# The Substrate Specificity of the Enzyme Amyloglucosidase (AMG). Part III. Synthesis of Epimers and Mono-*O*-methyl Ethers of Methyl β-Maltoside

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The synthesis of 3,4′ and 6′ mono-*O*-methyl ethers of methyl β-maltoside is described using suitably protected alcohols followed by methylation with diazomethane catalyzed by boron trifluoride. Similarly, the 3,4′ and 2′ epimers **4a**, **7a** and **9** of methyl β-maltoside have been prepared by chemical modification of maltose and lactosan derivatives for compounds **4a** and **7a**, respectively, whereas compound **9** has been prepared in a glycoside synthesis promoted by silver triflate and tetramethylurea.

All compounds have been tested and found not to be substrates towards the enzyme amyloglucosidase.

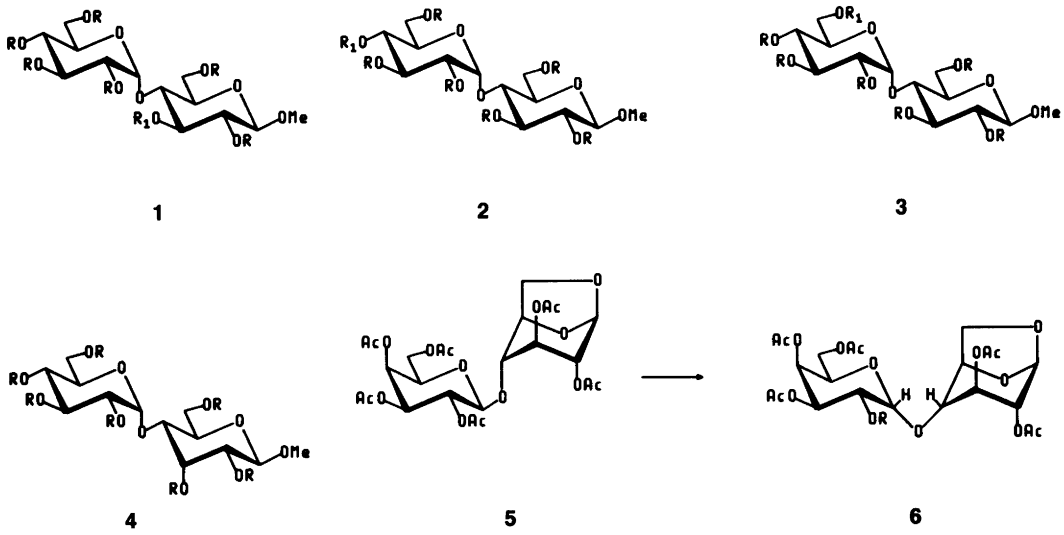
We have recently[1–3] discussed the substrate specificity of the enzyme amyloglucosidase (AMG) towards modified deoxy maltose derivatives[1,2] and 6-substituted maltose derivatives.[3] In this paper we report the synthesis and substrate activity of three *O*-methyl ethers of maltose and three epimeric α-1,4-linked oligosaccharides related to maltose. Previous results have shown[1,2] that three key polar hydroxy groups (3, 4′ and 6′) are essential for substrate activity of the parent synthetic compounds. It would therefore be of interest to study the behaviour of the corresponding three *O*-methyl ethers, which can act towards AMG as acceptors for hydrogen bonding but not as donors.

The 3-*O*-methyl maltoside derivative **1a** was prepared from the known[4] methyl 2,6,2′,3′,4′,6′-hexa-*O*-acetyl-β-maltoside by methylation with diazomethane in dichloromethane using boron trifluoride as catalyst.[5] The *O*-methyl compound **1b** was formed in 30 % yield, and 32 % of the starting material was recovered. Deprotection with sodium methoxide in methanol gave **1a** in 95 % yield. Similar methylation of methyl 2,3,6,2′,3′,6′-hexa-*O*-benzyl-β-maltoside (**2d**)[1] gave the 4′-*O*-methyl ether (**2e**) in 50 % yield. This compound was converted into **2a** in 82 % yield by catalytic hydrogenation of the *O*-benzyl groups. Finally, the 6-*O*-methyl ether was prepared analogously by methylation of the known[6] methyl 2,3,6,2′,3′,4′-hexa-*O*-acetyl-β-maltoside (**3c**) in 75 % yield. The unprotected compound was isolated in 71 % yield after deprotection. All the compounds were characterized by their $^1$H and $^{13}$C NMR parameters, which in all cases were consistent with the proposed structures.

None of the *O*-methyl ethers **1a**, **2a** or **3a** were substrates for the enzyme under the experimental conditions described previously.[1,3]

In order to further study the substrate specificity, it would be of interest to synthesize the corresponding 3,2′ and 4′ epimeric structures. The 3-epimeric compounds was prepared as described by Hough and Richardson,[4] and was de -*O*-acetylated to give the unprotected compound **4** in 90 % yield.

The preparation of the 4′-epimer was the result of an unsuccessful attempt to photobrominate hexa-*O*-acetyl-1,6-anhydrolactosan (**5**) as described by Ferrier and Fourneaux.[7] The compound decomposed partly during the reaction, but it was possible to isolate 20 % of a compound



1 2 3 4 5 6

**6** which had been anomerized at the non-reducing unit, together with 30 % of starting material. Repeated experiments showed the reaction to be reproducible. The α-linked 1,6-anhydro compound **6** was converted into the β-methyl glycoside **7b** which was characterized and de-*O*-acetylated to give **7a**.

