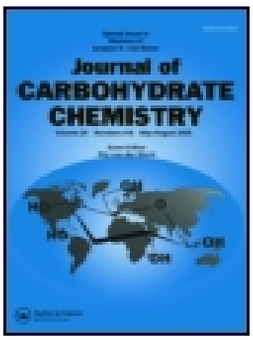

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THE SYNTHESIS OF FOUR DIDEOXYGENATED ANALOGUES OF β-MALTOSYL-(1→4)-TREHALOSE

Hans Peter Wessel,* Rudolf Minder and Michel Trumtel

F.Hoffmann-La Roche Ltd
Pharmaceuticals Division, Dept. PRPV-D, Building 15/30
CH-4070 Basel, Switzerland

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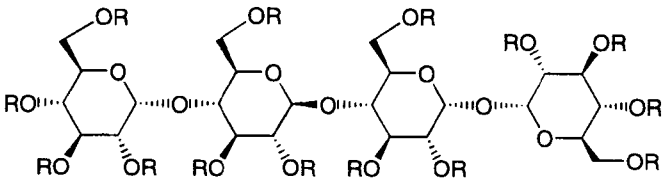
ABSTRACT

Four derivatives of β-maltosyl-(1→4)-trehalose were prepared, each with two deoxy functions in one of the constitutive disaccharide building blocks. 2,3-Di-*O*-acetyl-4,6-dideoxy-4,6-diiodo-α-D-galactopyranosyl- (1→4) -1,2,3,6-tetra-*O*-acetyl-D-glucopyranose (**3**) was employed as a precursor for the 4''',6'''-dideoxygenated tetrasaccharide **9**: ccupling of **3** with 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3,6-tri-*O*-benzylidene-α-D-glucopyranoside (**4**) furnished the tetrasaccharide **5** which was deiodinated and deprotected to yield the target tetrasaccharide **9**. Secondly, the dideoxygenated maltose derivative 3-deoxy-4,6-*O*-isopropylidene-2-*O*-pivaloyl-α-D-glucopyranosyl- (1→4) -1,6-anhydro-3-deoxy-2-*O*-pivaloyl-β-D-glucopyranose (**10**) was ring-opened to the anomeric acetate **11**. A [2+2] block synthesis with **4** in TMS triflate mediated glycosylation gave a tetrasaccharide which was deprotected to the 3'',3'''- dideoxygenated analogue of β-maltosyl-(1→4)-trehalose. For the third tetrasaccharide, 2,3,2',3'-tetra-*O*-benzyl-α,α-trehalose was iodinated at the primary positions and deiodinated in the presence of palladium-on-carbon, then this acceptor was selectively glycosylated with hepta-*O*-acetyl-maltosyl bromide (**20**). Removal of protective groups furnished the maltosyl trehalose tetrasaccharide deoxygenated at positions C-6 and C-6'. To prepare a 3,3'-dideoxygenated trehalose, the free hydroxyl groups of 2-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-α-D-glucopyranosyl 2-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-α-D-glucopyranoside (**25**) were reduced by Barton-McCombie deoxygenation. One of the benzylidene groups was opened reductively with sodium cyanoborohydride. The resulting free hydroxyl group at the 4'-position was glycosylated in a Koenigs-Knorr reaction with **20** to yield the 3,3'-dideoxygenated tetrasaccharide **32**, the fourth target oligosaccharide, after deprotection.



1 R = SO_3Na or H, DS ~ 2.8 (DS, the degree of sulfation, denotes the average number of sulfate groups per monosaccharide unit)

2 R = H

Scheme 1

INTRODUCTION

The tetrasaccharide sulfated β-maltosyl-(1→4)-trehalose (**1**) is a potent smooth muscle cell (SMC) proliferation inhibitor[1] which seems to mimic the action of heparan sulfate, an endogenous SMC growth regulator. In earlier publications[2,3] we have detailed our approach to investigate the relative importance of sulfate groups in the various positions of the sulfated tetrasaccharide **1** (Scheme 1) by selective removal of single hydroxyl groups of the unprotected tetrasaccharide **2**.

Derivatives of **2** deoxygenated at the primary positions have been synthesized via the respective iodinated compounds.[3] The syntheses of the tetrasaccharide analogues deoxygenated at secondary carbon atoms were achieved after Barton-McCombie deoxygenation[4] of the activated secondary hydroxyl groups. Thus, we have reported the preparation of the C-4- and C-4'''-deoxy derivatives,[5] the C-3"-deoxy derivative,[6] the C-3'- and C-3'''-deoxy derivatives,[7] and the C-2''-deoxy derivative.[8] While maltose and trehalose were favourably employed as starting materials for those analogues, one of the disaccharide units for the other 2-deoxy derivatives was assembled from monosaccharide precursors using a phenylselenyl chloride mediated coupling reaction[9] for the C-2'''-deoxy[8] and *N*-iodosuccinimide coupling[10,11] for the C-2- and C-2'-deoxygenated derivatives.[12] Here we report on the syntheses of four different dideoxygenated analogues of **2**.

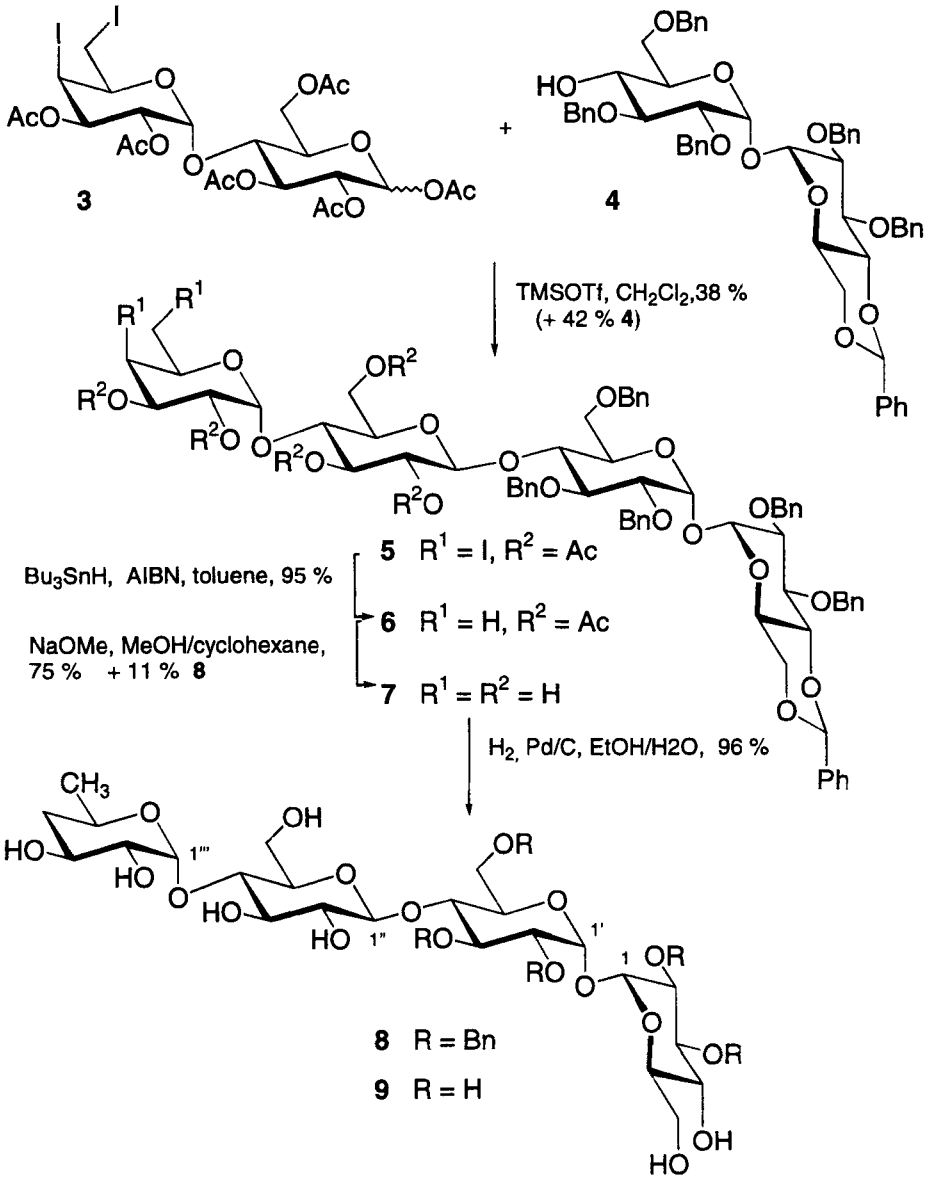
RESULTS AND DISCUSSION

Dideoxygenated derivatives of β-maltosyl-(1→4)-trehalose were planned to serve as controls for the antiproliferative activities of the monodeoxygenated analogues. These dideoxygenated derivatives were prepared in parallel to the monodeoxygenated analogues of **2**, so that the choice of the deoxygenated positions was not determined by the antiproliferative activity of the respective monodeoxygenated compounds but, in a very pragmatic approach, by ease of synthetic access.

