t, 0.6 H, $J_{4,5}$ 10.0 Hz, H-4), 3.90 (t, 0.4 H, $J_{4,5}$ 9.1 Hz, H-4), 3.80 (ddd, 0.4 H, H-5), 3.72 (dd, 0.4 H, H-2), 3.62 (dd, 0.6 H, H-2), 3.58–3.45 (m, 2 H, H-5′,6′b), 3.37–3.30 (m, 1 H, H-6′a), 2.23, 2.19, 2.13, 2.02, 1.98, 1.97, 1.95, 1.94, 1.93, 1.92 (10 s, 6 Ac); ^{13}C (50 MHz), δ 170.2, 170.0, 169.8, 169.1, 168.9, 168.6, 168.4, 164.8, 164.7, 133.5, 129.7, 129.5, 128.5, 100.9, 100.1, 92.6, 90.1, 75.7, 75.3, 73.6, 72.3, 70.8, 70.7, 70.6, 70.5, 69.2, 69.1, 66.3, 66.2, 63.1, 61.7, 61.6, 60.7, 60.1, 59.8, 26.8, 20.9, 20.7, 20.5, 20.4.

Anal. Calcd for $C_{31}H_{37}N_3O_{17}$: C, 51.45; H, 5.15; N, 5.81. Found: C, 51.25; H, 5.02; N, 5.70.

*6-*O*-Acetyl-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galacto-pyranosyl)-α,β-*D*-glucopyranose* (**15**).—Hydrazine acetate (0.159 g, 1.73 mmol) was added to a solution of **14** (0.90 g, 1.24 mmol) in dry *N,N*-dimethylformamide (7 mL) and the mixture was stirred at room temperature for 5 h. Dichloromethane

and water were added, the aqueous phase was washed twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated. Column chromatography (2:1 hexane–acetone) of the residue gave **15** (0.84 g, 99%) as a 3:2 α,β-mixture. NMR data ($CDCl_3$): ^1H (300 MHz), δ 8.10–7.39 (m, 5 H, Ph), 5.73 (t, 0.6 H, J 10.3 Hz, H-3), 5.35 (d, 0.6 H, $J_{1,2}$ 3.6 Hz, H-1α), 5.24 (t, 0.4 H, J 10.2 Hz, H-3), 5.09 (m, 1 H, H-4′), 5.02 (dd, 0.6 H, J 7.3 Hz, H-2′), 4.98 (dd, 0.4 H, $J_{1',2'}$ 7.7, $J_{2',3'}$ 10.5 Hz, H-2′), 4.80 (dd, 0.6 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.4 Hz, H-3′), 4.79 (dd, 0.4 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.3 Hz, H-3′), 4.74 (d, 0.4 H, $J_{1,2}$ 7.8 Hz, H-1β), 4.25 (m, 2 H, H-1′,6), 4.24 (m, 0.6 H, H-5), 4.07 (dd, 0.6 H, $J_{5,6}$ 4.4, $J_{6a,6b}$ 12.2 Hz, H-6), 4.03 (dd, 0.4 H, $J_{5,6}$ 5.1, $J_{6a,6b}$ 12.2 Hz, H-6), 3.84 (t, 0.6 H, J 9.8 Hz, H-4), 3.81 (t, 0.4 H, J 9.1 Hz, H-4), 3.66 (m, 0.4 H, H-5), 3.54–3.24 (m, 4 H, H-2,5′,6′a,6′b), 2.07, 1.94, 1.91, 1.87, 1.86 (5 s, each 3 H, 5 Ac); ^{13}C (50 MHz), δ 170.51, 170.10, 169.96, 169.10, 164.99, 164.92, 133.41, 129.79, 128.46, 100.65, 96.140, 92.22, 76.36, 75.93, 72.88, 72.55, 70.94, 70.49, 69.27, 68.38, 62.12, 61.96, 59.99, 20.85, 20.67, 20.43.

Anal. Calcd for $C_{29}H_{35}N_3O_{16}$: C, 51.10; H, 5.18; N, 6.16. Found: C, 50.85; H, 5.40; N, 6.13.

6-O-Acetyl-2-azido-3-O-benzoyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galacto-pyranosyl)-α,β-D-glucopyranosyl trichloroacetimidate (**10**).—To a solution of **15** (0.19 g, 0.28 mmol) in dry CH_2Cl_2 (4 mL) were added trichloroacetonitrile (0.10 mL, 0.99 mmol) and dry K_2CO_3 (0.040 g, 0.289 mmol), and the mixture was stirred at room temperature under Ar for 90 min, then filtered through Celite, and concentrated. Compound **10** was used in the next step without further purification or after flash-column chromatography (2:1 hexane–acetone); α,β-ratio, 1:3.8 (^1H NMR data).

