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Synthesis of β-D-mannosides from β-D-glucosides *via* an intramolecular SN2 reaction at C-2*

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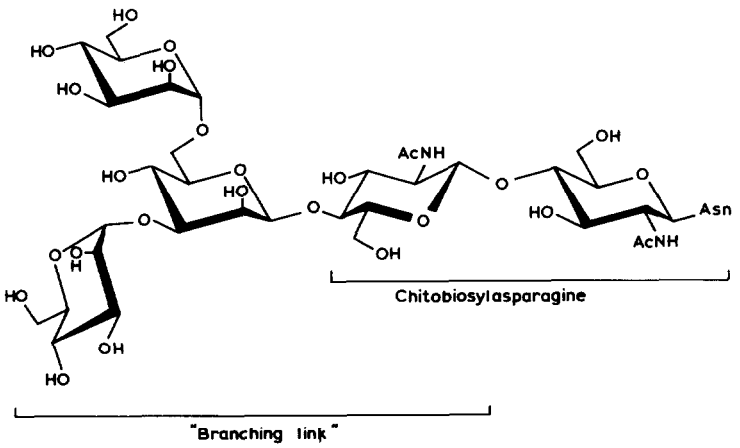
ABSTRACT

The selective synthesis of β-D-mannosides was achieved by first synthesizing β-D-glucosides that carry a *N*-phenylcarbamoyl protecting group at O-3. These derivatives were transformed into the corresponding β-D-mannosides by intramolecular nucleophilic substitution with inversion of configuration at C-2, the *O*-triflyl group being the leaving group. Subsequent intramolecular attack of the neighboring carbamoyl group resulted in the formation of the 2,3-carbonate of the desired β-D-mannoside.

INTRODUCTION

Of the glycoside bonds, the β-D-mannosyl linkage is especially difficult to be constructed, as both the neighboring group assistance in the sense of the Koenigs–Knorr reaction and the anomeric effect uniformly favor the formation of α-D-mannosides. However, the β-D-mannoside bond is an important structural element of the



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* Dedicated to Professor S. David on the occasion of his 70th birthday.
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N-glycoproteins, widespread in multicellular organisms as serum, cytosol, and membrane components. The β-D-mannose unit glycosidically linked to the chitobiosylasparagine component of the "core region" (**1**) of the *N*-glycoproteins is the branching link of the antennary oligosaccharide side-chains of the high-mannose, complex, and hybrid type.

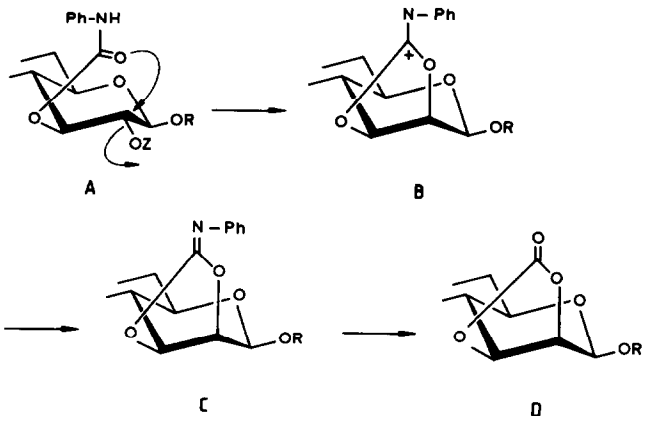
The β-D-mannoside syntheses starting from D-mannosyl donors only show a useful β-selectivity when the 2,3-*O*-carbonyl[2], 2-*O*-mesyl[3], or 2-*O*-benzyl protective groups are present. Oligosaccharides of *N*-glycoproteins have been synthesized especially with insoluble silver salt reagents, such as silver silicate[4] or silver zeolithe[5]. However, a satisfactory selectivity in the formation of the β-D-mannosyl bond to the 2-acetamido-2-deoxy-D-glucose unit was only achieved where reactive glycosyl acceptors, *e.g.*, 1,6-anhydro-2-azido derivatives[4], were applied. With less reactive acceptors, as for instance 2-acetamido-3,6-di-*O*-benzyl-D-glucose[6] or chitobiose derivatives[7], the silver silicate-promoted glycosylation either showed no β-selectivity[7], or even gave exclusively α-D-mannosides[6].

An alternative concept for the synthesis of β-D-mannosides, based on the work of Theander[8] and Ekborg *et al.*[9], has been extensively used by Augé *et al.*[10]. These authors started with the stereoselective synthesis of β-D-glucosides which were then epimerized at C-2 *via* an oxidation to give the 2-uloses and a subsequent reduction with sodium borohydride. Since the reduction is not completely selective, β-D-glucosides were formed again in various amounts[11].

The epimerization of β-D-glucosides to β-D-mannosides is also possible *via* a SN2 reaction with inversion of configuration at C-2. Since SN2-type reactions at C-2 of glucopyranose derivatives are difficult owing to the repulsive interaction between the approaching nucleophile and the lone pair at the ring oxygen atom, we have developed a transformation of β-D-glucosides to β-D-mannosides that overcomes this problem by use of an entropically favored, intramolecular presentation of the nucleophile in the form of the phenylcarbamoyl group at O-3[12,13]. During this investigation, David and assoc.[14] reported that β-D-galactosides can be converted to β-D-mannosides by a simultaneous inversion of configuration at C-2 and C-4 using the benzoate group as an external nucleophile. Also β-D-glucosides could be transformed to β-D-mannosides by use of the *N*-imidazolylsulfonate as the leaving group at C-2[15].

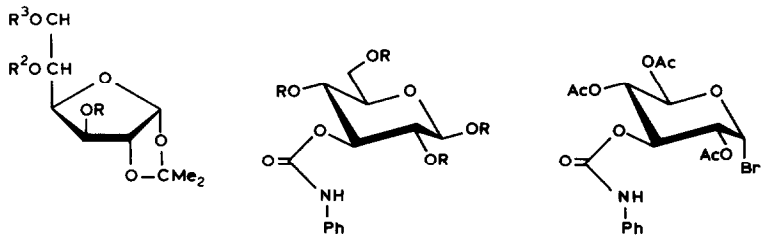
RESULTS AND DISCUSSION

In this new synthesis of β-D-mannosides, the principle of neighboring-group participation is applied in two different ways. In the first step, the classical neighboring-group assistance is exploited in a stereoselective, Koenigs–Knorr type formation of β-D-glucosides. The key step consists in the neighboring-group participation of the protecting group at O-3-position which, however, in contrast to the classical prototype[16], has to lock in the 2,3-*cis*-diol configuration. The usual acyl protecting groups do not meet these preconditions, because their acyloxonium intermediates are opened by nucleophilic attack with preferred *trans*-diol formation[16]. Thus, to achieve a stabiliza-



tion of the acyloxonium intermediate that embodies the desired 2,3-*cis*-diol structure, we used the *N*-phenylcarbamoyl group as the neighboring-group-active protection at O-3. The neighboring-group participation **A** (see Scheme 1) of this urethane-type protecting group results in an acyloxonium intermediate **B** which, after deprotonation, forms an iminocarbonate **C**. The hydrolysis of **C** gives the 2,3-carbonate **D** having the *cis*-diol structure[12,13,17].

In order to synthesize a suitable D-glucosyl donor carrying the 3-*O*-(*N*-phenyl)-carbamoyl protective group, 1,2-5,6-di-*O*-isopropylidene-D-glucofuranose was treated with phenyl isocyanate and a catalytic amount of 4-dimethylaminopyridine in toluene to give the known carbamate[18] **2**. Hydrolysis with aqueous acetic acid yielded the known 3-*O*-carbamoyl-1,2-*O*-isopropylidene derivative **3**. The selective removal of the 1,2-*O*-isopropylidene group was achieved without undesired side-reactions by treatment with



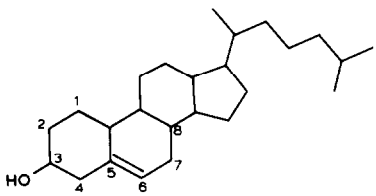
2 R^1 = CO–NH–Ph; R^2, R^3 = Me_2C 4 R = H 6

3 R^1 = CO–NH–Ph; R^2 = R^3 = H 5 R = Ac

0.05M sulfuric acid in 1,4-dioxane at 100°. 3-*O*-(*N*-Phenyl)carbamoyl-D-glucopyranose (**4**), obtained in a yield of 87%, was subsequently acetylated to yield **5**. Treatment of **5** with hydrobromic acid afforded the stable glucosyl donor **6** in 83% yield.

Synthesis of β-D-*glucosides using 2,4,6-tri*-O-*acetyl-3*-O-(N-*phenylcarbamoyl*)-D-*glucopyranosyl donors.* — The urethane-type protection in glucosyl donors such as **6** influences the glycosylation reactions. Glycosylation of cholesterol (**7**) or menthol (**8**)

using **6** and silver trifluoromethanesulfonate 1-*N,N,N',N'*-tetramethylurea[19] gave almost exclusively the undesired orthoester. Similar results were obtained with the monosaccharide acceptors **9–12**.



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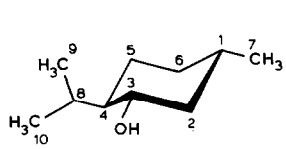

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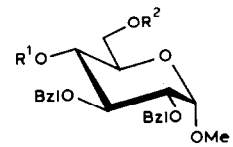
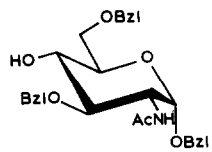


9 R^1 = Bzl ; R^2 = H

10 R^1 = H ; R^2 = Bzl



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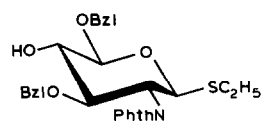
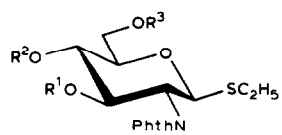


12

The *O*-benzyl-protected methyl α-D-glucopyranosides having a free OH-6[20] or OH-4[21] group, as well as the 2-acetamido-2-deoxy-D-glucose derivative[21], were obtained according to procedures described in the literature. The *N*-phthaloylthioglycoside **12** was synthesized starting from the thioglycoside[22] **13** which after deacetylation, was treated in a modified procedure with benzaldehyde dimethylacetal to give **14**. After introduction of a benzyl protective group at OH-3, the resulting compound **15** was subjected to the regioselective opening of the benzylidene acetal ring[21] to give the selectively deblocked derivative **12**.

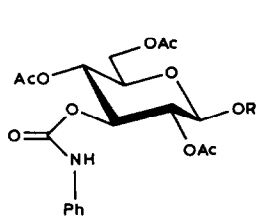


13 R^1 = R^2 = R^3 = Ac

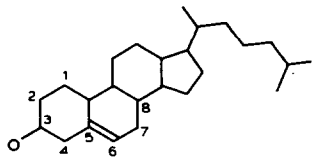
14 R^1 = H ; R^2, R^3 = PhCH

15 R^1 = Bzl ; R^2, R^3 = PhCH

Variations of the conditions of the glycosylation procedure revealed that cholesterol (**7**) and the 3-*O*-carbamoylglucosyl bromide **6**, in the presence of silver carbonate in refluxing benzene[23], gave several side products and the desired β-D-glucoside **16** in only a low yield. The application of silver 4-hydroxyvalerate in diethyl ether[24] as the activating reagent in this reaction afforded **16** in a satisfactory yield. However, under identical conditions, menthol (**8**) as the glycosyl acceptor gave almost exclusively the corresponding orthoester. Its β-D-glucoside **17** was accessible in moderate yield by treatment of the 1-*O*-acetyl derivative **5** with **8** in the presence of a catalytic amount of trimethylsilyl triflate[25].