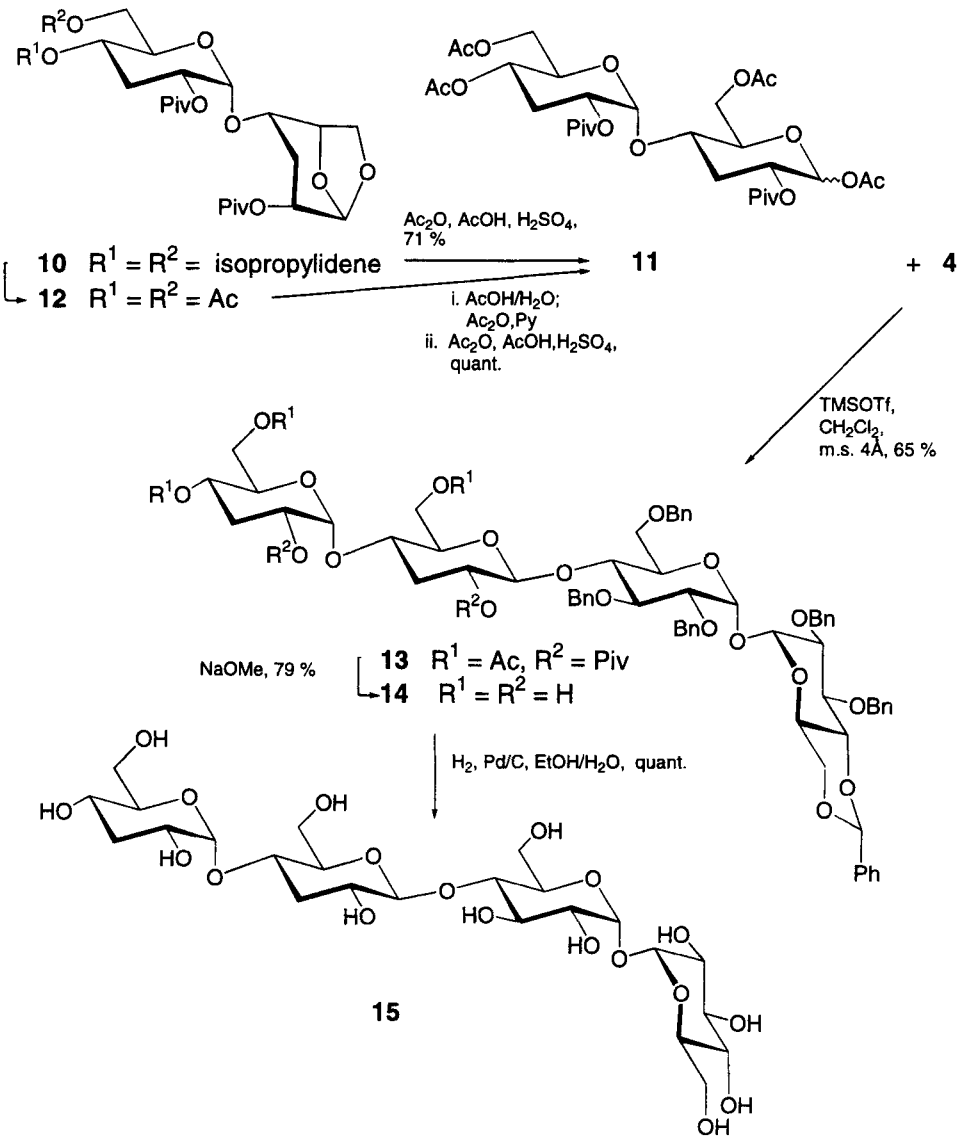
A suitable precursor for a dideoxygenated maltose moiety was 2,3-di-*O*-acetyl-4,6-dideoxy-4,6-diiodo-α-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-*O*-acetyl-D-glucopyranose (**3**)[13] which was prepared from allyl 2,2',3,3',6-penta-*O*-acetyl-β-maltoside, a common starting material for a number of our syntheses.[3,6] Although only β-D-acetates are suitable glycosyl donors in a trimethylsilyl triflate mediated glycosylation reaction[14] we have reacted the 3:2 α/β-mixture of anomeric acetates **3** to avoid a laborious separation. As a glycosyl acceptor 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3,6-tri-*O*-benzylidene-α-D-glucopyranoside[15] (**4**) was employed, and the tetrasaccharide **5** was obtained (Scheme 2) in a yield of 38 % along with unreacted glycosyl acceptor (42 %). The structure of **5** was fully supported by its ^{1}H NMR spectrum, again, a typical up-field shift (δ 1.71 ppm) was observed for one of the acetate signals, according to earlier observations[3,6] due to an interaction of 2''-OAc with the C-6' benzyl group.

The deoxy functions were introduced by treatment of **5** with tributyltin hydride in the presence of α,α'-azobisisobutyronitrile (AIBN) as radical starter to afford tetrasaccharide **6** in excellent yield (95 %). Deacetylation was achieved with sodium carbonate in methanol/cyclohexane to give **7** in up to 75 % yield, in addition, the debenzylidenated derivative **8** was obtained unexpectedly in variable amounts. This by-product was only faintly visible on TLC after the work-up procedure and was probably formed during chromatography. This side reaction was not relevant since both deacylated tetrasaccharides **7** and **8** gave, upon hydrogenolysis, in excellent yield (96 %) the completely deprotected saccharide **9**, the 4''',6'''-dideoxygenated analogue of tetrasaccharide **2**.

For the synthesis of the 3'',3'''-dideoxygenated β-maltosyl-(1→4)-trehalose we had obtained earlier[13] a suitable maltosyl precursor, namely 3-deoxy-4,6-*O*-isopropylidene-2-



Scheme 2



Scheme 3

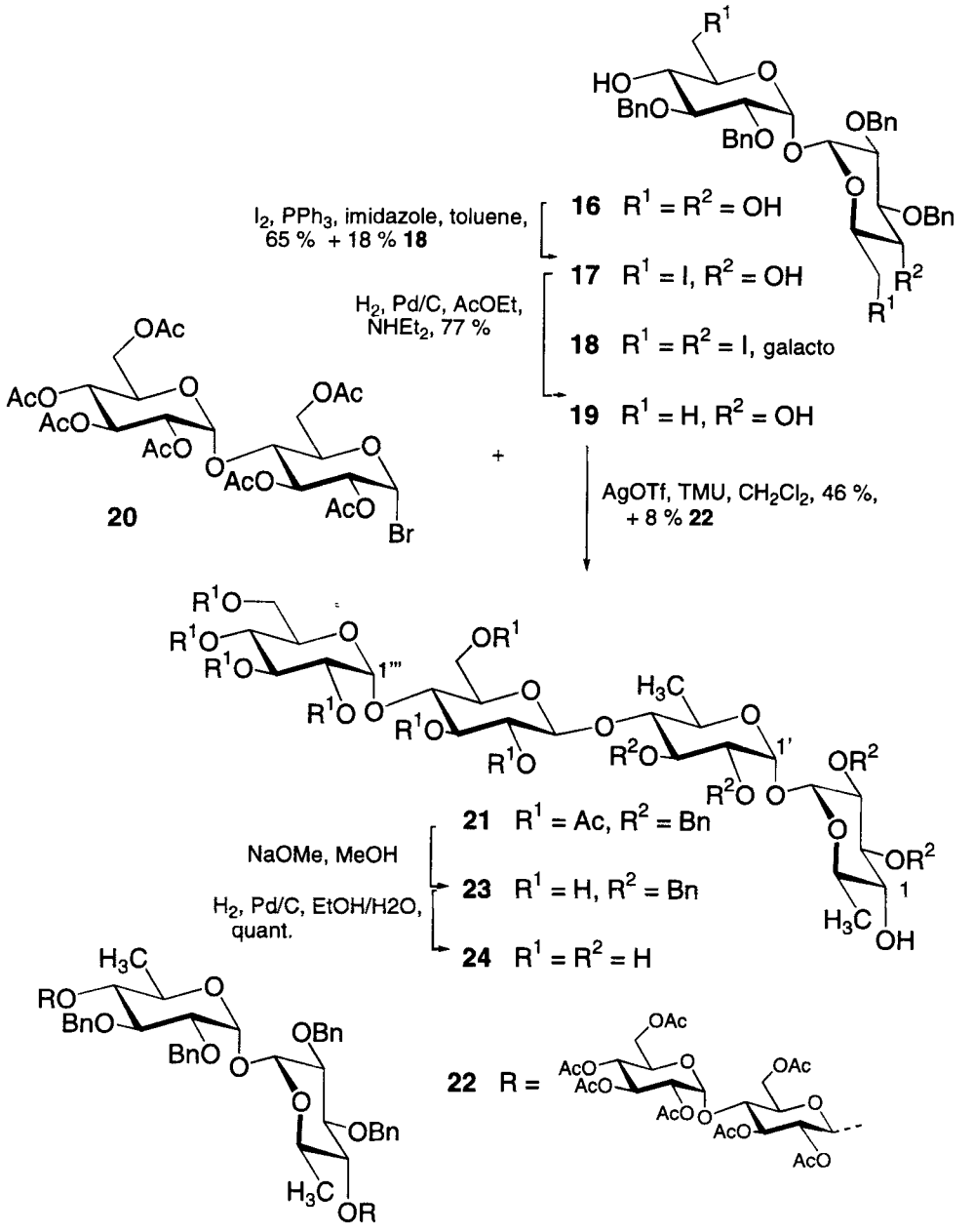
O-pivaloyl-α-D-glucopyranosyl- (1→4) -1,6-anhydro-3-deoxy-2-*O*-pivaloyl-β-D-glucopyranose (**10**), which already has the deoxy functions in place and can be converted to a glycosyl donor. Acetolysis of this compound opened up the 1,6-anhydro ring and concomitantly led to cleavage of the isopropylidene acetal to afford **11** in 71 % yield. A much

cleaner reaction occurred when the isopropylidene group was cleaved first with acetic acid followed by acetylation to afford **12**; opening of the 1,6-anhydro ring by acetolysis then gave a quantitative yield of **11** as an inseparable 1:1 mixture of α/β-anomers. Again, the anomeric mixture of acetates was reacted with glycosyl acceptor **4** to furnish, catalyzed by trimethylsilyl triflate, the tetrasaccharide **13** in 65 % yield. Transesterification of **13** gave **14** (79 %) the structure of which was confirmed by ^{1}H NMR. Hydrogenolysis of this compound then afforded quantitatively the free tetrasaccharide **15**, the 3'',3'''-dideoxygenated analogue of **2**.