*(±)-4-O-[6-O-Acetyl-2-azido-3-O-benzoyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-1-O-benzyl-2,3:5,6-di-O-isopropylidene-*myo*-inositol* (**16**).—To a solution of **4** (0.106 g, 0.303 mmol) and **10** (0.360 g, 0.364 mmol) in CH_2Cl_2 (10 mL) under Ar at −24° was added dropwise 0.1 M trimethylsilyl triflate in CH_2Cl_2 (0.24 mL). The temperature of the stirred solution was allowed to rise slowly from −24° to −10° during 3 h, solid $NaHCO_3$ and aq $NaHCO_3$ were added, and the mixture was diluted with CH_2Cl_2. The aqueous phase was washed with CH_2Cl_2 and the combined organic layers were washed with water and with brine, dried (Na_2SO_4), and concentrated. Column chromatography (2:1 hexane–acetone) of the residue gave **16** as a syrupy mixture (0.245 g, 80%) of diastereomers. Column chromatography (18:1 → 9:1 $CHCl_3$–acetone) of the mixture gave the diastereomer of higher R_F, mp 102–105°, $[\alpha]_D$ +102° (c 0.64, $CHCl_3$). ^1H NMR data (300 MHz, $CDCl_3$): δ 8.08–7.22 (m, 10 H, 2 Ph), 5.67 (dd, 1 H, $J_{3',4'}$ 9.0, $J_{2',3'}$ 10.7 Hz, H-3′), 5.37 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.08 (dd, 1 H, $J_{4'',5''}$ 1.0, $J_{3'',4''}$ 3.4 Hz, H-4″), 5.01 (dd, 1 H, $J_{1'',2''}$ 7.9, $J_{2'',3''}$ 10.4 Hz, H-2″), 4.79 (dd, 1 H, H-3″), 4.77 (AB q, 2 H, CH_2Ph), 4.49 (d, 1 H, H-1″), 3.38 (dd, 1 H, $J_{5',6'a}$ 2.2, $J_{6'a,6'b}$ 12.1 Hz, H-6′a), 4.30 (m, 1 H, H-5′), 4.27 (t, 1 H, $J_{1,2} = J_{2,3} = 4.3$ Hz, H-2), 4.13 (dd, 1 H, $J_{5',6'b}$ 3.3 Hz, H-6′b), 4.03 (dd, 1 H, $J_{3,4}$ 6.7 Hz, H-3), 3.94 (t, 1

H, *J* 9.8 Hz, H-4′ or H-6), 3.93 (t, 1 H, *J* 10.0 Hz, H-4′ or H-6), 3.86 (dd, 1 H, $J_{4,5}$ 10.6 Hz, H-4), 3.72 (dd, 1 H, $J_{1,6}$ 10.1 Hz, H-1), 3.54 (m, 2 H, 2 H-6″), 3.37 (m, 1 H, H-5″), 3.36 (dd, 1 H, $J_{5,6}$ 9.4 Hz, H-5), 3.12 (dd, 1 H, H-2′), 2.06, 1.93, 1.90, 1.86 (4 s, each 3 H, 4 Ac), 1.49, 1.39, 1.36, 1.26 (4 s, each 3 H, 2 CMe_2).

Anal. Calcd for $C_{48}H_{59}N_3O_{21}$: C, 56.86; H, 5.86; N, 4.14. Found: C, 56.71; H, 5.76; N, 3.98.