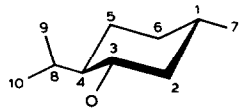


16 OR =



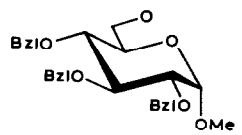
16 R = cholesteryl
17 R = menthyl

17 OR =

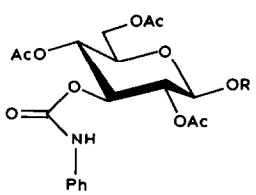


In view of the unsatisfying results of the various reaction conditions, and our major interest in the synthesis of the β-D-mannoside of the core region **1**, the optimization of the glycosylation conditions with 3-*O*-carbamoyl-D-glucosyl donors was carried out on the 2-amino-2-deoxy-D-glucose derivative **11** as the glycosyl acceptor. Neither the 1-*O*-acetyl derivative **5** in the presence of trimethylsilyl triflate nor the the corresponding 1-*O*-trichloroacetimidate[26] in the presence of boron trifluoride etherate or 4-toluenesulfonic acid, or the corresponding *S*-phenyl thioglycoside in the presence of electrophilic activating agents[27] reacted with **11** to give the desired β-glycosidically linked disaccharide. The major products of the reactions were the orthoester and compounds formed by its hydrolysis. These, as well as the aforementioned results, suggested that the *N*-phenylcarbamoyl group acts as an intramolecular weak base in the glycosylation processes with different donors and, thus, favors the formation of orthoesters. As a consequence, the glycosylation of the monosaccharide acceptors **9–12** with the *N*-phenylcarbamoylglycosyl bromide **6** was performed in the presence of silver triflate in dichloromethane[15] at −40 to −10° without addition of any external base.

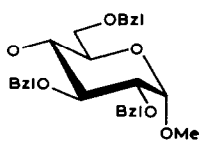
18 OR =



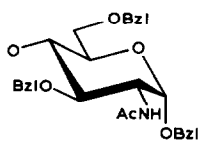
6 + 9-11 ⟶



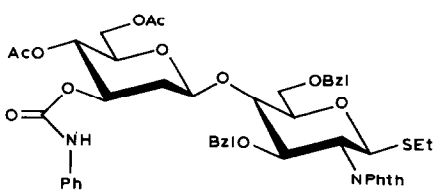
19 OR =



20 OR =



6 + 12 ⟶



21

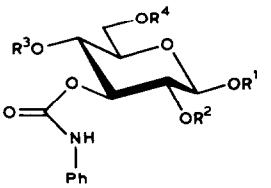
The disaccharide synthesis was carried out with two equivalents of silver triflate in the presence of molecular sieves and after addition of glucosyl bromide **6** (1.5 equiv.) at −40°, the reaction mixture was allowed to warm up to −10°. The (1→6)- and (1→4)-linked glucosyl glucosides **18** and **19** were obtained in a yield of 70%. The reaction with the 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-D-glucose derivative **11**, known as an acceptor of low reactivity[6], required a prolonged reaction time but afforded the disaccharide **20** in excellent yield. The conditions for the glycosylation of the *N*-phthaloyl thioglycoside **12** to give an intermediate in the synthesis of the "core region" were optimized. The condensation of **12** and donor **6** was performed at a reaction temperature < −20°, otherwise the thioglycoside **12** would have been attacked by the silver reagent. Thus, the desired thioglycoside **21** was formed in almost quantitative yield.

Conversion of β-D-*glucosides to* β-D-*mannosides.* — For the inversion of the configuration at C-2 to give the corresponding *β*-D-mannosides, the *β*-D-*gluco* epimers **16**–**21** were deacetylated with potassium carbonate–methanol, which kept the urethane structure intact. The resulting triol derivatives **22**, **23**, **28**, **31**, **34**, and **36** were treated with benzaldehyde dimethylacetal to give the corresponding 4,6-*O*-benzylidene derivatives **24**, **25**, **29**, **32**, **35**, and **37**. Interestingly, the benzylidenation only proceeded efficiently if the catalyzing tetrafluoroboric acid (54% in diethylether) was applied in excess (~ 2 equivs.), thus supporting the hypothesis that the urethane residue acts as an internal base. The benzylidene derivative **35** of the 2-acetamido-2-deoxy-D-glucose derivative **34** surprisingly showed an enhanced sensitivity towards acids and easily decomposed during workup. Therefore, the analogous 4-nitrobenzylidene acetal[28] **39**, more resistant to acidic conditions, was synthesized from **34**.

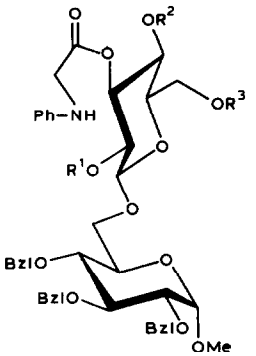
In order to perform the epimerization at C-2 of the *β*-D-glucoside precursors, the free OH-2 of the benzylidene derivatives **24**, **25**, **29**, **32**, and **37** was esterified with a triflate group. It should be noted that neither the benzylidene derivative **35** nor the 4-nitrobenzylidene derivative **39** of 2-acetamido-2-deoxy-D-glucose could be converted to a corresponding triflate pure enough for further application. Besides other side-reactions, an involvement of the acetamido group is highly probable. As has been demonstrated for the menthyl glucoside, triflate **27** could be isolated. However, in order to achieve epimerization at C-2, the isolation of these activated compounds **26**, **27**, **30**, **33**, and **38** is unnecessary. Instead, the inversion of configuration at C-2 proceeded after evaporation of the solvent and heating of the crude triflates in *N*,*N*-dimethylformamide–pyridine at 70°.

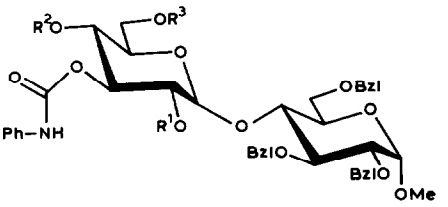
The intramolecular SN2-type reactions were complete after 1–2 h and yielded the 2,3-*O*-carbonyl-*β*-D-mannosides **40**–**44** without the formation of undesired stereoisomers. T.l.c. revealed that the *N*-phenyliminocarbonates corresponding to **40**–**44** were intermediates. However, they were hydrolyzed, at least during the workup. The iminocarbonate group of the 2-deoxy-2-phthalimido-4-*O*-*β*-D-mannopyranosyl-*β*-D-glucopyranoside derivative **45** was more stable. In this case, the intermediate could be separated from **44** and characterized. It was hydrolyzed by dilute acetic acid to give quantitatively the carbonate **44**. When the hydrolysis was carried out directly on the

mixture of **44** and **45**, the desired 2,3-carbonate **44** was isolated as the single product of the epimerization procedure in a yield of 96%.



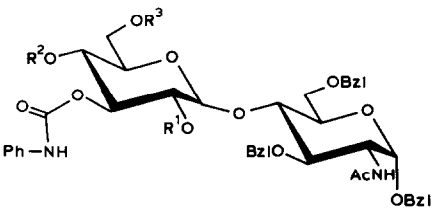
22 R^1 = cholesteryl; $R^2 = R^3 = R^4 = H$
23 R^1 = menthyl; $R^2 = R^3 = R^4 = H$
24 R^1 = cholesterol; $R^2 = H$; R^3, R^4 = CH–Ph
25 R^1 = menthyl; $R^2 = H$; $R^3 = R^4$ = CH–Ph
26 R^1 = cholesterol; $R^2 = SO_2F_3$; $R^3 = R^4$ = CH–Ph
27 R^1 = menthyl; $R^2 = SO_2F_3$; $R^3 = R^4$ = CH–Ph

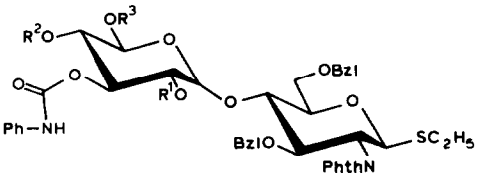




31 $R^1 = R^2 = R^3 = H$
32 $R^1 = H$; R^2, R^3 = CH–Ph
33 $R^1 = SO_2F_3$; R^2, R^3 = CH–Ph

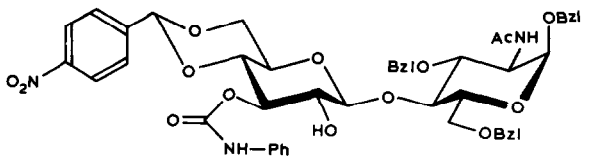
28 $R^1 = R^2 = R^3 = H$
29 $R^1 = H$; R^2, R^3 = CH–Ph
30 $R^1 = SO_2F_3$; R^2, R^3 = CH–Ph





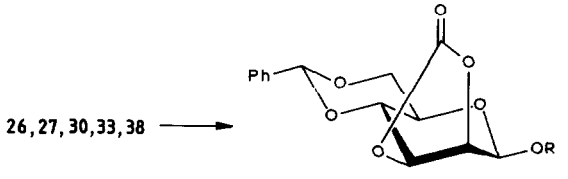
34 $R^1 = R^2 = R^3 = H$
35 $R^1 = H$; R^2, R^3 = CH–Ph

36 $R^1 = R^2 = R^3 = H$
37 $R^1 = H$; R^2, R^3 = CH–Ph
38 $R^1 = SO_2CF_3$; R^2, R^3 = CH–Ph



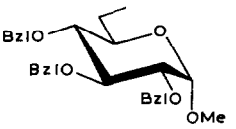
39

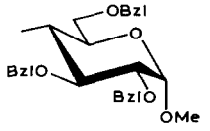
The structure of the β-D-mannosides **40–44** was confirmed by ^{1}H-n.m.r. spectroscopy. At first sight, the data obtained seemed to be incompatible with the β-D-mannoside configuration. In comparison to other β-D-mannosides, the signals of the anomeric protons are shifted downfield to $\delta \sim 5$ and showed an unusually large coupling constant of $J_{1,2} \sim 3$ Hz. The coupling between H-2 and H-3 is also relatively large ($J_{2,3} \sim 8$ Hz), as

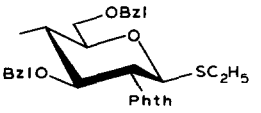


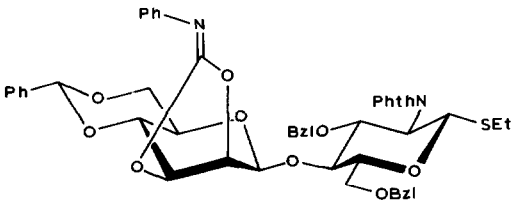
40 R = cholesteryl

41 R = menthyl

42 R = 

43 R = 

44 R = 



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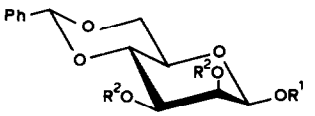
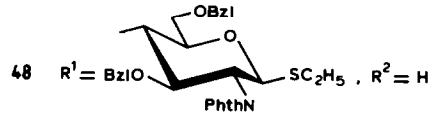


46 R^1= cholesteryl , R^2= H

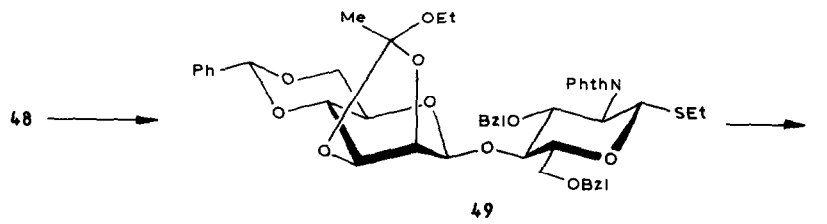
47 R^1= menthyl , R^2= Ac



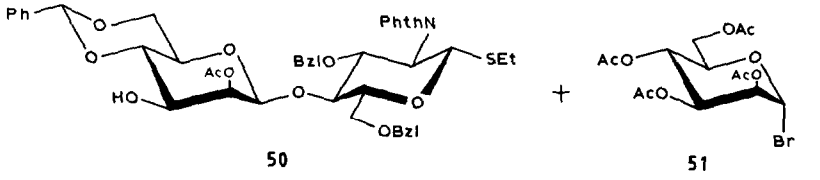
48 R^1= BzlO , SC_2H_5 , R^2= H

well as the anomeric heteronuclear coupling showing a value ($J_{C\text{-}1,H\text{-}1}$ ~ 171 Hz) which commonly is found for α-D-mannosides. These anomalies are due to the 2,3-carbonate group which obviously forces the D-mannose ring to adopt a $^{O}H_5$ (D) conformation[2]. To resolve these discrepancies, the carbonate group of cholesteryl (**40**) and menthyl (**41**) β-D-mannoside and of the disaccharide **44** was removed to give the corresponding diols **46** and **48** or, after acetylation, the diacetate **48**; the ^{1}H-n.m.r. data of which, *i.e.*, $J_{1,2} < 1$ Hz, $J_{2,3}$ ~ 3 Hz, $J_{C\text{-}1,H\text{-}1}$ ~ 157 Hz, clearly confirmed the β-D-mannoside configuration.