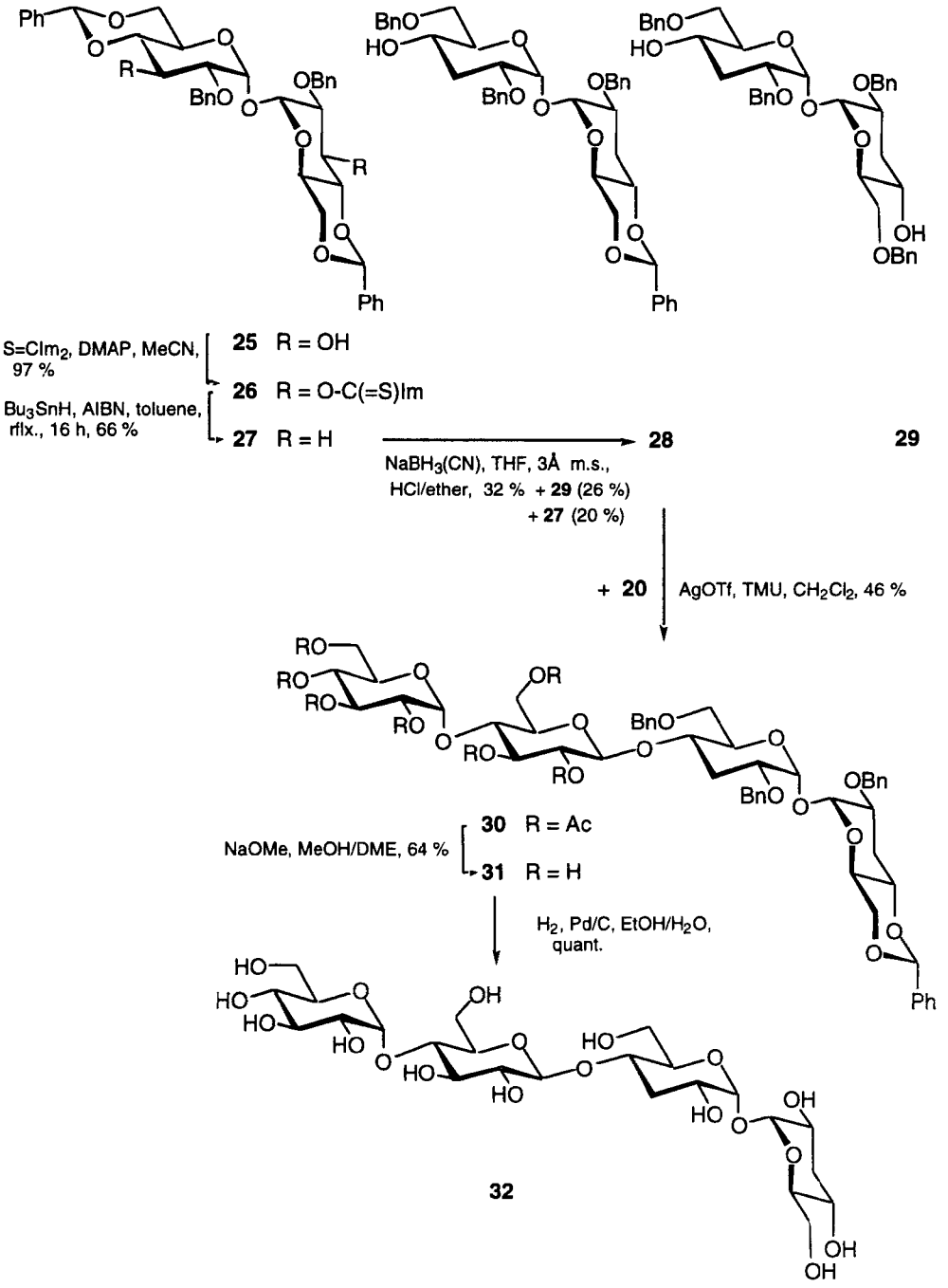
α,α-Trehalose is a C_2-symmetrical molecule, and the symmetrical introduction of two deoxy functions is straightforward. Thus, the known[16] 2,3,2',3'-tetra-*O*-benzyl-α,α-trehalose (**16**) was iodinated regioselectively with iodine in the presence of triphenylphosphine and imidazole[17] to afford the desired symmetrical diiodide **17** in 65 % yield together with some triiodo derivative **18** (18 %, Scheme 4). The diiodide was reduced selectively by hydrogenation in the presence of palladium-on-carbon and diethylamine[18] giving the symmetrical dideoxy derivative **19** in good yield (77 %).

The selective transformation of only one of the glucose moieties of the C_2-symmetrical trehalose system ("symmetry breaking") is usually a low yield process, but we could demonstrate[6,15] that glycosylation is a comparatively good symmetry breaking reaction. Thus, we have coupled hepta-*O*-acetyl-maltosyl bromide[19] **20** to glycosyl acceptor **19** in a Koenigs-Knorr glycosylation reaction, using silver triflate[20] and tetramethylurea as activating system, to give the tetrasaccharide **21** in a yield of 46 %. Beside unreacted starting material **19** (31 %), the symmetrical hexasaccharide **22** was obtained as a by-product in 8 % yield. Deblocking of **21** by transesterification to give **23** followed by hydrogenolysis quantitatively furnished the β-maltosyl trehalose tetrasaccharide **24** dideoxygenated at C-6 and C-6'.

For the synthesis of the 3,3'-dideoxygenated β-maltosyl-(1→4)-trehalose the known[21] 2-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-α-D-glucopyranosyl 2-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-α-D-glucopyranoside **25** was a suitable precursor. Activation of the hydroxyl groups of **25** with thiocarbonyldiimidazole in acetonitrile was achieved in an excellent yield of 97 % (Scheme 5). The resulting compound **26** was submitted to Barton-McCombie deoxygenation[5] using tributyltin hydride and AIBN in toluene to afford the



Scheme 4



Scheme 5

symmetrical dideoxygenated derivative **27** (66 %). The selective reductive opening of one of the benzylidene acetals with sodium cyanoborohydride in the presence of hydrochloric acid / ether proceeded, as expected, in moderate yield (32 %) to give the monohydroxy derivative **28** along with starting material **27** (20 %) and the symmetrical derivative **29** (26 %). Koenigs-Knorr glycosylation of **28** with hepta-*O*-acetylmaltosyl bromide[19] **20** as glycosyl donor and activation with silver triflate[20] and tetramethylurea furnished tetrasaccharide **30** in 46 % yield. Again, one of the acetate signals in the ^{1}H NMR spectrum was shifted upfield (δ = 1.77 ppm) supporting the earlier observed interaction of the acetate group at C-2'' with the C-6' benzyl group. As expected, this effect was not observed for tetrasaccharide **21** (highest acetate shift at δ = 1.89 ppm) which lacks the C-6' benzyl group.

Standard deprotection of **30** went on uneventfully to afford **31** after transesterification and, after hydrogenolysis, the free tetrasaccharide **32** in quantitative yield. Compound **32** is the 3,3'-dideoxygenated analogue of β-maltosyl-(1→4)-trehalose.

The investigation of the antiproliferative activities of the highly sulfated derivatives of the dideoxygenated tetrasaccharides described here showed that these compounds serve well as a control for the activities observed with the monodeoxygenated tetrasaccharide derivatives.[2] In consequence, the low relative antiproliferative activity of the highly sulfated derivative of the 3,3'-dideoxygenated β-maltosyl-(1→4)-trehalose could be used to predict that the sulfate at C-3 plays a role in the activity of the parent sulfated tetrasaccharide.

EXPERIMENTAL

General Procedures. Experimental conditions were essentially as described before.[3] Specific rotations were measured at 20 °C. Mass spectra were recorded on API III Sciex, Perkin Elmer (ionspray), CSP 46 Finnigan MAT, Bremen (thermospray), or MS 902 (FAB) with data system DS 2050 (VG).

2,3-Di-*O*-acetyl-4,6-dideoxy-4,6-diiodo-α-D-galactopyranosyl- (1→4) -2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-di-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**5**). A soln of glycosyl donor **3** (5.0 g of a 3:2 α/β-mixture, ca. 2.46 mmol of β-acetate) and acceptor **4** (2.17 g, 2.46 mmol) in

abs dichloromethane (12 mL) was stirred in the presence of molecular sieves (4 Å, ca. 1 g) at rt. A soln of trimethylsilyl triflate (45 µL, 0.246 mmol) in abs dichloromethane (2 mL) was added at -20 °C. The reaction mixture was allowed to reach rt and was stirred at rt for 18 h. Then it was poured into ice/aq sodium bicarbonate soln and extracted with ethyl acetate. The organic phases were dried over sodium sulfate, filtered, and concentrated. The residue was purified by MPLC using ethyl acetate/ hexane 1:3 as eluent to furnish acceptor **4** (910 mg, 42 %) followed by tetrasaccharide **5** (1.51 g, 38 %) as a colourless foam: $[\alpha]_D$ +92.0 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 1652.7 ([M + NH_4]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 - 7.47 (m, 2H, aromat), 7.44 - 7.23 (m, 28H, aromat), 5.53 (s, 1H, CHPh), 5.27 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1'''), 5.16 (dd, 1H, $J_{2''',3'''}$ = 10.7 Hz, $J_{3''',4'''}$ = 4.0 Hz, H-3'''), 5.13 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.11 (d, 1H, $J_{1',2'}$ = 3.8 Hz, H-1'), 5.01, 4.89 (2 d, 2H, J_{gem} = 10.5 Hz, CH_2Ph), 5.01, 4.75 (2 d, 2H, J_{gem} = 11.8 Hz, CH_2Ph), 4.99 (dd ~ t, 1H, $J_{3'',4''}$ = 8.7 Hz, H-3''), 4.91 (dd ~ t, 1H, $J_{4''',5'''}$ = 1.2 Hz, H-4'''), 4.73, 4.67 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.73, 4.40 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.72 (dd, 1H, $J_{2'',3''}$ = 9.3 Hz, H-2''), 4.68, 4.62 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.51 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.48 (dd, 1H, H-2'''), 4.26 (ddd ~ dt, 1H, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 10.2 Hz, H-5), 4.23 (dd, 1H, $J_{5'',6a''}$ = 3.0 Hz, H-6a''), 4.13 (dd ~ t, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.08 (dd, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6a), 4.04 (dd, 1H, $J_{6a'',6b''}$ = 12.2 Hz, H-6b''), 4.01 (ddd ~ br t, 1H, H-5'), 3.89, 3.86 (dd ~ t, 1H and dd ~ t, 2H, H-3', H-4', H-4''), 3.63 (dd ~ t, 1H, H-6b), 3.62 (dd ~ t, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 3.61 (br dd, 1H, H-6a'), 3.57 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 3.52 (dd, 1H, $J_{2',3'}$ = 9.2 Hz, H-2'), 3.44 (dd, 1H, $J_{5',6b'}$ = 1.5 Hz, $J_{6a',6b'}$ = 10.8 Hz, H-6b'), 3.28 (ddd, 1H, H-5'''), 3.21 (dd, 1H, $J_{5''',6a'''}$ = 5.9 Hz, H-6a'''), 3.19 (ddd, 1H, $J_{5'',6b''}$ = 4.8 Hz, H-5''), 3.08 (dd, 1H, $J_{5''',6b'''}$ = 8.1 Hz, $J_{6a''',6b'''}$ = 10.0 Hz, H-6b'''), 2.12, 2.10, 1.98, 1.95, 1.71 (5 s, 15H, OAc).

Anal. Calcd for $C_{76}H_{84}I_2O_{24}$ (1635.29): C, 55.82; H, 5.18; I, 15.52. Found: C, 55.68; H, 5.20; I, 15.47.