Conversion of ***16*** *into 4-O-[2-acetamido-3,6-di-O-acetyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-1,2,3,5,6-penta-O-acetyl-*myo*-inositol* (**24**).—The reactions were monitored by TLC and ^{1}H NMR spectroscopy without further characterisation. Compound **16** (30 mg, 0.0374 mmol) in MeOH (2 mL) was deacylated with methanolic M NaOMe (0.2 mL) at room temperature, and the mixture was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. A solution of the residue (26 mg) in MeOH (7 mL) was hydrogenated in the presence of Pd/C (10 mg) for 3 h at room temperature, then filtered through Celite, and concentrated. The residue was acetylated and the product was purified by column chromatography (4:1 EtOAc–hexane). The benzyl group was removed by hydrogenation of the product (25 mg) in the presence of Pd/C (10 mg) in 1:1 EtOAc–MeOH (6 mL) for 24 h at room temperature. The mixture was filtered through Celite and concentrated. A solution of the residue (24 mg) in MeOH (2 mL) was treated with Amberlite IR-120 (H^+) resin for 6 h at room temperature, then filtered, and concentrated. Column chromatography (6:1 $CHCl_3$–MeOH) of the residue (19 mg), acetylation of the product, and column chromatography (5:1 EtOAc–hexane) gave **24** (9 mg), mp 131–134°, $[\alpha]_D$ +36° (*c* 0.29, $CHCl_3$). NMR data ($CDCl_3$): ^{1}H (300 MHz), δ 5.59 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1′), 4.43 (d, 1 H, $J_{1'',2''}$ 7.7 Hz, H-1″), 2.15, 2.11, 2.10, 2.02, 2.01, 1.98, 1.97, 1.95, 1.94, 1.93, 1.92, 1.91 (s, 12 Ac); ^{13}C (50 MHz), δ 171.0, 170.5, 170.3, 170.0, 169.8, 169.6, 169.2, 169.1, 168.9, 101.3, 97.3, 76.0, 73.0, 72.3, 71.0, 70.9, 70.6, 69.9, 69.7, 69.3, 68.9, 68.3, 68.1, 66.5, 61.5, 60.7, 51.9, 20.8, 20.6, 20.5.

*2,3 : 5,6-Di-O-isopropylidene-1-O-menthoxycarbonyl-4-O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-*myo*-inositol* (**21**).–To a solution of **18** (0.030 g, 0.068 mmol) and **20**[44,45] (0.044 g, 0.092 mmol) in CH_2Cl_2 (2 mL) at −35° under Ar was added 0.1 M trimethylsilyl triflate in CH_2Cl_2 (0.006 mL). The mixture was stirred for 2 h and the temperature was allowed to rise slowly during this period to −15°. Solid and aq $NaHCO_3$ were added, the mixture was diluted with CH_2Cl_2 the aqueous layer was washed twice with CH_2Cl_2, and the combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography (6:1 hexane–EtOAc) of the residue gave **21** (0.044 g, 86%), mp 164–166° (from MeOH), $[\alpha]_D$ +65° (*c* 0.54, $CHCl_3$). NMR data ($CDCl_3$): ^{1}H (300 MHz), δ 5.44 (dd, 1 H, $J_{2',3'}$ 10.7, $J_{3',4'}$ 9.4 Hz, H-3′), 5.42 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.07 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′), 4.88 (dd, 1 H, $J_{1,2}$ 4.3, $J_{1,6}$ 10.5 Hz, H-1), 4.69 (t, 1 H, $J_{2,3}$ 4.6 Hz, H-2), 4.56 (td, 1 H, *J* 11.0, and 4.5 Hz, CHOCO), 4.36–4.29 (m, 2 H, H-5′,6′), 4.17 (dd, 1 H, *J* 5.0, and 6.7 Hz, H-3), 4.01 (t, 1 H, *J* 9.6 Hz, H-6), 3.91 (dd, 1 H, *J* 6.8, and 10.8 Hz, H-4), 3.97 (m, 1 H, H-6′), 3.51 (dd,

1 H, *J* 9.5, 10.6 Hz, H-5), 3.28 (dd, 1 H, H-2′), 2.04, 2.03, 2.00 (3 s, each 3 H, 3 Ac), 1.47, 1.41, 1.40, 1.28 (4 s, each 3 H, 2 CMe_2), 0.88 (d, 3 H, *J* 6.6 Hz, CH_3CH), 0.84 (d, 3 H, *J* 7.1 Hz, CH_3CH), 0.75 (d, 3 H, *J* 6.9 Hz, CH_3CH); ^{13}C (50 MHz), δ 170.7, 170.0, 169.6, 154.8, 133.2, 110.1, 96.5, 79.2, 79.1, 78.2, 78.0, 74.6, 73.3, 70.1, 68.0, 67.3, 61.4, 60.5, 47.2, 40.6, 33.9, 31.4, 28.1, 26.9, 26.7.

Anal. Calcd for $C_{35}H_{53}N_3O_{15}$: C, 55.62; H, 7.07; N, 5.56. Found: C, 55.90; H, 7.27; N, 5.28.