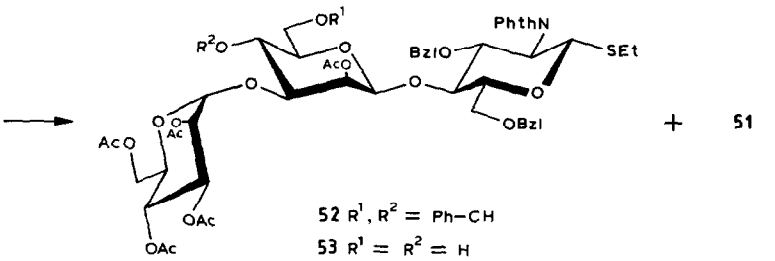
The 2′,3′-carbonate protective group of **44** and its easy selective removal to give the diol **48** allowed a convenient synthesis of the branching link of the oligosaccharide side-chains of *N*-glycoproteins. Regioselective acetylation of axial OH-2′ of **48** was achieved *via* formation of the 2′,3′-orthoester **49**, and regioselective opening of the orthoacetate ring[29] gave the disaccharide derivative **50** having selectively unblocked OH-3′. This was condensed, as the glycosyl acceptor, with 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (**51**) to furnish the protected trisaccharide derivative **52** in a yield of 74%. Neither the benzylidene acetal group nor the thioglycoside structure was affected. The structure of **52** was confirmed by 2D ^{1}H-n.m.r. spectroscopy. The α-D-mannosyl configuration was ascertained by the doublet signal for its anomeric proton at δ ~ 5.16 with a coupling constant of $J_{1'',2''}$ ~ 1.7 Hz. After hydrolysis of the benzylidene acetal group of **52** to give the diol **53** in high yield, condensation with **51** furnished the branched tetrasaccharide **54** in a yield of 74%. Its structure was confirmed by 2D ^{1}H-n.m.r. spectroscopy and by derivatization of free OH-4″ with trichloroacetyl isocyanate[30]. Tetrasaccharide **54** represents the branching link of the antennary oligosaccharide side-chains of typical *N*-glycoproteins and its synthesis illustrates the efficiency of the β-D-mannoside synthesis just described.



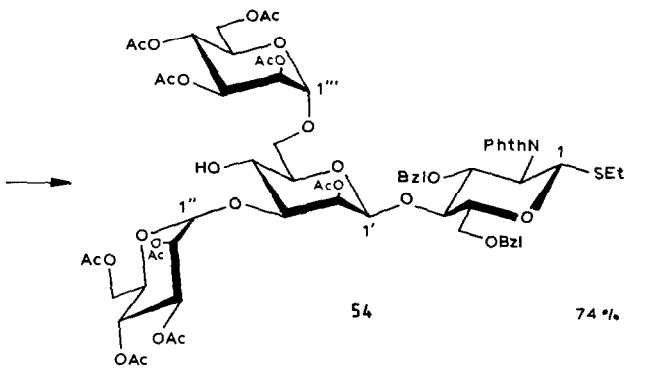
49



50 51



52 R^1, R^2 = Ph–CH
53 R^1 = R^2 = H



54 74 %

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi melting-point apparatus (Tottoli) and are uncorrected. Optical rotations were measured with a Perkin–Elmer-241 polarimeter. I.r. spectra were recorded with a Beckmann-IR spec-

trometer 4220. ^{1}H-N.m.r. spectra at 200 MHz and 400 MHz were recorded with a Bruker WT 200 and a Bruker AM 400 spectrometer, respectively. The values of δ are expressed relative to the signal of Me_4Si for solutions in $CDCl_3$, unless otherwise noted. All reactions were monitored by t.l.c. in Silica gel-60 F_{254} (Merck), with detection by u.v. fluorescence or spraying with a 1:1 mixture (v/v) of 2M H_2SO_4 and a 0.2% solution of resorcinol monomethyl ether in ethanol. Flash chromatography was performed in columns of Silica gel-60 (Merck, 0.04–0.06 mm). Evaporation of solvents was done at $<40°$ (bath) under vacuum. Glycosylation reactions were performed in freshly dried solvents under an Ar atmosphere; the solvents were dried as described by Perrin and Armarego[31].

1,2-5,6-Di-O-isopropylidene-3-O-(N-phenylcarbamoyl)-α-D-glucofuranose (**2**). — To a solution of 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose (100 g, 0.38 mol) and 4-dimethylaminopyridine (1 g, 8 mmol) in dry toluene (350 mL) was added phenyl isocyanate (42 mL, 0.38 mol), and the mixture was heated for 3 h at 100°. After cooling and diluting with toluene, the solution was extracted with 2M HCL, washed with water, dried ($MgSO_4$), and evaporated to yield **2** (134 g, 92%), $[\alpha]_D^{23}$ −31° *c* 1.0, chloroform) {lit. $^{18}[\alpha]_D$ −33° (*c* 1.1, chloroform)}; R_F 0.34 (19:1 chloroform–acetone).

3-O-(N-Phenylcarbamoyl)-D-glucopyranose (**4**). — A solution of **3** (0.315 mol) in 1,4-dioxane (700 mL) and 0.05M H_2SO_4 (1000 mL) was heated at 100° for 5 h, when t.l.c. showed complete conversion of **3**. The cooled mixture was made neutral with K_2CO_3, filtered, and evaporated to dryness. The resulting residue was taken up in warm methanol, the solution filtered from undissolved material and concentrated to give crystalline **4** (82 g, 87%), which was pure enough for further usage. For characterization, a small quantity was recrystallized from a large volume of ethyl acetate to yield pure **4**, m.p. 153°, $[\alpha]_D^{23}$ +58.5° (*c* 1.0, methanol), R_F 0.75 (methanol).

Anal. Calc. for $C_{13}H_{17}NO_7$: C, 52.17; H, 5.72; N, 4.68. Found: C, 52.02; H, 5.84; N, 4.86.

1,2,4,6-Tetra-O-acetyl-3-O-(N-phenylcarbamoyl)-β-D-glucopyranose (**5**). — To a cooled solution (−15°) of **4** (34 g, 0,11 mol) in pyridine (125 mL) and 4-dimethylaminopyridine (1.2 g) was added dropwise acetic anhydride (85 mL) with stirring. After completion of the addition, the mixture was stirred for 5 h at room temperature. Then the bulk of solvent was evaporated *in vacuo* and the resulting oily residue was dissolved in chloroform (400 mL) and washed with 2M HCl, aq. $NaHCO_3$, and water. Concentration of the dried solution afforded analytically pure **5** (49 g, 93%), m.p. 133°, $[\alpha]_D^{23}$ +20° (*c* 1.0, dichloromethane), R_F 0.78 (1:1, chloroform–acetone); ^{1}H-n.m.r.: δ 7.45–7.00 (m, 5 H, arom.), 6.96 (s, 1 H, urethane-NH), 5.72 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 5.31–5.15 (m, 3 H, H-2,3,4), 4.28 (dd, 1 H, J_{gem} 11.5, J_{vic} 4.5 Hz, H-6a), 4.10 (dd, 1 H, J_{vic} 2.5, J_{gem} 11.5 Hz, H-6b), 3.85 (m, 1 H, H-5), and 2.10–2.00 (4s, 12 H, OAc).

Anal. Calc. for $C_{21}H_{25}NO_{11}$: C, 53.96; H, 5.39; N, 2.99. Found: C, 54.12; H, 5.46; N, 2.81.

2,4,6-Tri-O-acetyl-3-O-(N-phenylcarbamoyl)-α-D-glucopyranosyl bromide (**6**). — To a solution of **5** (28 g, 0.06 mol) in dry chloroform (90 mL) was added dropwise a solution of 33% HBr–AcOH (32 mL) at 0°. After being stirred for 5.5 h at room

temperature, the mixture was diluted with chloroform and washed successively with water, aq. $NaHCO_3$, and water. After drying ($MgSO_4$), the solvent was evaporated to 2/3 of the starting volume. Addition of light petroleum yielded **6** as colorless needles in analytically pure form (24 g, 82%), m.p. 151°, $[\alpha]_D^{23}$ + 145° (*c* 1, dichloromethane); R_F 0.7 (3:2 light petroleum–ethyl acetate); 1H-n.m.r.: δ 7.36–7.08 (m, 5 H, arom.), 6.80 (s, 1 H, urethane-NH), 6.58 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.54 (dd, 1 H, $J_{2,3} = J_{3,4}$ 10.0 Hz, H-3), 5.19 (m, 1 H, H-4), 4.87 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 10.0 Hz, H-2), 4.32 (m, 2 H, H-5,6a), 4.10 (m, 1 H, H-6b), and 2.08–2.02 (3 s, 9 H, OAc).

Anal. Calc. for $C_{19}H_{22}BrNO_9$: C, 46.73; H, 4.54; N, 2.87. Found: C, 46.71; H, 4.68; N, 2.85.

Ethyl 4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**14**). — To a solution of **13**[22] (30 g, 62.6 mmol) in dichloromethane (90 mL) and methanol (60 mL) was added a 0.3M solution of sodium methoxide in methanol (30 mL), and the mixture was stirred at room temperature until t.l.c. (3:1 toluene–methanol) showed the conversion of the starting material (R_F 0.33; 1.5–2.5 h). After neutralization with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtration and evaporation of the solvent, toluene was distilled three times from the residue. This was taken up in *N,N*-dimethylformamide (200 mL) and treated with benzaldehyde dimethylacetal (16 mL, 107 mmol) and etheral HBF_4 (8.5 mL, 54%) for 4 h at room temperature. The mixture was made neutral with triethylamine, diluted with toluene, and washed with aq. $KHCO_3$, 2M HCl, aq. $KHCO_3$ again, and water. The solvent was removed *in vacuo* and the remaining sirup crystallized from ethyl acetate–light petroleum to give pure **14** (23.9 g, 87%), m.p. 168° (lit.[22] m.p. 168°), $[\alpha]_D^{23}$ − 8.7° (*c* 1.0, dichloromethane) {lit.[22] $[\alpha]_D$ − 9° (*c* 0.9, dichloromethane)], R_F 0.62 (3:1 toluene–acetone).

Ethyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**15**). — Sodium hydride (2 g, 66.7 mmol, 80% suspension in mineral oil) was added to a solution of **14** (26.6 g, 60.3 mmol) in *N,N*-dimethylformamide (320 mL) and the mixture was stirred at room temperature for 45 min. After the addition of benzyl bromide (8.6 mL, 72.4 mmol) and heating for 4 h at 50°, the solution was concentrated *in vacuo* and the oily residue taken up in ether. After filtration, the organic layer was washed with water, dried, and concentrated to dryness. Crude, sirupy **15** was purified by flash chromatography (40:1 dichloromethane–ethyl acetate) to give crystalline **15** (25.7 g, 80%), m.p. 58°, $[\alpha]_D^{23}$ + 44° (*c* 1.4, dichloromethane, R_F 0.51 (2:1 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.83–6.84 (m, 14 H, arom.), 5.62 (s, 1 H, PhCH), 5.32 (d, 1 H, $J_{1,2}$ 10.5 Hz, H-1), 4.78 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.49 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.47–4.38 (m, 2 H, H-4,3), 4.29 (dd, 1 H, $J_{1,2} = J_{2,3}$ 10.5 Hz, H-2), 3.85–3.79 (m, 2 H, H-6a,6b), 3.69 (m_c, 1 H, H-5), 2.75–2.58 (m, 2 H, SCH_2), and 1.15 (t, 1 H, *J* 7.4 Hz, CH_3).

Anal. Calc. for $C_{30}H_{29}NO_6S$: C, 67.78; H, 5.50; N, 2.64. Found: C, 67.56; H, 5.65; N, 2.64.