2,3-Di-*O*-acetyl-4,6-dideoxy-α-D-*xylo*-hexopyranosyl- (1→4) -2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-di-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (6). A soln of diiodo derivative **5** (1.0 g, 0.61 mmol) in abs toluene (10 mL) was stirred at 100 °C in the presence of tributyltin hydride

(355 μL, 1.34 mmol) and AIBN (10 mg, 0.06 mmol) for 30 min, then the same amounts of tributyltin hydride and AIBN were added, and stirring at 100 °C was continued for another 30 min. The reaction mixture was concentrated and chromatographed on silica gel using ethyl acetate/ hexane 1:2 as eluent to afford pure **6** (801 mg, 95 %) as a colourless syrup: $[\alpha]_D$ +79.0 ° (*c* 0.2, dioxane); MS (FAB) *m/z* 1421.5 ($[M + K]^+$), 1405.6 ($[M + Na]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 - 7.48 (m, 2H, aromat), 7.46 - 7.10 (m, 28H, aromat), 5.53 (s, 1H, CHPh), 5.24 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.17 (ddd ~ dt, 1H, $J_{3''',4eq'''}$ = 4.9 Hz, $J_{3''',4ax'''}$ = 11.4 Hz, H-3'''), 5.13, 5.12 (2 d, 2H, H-1, H-1'), 5.03, 4.74 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 5.02 (dd ~ t, 1H, $J_{3'',4''}$ = 8.7 Hz, H-3''), 5.00, 4.90 (2 d, 2H, J_{gem} = 11.1 Hz, CH_2Ph), 4.48 (dd, 1H, $J_{2''',3'''}$ = 10.5 Hz, H-2'''), 4.73, 4.67 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.73, 4.40 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.73 (dd, 1H, $J_{2'',3''}$ = 9.5 Hz, H-2''), 4.67, 4.61 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.51 (d, 1H, $J_{1'',2''}$ = 8.1 Hz, H-1''), 4.25 (ddd ~ dt, 1H, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.3 Hz, H-5), 4.16 (dd, 1H, $J_{5'',6a''}$ = 2.0 Hz, H-6a''), 4.14 (dd ~ t, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 4.08 (dd, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6a), 4.01 (dd, 1H, $J_{5'',6b''}$ = 3.8 Hz, $J_{6a'',6b''}$ = 12.2 Hz, H-6b''), 4.01 (ddd ~ br t, 1H, H-5'), 3.92 (dd ~ t, 1H, $J_{4'',5''}$ = 9.8 Hz, H-4''), 3.89 (dd ~ t, 1H, $J_{4',5'}$ = 10.0 Hz, H-4'), 3.84 (dd ~ t, 1H, $J_{3',4'}$ = 9.9 Hz, H-3'), 3.28 (ddq, 1H, $J_{4eq''',5'''}$ = 2.0 Hz, $J_{4ax''',5'''}$ = 11.3 Hz, H-5'''), 3.63 (dd ~ t, 1H, H-6b), 3.63 (dd, 1H, $J_{5',6a'}$ = 2.8 Hz, H-6a'), 3.61 (dd ~ t, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.57 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 3.52 (dd, 1H, $J_{1',2'}$ = 3.7 Hz, $J_{2',3'}$ = 9.2 Hz, H-2'), 3.47 (dd, 1H, $J_{5',6b'}$ = 1.0 Hz, $J_{6a',6b'}$ = 10.8 Hz, H-6b'), 3.14 (ddd, 1H, H-5''), 2.12 (ddd, 1H, H-4_{eq}'''), 2.10, 2.02, 1.96, 1.86, 1.71 (5 s, 15H, OAc), 1.42 (ddd ~ q, 1H, $J_{4eq''',4ax'''}$ = 14.5 Hz, H-4_{ax}'''), 1.12 (d, 1H, $J_{5''',6'''}$ = 6.1 Hz, H-6''').

Anal. Calcd for $C_{76}H_{86}O_{24}$ (1383.50): C, 65.98; H, 6.27. Found: C, 65.78; H, 6.31.

4,6-Dideoxy-α-D-*xylo*-hexopyranosyl- (1→4) -β-D-glucopyranosyl- (1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (7). A soln of tetrasaccharide **6** (190 mg, 0.137 mmol) in methanol (3 mL) and cyclohexane (1 mL) was stirred in the presence of sodium methanolate (0.1 mL of 2.0 g Na/100 mL methanol) at rt. After 18 h at rt the reaction mixture was neutralized with Amberlite IR 120 (H^+), and filtered. The filtrate and methanol washings were

concentrated. The residue was purified by MPLC using ethyl acetate as eluent to obtain **7** (120 mg, 75 %) followed by 4,6-dideoxy-α-D-*xylo*-hexopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (**8**, 17 mg, 11 %).

Data for **7**: Colorless foam, $[\alpha]_D$ +107.5 ° (*c* 0.2, dioxane); MS (FAB) *m/z* 1211.5 ([M + K]$^+$), 1195.5 ([M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 - 7.49 (m, 2H, aromat), 7.41 - 7.25 (m, 28H, aromat), 5.55 (s, 1H, CHPh), 5.14, 5.13 (2 d, 2H, H-1, H-1'), 5.00 (d, 1H, $J_{1''',2'''}$ Å 3.8 Hz, H-1'''), 4.98, 4.85 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 4.94, 4.90 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 4.81, 4.62 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.72, 4.68 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.59, 4.43 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.38 (d, 1H, $J_{1'',2''}$ = 7.7 Hz, H-1''), 4.25 (ddd ~ dt, 1H, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 10.0 Hz, H-5), 4.13 (dd ~ t, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 4.12 (ddd ~ br d, 1H, H-5'), 4.11 (dd, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6a), 4.06 (br s, 1H, OH), 3.97 (dd ~ t, 1H, $J_{4',5'}$ = 9.8 Hz, H-4'), 3.92 (dd ~ t, 1H, $J_{3',4'}$ = 8.8 Hz, H-3'), 3.92 (ddq, 1H, $J_{4eq''',5'''}$ = 2.0 Hz, H-5'''), 3.80 (br d, 1H, OH), 3.79 (ddd, 1H, $J_{2''',3'''}$ = 9.5 Hz, $J_{3''',4eq'''}$ = 4.9 Hz, $J_{3''',4ax'''}$ = 11.4 Hz, H-3'''), 3.66 (dd ~ t, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6b), 3.64 (dd ~ t, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.63 (dd, 1H, H-6a'), 3.62 (dd, 1H, H-6a''), 3.60 (dd, 1H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 3.56 (dd, 1H, $J_{1',2'}$ = 3.7 Hz, $J_{2',3'}$ = 9.2 Hz, H-2'), 3.46 - 3.37 (m, 4H, H-2''', H-3''', H-3'', H-6b''), 3.34 (dd, 1H, $J_{5',6b'}$ = 1.4 Hz, $J_{6a',6b'}$ = 11.3 Hz, H-6b'), 3.26 (ddd ~ dt, 1H, $J_{2'',3''}$ = 9.2 Hz, H-2''), 3.16 (d, 1H, $J_{2'',2''\text{-OH}}$ = 2.3 Hz, 2''-OH), 2.98 (ddd, 1H, H-5''), 2.59 (br s, 1H, OH), 2.09 (br t, 1H, 6''-OH), 1.93 (ddd, 1H, H-4_{eq}'''), 1.31 (ddd ~ q, 1H, H-4_{ax}'''), 1.14 (d, 1H, $J_{5''',6'''}$ = 6.3 Hz, H-6''').

Anal. Calcd for $C_{66}H_{76}O_{19}$ (1173.32): C, 67.56; H, 6.53. Found: C, 67.39; H, 6.55.

Data for **8**: Colorless foam, MS (FAB) *m/z* 1123.4 ([M + K]$^+$), 1107.5 ([M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 - 7.13 (m, 25H, aromat), 5.18, 5.17 (2 d, 2H, H-1, H-1'), 5.01, 4.81 (2 d, 2H, J_{gem} = 11.3 Hz, CH_2Ph), 4.99, 4.93 (2 d, 2H, J_{gem} = 10.8 Hz, CH_2Ph), 5.00 (d, 1H, $J_{1''',2'''}$ Å 3.6 Hz, H-1'''), 4.86 (br s, 1H), 4.72, 4.65 (2 d, 2H, J_{gem} = 11.9 Hz, CH_2Ph), 4.71, 4.67 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.54, 4.42 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 3.86 (ddq, 1H, $J_{4eq''',5'''}$ = 1.8 Hz, H-5'''), 3.74 (ddd, 1H,

$J_{2''',3'''}$ = 9.5 Hz, $J_{3''',4eq'''}$ = 4.8 Hz, $J_{3''',4ax'''}$ = 11.0 Hz, H-3'''), 1.84 (ddd, 1H, H-4_{eq}'''), 1.24 (ddd ~ q, 1H, H-4_{ax}'''), 1.13 (d, 1H, $J_{5''',6'''}$ = 6.2 Hz, H-6''').

Anal. Calcd for $C_{59}H_{72}O_{19}$ (1085.21): C, 65.30; H, 6.69. Found: C, 65.22; H, 6.73.

4,6-Dideoxy-α-D-*xylo*-hexopyranosyl- (1→4) -β-D-glucopyranosyl- (1→4) -α-D-glucopyranosyl α-D-Glucopyranoside (9). A soln of **7** (160 mg, 0.136 mmol) in ethanol (6 mL) and water (2 mL) was hydrogenated in the presence of 10 % palladium on charcoal (100 mg) at 1.1 bar and rt for 18 h. The reaction mixture was filtered over a pad of celite and washed with ethanol/ water. After addition of a few drops of triethylamine the filtrate was concentrated. The residue was chromatographed on silica gel using ethyl acetate/ methanol/ water 6:3:1 as eluent. The product fractions were concentrated and the residue was lyophilized to obtain pure **9** (83 mg, 96 %) as an amorphous colourless powder: $[\alpha]_D$ +154.5 ° (*c* 0.2, water); MS (FAB) *m/z* 673.0 ($[M + K]^+$), 657.0 ($[M + Na]^+$); ^{1}H NMR (D_2O, 400 MHz) δ 5.34 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.20, 5.19 (2 d, 2H, $J_{1,2}$ = 3.6 Hz, $J_{1',2'}$ = 3.9 Hz, H-1, H-1'), 4.54 (d, 1H, $J_{1'',2''}$ = 7.9 Hz, H-1''), 2.07 (ddd, 1H, H-4eq'''), 1.38 (ddd ~ q, 1H, H-4ax'''), 1.21 (d, 1H, $J_{5''',6'''}$ = 6.3 Hz, H-6''').

Anal. Calcd for $C_{24}H_{42}O_{19}$ (634.58): C, 45.43; H, 6.67. Found: C, 45.20; H, 6.71.