*2,3 : 4,5-Di-*O*-isopropylidene-1-*O*-menthoxycarbonyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-*D*-glucopyranosyl)*-myo*-inositol* (**22**).—To a solution of **19** (0.150 g, 0.34 mmol) and **20** (0.220 g, 0.463 mmol) in dry CH_2Cl_2 (10 mL) under Ar at −25° was added 0.1 M trimethylsilyl triflate in CH_2Cl_2 (0.018 mL). The mixture was stirred for 5 h and the temperature was allowed to rise slowly from −25° to 0° during this period. Work-up, as described for **21**, afforded **22** (0.132 g, 51%) as a syrup, $[\alpha]_D$ +63° (*c* 0.65, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 5.45 (dd, 1 H, $J_{2',3'}$ 10.2, $J_{3',4'}$ 9.3 Hz, H-3′), 5.32 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1′), 5.07 (t, 1 H, $J_{4',5'}$ 9.8 Hz, H-4′), 4.91 (t, 1 H, $J_{1,2} = J_{2,3} = 4.0$ Hz, H-2), 4.57 (dd, 1 H, $J_{1,6}$ 6.7 Hz, H-1), 4.52 (td, 1 H, *J* 11.7, and 4.1 Hz, CHOCOO), 4.36 (t, 1 H, *J* 7.5 Hz, H-6), 4.32 (dd, 1 H, $J_{6a',6b'}$ 12.6, $J_{5',6a'}$ 3.2 Hz, H-6′a), 4.21 (m, 1 H, H-5′), 4.04 (dd, 1 H, *J* 3.9, 8.5 Hz, H-3), 4.01 (dd, 1 H, $J_{5',6'b}$ 2.2 Hz, H-6′b), 3.93 (dd, 1 H, *J* 7.8, 10.4 Hz, H-5), 3.54 (dd, 1 H, *J* 8.8, 10.5 Hz, H-4), 3.35 (dd, 1 H, H-2′), 2.06, 2.04, 2.01 (3 s, each 3 H, 3 Ac), 1.47, 1.43, 1.39, 1.31 (s, each 3 H each, 2 CMe_2), 0.89 (d, 3 H, *J* 6.5 Hz, CH_3CH), 0.84 (d, 3 H, *J* 8.1 Hz, CH_3CH), 0.74 (d, 3 H, *J* 7.0 Hz, CH_3CH); ^{13}C (50 MHz), δ 170.6, 170.1, 169.5, 154.1, 112.7, 111.4, 97.2, 79.3, 77.5, 76.4, 76.2, 73.5, 70.5, 68.1, 67.7, 61.2, 60.7, 47.0, 40.5, 34.0, 31.9, 27.1, 27.0, 26.8, 26.0, 25.2, 23.2, 21.9, 20.6, 16.2.

Anal. Calcd for $C_{35}H_{53}N_3O_{15}$: C, 55.62; H, 7.07; N, 5.56. Found: C, 55.90; H, 7.27; N, 5.28.

*4-*O*-[6-*O*-Acetyl-2-azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-α-*D*-glucopyranosyl]-2,3 : 5,6-di-*O*-isopropylidene-1-*O*-menthoxycarbonyl*-myo*-inositol* (**23**).—To a solution of **18** (0.234 g, 0.529 mmol) and trichloroacetimidate **10** (0.500 g, 0.607 mmol) in CH_2Cl_2 (16 mL) under Ar at −28° was added dropwise 0.88 M trimethylsilyl triflate in CH_2Cl_2 (0.048 mL), and the mixture was stirred for 2 h. Solid and aq $NaHCO_3$ were added, the mixture was diluted with CH_2Cl_2 the aqueous layer was washed twice with CH_2Cl_2, and the combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography (2:1 hexane–EtOAc) of the residue gave **23** (0.250 g, 45.5%) isolated as a syrup, $[\alpha]_D$ −61° (*c* 1.0, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 8.11–7.46 (m, 5 H, Ph), 5.74 (dd, 1 H, $J_{3',4'}$ 9.0, $J_{2',3'}$ 10.5 Hz, H-3′), 5.42 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1′), 5.13 (dd, 1 H, $J_{3'',4''}$ 3.4, $J_{4'',5''}$ 0.8 Hz, H-4″), 5.07 (dd, 1 H, $J_{1'',2''}$ 7.7, $J_{2'',3''}$ 10.4 Hz, H-2″), 4.91 (dd, 1 H, $J_{1,2}$ 4.3, $J_{1,6}$ 10.4 Hz, H-1), 4.84 (dd, 1 H, $J_{2'',3''}$ 10.4, $J_{3'',4''}$ 3.4 Hz, H-3″), 4.72 (t, 1 H, $J_{2,3}$ 4.6 Hz, H-2), 4.59 (td, 1 H, *J* 4,6, 11.1 Hz, CHOCO), 4.55 (d, 1 H, H-1″), 4.44 (dd, 1 H, $J_{5',6'a}$ 2.1, $J_{6'a,6'b}$ 12.0 Hz, H-6′a), 4.36–4.31 (m, 1 H, H-5′), 4.22 (dd, 1 H, $J_{3,4}$ 6.6