Ethyl 3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**12**). — A solution of **15** (24.3 g, 45.7 mmol) in oxolane (600 mL) containing molecular sieves 3A (15 g) and $NaBH_3CN$ (26 g) was cooled to 0° and acidified with a solution of HCl in ether. When t.l.c. (2:1 light petroleum–ethyl acetate) showed the end of the reaction, the

mixture was diluted with dichloromethane (800 mL), stirred for 15 min at room temperature after the addition of water (20 mL), and filtered through a pad of Celite. The organic layer was extracted with aqueous sodium hydrogencarbonate, then with water, dried and concentrated. The oily residue was purified by flash chromatography (2:1 light petroleum–ethyl acetate) to give crystalline **12** (21.2 g, 86%), m.p. 102°, $[\alpha]_D^{23}$ + 33° (*c* 0.9, dichloromethane), R_F 0.46 (2:1 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.80–7.65 (m, 4 H, Phth-H), 7.66–6.92 (m, 10 H, arom.), 5.26 (d, 1 H, $J_{1,2}$ 9.7 Hz, H-1), 4.74 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.62 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.57 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.53 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.28–4.21 (m, 2 H, H-2,3), 3.85–3.74 (m, 3 H, H-6a,6b,4), 3.67 (m_c, 1 H, H-5), 3.04 (s, 1 H, OH-4), 2.67–2.54 (m, 2 H, SCH_2), and 1.14 (t, 1 H, *J* 7.4 Hz, CH_3).

Anal. Calc. for $C_{30}H_{31}NO_6S$: C, 67.52; H, 5.86; N, 2.63. Found: C, 67.73; H, 5.67; N, 2.60.

*Cholesteryl 2,4,6-tri-*O*-acetyl-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranoside* (**16**). — A mixture of silver 4-hydroxy valerate (8.4 g, 37.3 mmol), cholesterol (5.3 g, 13.7 mmol), and **6** (16.5 g, 33.8 mmol) in diethyl ether was stirred for 6 h at room temperature and then it was filtered, and the filtrate was concentrated to dryness. Flash chromatography (2:1 light petroleum–ethyl acetate) of the residue gave crystalline **16** (3.7 g, 34%), m.p. 157–158°, $[\alpha]_D^{23}$ − 67.5° (*c* 1.0, dichloromethane), R_F 0.65 (1:1 light petroleum–ethyl acetate); ^{1}H-n.m.r. d: δ 7.40–7.05 (m, 5 H, arom.), 6.82 (s, 1 H, urethane-NH), 5.05–5.18 (m, 2 H, H-4,3), 4.95 (dd, 1 H, $J_{1,2} = J_{2,3}$ 8.0 Hz, H-2), 4.62 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.25 (dd, 1 H, J_{vic} 5.0, J_{gem} 12.5 Hz, H-6a), 4.10 (m, 1 H, H-6b), 3.7 (m, 1 H, H-5), and 2.10–1.90 (3 s, 9 H, 3 OAc).

Anal. Calc. for $C_{46}H_{67}NO_{10}$: C, 69.58; H, 8.50; N, 1.76. Found: C, 69.52; H, 8.67; N, 1.68.

*(−)-Menthyl 2,4,6-tri-*O*-acetyl-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranoside* (**17**). — To a solution of menthol (**8**; 4.4 g, 28.2 mmol) and **5** (5 g, 10.7 mmol) in dichloromethane (35 mL) was added trimethylsilyl triflate (0.4 mL, 2.2 mmol). After stirring for 6 days at room temperature, the reaction was quenched by addition of triethylamine and the solution was evaporated to dryness. Flash chromatography of the residue gave crystalline **17** (2.4 g, 40%), m.p. 138–140°, $[\alpha]_D^{23}$ − 35.5° (*c* 1.0, chloroform), R_F 0.42 (4:1 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.34–7.03 (m, 5 H, arom.), 6.77 (s, 1 H, urethane-NH), 5.15 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3), 5.05 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 4.95 (dd, 1 H, $J_{2,3}$ 9.5, $J_{1,2}$ 8.0 Hz, H-2), 4.56 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.19 (dd, 1 H, J_{gem} 12.1, J_{vic} 5.6 Hz, H-6a), 4.10 (dd, 1 H, J_{gem} 12.1, J_{vic} 2.7 Hz, H-6b), 3.67 (ddd, 1 H, $J_{5,6a}$ 5.6, $J_{5,6b}$ 2.7, $J_{4,5}$ 9.5 Hz, H-5), and 2.04, 2.01, 1.99 (3 s, 9 H, 3 OAc).

Anal. Calc. for $C_{29}H_{41}NO_{10}$: C, 61.79; H, 7.33; N, 2.48. Found: C, 61.51; H, 7.10; N, 2.25.

*Methyl 6-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranosyl]-2,3,4-tri-*O*-benzyl-α-*D*-glucopyranoside* (**18**). — A solution of **9**[20] (2 g, 4.3 mmol) and silver triflate (2.2 g, 8.6 mmol) in dichloromethane (35 mL) containing molecular sieves 4A (2 g) was stirred at room temperature for 30 min. After cooling at −40°, bromide **6** (3 g, 6.8 mmol), dissolved in dichloromethane (20 mL) was added dropwise,

and then the temperature was allowed to rise but not exceeding −10°. After 45 min, t.l.c. (3:2 light petroleum–ethyl acetate) indicated the end of the reaction. For workup, the mixture was made neutral with triethylamine, diluted with dichloromethane, and filtered through a pad of Celite. The filtrate was washed with water, dil. HCl, aq. $NaHCO_3$, and water, dried, and concentrated to dryness. The resulting residue was purified by flash chromatography (3:2 light petroleum–ethyl acetate) to give amorphous **18** (2.6 g, 70%), $[\alpha]_D^{23}$ +55.5° (*c* 0.44, chloroform), R_F 0.40 (3:2 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.36–6.94 (m, 20 H, arom.), 6.81 (s, 1 H, urethane-NH), 5.14–5.06 (m, 3 H, H-2',3',4'), 4.97 (d, 1 H, J_{gem} 11.0 Hz, OCH_2Ph), 4.85 (d, 1 H, J_{gem} 10.8 Hz, OCH_2Ph), 4.78 (d, 1 H, J_{gem} 10.8 Hz, OCH_2Ph), 4.77 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.64 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.58 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.55 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1'), 4.53 (d, 1 H, J_{gem} 11.0 Hz, OCH_2Ph), 4.25 (dd, 1 H, J_{gem} 12.3, J_{vic} 4.7 Hz, H-6a'), 4.13 (dd, 1 H, J_{gem} 12.3, J_{vic} 2.4 Hz, H-6b'), 4.07 (dd, 1 H, J_{gem} 10.6, J_{vic} 1.4 Hz, H-6a), 3.97 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.3 Hz, H-3), 3.76 (m_c, 1 H, H-5), 3.72–3.66 (m, 2 H, H-5',6b), 3.51 (dd, 1 H, $J_{2,3}$ 9.3, $J_{1,2}$ 3.6 Hz, H-2), 3.43 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.3 Hz, H-4), 3.35 (s, 3 H, OCH_3), and 2.04, 2.00, 1.94 (3 s, 9 H, 3 OAc).

Anal. Calc. for $C_{47}H_{53}NO_{15}$: C, 64.74; H, 6.13; N, 1.61. Found: C, 65.00; H, 6.05; N, 1.45.

Methyl O-*[2,4,6,tri*-O-*acetyl-3*-O-*(*N-*phenylcarbamoyl)-β-*D-*glucopyranosyl]-(1→4)-2,3,6-tri*-O-*benzyl-α-*D-*glucopyranoside* (**19**). – Glycosylation of **10**[21] (2 g, 4.3 mmol) with **6** (3.3 g, 6.8 mmol), as described for the synthesis of **18**, yielded after flash chromatography (2:1 light petroleum–ethyl acetate) crystalline **19** (2.5 g, 68%), m.p. 167°, $[\alpha]_D^{23}$ +14.8° (*c* 1.0, chloroform), R_F 0.38 (3:2 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.42–7.04 (m, 20 H, arom.), 6.70 (s, 1 H, urethane-NH), 5.06–4.88 (m, 4 H, H-4',3',2', OCH_2Ph), 4.78–4.70 (m, 3 H, 3 OCH_2Ph), 4.57 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.56 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.53 (d, 1 H, $J_{1',2'}$ 7.2 Hz, H-1'), 4.43 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.14 (dd, 1 H, J_{gm} 12.4, J_{ic} 4.0 Hz, H-6a'), 3.89–3.81 (m, 3 H, H-6b',3,4), 3.76 (dd, 1 H, J_{gem} 10.7, J_{vic} 3.0 Hz, H-6a), 3.61–3.58 (m, 2 H, H-6b,5), 3.46 (dd, 1 H, $J_{2,3}$ 9.2, $J_{1,2}$ 3.6 Hz, H-2), 3.35 (s, 3 H, OCH_3), 3.29 (ddd, 1 H, $J_{5',6b'}$ 2.4, $J_{4',5'}$ 6.2, $J_{5',6a'}$ 4.0 Hz, H-5'), and 1.98, 1.94, 1.93 (3 s, 9 H, 3 OAc).

Anal. Calc. for $C_{47}H_{53}NO_{15}$: C, 64.74; H, 6.13; N, 1.61. Found: C, 64.96; H, 5.94; N, 1.51.

Benzyl O-*[2,4,6-tri*-O-*acetyl-3*-O-*(*N-*phenylcarbamoyl)-β-*D-*glucopyranosyl]-(1→4)-2-acetamido-3,6-di*-O-*benzyl-2-deoxy-α-*D-*glucopyranoside* (**20**). — A mixture of **11** (5 g, 10.4 mmol) and silver triflate (5 g, 19.5 mmol) in dichloromethane (80 mL) containing powdered molecular sieves 4A (6 g) was stirred for 1 h at room temperature and cooled to −40°. A solution of bromide **6** (7.6 g, 15.6 mmol) in dichloromethane (30 mL) was added dropwise and the temperature was allowed to rise to −10°. When t.l.c. indicated completion of the reaction (4–5 h), the mixture was made neutral with triethylamine, diluted with dichloromethane, and filtered through a pad of Celite. The filtrate was washed with water, 2M HCl, aq. $NaHCO_3$, and water, dried, and evaporated *in vacuo*. Flash chromatography of the residue (2:1 ethyl acetate–light petroleum) gave crystalline **20** (8.2 g, 88%), m.p. 206°, $[\alpha]_D^{23}$ +48° (*c* 1.0, chloroform), R_F 0.23 (2:3 light

petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.44–7.04 (m, 20 H, arom.), 6.74 (s, 1 H, urethane-NH), 5.15 (d, 1 H, $J_{NH,2}$ 8.9 Hz, NHAc), 5.05–4.94 (m, 3 H, H-4′,2′,3′), 4.91 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.86 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.77 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.63 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.61–4.43 (m, 4 H, 3 OCH_2Ph, H-1′), 4.20–4.13 (m, 2 H, H-6a′,2), 4.02 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 3.91 (dd, 1 H, J_{gem} 12.4, J_{vic} 2.2 Hz, H-6b′), 3.74 (dd, 1 H, J_{gem} 10.9, J_{vic} 3.0 Hz, H-6a), 3.63–3.54 (m, 3 H, H-3,6b,5), 3.35 (ddd, 1 H, $J_{4',5'}$ 10.0, $J_{5',6a'}$ 4.4, $J_{5',6b'}$ 12.4 Hz, H-5′), 1.98, 1.95, 1.91 (3 s, 9 H, 3 OAc), and 1.71 (s, 3 H, NAc).

Anal. Calc. for $C_{48}H_{54}N_2O_{15}$: C, 64.13; H, 6.05; N, 3.12. Found: C, 63.98; H, 6.00; N, 3.38.