4,6-Di-*O*-acetyl-3-deoxy-2-*O*-pivaloyl-α-D-*ribo*-hexopyranosyl- (1→4) -1,6-di-*O*-acetyl-3-deoxy-2-*O*-pivaloyl-D-*ribo*-hexopyranose (11). A. A soln of compound **10** (0.20 g, 0.4 mmol) in a mixture of acetic anhydride/ acetic acid/ concd sulfuric acid 140:60:1 v/v/v (1.5 mL) was stirred for 3 h under argon. Then anhyd sodium acetate (0.1 g) was added, and stirring was continued for 45 min. The reaction mixture was poured into ice/water and extracted with ethyl acetate. Organic phases were washed with sodium bicarbonate soln and water, dried over sodium sulfate, and concentrated. The residue was purified by MPLC using toluene/ ethyl acetate 4:1 as eluent to afford pure **11** (170 mg, 71 %). B. A soln of crude **12** (3.0 g, 5.5 mmol) in a mixture of acetic anhydride/ acetic acid/ concd sulfuric acid 140:60:1 v/v/v (12 mL) was stirred for 3.5 h under argon. Work-up as under A. furnished **11** (3.6 g) quantitatively as a 1:1 mixture of anomers: colorless foam, MS (thermospray) *m/z* 664 ($[M + NH_4]^+$), 562 ($[(M - Piv + H) + NH_4]^+$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.24 (d, 0.5H, $J_{1,2}$ = 3.4 Hz, H-$1_{a\text{-}OAc}$), 5.72 (d, 0.5H, $J_{1,2}$ = 8.3 Hz, H-$1_{b\text{-}OAc}$), 5.16 (d, 0.5H, $J_{1',2'}$ = 3.6 Hz, H-$1'_{a\text{-}OAc}$), 5.08 (d, 0.5H, $J_{1',2'}$ = 3.6 Hz, H-$1'_{b\text{-}}$

$_{OAc}$), 2.14, 2.11, 2.10, 2.06 (4 s, 6H, $Ac_{a\text{-}OAc}$), 2.11, 2.10, 2.09, 2.05 (4 s, 6H, $Ac_{b\text{-}OAc}$), 1.20, 1.15 (2 s, 9H, $^tBu_{a\text{-}OAc}$), 1.17, 1.16 (2 s, 9H, $^tBu_{b\text{-}OAc}$).

Anal. Calcd for $C_{30}H_{46}O_{15}$ (646.68): C, 55.72; H, 7.17. Found: C, 55.58; H, 7.21.

4,6-Di-*O*-acetyl-3-deoxy-2-*O*-pivaloyl-α-D-*ribo*-hexopyranosyl- (1→4)-1,6-anhydro-3-deoxy-2-*O*-pivaloyl-β-D-*ribo*-hexopyranose (12). A soln of **10** (3.0 g, 5.99 mmol) in 80 % aqueous acetic acid was warmed for 1 h at 50 °C and concentrated. The residue was taken up in toluene and concentrated. This residue was acetylated with acetic anhydride (10 mL) in pyridine (20 mL) for 18 h at rt. The solvents were evaporated, and the residue was taken up in toluene and concentrated. An analytical sample was purified by MPLC using ethyl acetate/ hexane 1:1 as eluent to give pure **12**, $[\alpha]_D$ +44.0 ° (*c* 0.2, dioxane); MS (thermospray) *m/z* 562 ($[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 250 MHz) δ 5.41 (br s, 1H, H-1), 5.12 (d, 1H, $J_{1',2'}$ = 3.8 Hz, H-1'), 4.94 (m_c, 1H, H-2), 4.83 (ddd ~ dt, 1H, $J_{3'eq,4'}$ = 5.0 Hz, $J_{3'ax,4'}$ = 11.5 Hz, H-4'), 4.74 (dd, 1H, $J_{2',3'eq}$ = 5.0 Hz, $J_{2',3'ax}$ = 12.5 Hz, H-2'), 4.62 (ddd ~ dt, 1H, H-5), 4.49 (ddd ~ dt, 1H, $J_{4',5'}$ = 10.0 Hz, H-5'), 4.26 (dd, 1H, $J_{5',6a'}$ = 2.5 Hz, $J_{6a',6b'}$ = 11.5 Hz, H-6a'), 4.17 (dd ~ t, 1H, $J_{5',6b'}$ = 5.2 Hz, H-6b'), 3.78 (dd, 1H, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 8.0 Hz, H-6a), 3.76 (dd, 1H, $J_{5,6b}$ = 1.6 Hz, H-6b), 3.48 (br d, 1H, H-4), 2.35 - 2.14 (m, 3H, H-3a, H-3'eq, 3'ax), 1.80 (br d, 1H, $J_{3a,3b}$ = 16 Hz, H-3b), 2.07, 2.05 (2 s, 6H, Ac), 1.28, 1.16 (2 s, 18H, ^{t}Bu).

Anal. Calcd for $C_{26}H_{40}O_{12}$ (544.59): C, 57.34; H, 7.40. Found: C, 57.25; H, 7.44.

4,6-Di-*O*-acetyl-3-deoxy-2-*O*-pivaloyl-α-D-*ribo*-hexopyranosyl- (1→4) -6-*O*-acetyl-3-deoxy-2-*O*-pivaloyl-β-D-*ribo*-hexopyranosyl- (1→4) -2,3,6-di-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (13). A soln of crude glycosyl donor **11** (1.0 g of a 1:1 α/β-mixture, ca. 0.77 mmol of β-acetate) and acceptor **4** (683 mg, 0.77 mmol) in abs dichloromethane (5 mL) was stirred in the presence of molecular sieves (4 Å, ca. 1 g) at rt. A soln of trimethylsilyl triflate (29 µL, 0.155 mmol) in abs dichloromethane (0.5 mL) was added at -25 °C. The reaction mixture was allowed to reach rt and was stirred at rt for 2.5 h. Then it was poured into ice/aq sodium bicarbonate soln and extracted with ethyl acetate. The organic phases were dried over sodium sulfate, filtered, and concentrated. The residue was purified by MPLC using toluene/ ethyl acetate 9:2 as eluent to furnish tetrasaccharide **13** (740 mg, 65 %) as a colourless foam: $[\alpha]_D$ +86.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 1505.0 ($[M + K]^+$),

1498.5 ([M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 - 7.47 (m, 2H, aromat), 7.40 - 7.19 (m, 28H, aromat), 5.51 (s, 1H, CHPh), 2.06, 2.05, 1.93 (3 s, 9H, OAc), 1.16, 1.05 (2 s, 18H, ^{t}Bu).

Anal. Calcd for $C_{82}H_{98}O_{24}$ (1467.66): C, 67.11; H, 6.73. Found: C, 67.02; H, 6.73.

3-Deoxy-α-D-*ribo*-hexopyranosyl- (1→4) -3-deoxy-β-D-*ribo*-hexopyranosyl-(1→4)-2,3,6-di-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (14). A soln of tetrasaccharide **13** (550 mg, 0.375 mmol) was stirred in the presence of sodium methanolate (4 mL of 2.0 g Na/100 mL methanol) at rt. After 10 d at 12 °C the reaction mixture was neutralized with Amberlite IR 120 (H^+) and filtered. The filtrate and methanol washings were concentrated. The residue was chromatographed using ethyl acetate/ methanol/ water 92.5:5:2.5 as eluent to obtain pure **14** (348 mg, 79 %) as a syrup: $[\alpha]_D$ +120.0 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 1211.4 ([M + K]$^+$), 1195.5 ([M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz; 1D TOCSY) δ 7.51 - 7.49 (m, 2H, aromat), 7.41 - 7.26 (m, 28H, aromat), 5.56 (s, 1H, CHPh), 5.16, (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.15 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 4.99, 4.86 (2 d, 2H, J_{gem} = 11.1 Hz, CH_2Ph), 4.95, 4.91 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 4.83 (d, 1H, H-1'''), 4.82, 4.63 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.73, 4.69 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.60, 4.43 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.33 (d, 1H, $J_{1'',2''}$ = 7.6 Hz, H-1''), 4.27 (ddd ~ dt, 1H, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 9.7 Hz, H-5), 4.13 (dd ~ t, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 4.13 (dd, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6a), ~4.10 (ddd ~ br d, 1H, H-5'), 3.94 (m_c, 2H, H-3', H-4'), 3.83 (dd ~ br d, 1H, H-6a'''), 3.79 (ddd, 1H, $J_{3eq'',4''}$ = 4.9 Hz, $J_{3ax'',4''}$ = 11.1 Hz, H-4''), 3.70 (dddd ~ ddt, 1H, $J_{3eq'',4''}$ = 4.6 Hz, $J_{2''',3eq'''}$ = 11 Hz, H-2'''), ~3.67 (br dd, 1H, H-6a''), 3.66 (dd ~ t, 1H, H-4), (dd, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.59 (dd, 1H, $J_{5',6a'}$ Å 3 Hz, H-6a'), 3.58 (dd, 1H, $J_{2',3'}$ = 9 Hz, H-2'), 3.56, 3.55 (2 dd, 2H, H-6b'', H-6b'''), 3.47 (br, 1H, H-4'''?), 3.41 (ddd, 1H, H-5'''), 3.34 (dd, 1H, $J_{5',6b'}$ = 1.8 Hz, $J_{6a',6b'}$ = 11.3 Hz, H-6b'), 3.33 (dddd, 1H, $J_{2'',3eq''}$ = 4.9 Hz, $J_{2'',3ax''}$ = 10.5 Hz, H-2''), 3.12 (ddd ~ dt, 1H, $J_{4'',5''}$ = 9.5 Hz, H-5''), 2.67 (d, 1H, $J_{2'',2''\text{-OH}}$ = 2.4 Hz, 2''-OH), 2.41 (ddd ~ dt, 1H, $J_{3eq'',4''}$ Å 5 Hz, $J_{3eq'',3ax''}$ = 12.0 Hz, H-3_{eq}''), 2.31 (br, 1H, OH), 2.20 (ddd ~ dt, 1H, $J_{3eq''',3ax'''}$ = 11.6 Hz, H-3_{eq}'''), 2.01 (d, 1H, $J_{4''',4'''\text{-OH}}$ = 5.0 Hz, 4'''-OH), 1.79 (d, 1H, $J_{2''',2'''\text{-OH}}$ = 11.0 Hz, 2'''-OH), 1.57 (ddd ~ q, 1H, H-3_{ax}'''), 1.20 (ddd ~ q, 1H, H-3_{ax}'').

Anal. Calcd for $C_{66}H_{76}O_{19}$ (1173.31): C, 67.56; H, 6.53. Found: C, 65.49; H, 6.55.