Hz, H-3), 4.18 (dd, 1 H, $J_{5',6'b}$ 3.0 Hz, H-6'b), 3.95 (t, 1 H, *J* 9.8 Hz, H-4' or H-6), 3.94 (t, 1 H, *J* 9.8 Hz, H-4' or H-6), 3.93 (dd, 1 H, $J_{4,5}$ 10.9 Hz, H-4), 3.63–3.48 (m, 3 H, H-5,6"a,6"b), 3.43–3.38 (m, 1 H, H-5"), 3.20 (dd, 1 H, H-2'), 2.11, 1.99, 1.95, 1.91 (4 s, each 3 H, 4 Ac), 1.52, 1.41, 1.29 (3 s, 12 H, 2 CMe_2), 0.89 (d, 3 H, *J* 6.5 Hz, CH_3CH), 0.86 (d, 3 H, *J* 6.9 Hz, CH_3CH), 0.77 (d, 3 H, *J* 6.9 Hz, CH_3CH); ^{13}C (50 MHz), δ 170.2, 168.9, 169.6, 168.9, 164.7, 153.7, 133.2, 129.7, 128.4, 113.0, 109.9, 100.5, 96.7, 79.1, 78.9, 78.5, 77.9, 75.9, 74.5, 73.3, 70.8, 70.4, 70.3, 69.2, 67.9, 66.1, 61.7, 60.8, 59.6, 47.1, 40.5, 33.9, 31.3, 28.0, 26.8, 26.5, 26.0, 25.4, 23.3, 21.8, 20.7, 20.5, 20.3, 16.2.

Anal. Calcd for $C_{52}H_{71}N_3O_{23}$: C, 56.46; H, 6.47; N, 3.80. Found: C, 56.70; H, 6.71; N, 3.90.

Conversion of ***23*** *into 4-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-α-*D*-glucopyranosyl]-1,2,3,5,6-penta-*O*-acetyl-*myo*-inositol* (**24**).—The reactions were monitored by TLC and ^1H NMR spectroscopy without further characterisation. Compound **23** (53 mg, 0.048 mmol) was deacylated with methanolic 0.2 M NaOMe (0.5 mL) for 20 h at room temperature. The mixture was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. A solution of the residue (32 mg) in MeOH (10 mL) was hydrogenated in the presence of Pd/C (10 mg) overnight, then filtered through Celite, and concentrated, the residue was acetylated, and the product (34 mg) was purified by column chromatography (5 : 1 hexane–EtOAc). To a solution of product (20 mg) in CH_2Cl_2 (0.8 mL) was added trifluoroacetic acid (0.074 mL), the mixture was stirred for 6 h, then 1 : 1 toluene–EtOAc was added, and the solvents were evaporated. To a solution of the residue (22 mg) in MeOH (2 mL) was added toluene-*p*-sulfonic acid (2 mg), the mixture was stirred for 1 h, triethylamine was added, and the mixture was concentrated. Column chromatography (10 : 1 $CHCl_3$–MeOH) of the residue, acetylation, and column chromatography (5 : 1 EtOAc–hexane) gave **24** (4 mg), mp 132–135°, $[\alpha]_D$ +35° (*c* 0.3, $CHCl_3$). The ^1H NMR data (300 MHz, $CDCl_3$) were identical to those of the product described above.

Anal. Calcd for $C_{42}H_{57}NO_{27}$: C, 50.05; H, 5.70; N, 1.39. Found: C, 49.78; H, 5.66; N, 1.15.

ACKNOWLEDGMENTS

We thank the Dirección General de Investigacion Científica y Técnica (Grant 87-0367) and Europharma S.A. for financial support, Dr. S. Penadés and Mr. A. Aguiló for helpful discussions, and the Ministerio de Educación y Ciencia for a fellowship (to A.Z.).

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