Ethyl O-[2,4,6-tri-O-acetyl-3-O-(N-phenylcarbamoyl)-β-D-glucopyranosyl]-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**21**). — A solution of **12** (5.9 g, 11 mmol) and bromide **6** (6.2 g, 12.7 mmol) in dichloromethane (120 mL) was stirred with powdered molecular sieves 4A (7 g) for 1 h at room temperature. The mixture was cooled to −45° and a solution of silver triflate (6.4 g, 25 mmol) in toluene (90 mL) was rapidly added dropwise. The temperature was maintained until t.l.c. (3:2 light petroleum–ethyl acetate) showed completion of the reaction (~ 45 min). After neutralization with triethylamine, the mixture was diluted with dichloromethane and immediately washed with ice-cold aq. $Na_2S_2O_3$ and filtered through a pad of Celite. The filtrate was successively extracted with 2M HCl, aq. $NaHCO_3$, and water. The residue obtained after evaporation of the dried solvent gave quantitatively crude **21** in a form almost pure enough for further usage. It may be purified by crystallization from dichloromethane–hexane or flash chromatography (1:2 ethyl acetate–chloroform) to give pure **21** (9.8 g, 94%), m.p. 103–105°, $[\alpha]_D^{23}$ +2.3° (*c* 1.0, dichloromethane), R_F 0.35 (3:2 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.74–7.56 (m, 4 H, Phth-H), 7.41–6.77 (m, 15 H, arom.), 6.71 (s, 1 H, urethane-NH), 5.17 (d, 1 H, $J_{1,2}$ 10.0 Hz, H-1), 5.05–4.99 (m, 3 H, H-2′,3′,4′), 4.78 (d, 1 H, J_{gem} 12.4 Hz, OCH_2Ph), 4.76 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.69 (d, 1 H, $J_{1',2'}$ 7.4 Hz, H-1′), 4.52 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.38 (d, 1 H, J_{gem} 12.4 Hz, OCH_2Ph), 4.27–4.16 (m, 3 H, H-2,3,6a′), 4.07 (m_c, 1 H, H-4), 3.96 (dd, 1 H, J_{gem} 12.3, J_{vic} 2.3 Hz, H-6b′), 3.8 (m, 2 H, H-6a,6b), 3.52 (m_c, 1 H, H-5), 3.43 (m_c, 1 H, H-5′), 2.67–2.53 (m, 2 H, SCH_2), 2.00, 1.97, 1.93 (3 s, 9 H, 3 OAc), and 1.14 (t, 3 H, *J* 7.4 Hz, CH_3).

Anal. Calc. for $C_{49}H_{52}N_2O_{15}S$: C, 62.54; H, 5.57; N, 2.98. Found: C, 62.63; H, 5.45; N, 2.74.

Cholesteryl 4,6-O-benzylidene-3-O-(N-phenylcarbamoyl)-β-D-glucopyranoside (**24**). — To a solution of **16** (3.81 g, 4.8 mmol) in methanol (130 mL) was added K_2CO_3 (0.60 g), and the mixture was stirred at room temperature for 4.5 h. The filtered solution was made neutral with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtered, and evaporated to dryness. The residue of crude **22** was dried, taken up in *N,N*-dimethylformamide, and treated with benzaldehyde dimethylacetal (0.72 mL) and 54% etheral HBF_4 (1.2 mL) for 27 h at room temperature. The solution was made neutral with triethylamine and evaporated to dryness. The residue was taken up in chloroform, the solution filtered through a short column of silica gel and purified by

flash chromatography (5:1 toluene–acetone) (after removal of the chloroform) to give crystalline **24** (2.24 g, 62%), m.p. 208°, $[\alpha]_D^{23}$ −26° (*c* 1.0, dichloromethane), R_F 0.35 (3:1 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.50–7.03 (m, 10 H, arom.), 6.73 (s, 1 H, urethane-NH), 5.49 (s, 1 H, PhCH), 5.37 (m, 1 H, H-6 of cholesterol), 5.13 (dd, 1 H, $J_{3,4} = J_{2,3}$ 9.4 Hz, H-3), 4.59 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.33 (dd, 1 H, J_{vic} 5.0, J_{gem} 10.7 Hz, H-6a), 3.78 (dd, 1 H, $J_{gem} = J_{vic}$ 10.7 Hz, H-6b), 3.67 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.4 Hz, H-4), 3.62–3.50 (m, 3 H, H-5,2,3 of cholesterol), and 2.97 (s, 1 H, OH).

Anal. Calc. for $C_{47}H_{65}NO_7$: C, 74.67; H, 8.67; N, 1.85. Found: C, 74.84; H, 8.61; N, 1.84.

*(−)-Menthyl 4,6-*O*-benzylidene-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranoside* (**25**). — A solution of **17** (1.8 g, 3.2 mmol) in methanol was stirred with K_2CO_3 (0.5 g) for 5.5 h at room temperature. The filtered solution was made neutral with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtered, and concentrated to dryness. The residue was dried and treated with benzaldehyde dimethylacetal (0.5 mL) and 54% etheral HBF_4 (0.9 mL) in *N,N*-dimethylformamide at room temperature for 2 h. Workup was done as described for compound **29**. The residue was purified by filtration through a short column of silica gel (eluent; 1:1 light petroleum–acetone) to give crystalline **25** (1.5 g, 90%), m.p. 84°, $[\alpha]_D^{23}$ −87.5° (*c* 1.1, chloroform), R_F 0.76 (1:1 light petroleum–acetone); ^{1}H-n.m.r.: δ 7.46–6.99 (m, 10 H, arom.), 6.82 (s, 1 H, urethane-NH), 5.49 (s, 1 H, PhCH), 5.15 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3), 4.55 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.30 (dd, 1 H, J_{gem} 10.4, J_{vic} 4.9 Hz, H-6a), 3.77 (dd, 1 H, $J_{gem} = J_{vic}$ 10.4 Hz, H-6b), 3.68 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.4 Hz, H-4), 3.58–3.45 (m, 3 H, H-2,5, H-3 of menthyl), and 2.90 (s, 1 H, OH).

Anal. Calc. for $C_{30}H_{39}NO_7$: C, 68.55; H, 7.48; N, 2.66. Found: C, 68.62; H, 7.29; N, 2.78.

Methyl O*-[4,6-*O*-benzylidene-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-*D*-glucopyranoside* (**29**). — Potassium carbonate (0.25 g, 1.8 mmol) was added to a solution of **18** (2 g, 2.3 mmol) in methanol (100 mL). After stirring for 7 h at room temperature, the base was neutralized with an excess of Amberlite IR-120 (H^+) cation-exchange resin, the suspension filtered, and the filtrate concentrated to dryness. The residue of crude **28** was dried, taken up in *N,N*-dimethylformamide (30 mL), and treated with benzaldehyde dimethylacetal (0.5 mL) and 54% etheral HBF_4 (0.85 mL). When t.l.c. (3:1 toluene–acetone) indicated the end of the reaction (~ 12 h), the solution was made neutral with triethylamine, diluted with toluene, and washed with ice-cold aq. $NaHCO_3$, 2M HCl, aq. $NaHCO_3$ again, and water. The residue obtained after evaporation of the solvent was purified by flash chromatography (3:2 light petroleum–ethyl acetate) to give **29** (1.7 g, 86%), m.p. 196°, $[\alpha]_D^{23}$ −22° (*c* 1.1, chloroform), R_F 0.47 (3:1 toluene–acetone); ^{1}H-n.m.r.: δ 7.45–7.02 (m, 25 H, arom.), 6.79 (s, 1 H, urethane-NH), 5.47 (s, 1 H, PhCH), 5.07 (dd, 1 H, $J_{2',3'} = J_{3',4'}$ 9.3 Hz, H-3'), 4.97 (d, 1 H, J_{gem} 11.0 Hz, OCH_2Ph), 4.88 (d, 1 H, J_{gem} 11.0 Hz, OCH_2Ph), 4.82 (d, 1 H, J_{gem} 11.0 Hz, OCH_2Ph), 4.77 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.67 (d, 1 H, J_{gem} 11.0 Hz, OCH_2Ph), 4.63 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.59 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.44 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1'), 4.32 (dd, 1 H, J_{gem} 10.6, J_{vic} 5.0 Hz, H-6a'), 4.11 (m_c, 1 H, H-6a), 3.99

(dd, 1 H, $J_{2,3}$ = $J_{3,4}$ 9.4 Hz, H-3), 3.80–3.73 (m, 3 H, H-6b',5,6b), 3.67–3.62 (m, 2 H, H-2,4'), 3.57 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ 9.4 Hz, H-4), 3.52 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.4 Hz, H-2), 3.45 (m_c, 1 H, H-5'), 3.40 (s, 1 H, 2'-OH), and 3.36 (s, 3 H, OCH_3).

Anal. Calc. for $C_{48}H_{51}NO_{12}$: C, 69.13; H, 6.16; N, 1.68. Found: C, 69.16; H, 5.92; N, 1.59.

Methyl O-*[4,6-*O*-benzylidene-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-*D*-glucopyranoside* (**32**). — Compound **32** was prepared as described for **29**. The benzylidenation reaction was finished after 24 h, and **32** was isolated by flash chromatography (3:2 light petroleum–ethyl acetate) as crystals (1.68 g, 86%), m.p. 138–139°, $[\alpha]_D^{23}$ +11.9° (*c* 1.0, dichloromethane), R_F 0.56 (3:1 toluene–acetone); ^{1}H-n.m.r.: δ 7.44–7.03 (m, 25 H, arom.), 6.78 (s, 1 H, urethane-NH), 5.39 (s, 1 H, PhCH), 4.89–4.82 (m, 2 H, 2 OCH_2Ph), 4.84 (dd, 1 H, $J_{2',3'}$ = $J_{3',4'}$ 9.4 Hz, H-3'), 4.75 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.67 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.61 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.57 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.47 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1'), 4.46 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.06–4.00 (m, 2 H, H-6a',6a), 3.96 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ 9.2 Hz, H-4), 3.90 (dd, 1 H, $J_{2,3}$ = $J_{3,4}$ 9.2 Hz, H-3), 3.83 (s, 1 H, OH-2'), 3.75 (m_c, 1 H, H-5), 3.66 (dd, 1 H, J_{gem} 11.1, J_{vic} 2.1 Hz, H-6b), 3.54–3.44 (m, 4 H, H-6b',2',4',2), 3.34 (s, 3 H, OCH_3), and 3.09 (m_c, 1 H, H-5').

Anal. Calc. for $C_{48}H_{51}NO_{12}$: C, 69.13; H, 6.16; N, 1.68. Found: C, 68.94; H, 5.89; N, 1.60.

*Benzyl O-[4,6-*O*-benzylidene-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranosyl]-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**35**). — A mixture of **20** (2.5 g, 2.8 mmol) and K_2CO_3 (0.5 g) in methanol (150 mL) was stirred for 6 h at room temperature. The solution was filtered, made neutral with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtered, and concentrated to dryness. The crude residue was dried and treated with benzaldehyde dimethylacetal as described above to give, after workup and flash chromatography (8:1 dichloromethane–ethyl acetate), amorphous **35** (1.2 g, 50%), $[\alpha]_D^{23}$ +28.3° (*c* 1.0, chloroform), R_F 0.36 (10:1 chloroform–acetone); ^{1}H-n.m.r. [$(CD_3)SO$]: δ 9.62 (s, 1 H, urethane-NH), 8.12 (d, 1 H, $J_{NH,2}$ 8.7 Hz, H-2), 7.45–6.94 (m, 25 H, arom.), 5.83 (d, 1 H, $J_{2',OH}$ 5.8 Hz, OH-2'), 5.57 (s, 1 H, PhCH), 4.97 (dd, 1 H, $J_{2',3'}$ = $J_{3',4'}$ 9.6 Hz, H-3'), 4.84 (d, 1 H, J_{gem} 10.6 Hz, OCH_2Ph), 4.75 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.67 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.61–4.58 (m, 4 H, 3 OCH_2Ph, H-1'), 4.47 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.02 (dd, 1 H, J_{gem} 10.2, J_{vic} 4.8 Hz, H-6a'), 3.97–3.80 (m, 2 H, H-2), 3.71 (dd, 1 H, $J_{2,3}$ 10.6, $J_{3,4}$ 8.5 Hz, H-3), 3.61 (dd, 1 H, $J_{3',4'}$ = $J_{4',5'}$ 9.6 Hz, H-4'), 3.31–3.25 (m, 2 H, H-5',2'), and 1.84 (s, 3 H, NAc).

Anal. Calc. for $C_{49}H_{52}N_2O_{12}$: C, 68.34; H, 6.09; N, 3.25. Found: C, 68.25; H, 6.01; N, 3.08.