3-Deoxy-α-D-*ribo*-hexopyranosyl- (1→4) -3-deoxy-β-D-*ribo*-hexopyranosyl-(1→4)-α-D-glucopyranosyl α-D-Glucopyranoside (15). A soln of **14** (290 mg, 0.247 mmol) in ethanol (6 mL) and water (2 mL) was hydrogenated in the presence of 10 % palladium on charcoal (100 mg) at 1.1 bar and rt for 2 d. The reaction mixture was filtered over a pad of celite and washed with ethanol/ water. After addition of a few drops of triethylamine the filtrate was concentrated. The residue was filtered over silica gel using ethyl acetate/ methanol/ water 6:3:1 as eluent. The product fractions were concentrated and the residue was lyophilized to obtain pure **15** (157 mg) quantitatively as an amorphous colourless powder: $[\alpha]_D$ +173.0 ° (*c* 0.2, water); MS (FAB) *m/z* 673.0 ([M + K]$^+$), 657.0 ([M + Na]$^+$); ^{1}H NMR (D_2O, 400 MHz) δ 5.19 (br s, 2H, H-1, H-1'), 5.00 (d, 1H, $J_{1''',2'''}$ = 2.4 Hz, H-1'''), 4.52 (d, 1H, $J_{1'',2''}$ = 7.8 Hz, H-1''), 2.63 (ddd ~ dt, 1H, H-3eq''), 2.18 (ddd ~ dt, 1H, H-3eq'''), 1.72 (ddd ~ q, 1H, H-3ax'''), 1.52 (ddd ~ q, 1H, H-3ax'').

Anal. Calcd for $C_{24}H_{42}O_{19}$ (634.58): C, 45.43; H, 6.67. Found: C, 45.22; H, 6.73.

2,3-Di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside (17) and **2,3-Di-*O*-benzyl-4,6-dideoxy-4,6-diiodo-α-D-galactopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside (18).** A soln of **16** (1.815 g, 2.6 mmol) in abs toluene (70 mL) was reacted with iodine (1.835 g, 7.23 mmol) in the presence of triphenylphosphine (2.032 g, 7.75 mmol) and imidazole (1.055 g, 15.5 mmol) at 70 °C for 2.5 h. The reaction mixture was diluted with ethyl acetate and washed with an aq soln of sodium thiosulfate, a saturated aq soln of sodium chloride and with water and was then dried over sodium sulfate and concentrated. The residue was separated by flash chromatography using toluene/ ethyl acetate 95:5 as eluent to give **18** (480 mg, 18 %) followed by pure **17** (1.555 g, 65 %).

Data for **17**: $[\alpha]_D$ +101.2 ° (*c* 0.3, chloroform); MS (FAB) *m/z* 945 ([M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.36 - 7.26 (m, 10H, aromat), 5.34 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.03, 4.74 (2 d, 2H, J_{gem} = 11.3 Hz, CH_2Ph), 4.80, 4.73 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 3.91(dd ~ t, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 3.62 (ddd, 1H, H-5), 3.61 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 3.40 (ddd ~ dt, 1H, $J_{4,4\text{-OH}}$ = 1.8 Hz, $J_{4,5}$ = 9.3 Hz, H-4), 3.24 (dd, 1H, $J_{5,6a}$ = 3.5 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6a), 3.18 (dd, 1H, $J_{5,6b}$ = 4.8 Hz, H-6b), 2.15 (d, 1H, 4-OH).

Anal. Calcd for $C_{40}H_{44}I_2O_9$ (922.59): C, 52.08; H, 4.81. Found: C, 51.92; H, 4.88.

Data for **18**: $[\alpha]_D$ +113.8 ° (*c* 0.16, chloroform); MS (FAB) *m/z* 1070.9 ([M + K]$^+$), 1054.9 ([M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 - 7.44 (m, 2H, aromat), 7.38 - 7.16 (m, 18H, aromat), 5.29 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.23 (d, 1H, $J_{1',2'}$ = 3.8 Hz, H-1'), 4.98, 4.72 (2 d, 2H, J_{gem} = 11.3 Hz, CH_2Ph), 4.87, 4.69 (2 d, 2H, J_{gem} = 11.6 Hz, CH_2Ph), 4.83 (dd, 1H, $J_{4',5'}$ = 1.7 Hz, H-4'), 4.81, 4.73 (2 d, 2H, J_{gem} = 11.9 Hz, CH_2Ph), 4.79, 4.60 (2 d, 2H, J_{gem} = 11.4 Hz, CH_2Ph), 3.92 (dd, 1H, $J_{2',3'}$ = 9.5 Hz, H-2'), 3.84 (dd ~ t, 1H, $J_{3,4}$ = 8.4 Hz, H-3), 3.63 (ddd, 1H, $J_{5,6a}$ = 2.8 Hz, $J_{5,6b}$ = 5.7 Hz, H-5), 3.58 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.46 (ddd ~ dt, 1H, H-5'), 3.37 (ddd ~ dt, 1H, $J_{4,4\text{-OH}}$ = 3.5 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 3.33 (dd, 1H, $J_{3',4'}$ = 4.0 Hz, H-3'), 3.24 (dd, 1H, $J_{5',6a'}$ = 6.5 Hz, $J_{6a',6b'}$ = 10.0 Hz, H-6a'), 3.22 (dd, 1H, $J_{6a,6b}$ = 10.8 Hz, H-6a), 3.15 (dd, 1H, H-6b), 3.03 (dd, 1H, $J_{5',6b'}$ = 7.5 Hz, H-6b'), 2.02 (d, 1H, 4-OH).

Anal. Calcd for $C_{40}H_{43}I_3O_8$ (1032.45): C, 46.53; H, 4.20. Found: C, 46.82; H, 4.24.

2,3-Di-*O*-benzyl-6-deoxy-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (19). A soln of **17** (1.444 g, 1.565 mmol) in ethyl acetate (30 mL) and diethylamine (1 mL) was hydrogenated in the presence of 10% palladium on charcoal (300 mg) for 24 h at rt. The reaction mixture was filtered over a pad of celite and extracted with aq sodium thiosulfate soln and water. The organic phases were dried over sodium sulfate and concentrated. The residue was purified by flash chromatography using chloroform/ acetone 99:1 as eluent. The chromatographically pure material (980 mg, 93 %) was crystallized from dichloromethane/ hexane to yield crystalline **19** (807 mg, 77 %): mp 136 -136 °C; $[\alpha]_D$ +111.0 ° (*c* 0.32, chloroform); MS (thermospray) *m/z* 688 ([M + NH_4]$^+$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.38 - 7.29 (m, 10H, aromat), 5.16 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.05, 4.74 (2 d, 2H, J_{gem} = 11.4 Hz, CH_2Ph), 4.74, 4.66 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.09 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.82 (dd ~ t, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 3.56 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 3.20 (ddd ~ dt, 1H, $J_{4,4\text{-OH}}$ = 2.7 Hz, H-4), 2.18 (d, 1H, 4-OH), 1.15 (d, 3H, H-6).

Anal. Calcd for $C_{40}H_{46}O_9$ (670.80): C, 71.62; H, 6.91; Found: C, 71.43; H, 6.93.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (**21**). To a soln of glycosyl acceptor **19** (304 mg, 0.453 mmol) and acetobromomaltose **20** (380 mg, 0.544 mmol) in abs dichloromethane (5 mL) was added tetramethylurea (98 μL, 0.816 mmol) and silver triflate (141 mg, 0.549 mmol) at -78 °C. The reaction mixture was stirred at rt for 1 d and more **20** (95 mg, 0.136 mmol) and silver triflate (35 mg, 0.137 mmol) were added. After 1 d the reaction mixture was filtered through a pad of filter aid directly into an aq sodium bicarbonate soln. The filtrate and the dichloromethane washings were combined and washed twice with aq sodium bicarbonate soln. The organic phases were dried over magnesium sulfate and concentrated. The residue was separated by flash chromatography using chloroform/ethyl acetate 9:1 as eluent to furnish unreacted starting material **19** (94 mg, 31 %), the main product **21** (265 mg, 46 %) and the symmetrical hexasaccharide 2,3-di-*O*-benzyl-6-deoxy-4-*O*-(hepta-*O*-acetyl-β-maltosyl)-α-D-glucopyranosyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-(hepta-*O*-acetyl-β-maltosyl)-α-D-glucopyranoside (**22**, 70 mg, 8%).

Data for **21**: $[\alpha]_D$ +95.3 ° (*c* 0.13, chloroform); MS (FAB) *m/z* 1327.2 ($[M + K]^+$), 1311.1 ($[M + Na]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz; 1D TOCSY) δ 7.39 - 7.17 (m, 20H, aromat), 5.36 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1'''), 5.30 (dd ~ t, 1H, $J_{3''',4'''}$ = 9.5 Hz, H-3'''), 5.18 (dd ~ t, 1H, $J_{3'',4''}$ = 8.8 Hz, H-3''), 5.09 (d, 1H, H-1), 5.08 (d, 1H, H-1'), 5.07, 4.79 (2 d, 2H, J_{gem} = 11.4 Hz, CH_2Ph), 5.04 (dd ~ t, 1H, $J_{4''',5'''}$ = 10.1 Hz, H-4'''), 5.01, 4.97 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.89 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.83 (dd, 1H, $J_{2''',3'''}$ = 10.5 Hz, H-2'''), 4.81 (dd, 1H, $J_{2'',3''}$ = 9.4 Hz, H-2''), 4.69, 4.63 (2 d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.62, 4.57 (2 d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.21 (dd , 1H, $J_{5''',6a'''}$ = 3.5 Hz, $J_{6a''',6b'''}$ = 12.6 Hz, H-6a'''), 4.12 (dq, 1H, $J_{4',5'}$ = 9.6 Hz, $J_{5',6a'}$ = 6.0 Hz, H-5'), 4.08 (dd, 1H, $J_{5'',6a''}$ = 2.8 Hz, $J_{6a'',6b''}$ = 12.2 Hz, H-6a''), 4.05 (dq, 1H, $J_{5,6}$ = 6.1 Hz, H-5), 3.97 (2 dd, 1H, H-6b'', H-6b'''), 3.96 (dd ~ t, 1H, H-4''), 3.93 (dd ~ t, 1H, H-3'), 3.82 (ddd, 1H, $J_{5''',6b'''}$ = 2.3 Hz, H-5'''), 3.81 (dd ~ t, 1H, $J_{3,4}$ = 9.0 Hz, H-3), 3.54 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.51 (dd, 1H, $J_{1',2'}$ = 3.7 Hz, $J_{2',3'}$ = 9.5 Hz, H-2'), 3.39 (ddd ~ dt, 1H, $J_{4'',5''}$ = 9.8 Hz, $J_{5'',6b''}$ = 3.4 Hz, H-5''), 3.34 (dd ~ t, 1H, $J_{3',4'}$ = 9.0 Hz, H-4'), 3.17 (ddd ~ dt, 1H, $J_{4,4\text{-OH}}$ = 2.9 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 2.12

(d, 1H, 4-OH), 2.07, 2.05, 2.04, 2.02, 2.00, 1.98, 1.89 (7 s, 21H, OAc), 1.14 (d, 3H, H-6), 1.12 (d, 3H, H-6').

Anal. Calcd for $C_{66}H_{80}O_{26}$ (1289.34): C, 61.48; H, 6.25; Found: C, 61.39; H, 6.33.

Data for **22**: MS (FAB) *m/z* 1945.7 ($[M + K]^+$), 1929.7 ($[M + Na]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 - 7.15 (m, 10H, aromat), 5.35 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1'''), 5.30 (dd ~ t, 1H, $J_{3''',4'''}$ = 9.5 Hz, H-3'''), 5.17 (dd ~ t, 1H, $J_{3'',4''}$ = 9.0 Hz, H-3''), 5.05, 4.99 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 5.04 (dd ~ t, 1H, H-4'''), 5.03 (d, 1H, H-1'), 4.87 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.83 (dd, 1H, $J_{2''',3'''}$ = 10.5 Hz, H-2'''), 4.80 (dd, 1H, $J_{2'',3''}$ = 9.5 Hz, H-2''), 4.59, 4.54 (2 d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.21 (dd , 1H, $J_{5''',6a'''}$ = 3.5 Hz, $J_{6a''',6b'''}$ = 12.6 Hz, H-6a'''), 4.08 (dq, 1H, H-5'), 4.07 (dd, 1H, $J_{5'',6a''}$ = 2.8 Hz, $J_{6a'',6b''}$ = 12.5 Hz, H-6a''), 3.98 (dd, 1H, H-6b''), 3.96 (dd, 1H, H-6b'''), 3.96, 3.93 (2 dd ~ t, 2H, H-3', H-4''), 3.82 (ddd, 1H, $J_{4''',5'''}$ = 10.0 Hz, $J_{5''',6b'''}$ = 2.3 Hz, H-5'''), 3.48 (dd, 1H, $J_{1',2'}$ = 3.7 Hz, $J_{2',3'}$ = 9.6 Hz, H-2'), 3.39 (ddd ~ dt, 1H, $J_{4'',5''}$ = 9.6 Hz, $J_{5'',6b''}$ = 3.2 Hz, H-5''), 3.32 (dd ~ t, 1H, H-4'), 2.07, 2.03, 2.02, 1.99 (4s, 12H, OAc), 1.98 (s, 6H, OAc), 1.87 (s, 3H, OAc), 1.12 (d, 3H, $J_{5',6a'}$ = 6.2 Hz, H-6').

Anal. Calcd for $C_{92}H_{114}O_{43}$ (1907.88): C, 57.92; H, 6.02; Found: C, 57.80; H, 6.07.

α-D-Glucopyranosyl-(1→4)-β-D-glucopyranosyl- (1→4) -2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (**23**). To a soln of the protected tetrasaccharide **21** (205 mg, 0.159 mmol) in MeOH (7 mL) was added a catalytic amount of sodium (~5 mg). After 40 min the reaction mixture was neutralized by addition of acidic ion exchange resin (IR 120 H^+) and filtered. The filtrate was concentrated and purified by flash chromatography using chloroform/ 12 % methanol as eluent to furnish pure **23** (158 mg) quantitatively as a colourless syrup, MS (FAB) *m/z* 1033.4 ($[M + K]^+$), 1017.5 ($[M + Na]^+$).

α-D-Glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-6-deoxy-α-D-glucopyranosyl 6-Deoxy-α-D-glucopyranoside (**24**). A soln of **23** (140 mg, 0.122 mmol) in ethanol (12 mL) and water (3 mL) was hydrogenated in the presence of 10 % palladium on charcoal (60 mg) at 1.1 bar and rt for 2 h. The reaction mixture was filtered over a pad of celite and washed with ethanol/ water. After addition of a few drops of triethylamine the filtrate was concentrated. The residue was filtered over silica gel using ethanol/ water

1:1 as eluent. The product fractions were concentrated, and the residue was lyophilized to obtain pure **24** (89 mg) quantitatively as an amorphous colourless powder: $[\alpha]_D$ +160.5 ° (*c* 0.2, water); MS (FAB) *m/z* 673.0 ($[M + K]^+$), 657.0 ($[M + Na]^+$); ^{1}H NMR (D_2O, 400 MHz) δ 5.42 (d, 1H, $J_{1''',2'''}$ = 3.8 Hz, H-1'''), 5.10 (d, 2H, J = 3.9 Hz, H-1, H-1'), 4.58 (d, 1H, $J_{1'',2''}$ = 7.9 Hz, H-1''), 1.34, 1.27 (2 d, 6H, $J_{5,6a} = J_{5',6a'}$ = 6.3 Hz, H-6, H-6').

Anal. Calcd for $C_{24}H_{42}O_{19}$ (634.58): C, 45.43; H, 6.67. Found: C, 45.66; H, 6.75.

2-*O*-Benzyl-4,6-*O*-(*R*)-benzylidene-3-*O*-(imidazol-1-yl-thiocarbonyl)-α-D-glucopyranosyl 2-*O*-Benzyl-4,6-*O*-(*R*)-benzylidene-3-*O*-(imidazol-1-yl-thiocarbonyl)-α-D-glucopyranoside (26). To a solution of **25** (13.96 g, 20.0 mmol) in acetonitrile (450 mL) were added 1,1'-thiocarbonyldiimidazole (10.7 g, 60.0 mmol) and 4-dimethylaminopyridine (0.12 g, 1.0 mmol) at rt. The reaction mixture was refluxed for 65 h, then concentrated under reduced pressure. The residue was chromatographed over silica gel using hexane/ acetone 2:1 and 1:1 as eluents to afford after precipitation from acetone/ether **26** (17.8 g, 97 %) as a beige solid: $[\alpha]_D$ +119.2 ° (*c* 0.5, chloroform); MS (FAB) *m/z* 919.5 ($[M+H]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (~s, 1H, Im), 7.59 (dd ~ t, 1H, Im), 7.38 - 7.36 (m, 2H, aromat), 7.33 - 7.31 (m, 3H, aromat), 7.26 - 7.22 (m, 5H, aromat), 7.03 (dd ~ t, 1H, Im), 6.55 (dd ~ t, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 5.45 (s, 1H, CHPh), 5.35 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.70, 4.53 (2 d, 2H, J_{gem} = 12.3 Hz, CH_2Ph), 4.39 (ddd ~ dt, 1H, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 10.3 Hz, H-5), 4.16 (dd, 1H, $J_{6a,6b}$ = 10.3 Hz, H-6a), 3.86 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 3.77 (dd ~ t, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.72 (d, 1H, H-6).

Anal. Calcd for $C_{48}H_{46}N_4O_{11}S_2$ (919.02): C, 62.73; H, 5.05; N, 6.10; S, 6.98. Found: C, 62.52; H, 5.35; N, 6.05; S, 6.52.

2-*O*-Benzyl-4,6-*O*-(*R*)-benzylidene-3-deoxy-α-D-*ribo*-hexopyranosyl 2-*O*-Benzyl-4,6-*O*-(*R*)-benzylidene-3-deoxy-α-D-*ribo*-hexopyranoside (27). To a soln of **26** (10.0 g, 11.0 mmol) in abs toluene (950 mL) was added α,α'-azodiisobutyronitrile (2.5 g, 15.2 mmol) and then, at reflux temperature, a soln of tributyltin hydride (25 mL, 104 mmol) in toluene (50 mL) dropwise within 10 min. After reflux for 16 h the reaction mixture was concentrated. The residue was purified over silica gel (1 kg) using toluene/ ethyl acetate 19:1 and 9:1 as eluents to produce after crystallization from ether/hexane pure **27** (4.84 g, 66 %) as a colourless solid: mp 130 °C; $[\alpha]_D$ +83.0 ° (*c* 0.4,

chloroform); MS (FAB) *m/z* 705 ([M+K]$^+$), 689 ([M+Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 - 7.44 (m, 2H, aromat), 7.38 - 7.24 (m, 8H, aromat), 5.48 (s, 1H, CHPh), 5.22 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 4.64 (s, 2H, CH_2Ph), 4.20 (ddd ~ dt, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6a}$ = 5.0 Hz, H-5), 4.12 (dd, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6a), 3.69 (ddd, 1H, $J_{2,3eq}$ = 4.5 Hz, $J_{2,3ax}$ = 11.8 Hz, H-2), 3.63 (dd, 1H, $J_{5,6b}$ = 10.1 Hz, H-6b), 3.53 (ddd, 1H, $J_{3eq,4}$ = 4.1 Hz, $J_{3ax,4}$ = 11.6 Hz, H-4), 2.33 (ddd ~ dt, 1H, H-3eq), 2.19 (ddd ~ q, 1H, $J_{3eq,3ax}$ = 11.4 Hz, H-3ax).

Anal. Calcd for $C_{40}H_{42}O_9$ (666.74): C, 72.06; H, 6.35. Found: C, 72.40; H, 6.66.

2,6-Di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranosyl 2-*O*-Benzyl-4,6-*O*-(*R*)-benzylidene-3-deoxy-α-D-*ribo*-hexopyranoside (28) and **2,6-Di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranosyl 2,6-Di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranoside (29)**. To a soln of **27** (4.64 g, 7.0 mmol) in abs tetrahydrofuran (105 mL) were added pulverized molecular sieves (3Å, 6.2 g) at 0 °C followed by sodium cyanoborohydride (3.55 g, 56.5 mmol) and a few crystals of methyl orange. The reaction mixture was stirred for 30 min, and hydrogen chloride in diethyl ether (30 mL of a 1.82 M soln, 54.6 mmol) was added dropwise over 2 h at 0 °C to the milky reaction mixture. After stirring for 3 h at 0 °C, the orange-red reaction mixture was poured into sodium bicarbonate soln, and tetrahydrofuran was evaporated under reduced pressure. The aqueous residue was extracted twice with ethyl acetate. The organic phases were washed with ice water and brine, dried over magnesium sulfate, and concentrated. The residue was chromatographed on silica gel (200 g) using ethyl acetate/ toluene 1:9 containing 1 % methanol as eluent to give starting material **27** (930 mg, 20 %) followed by **28** (1.48 g, 32 %) and **29** (1.20 g, 26 %) as colourless syrups.