Ethyl O-*[4,6-*O*-benzylidene-3-*O*-(*N*-phenylcarbamoyl)-β-*D*-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside* (**37**). — To a solution of **21** (10 g, 10.6 mmol) in methanol (650 mL) was added K_2CO_3 (1.65 g, 12 mmol), and the mixture was stirred for 4 h at room temperature. It was made neutral with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtered, and concentrated to dryness. The residue of **36** was dissolved in *N,N*-dimethylformamide (170 mL),

and benzaldehyde dimethylacetal (3 mL) and 54% etheral HBF_4 (3.6 mL) were added. After reaction overnight, t.l.c. (3:1 toluene–acetone) indicated complete conversion of the starting material. The mixture was made neutral with triethylamine, partitioned between toluene and ice-cold 2M aq. $KHCO_3$, and the organic layer was extracted with 2M aq. $KHCO_3$, 2M HCl, and water. The dried solvent was removed and the product isolated by flash chromatography (12:1 dichloromethane–ethyl acetate) as an amorphous powder (8.1 g, 85%), $[\alpha]_D^{23}$ + 3.0° (*c* 1.1, dichloromethane), R_F 0.56 (3:1 toluene–acetone); ^{1}H-n.m.r.: δ 7.76–7.62 (m, 4 H, Phth-H), 7.42–6.58 (m, 21 H, arom., urethane-NH), 5.40 (s, 1 H, PhCH), 5.20 (d, 1 H, $J_{1,2}$ 10.4 Hz, H-1), 4.49 (dd, 1 H, $J_{2',3'} = J_{3',4'}$ 9.4 Hz, H-3'), 4.79 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.73 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.66 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1'), 4.55 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.42 (d, 1 H, J_{gem} 12.2 Hz, OCH_2Ph), 4.39 (dd, 1 H, $J_{3,4}$ 8.6, $J_{2,3}$ 10.4 Hz, H-3), 4.26 (dd, 1 H, $J_{1,2} = J_{2,3}$ 10.4 Hz, H-2), 4.22–4.11 (m, 2 H, H-4,6a'), 4.07 (dd, 1 H, J_{gem} 11.3, J_{vic} 3.1 Hz, H-6a), 3.98 (s, 1 H, OH), 3.83 (dd, 1 H, J_{gem} 11.3, J_{vic} 1.9 Hz, H-6b), 3.66 (m_c, 1 H, H-5), 3.51–3.46 (m, 3 H, H-6b'),2',4'), 3.22 (ddd, 1 H, $J_{4',5'} = J_{5',6a'} = J_{5',6b'}$ 4.9 Hz, H-5'), 2.68–2.55 (m, 2 H, SCH_2), and 1.15 (t, 3 H, *J* 7.4 Hz, CH_3).

Anal. Calc. for $C_{50}H_{50}N_2O_{12}S$: C, 66.51; H, 5.58; N, 3.10. Found: C, 66.76; H, 5.46; N, 2.78.

Benzyl O-*[4,6*-O-*(4-nitrobenzylidene)-3*-O-*(*N-*phenylcarbamoyl)-β*-D-*glucopyranosyl]-(1→4)-2-acetamido-3,6-di*-O-*benzyl-2-deoxy-α*-D-*glucopyranoside* (**39**). — In a flask equipped with a Soxhlett apparatus containing $CaCl_2$, was heated under reflux a solution of **36** (0.31 g, 0.4 mmol) and 4-toluenesulfonic acid monohydrate (0.14 g, 0.7 mmol) in 1:1 (v/v) benzene–*N,N*-dimethylformamide (40 mL). After 15 min, 4-nitrobenzaldehyde dimethylacetal (0.15 g, 0.88 mmol) was added and heating was continued for another 3 h. The solvents were removed and the residue was taken up in dichloromethane. The solution was washed with aq. $NaHCO_3$ and water, dried, and concentrated to dryness. The residue was dissolved in methanol (30 mL) and stirred for 1.5 h at room temperature. The residue obtained after evaporation of the solvent was purified by flash chromatography (25:1 dichloromethane–ethyl acetate) to give amorphous **39** (0.29 g, 81%); ^{1}H-n.m.r. [$(CD_3)_2SO$]: δ 9.68 (s, 1 H, urethane-NH), 8.21 (d, 2 H, J_{vic} 8.9 Hz, $4NO_2$-arom., H-ortho), 8.13 (d, 1 H, $J_{2,NH}$ 8.8 Hz, NHAc), 7.61 (d, 2 H, J_{vic} 8.9 Hz, $4NO_2$-Ar-H-meta), 7.47–6.95 (m, 20 H, arom.), 5.87 (d, 1 H, $J_{2,OH}$ 5.8 Hz, OH-2'), 5.75 (s, 1 H, PhCH), 5.00 (dd, 1 H, $J_{3',4'} = J_{2',3'}$ 9.5 Hz, H-3'), 4.84 (d, 1 H, J_{gem} 10.6 Hz, OCH_2Ph), 4.76 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.68 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.61–4.54 (m, 4 H, 3 OCH_2Ph, H-1'), 4.48 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.07 (dd, 1 H, J_{gem} 10.3, J_{vic} 4.9 Hz, H-6a'), 3.94 (m_c, 2 H, H-2), 3.71 (dd, 1 H, $J_{2,3}$ 10.6, $J_{3,4}$ 8.4 Hz, H-3), 3.67 (dd, 1 H, $J_{3',4'} = J_{4',5'}$ 9.5 Hz, H-4'), 3.43–3.22 (m, 2 H, H-2',5'), and 1.85 (s, 3 H, NAc).

(−)-Menthyl 4,6-O-*benzylidene-3*-O-*(*N-*phenylcarbamoyl)-2*-O-*trifluoromethanesulfonyl-β*-D-*glucopyranoside* (**27**). — To a stirred mixture of **25** (0.5 g, 0.95 mmol) and pyridine (0.15 mL, 1.9 mmol) in dichloromethane (10 mL) was added triflic anhydride (0.17 mL, 1 mmol) at −15° under an Ar atmosphere. When t.l.c. indicated the completion of the reaction (~ 45 min.), the solvent was removed and the residue was purified by filtration through a short column of silica gel (chloroform) to give crystalline

27 (0.54 g, 87%), m.p. 131° (dec.), $[\alpha]_D^{23}$ −67.5° (*c* 0.9, chloroform), R_F 0.72 (2:1 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.46–7.03 (m, 10 H, arom.), 6.71 (s, 1 H, urethane-NH), 5.49 (s, 1 H, PhCH), 5.46 (dd, 1 H, $J_{2,3}$ = $J_{3,4}$ 9.4 Hz, H-3), 4.83 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.67 (dd, 1 H, $J_{2,3}$ 9.4, $J_{1,2}$ 7.8 Hz, H-2), 4.35 (dd, 1 H, J_{gem} 10.3, J_{vic} 4.7 Hz, H-6a), 3.78 (dd, 1 H, J_{gem} = J_{vic} 10.3 Hz, H-6b), 3.71 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ 9.4 Hz, H-4), and 3.61–3.47 (m, 2 H, H-5 and H-3 of menthyl).

Cholesteryl 4,6-O-benzylidene-2,3-O-carbonyl-β-D-mannopyranoside (**40**). — To a solution of **24** (0.22 g, 0.29 mmol) in chloroform (5 mL) and pyridine (0.04 mL) was added triflic anhydride (0.05 mL) under an Ar atmosphere at −15°. When t.l.c. (3:1 light petroleum–ethyl acetate) indicated the end of the reaction (~ 3 h), the solvent was evaporated and the residue was dried for 15 min under high vacuum. It was taken up in *N,N*-dimethylformamide (6 mL), pyridine (0.1 mL) was added, and the mixture was heated at 75° for 3.5 h. Flash chromatography (4:1 light petroleum–ethyl acetate) of the residue obtained after evaporation of the solvent yielded crystalline **40** (0.12 g, 64%), m.p. 220°, $[\alpha]_D^{23}$ −92° (*c* 0.5, dichloromethane), R_F 0.85 (4:1 toluene–acetone), ν_{max} (KBr) 1815 cm^{-1} (C–O cycl. carbonate); ^{1}H-n.m.r.: δ 7.47–7.37 (m, 5 H, arom.), 5.56 (s, 1 H, PhCH), 5.33 (m, 1 H, H-6 of cholesteryl), 5.06 (d, 1 H, $J_{1,2}$ 3.1 Hz, H-1), 4.77 (dd, 1 H, $J_{1,2}$ 3.1, $J_{2,3}$ 8.4 Hz, H-2), 4.84 (dd, 1 H, $J_{2,3}$ 8.4, $J_{3,4}$ 6.9 Hz, H-3), 4.66 (dd, 1 H, $J_{3,4}$ 6.9, $J_{4,5}$ 10.0 Hz, H-4), 4.35 (m, 1 H, H-6a), 3.73–3.61 (m, 2 H, H-5,6b), and 3.5 (m, 1 H, H-3 of cholesteryl).

Anal. Calc. for $C_{41}H_{58}O_7$: C, 74.29; H, 8.82. Found; C, 74.61; H, 8.92.

(−)-Menthyl 4,6-O-benzylidene-2,3-O-carbonyl-β-D-mannopyranoside (**41**). — A solution of **27** (0.41 g, 0.62 mmol) in *N,N*-dimethylformamide (15 mL) and pyridine (0.3 mL, 3.7 mmol) was heated at 70° for 2 h. It was diluted with toluene, extracted with M aq. $KHCO_3$, M HCl, M aq. $KHCO_3$, and water. Evaporation of the dried solvent, followed by flash chromatography (2:1 light petroleum–ethyl acetate) of the residue, gave crystalline **41** (0.22 g, 82%); m.p. 154–156°, $[\alpha]_D^{23}$ −149° (*c* 1.0, dichloromethane), R_F 0.57 (2:1 light petroleum–ethyl acetate), ν_{max} (KBr) 1800 cm^{-1} (C–O cycl. carbonate); ^{1}H-n.m.r.: δ 7.51–7.31 (m, 5 H, arom.), 5.52 (s, 1 H, PhCH), 5.10 (d, 1 H, $J_{1,2}$ 3.1 Hz, H-1), 4.85 (dd, 1 H, $J_{2,3}$ 8.4, $J_{3,4}$ 6.3 Hz, H-3), 4.76 (dd, 1 H, $J_{2,3}$ 8.4, $J_{1,2}$ 3.1 Hz, H-2), 4.61 (dd, 1 H, $J_{3,4}$ 6.3, $J_{4,5}$ 10.1 Hz, H-4), 4.35 (dd, 1 H, J_{gem} 9.3, J_{vic} 3.6 Hz, H-6a), and 3.74–3.61 (m, 2 H, H-6b,5).

Anal. Calc. for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.94; H, 7.70.

Methyl O-(4,6-O-benzylidene-2,3-O-carbonyl-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**42**). — To a cooled solution (−15°) of **29** (0.2 g, 0.24 mmol) and pyridine (0.04 mL, 0.5 mmol) in dichloromethane (10 mL) was added triflic anhydride (0.045 mL, 0.27 mmol) under an Ar atmosphere. When t.l.c. (2:1 light petroleum–ethyl acetate) showed complete conversion of the starting material (~ 1.5 h), the solvent was removed and the residue was dried for 15 min under high vacuum. The triflate was dissolved in *N,N*-dimethylformamide (5 mL) and heated at 70° for 1.5 h after the addition of pyridine (0.1 mL, 1.2 mmol). T.l.c. (1:1 light petroleum–ethyl acetate) showed complete conversion of the triflate **30** to two new compounds having R_F 0.46 and R_F 0.57 (*i.e.*, the carbonate and the corresponding iminocarbonate). For workup, the

mixture was diluted with toluene, extracted with M aq. $KHCO_3$, 2M HCl, M aq. $KHCO_3$, and water. After evaporation of the solvent, t.l.c. of the residue revealed that the iminocarbonate had been hydrolyzed to the carbonate during workup. Flash chromatography (2:1 light petroleum–ethyl acetate) of the residue yielded amorphous **42** (146 mg, 82%), $[\alpha]_D^{23}$ −33° (*c* 1.0, dichloromethane), R_F 0.57 (1:1 light petroleum–ethyl acetate), ν_{max} (KBr) 1815 cm^{-1} (C–O cycl. carbonate); ^{1}H-n.m.r.: δ 7.46–7.18 (m, 20 H, arom.), 5.41 (s, 1 H, PhCH), 4.97 (d, 1 H, J_{gem} 10.9 Hz, OCH_2Ph), 4.91 (d, 1 H, J_{gem} 11.3 Hz, OCH_2Ph), 4.88 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1'), 4.85–4.78 (m, 3 H, H-3', 2 OCH_2Ph), 4.75 (dd, 1 H, $J_{2',3'}$ 8.5, $J_{1',2'}$ 3.0 Hz, H-2'), 4.57 (d, 1 H, J_{gem} 11.3 Hz, OCH_2Ph), 4.52 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 3.51 (dd, 1 H, $J_{2,3}$ 9.5, $J_{1,2}$ 3.5 Hz, H-2), 3.43 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), and 3.37 (s, 3 H, OCH_3).

Anal. Calc. for $C_{42}H_{44}O_{12}$: C, 68.10; H, 5.99. Found: C, 68.02; H, 5.80.

Methyl O-*(4,6-*O*-benzylidene-2,3-*O*-carbonyl-β-*D*-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-*D*-glucopyranoside* (**43**). — Compound **32** (0.2 g, 0.24 mmol) was transformed into the corresponding triflate and used directly for the inversion procedure as described for compound **29**. After flash chromatography (2:1 light petroleum–ethyl acetate), **43** was obtained as an amorphous solid (150 mg, 84%), $[\alpha]_D^{23}$ −43° (*c* 1.0, dichloromethane), R_F 0.4 (2:1 light petroleum–ethyl acetate), ν_{max} (KBr) 1810 cm^{-1} (C–O cycl. carbonate); ^{1}H-n.m.r.: δ 7.38–7.22 (m, 20 H, arom.), 5.14 (d, 1 H, J_{gem} 11.8 Hz, OCH_2Ph), 5.00 (s, 1 H, PhCH), 4.89 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1'), 4.82 (d, 1 H, J_{gem} 11.8 Hz, OCH_2Ph), 4.72 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.69 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.63–4.56 (m, 3 H, $J_{1,2}$ 3.4 Hz, J_{gem} 12.0 Hz, OCH_2Ph; H-1,3'), 4.39 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.22 (m_c, 1 H, H-4'), 4.20 (dd, 1 H, $J_{2',3'}$ 7.9, $J_{1',2'}$ 3.0 Hz, H-2'), 3.98 (dd, 1 H, J_{gem} 10.3, J_{vic} 5.0 Hz, H-6a'), 3.89–3.85 (m, 2 H, H-3,4), 3.77 (dd, 1 H, J_{gem} 11.1, J_{vic} 2.6 Hz, H-6a), 3.69 (m_c, 1 H, H-5), 3.61–3.57 (m, 2 H, H-6b), 3.45 (dd, 1 H, $J_{gem} = J_{vic}$ 10.3 Hz, H-6b'), 3.36 (s, 3 H, OCH_3), and 3.29 (m_c, 1 H, H-5').

Anal. Calc. for $C_{42}H_{44}O_{12}$: C, 68.10; H, 5.99. Found: C, 68.07; H, 5.97.

Ethyl O-*(4,6-*O*-benzylidene-2,3-*O*-carbonyl-β-*D*-mannopyranosyl)-(1→4)-3,6-dibenzyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside* (**44**) *and ethyl* O-*[4,6-*O*-benzylidene-2,3-*O*-(*N*-phenyliminocarbonyl)-β-*D*-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside* (**45**). — To a solution of **37** (7.4 g, 8.2 mmol) in dichloromethane (120 mL) and pyridine (1.2 mL, 1.5 mmol) cooled to −15°, was added dropwise triflic anhydride (1.5 mL, 9 mmol) under an Ar atmosphere. After stirring for 2.5 h, t.l.c. (2:1 light petroleum–ethyl acetate; R_F 0.42) showed the complete conversion of the starting material. The solvent was evaporated and the residue was dried for 15 min under high vacuum. It was dissolved in *N,N*-dimethylformamide, diluted with toluene (300 mL), and extracted with M aq. $KHCO_3$, 2M HCl, M aq. $KHCO_3$, and water. The dried solvent was evaporated and the residue, consisting of a mixture of **44** and **45**, was dissolved in 1,4-dioxane (170 mL) and 40% acetic acid (75 mL), and stirred at room temperature until t.l.c. (3:2 light petroleum–ethyl acetate) indicated complete hydrolysis of **45** to **44** (4–5 h). Then 3/4 of the solvent was removed, toluene (150 mL) was added, and the organic layer was washed with water, aq. $NaHCO_3$, and water. Crude **44**, obtained by evaporation of the dried solvent, was

almost pure enough to be used directly for further work. Flash chromatography (3:2 light petroleum–ethyl acetate) of the residue afforded amorphous, analytically pure **44** (6.4 g, 96%), $[\alpha]_D^{23}$ −24.5° (*c* 1.0, dichloromethane), R_F 0.5 (3:2 light petroleum–ethyl acetate), ν_{max} (KBr) 1820 cm^{-1} (C–O cycl.carbonate); ^{1}H-n.m.r.: δ 7.25–7.13 (m, 4 H, Phth-H), 7.45–6.45 (m, 15 H, arom.), 5.24 (d, 1 H, $J_{1,2}$ 10.3 Hz, H-1), 5.20 (s, 1 H, PhCH), 4.98 (d, 1 H, $J_{1',2'}$ 2.7 Hz, H-1'), 4.77 (m_c, 2 H, 2 OCH_2Ph), 4.57 (dd, 1 H, $J_{2',3'} = J_{3',4'}$ 7.3 Hz, H-3'), 4.47–4.38 (m, 3 H, 2 OCH_2Ph, H-3), 4.35–4.30 (m, 2 H, H-2,2'), 4.13 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.3 Hz, H-4), 4.09 (dd, 1 H, J_{gem} 10.5, J_{vic} 4.9 Hz, H-6a'), 4.00 (dd, 1 H, $J_{3',4'}$ 7.3, $J_{4',5'}$ 10.3 Hz, H-4'), 3.86 (dd, 1 H, J_{gem} 11.4, J_{vic} 2.9 Hz, H-6a), 3.77 (dd, 1 H, J_{gem} 11.4, J_{vic} 1.7 Hz, H-6b), 3.63 (m_c, 1 H, H-5), 3.43 (dd, 1 H, $J_{gem} = J_{vic}$ 10.5 Hz, H-6b'), 3.24 (m_c, 1 H, H-5'), 2.70–2.57 (m, 2 H, SCH_2), and 1.17 (t, *J* 7.4 Hz, 3 H, CH_3).

Anal. Calc. for $C_{44}H_{43}NO_{12}S$: C, 65.23; H, 5.35; N, 1.73. Found: C, 65.41; H, 5.33; N, 1.98.

For characterization, a small portion of the iminocarbonate **45** was isolated chromatographically as an amorphous solid, $[\alpha]_D^{23}$ −14.5° (*c* 0.5, dichloromethane), R_F 0.32 (3:2 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.77–6.66 (m, 24 H, arom.), 5.48 (s, 1 H, PhCH), 5.23 (d, 1 H, $J_{1',2'}$ 2.6 Hz, H-1'), 5.17 (d, 1 H, $J_{1,2}$ 10.1 Hz, H-1), 4.80–4.74 (m, 3 H, 2 OCH_2Ph, H-3'), 4.51 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.43 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.29–4.13 (m, 4 H, H-2,3,4,4'), 3.89 (dd, 1 H, J_{gem} 11.4, J_{vic} 3.1 Hz, H-6a), 3.78 (dd, 1 H, J_{gem} 11.4, J_{vic} 1.3 Hz, H-6b), 3.74–3.59 (m, 4 H, H-5,2',6a',6b'), 3.17 (m_c, 1 H, H-5), 2.67–2.54 (m, 2 H, SCH_2), and 1.15 (t, *J* 7.4 Hz, 3 H, CH_3).

Anal. Calc. for $C_{50}H_{48}N_2O_{11}S$: C, 67.86; H, 5.47; N, 3.17. Found: C, 67.66; H, 5.52; N, 2.99.

Cholesteryl 4,6-O-benzylidene-β-D-mannopyranoside (**46**). — To a solution of carbonate **40** (0.1 g, 0.15 mmol) in dichloromethane (5 mL) was added 0.1% sodium methoxide in methanol (3.5 mL), and the mixture was stirred for 15 min at room temperature. Neutralization with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtration, and evaporation of the solvent afforded amorphous, analytically pure **46** (95 mg, quantitative), $[\alpha]_D^{23}$ −55° (*c* 0.5, chloroform), R_F 0.33 (3:1 toluene–acetone); ^{1}H-n.m.r.: δ 7.49–7.32 (m, 5 H, arom.), 5.53 (s, 1 H, PhCH), 5.36 (m_c, 1 H, H-6 of cholesteryl), 4.69 (d, 1 H, $J_{1,2} < 1$ Hz, H-1), 4.29 (dd, 1 H, J_{gem} 10.4, J_{vic} 5.0 Hz, H-6a), 4.03 (d, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 3.90–3.79 (m, 3 H, H-3,4,6b), 3.63 (m_c, 1 H, H-3 of cholesteryl), 3.33 (m_c, 1 H- H-5), 2.69 (d, 1 H, $J_{3,OH}$ 6.4 Hz, OH-3), and 2.68 (s, 1 H, OH-2).

Anal. Calc. for $C_{40}H_{60}O_6$: C, 75.43; H, 9.49. Found: C, 75.63; H, 9.44.

(−)-Menthyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-mannopyranoside (**47**). — To a solution of carbonate **41** (70 mg, 0.16 mmol) in dichloromethane (5 mL) was added 0.1% sodium methoxide in methanol (3.5 mL). After being stirred for 10 min at room temperature, the mixture was made neutral with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtered, and evaporated to dryness. The sirupy residue was dissolved in dichloromethane (10 mL), and then pyridine (0.1 mL), a catalytic amount of 4-dimethylaminopyridine, and acetic acid anhydride (0.08 mL) were added. After an overnight reaction, the mixture was diluted with dichloromethane and extracted with

2M HCl, aq. $NaHCO_3$, and water. Evaporation of the dried solvent afforded amorphous **47** (76 mg, 96%), $[\alpha]_D^{23}$ −57.5° (*c* 1.1, chloroform), R_F 0.8 (3:2 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.45–7.27 (m, 5 H, arom.), 5.53 (s, 1 H, PhCH), 5.44 (d, 1 H, $J_{2,3}$ 3.4 Hz, H-2), 5.12 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.3 Hz, H-3), 4.79 (s, 1 H, H-1), 4.30 (dd, 1 H, J_{gem} 10.4, J_{vic} 5.0 Hz, H-6a), 4.00 (dd, 1 H, $J_{3,4} = J_{4,5}$ 10.3 Hz, H-4), 3.88 (dd, 1 H, $J_{gem} = J_{vic}$ 10.4 Hz, H-6b), 3.50–3.42 (m, 2 H, H-5, H-3 of menthyl), 2.15 (s, 3 H, OAc), 2.00 (s, 3 H, OAc).

Anal. Calc. for $C_{27}H_{37}O_8$: C, 66.24; H, 7.62. Found: C, 65.88; H, 8.18.

Ethyl O-*(4,6-*O*-benzylidene-β-*D*-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside* (**48**). — To a solution of carbonate **44** (2 g, 2.5 mmol) in dichloromethane (50 mL) was added 0.1% sodium methoxide in methanol (25 mL). After stirring for 10 min at room temperature, the mixture was made neutral with an excess of Amberlite IR-120 (H^+) cation-exchange resin, filtered, and evaporated to dryness to give amorphous, analytically pure **48** (1.94 g, quantitative), $[\alpha]_D^{23}$ +36.5° (*c* 1.0, chloroform), R_F 0.14 (1:1 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.78–7.64 (m, 4 H, Phth-H), 7.45–6.86 (m, 15 H, arom.), 5.44 (s, 1 H, PhCH), 5.21 (d, 1 H, $J_{1,2}$ 10.4 Hz, H-1), 4.80 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.73 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.72 (s, 1 H, H-1′), 4.49 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.43–4.37 (m, 2 H, OCH_2Ph, H-3), 4.25 (dd, 1 H, $J_{2,3} = J_{1,2}$ 10.4 Hz, H-2), 4.13 (dd, 1 H, $J_{gem} \sim$ 10.4, J_{vic} 4.9 Hz, H-6a′), 4.09 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.1 Hz, H-4), 3.91 (d, 1 H, $J_{2',3'}$ 2.8 Hz, H-2′), 3.83–3.77 (m, 2 H, H-6a,6b), 3.74 (dd, 1 H, $J_{3',4'} = J_{4',5'}$ 9.5 Hz, H-4′), 3.64 (m_c, 1 H, H-3′), 3.58 (m_c, 1 H, H-5), 3.54 (dd, 1 H, $J_{gem} = J_{vic}$ 10.4 Hz, H-6b′), 3.11 (m_c, 1 H, H-5′), 2.79 (s, 1 H, OH-2′), 2.69–2.56 (m, 3 H, SCH_2, OH-3′), and 1.16 (t, *J* 7.4 Hz, 3 H, CH_3).