Data for **28**: $[\alpha]_D$ +88.8 ° (*c* 0.4, chloroform); MS (ionspray) *m/z* 691 ([M + Na]$^+$), 686 ([M + NH_4]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 - 7.44 (m, 2H, aromat), 7.37 - 7.25 (m, 18H, aromat), 5.47 (s, 1H, CHPh), 5.23, 5.21 (2 d, 2H, $J_{1,2}$ = 3.3 and 3.2 Hz, H-1, H-1'), 4.61, 4.58 (2 s, 4H, CH_2Ph), 4.49, 4.42 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.18 (ddd ~ dt, 1H, $J_{5,6a}$ = 5.0 Hz, H-5), 4.10 (dd, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6a), 4.02 (ddd ~ dt, 1H, $J_{4',5'}$ = 9.4 Hz, H-5'), 3.70 - 3.48 (m, 7H), 2.33 - 2.24 (m, 3H, H-3eq, H-3eq', 4'-OH), 2.20, 1.99 (2 ddd ~ q, 2H, H-3ax, H-3ax').

Anal. Calcd for $C_{40}H_{44}O_9$ (668.76): C, 71.84; H, 6.63. Found: C, 71.58; H, 6.93.

Data for **29**: $[\alpha]_D$ +87.8 ° (*c* 0.5, chloroform); MS (ionspray) *m/z* 693 ($[M+Na]^+$), 688 ($[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.34 - 7.21 (m, 10H, aromat), 5.20 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 4.59, 4.53 (2 d, 2H, J_{gem} = 12.2 Hz, C-2-OCH_2Ph), 4.48, 4.41 (2 d, 2H, J_{gem} = 12.0 Hz, C-6-OCH_2Ph), 4.00 (ddd ~ dt, 1H, $J_{4,5}$ = 9.5 Hz, H-5), 3.65 (ddd, 1H, $J_{3eq,4}$ = 4.6 Hz, $J_{3ax,4}$ = 11.2 Hz, H-4), 3.56 (ddd, 1H, $J_{2,3eq}$ = 4.3 Hz, H-2), 3.54 (dd, 1H, $J_{5,6a}$ = 4.5 Hz, H-6a), 3.49 (d, 1H, $J_{5,6b}$ = 5.0 Hz, $J_{6a,6b}$ = 10.1 Hz, H-6b), 2.35 (br s, 1H, 4-OH), 2.23 (ddd ~ dt, 1H, $J_{3eq,3ax}$ = 11.4 Hz, H-3eq), 1.98 (ddd ~ q, 1H, $J_{2,3ax}$ = 12.0 Hz, H-3ax).

Anal. Calcd for $C_{40}H_{46}O_9$ (670.77): C, 71.62; H, 6.91. Found: C, 71.92; H, 6.76.

2,3,4,6- Tetra-*O*-acetyl-α-D-glucopyranosyl- (1→4) - *O* - (2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,6-di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranosyl 2-*O*-Benzyl-4,6-*O*-(*R*)-benzylidene-α-D-*ribo*-hexopyranoside (30). To a soln of glycosyl acceptor **28** (1.48 g, 2.21 mmol) and acetobromomaltose **20** (3.09 g, 4.4 mmol) in abs dichloromethane (15 mL) were added tetramethylurea (0.80 mL, 6.62 mmol) and silver triflate (1.13 g, 4.4 mmol) at -10 °C. The reaction mixture was stirred at rt for 18 h and then filtered through a pad of filter aid. The filtrate and dichloromethane washings were combined and washed twice with aq sodium bicarbonate soln. The organic phases were dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel using ethyl acetate/ hexane 1:2 and 1:1 as eluents to furnish **30** (1.30 g, 46 %) as a colorless foam: $[\alpha]_D$ +92.0 ° (*c* 0.5, chloroform); MS (FAB) *m/z* 1325 ($[M + K]^+$), 1309 ($[M + Na]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47 - 7.44 (m, 2H, aromat), 7.42 - 7.23 (m, 18H, aromat), 5.46 (s, 1H, CHPh), 5.39 (d, 1H, H-1'''), 5.38 (dd ~ t, 1H, $J_{3''',4'''}$ = 9.6 Hz, H-3'''), 5.23, 5.22 (2 d, 2H, H-1, H-1'), 5.11 (dd ~ t, 1H, $J_{3'',4''}$ = 8.8 Hz, H-3''), 5.06 (dd ~ t, 1H, $J_{4''',5'''}$ = 10.0 Hz, H-4'''), 4.87 (dd, 1H, $J_{1''',2'''}$ = 4.0 Hz, $J_{2''',3'''}$ = 10.4 Hz, H-2'''), 4.74 (dd, 1H, $J_{2'',3''}$ = 9.3 Hz, H-2''), 4.62, 4.37 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.62, 4.56 (2 s, 4H, CH_2Ph), 4.47 (dd, 1H, $J_{5'',6a''}$ = 2.9 Hz, $J_{6a'',6b''}$ = 12.0 Hz, H-6a''), 4.44 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.27 (dd , 1H, $J_{5''',6a'''}$ = 4.0 Hz, $J_{6a''',6b'''}$ = 12.4 Hz, H-6a'''), 4.18 (ddd ~ dt, 1H, $J_{5,6a}$ = 5.0 Hz, H-5), 4.16 (dd, 1H, $J_{5'',6b''}$ = 4.5 Hz, H-6b''), 4.07 (dd, 1H, $J_{6a,6b}$ = 10.5 Hz, H-6a), 4.05 (dd , 1H, $J_{5''',6b'''}$ = 2.0 Hz, H-6b'''), 3.99 (ddd ~ dt, 1H, H-5'), ~3.95 (ddd, 1H, H-5'''), 3.94 (dd ~ t, 1H, $J_{4'',5''}$ = 9.7 Hz, H-4''), 3.73 (ddd, 1H, $J_{3'eq,4'}$ = 4.5 Hz, $J_{4',5'}$ = 10.0 Hz, $J_{3'ax,4'}$ = 11.5

Hz, H-4'), 3.66 - 3.57 (m, 3H), 3.50 (ddd, 1H, $J_{3eq,4}$ = 4.0 Hz, $J_{4,5}$ = 9.4 Hz, $J_{3ax,4}$ = 11.5 Hz, H-4), 3.47 - 3.43 (m, 2H), 3.39 (dd, 1H, $J_{5',6b'}$ = 1.7 Hz, $J_{6a',6b'}$ = 10.6 Hz, H-6b'), 2.35, 2.31 (2 ddd ~ dt, 2H, H-3'eq, H-3eq), 2.16, 2.07 (2 ddd ~ q, 2H, H-3'ax, H-3ax), 2.11 (2 s, 6H, OAc), 2.09, 2.03, 2.01, 1.98, 1.77 (5 s, 15H, OAc).

Anal. Calcd for $C_{66}H_{78}O_{26}$ (1287.28): C, 61.58; H, 6.11. Found: C, 61.76; H, 6.44.

α-D-Glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-2,6-di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranosyl 2-*O*-Benzyl-4,6-*O*-(*R*)-benzylidene-α-D-*ribo*-hexopyranoside (31). To a soln of **30** (1.21 g, 0.94 mmol) in dimethoxyethane (2.5 mL) and methanol (12 mL) was added a soln of sodium methanolate (2.5 mL of 2.0 g Na/ 100 mL methanol) at rt. The reaction mixture was kept for 5 h at rt, then was neutralized with Amberlite IR 120 (H^+) and filtered. After addition of a few drops of triethylamine, the filtrate and methanol washings were concentrated. The residue was chromatographed on silica gel using ethyl acetate/ methanol/ water 17:2:1 and 8:1:1 as eluents to obtain **31** as colorless crystals, which were recrystallized from methanol/ether (0.595 g, 64 %): mp 219 °C; $[\alpha]_D$ +101.5 ° (*c* 0.2, chloroform); MS (FAB) *m/z* 1031 ($[M + K]^+$), 1015 ($[M + Na]^+$); ^1H NMR [$(CD_3)_2SO$, 400 MHz] δ 7.38 - 7.28 (m, 20H, aromat), 5.56 (s, 1H, CHPh), 5.52 (d, 1H, J = 3.0 Hz, OH), 5.46 (d, 1H, J = 6.0 Hz, OH), 5.23 (d, 1H, J = 5.0 Hz, OH), 5.21, 5.20 (2 d, 2H, H-1, H-1'), 5.01 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1'''), 4.92 (d, 1H, J = 5.5 Hz, OH), 4.89 (d, 1H, J = 5.0 Hz, OH), 4.60, 4.58 (2 s, 4H, CH_2Ph), 4.52, 4.49 (2 dd ~ t, 2H, J = 5.4 Hz, 6-OH, 6'-OH), 4.48, 4.44 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.26 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 2.40, 2.19 (2 ddd ~ dt, 2H, H-3'eq, H-3eq), 1.87, 1.85 (2 ddd ~ q, 2H, H-3'ax, H-3ax).

Anal. Calcd for $C_{52}H_{64}O_{19}$ (993.03): C, 62.89; H, 6.50. Found: C, 62.97; H, 6.40.

α-D-Glucopyranosyl- (1→4) - *O*-β-D-glucopyranosyl- (1→4) - 3-deoxy-α-D-*ribo*-hexopyranosyl 3-Deoxy-α-D-*ribo*-hexopyranoside (32). A soln of **31** (550 mg, 0.55 mmol) in ethanol (15 mL) and water (5 mL) was hydrogenated in the presence of 10% palladium on charcoal (300 mg) at 1.1 bar and rt for 6 h. The reaction mixture was filtered over a pad of celite and washed with ethanol/ water 1:1. After addition of a few drops of triethylamine, the filtrate was concentrated. The aqueous residue was lyophilized to obtain **32** (355 mg) quantitatively as an amorphous colourless powder:

$[\alpha]_D$ +144.0 ° (*c* 0.1, water); MS (ionspray) *m/z* 657 ($[M + Na]^+$), 652 ($[M + NH_4]^+$); ^1H NMR (D_2O, 400 MHz) δ 5.41 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1'''), 5.13 (d, 2H, J = 3.3 Hz, H-1, H-1'), 4.57 (d, 1H, $J_{1'',2''}$ = 7.9 Hz, H-1''), 2.43, 2.22 (2 ddd ~ dt, 2H, H-3eq, H-3'eq), 2.03, 1.92 (ddd ~ q and m_c, 2H, H-3ax, H-3'ax).

Anal. Calcd for $C_{24}H_{42}O_{19}$ (634.58): C, 45.43; H, 6.67. Found: C, 45.21; H, 6.45.

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