Anal. Calc. for $C_{43}H_{45}NO_{11}S$: C, 65.88; H, 5.79; N, 1.79. Found: C, 65.69; H, 5.98; N, 2.00.

Ethyl O-*(2-*O*-acetyl-4,6-*O*-benzylidene-β-*D*-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside* (**50**). — To a solution of diol **48** (800 mg, 1.02 mmol) in benzene (40 mL) were added triethylorthoacetate (4.7 mL, 26 mmol) and a catalytic amount of 4-toluenesulfonic acid. After stirring for 1 h at room temperature, t.l.c. (1:1 light petroleum–ethyl acetate) indicated the quantitative formation of compound **49**. The reaction mixture was made neutral with triethylamine, poured into ice–water, and the product extracted with ether. Crude **49**, obtained by evaporation of the dried solvent, was directly used for the synthesis of **50**. For this purpose crude **49** was dissolved in 80% acetic acid (10 mL) and stirred at room temperature for 5 min. The solvent was removed under high vacuum and toluene was distilled from the residue several times. Flash chromatography gave amorphous **50** (810 mg, 96%), $[\alpha]_D^{23}$ +22.7° (*c* 1.0, chloroform), R_F 0.36 (1:1 light petroleum–ethyl acetate); ^{1}H-n.m.r.: δ 7.78–7.59 (m, 4 H, Phth-H), 7.45–6.86 (m, 15 H, arom.), 5.45 (s, 1 H, PhCH), 5.26 (d, 1 H, $J_{2',3'}$ 3.0 Hz, H-2′), 5.10 (d, 1 H, $J_{1,2}$ 10.0 Hz, H-1), 4.81 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.75 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.73 (s, 1 H, H-1′), 4.47 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.38 (d, 1 H, J_{gem} 12.1 Hz, OCH_2Ph), 4.28–4.19 (m, 2 H, H-2,3), 4.16–4.09 (m, 2 H, H-6a′,4), 3.82 (dd, 1 H, J_{gem} 11.4, J_{vic} 3.0 Hz, H-6a), 3.74 (dd, 1 H, J_{gem} 11.4, J_{vic} 1.5 Hz, H-6b), 3.70 (m_c, 1 H, $J_{3',4'} \approx J_{4',5'} \approx$ 9.6 Hz, H-4′), 3.63 (m_c, 1 H, H-3′),

3.57–3.51 (m, 2 H, H-5,6b'), 3.13 (m_c, 1 H, H-5'), 2.67–2.55 (m, 2 H, SCH_2), 2.31 (d, 1 H, $J_{3',OH}$ 3.2 Hz, OH-3'), 2.16 (s, 3 H, OAc), and 1.15 (t, 3 H, J 7.5 Hz, CH_3).

Anal. Calc. for $C_{45}H_{47}NO_{12}S$: C, 65.44; H, 5.74; N, 1.70. Found: C, 65.24; H, 5.82; N, 1.56.

Ethyl O-*(2,3,4,6-tetra*-O-*acetyl-α*-D-*mannopyranosyl)-(1→3)*-O-*(2*-O-*acetyl-4,6*-O-*benzylidene-β*-D-*mannopyranosyl)-(1→4)-3,6-di*-O-*benzyl-2-deoxy-2-phthalimido-1-thio-β*-D-*glucopyranoside* (**52**). — A mixture of silver triflate (0.46 g, 1.8 mmol) and molecular sieves 4A (1 g) in dichloromethane (25 mL) was stirred for 15 min at room temperature. After cooling to −50°, a solution of acceptor **50** (0.5 g, 0.58 mmol) in dichloromethane (10 mL) was added and stirring was continued for another 15 min. A solution of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide[32] (**51**; 0.37 g, 0.9 mmol) in dichloromethane was added dropwise. When t.l.c. indicated the end of the reaction, the solution was made neutral with triethylamine, washed with ice-cold aq. $Na_2S_2O_3$, and filtered through a pad of Celite. The filtrate was washed with M HCl, aq. $NHCO_3$, and water, dried, and evaporated to dryness. Flash chromatography of the residue gave amorphous **52** (512 mg, 76%), $[\alpha]_D^{23}$ +21° (*c* 1.0, chloroform), R_F 0.5 (15:1 dichloromethane–acetone); ^{1}H-n.m.r.: δ 7.79–7.60 (m, 4 H, Phth-H), 7.37–6.89 (m, 15 H, arom.), 5.45 (s, 1 H, PhCH), 5.35 (d, 1 H, $J_{2',3'}$ 3.0 Hz, H-2'), 5.33–5.29 (m, 2 H, H-2'',4''), 5.17 (d, 1 H, $J_{1,2}$ 11.2 Hz, H-1), 5.16 (d, 1 H, $J_{1'',2''}$ 1.7 Hz, H-1''), 5.13 (dd, 1 H, $J_{3'',4''}$ 10.3, $J_{2'',3''}$ 3.3 Hz, H-3''), 4.81 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.77 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.73 (s, 1 H, H-1'), 4.48 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.41 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.31 (dd, 1 H, J_{gem} 12.9, J_{vic} 4.6 Hz, H-6a''), 4.29–4.22 (m, 2 H, H-2,3), 4.19–4.13 (m, 2 H, H-6a',4), 4.09–4.06 (m, 2 H, H-5'',6b''), 3.87–3.75 (m, 4 H, H-4',3',6a,6b), 3.55 (m_c, 1 H, H-5), 3.49 (dd, 1 H, J_{gem} = J_{vic} 10.3 Hz, H-6b'), 3.09 (m_c, 1 H, H-5'), 2.72–2.53 (m, 2 H, SCH_2), 2.20, 2.07, 2.05, 2.03, 1.93 (5 s, 15 H, 5 OAc), and 1.15 (t, 3 H, J 7.4 Hz, CH_3).

Anal. Calc. for $C_{59}H_{65}NO_{12}S$: C, 61.29; H, 5.66; N, 1.21. Found: C, 61.65; H, 5.40; N, 1.68.

Ethyl O-*(2,3,4,6-tetra*-O-*acetyl-α*-D-*mannopyranosyl)-(1→3)*-O-*(2*-O-*acetyl-β*-D-*mannopyranosyl)-(1→4)-3,6-di*-O-*benzyl-2-deoxy-2-phthalimido-1-thio-β*-D-*glucopyranoside* (**53**). — Trisaccharide **52** (0.38 g, 0.33 mmol) was dissolved in 1,4-dioxane (15 mL) and acetic acid (65%, 40 mL), and heated at 75° for 24 h. When t.l.c. showed complete conversion of the starting material, the solvent was removed *in vacuo* (0.1 kPa), and toluene was distilled from the residue. Flash chromatography afforded amorphous **63** (304 mg, 87%), $[\alpha]_D^{23}$ +22.5° (*c* 0.4, chloroform), R_F 0.38 (3:1 toluene–acetone); ^{1}H-n.m.r.: δ 7.78–7.58 (m, 4 H, Phth-H), 7.36–6.89 (m, 10 H, arom.), 5.30 (dd, 1 H, $J_{3'',4''}$ = $J_{4'',5''}$ 10.2 Hz, H-4''), 5.27–5.24 (m, 2 H, H-2'',2'), 5.19–5.16 (m, 2 H, H-1'',1), 5.14 (dd, 1 H, $J_{2'',3''}$ 3.2, $J_{3'',4''}$ 10.2 Hz, H-3''), 4.82 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.74 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.64 (s, 1 H, H-1'), 4.45 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.39 (d, 1 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.28 (dd, 1 H, J_{gem} 12.4, J_{vic} 4.3 Hz, H-6a''), 4.23–4.17 (m, 2 H, H-2,3), 4.17–4.06 (m, 3 H, H-5'',6b'',4), 3.80–3.69 (m, 4 H, H-6a,6b,6a',4'), 3.56–3.53 (m, 2 H, H-5,6b'), 3.51 (dd, 1 H, $J_{2',3'}$ 3.4, $J_{3',4'}$ 9.5 Hz, H-3'), 3.32 (d, 1 H, $J_{4',OH}$ 4.6 Hz, OH-4'), 3.04 (m_c, 1 H, H-5'), 2.67–2.54 (m, 3 H, SCH_2, OH-6'), 2.12, 2.11, 2.09, 2.04, 1.95 (5 s, 15 H, 5 OAc), and 1.14 (t, 3 H, J 7.5 Hz, CH_3).

Anal. Calc. for $C_{52}H_{61}NO_{12}S$: C, 58.48; H, 5.76; N, 1.31. Found: C, 58.25; H, 5.71; N, 1.95.

Ethyl O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-[(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-(1→6)]-O-(2-O-acetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**54**). — A mixture of **53** (50 mg, 46.8 μmol), 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide[32] (**51**; 20.2 mg, 49.1 μmol), and molecular sieves (4A) in dichloromethane (5 mL) was stirred for 1 h at room temperature. After cooling to −20°, a solution of silver triflate (23 mg, 89.5 μmol) and *N,N,N',N'*-tetramethylurea (7 μL, 56.6 μmol) in toluene (0.5 mL) was added. When t.l.c. (20:1 chloroform–methanol) indicated the end of the reaction (~ 20 min.), the mixture was diluted with cold dichloromethane and washed with ice-cold M HCl, aq. $NaHCO_3$, and water. Evaporation of the dried solvent, followed by flash chromatography (30:1 chloroform–methanol) of the residue gave amorphous **54** (48.4 mg, 74%), $[\alpha]_D^{23}$ +18.5° (*c* 0.5, chloroform), R_F 0.66 (20:1 chloroform–methanol); ^{1}H-n.m.r.: δ 7.75–7.59 (m, 4 H, Phth-H), 7.38–7.29 (m, 5 H, arom.), 6.94–6.82 (m, 5 H, arom.), 5.40 (d, 1 H, $J_{1''',2'''}$ 2.5 Hz, H-1'''), 5.31–5.17 (m, 7 H, H-4'',2'',1'',2',4''',1,3'''), 5.14 (dd, 1 H, $J_{2'',3''}$ 3.2, $J_{3'',4''}$ 10.3 Hz, H-3''), 4.84 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.80 (d, 1 H, J_{gem} 11.8 Hz, OCH_2Ph), 4.69 (s, 1 H, H-1'), 4.56 (m_c, 1 H, H-2'''), 4.45 (d, 1 H, J_{gem} 11.8 Hz, OCH_2Ph), 4.38 (d, 1 H, J_{gem} 12.3 Hz, OCH_2Ph), 4.28 (dd, 1 H, J_{gem} 13.0, J_{vic} 4.9 Hz, H-6a''), 4.23–4.19 (m, 3 H, H-2,3), 4.15–4.07 (m, 4 H, H-6b'',5''), 3.80–3.73 (m, 4 H, H-4',5'''), 3.75–3.66 (m, 2 H, H-6a',6b'), 3.56–3.53 (m, 2 H, H-3'), 3.13 (m_c, 1 H, H-5'), 2.91 (d, 1 H, $J_{4',OH}$ 3.6 Hz, OH-4'), 2.64–2.57 (m, 2 H, SCH_2), 2.14–1.69 (9 s, 27 H, 9 OAc), and 1.15 (t, 3 H, *J* 7.4 Hz, CH_3).

Anal. Calc. for $C_{66}H_{79}NO_{30}S \cdot H_2O$: C, 55.26; H, 5.83; N, 0.97. Found: C, 55.43; H, 6.12; N, 1.04.

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