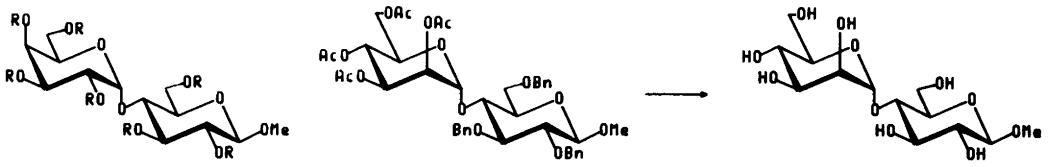
The 2′ epimeric compound **9** was synthesized from methyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside and acetobromomannose using silver triflate and tetramethylurea as promoter. The disaccharide **8** was isolated in 25 % yield and characterized by its $^1$H and $^{13}$C NMR spectral data. Removal of the protecting groups to give **9** was accomplished in 65 % yield.

None of the epimeric compounds **4a**, **7a** or **9** were substrates for the enzyme AMG under the experimental conditions described previously.[1,3] These results are all in complete agreement with the proposal made by Lemieux,[10] that key polar groups are essential for recognition of substrates for the enzyme.

## Experimental

Melting points are uncorrected. Optical rotations were measured on a Perkin Elmer 241 polarimeter. NMR spectra were recorded on Bruker WH-90, HX-270 and AM-500 NMR instruments. The spectra of protected compounds were measured in $CDCl_3$, while those of unprotected compounds were measured in $D_2O$ relative to the internal references: acetone (δ 2.22) for $^1$H NMR spectra and dioxane (67.4 ppm) for $^{13}$C NMR spectra. Microanalyses were performed by Novo Microanalytical Laboratory, Copenhagen, Denmark. TLC was performed on silica gel-coated plates (Merck F-254). Preparative TLC was performed on 20×40 cm plates coated with 1 mm of silica gel. The enzyme amyloglucosidase, AMG (EC. 3.2.1.3), was a gift from Novo A/S, Denmark.

*Methyl 2,6,2′,3′,4′,6′-hexa-O-acetyl-3-O-methyl-β-maltoside* (**1b**). To a solution of methyl 2,6,2′,3′,4′,6′-hexa-*O*-acetyl-β-maltoside[4] (**1c**) (200 mg, 0.33 mmol) in dichloromethane (10 ml) was added 2 drops of boron trifluoride etherate and an excess of diazomethane in dry ether, and the solution was left for 5 min at room temperature. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was purified by preparative TLC using diethyl ether as eluent. The main fraction (62 mg, 30 %) was crystallized from ethanol to give **1b** with m.p. 79–80 °C and $[\alpha]_D^{23}$ + 22.9° (*c* 0.5, chloroform). Anal. $C_{26}H_{38}O_{17}$: C, H. $^1$H NMR (270 MHz, $CDCl_3$): δ 5.48 (H-1′); 4.91 (H-2′); 5.42 (H-3′); 5.19 (H-4′); 4.04 (H-5′); 4.05 (H-6a′); 4.25 (H-6b′); 4.31 (H-1); 4.92 (H-2); 3.50 (H-3); 3.78 (H-4); 3.59 (H-5); 4.49 (H-6a); 4.22 (H-6b); 3.45, 3.36 (OMe). $^{13}$C NMR (67.89 MHz, $CDCl_3$): 96.6



**7** **8** **9**

**a** : R = H, $R_1$ = Me
**b** : R = Ac, $R_1$ = Me
**c** : R = Ac, $R_1$ = H
**d** : R = Bn, $R_1$ = H
**e** : R = Bn, $R_1$ = Me

ppm (C-1′); 70.5 (C-2′); 69.6 (C-3′); 68.3 (C-4′); 68.4 (C-5′); 61.9 (C-6′); 101.5 (C-1); 72.1 (C-2); 83.5 (C-3); 75.1 (C-4); 72.5 (C-5); 63.2 (C-6); 56.7, 58.0 (OMe).

Unchanged starting material (**1c**) was also isolated (65 mg, 0.11 mmol, 32 %), raising the effective yield of **1b** to 62 %.

*Methyl 3-O-methyl-β-maltoside* (**1a**). De-*O*-acetylation of **1b** (25 mg, 0.040 mmol) with 0.1 % sodium methoxide in methanol (5 ml) yielded **1b** (14 mg, 95 %) as a syrup. $^1$H NMR (270 MHz, $D_2O$): δ 5.34 (H-1′); 3.50 (H-2′); 3.63 (H-3′); 3.39 (H-4′); 3.89 (H-6a′); 3.72 (H-6b′); 4.35 (H-1); 3.37 (H-2); 3.69 (H-4); 3.76 (H-6a); 3.73 (H-6b); 3.53, 3.52 (OMe). $^{13}$C NMR (125.7 MHz, $D_2O$): 99.2 ppm (C-1′); 72.1 (C-2′); 73.5 (C-3′); 70.2 (C-4′); 73.5 (C-5′); 61.6 (C-6′); 103.8 (C-1); 73.0, 74.0, 75.3 (C-2,4,5); 87.0 (C-3); 61.2 (C-6); 58.0 (OMe); 60.2 (3-OMe).

*Methyl 2,3,6,2′,3′,6′-hexa-O-benzyl-4′-O-methyl-β-maltoside* (**2e**). To a solution of methyl 2,3,6,2′,3′,6′-hexa-*O*-benzyl-β-maltoside (**2d**)[1] (100 mg, 0.11 mmol) was added 2 drops of boron trifluoride etherate and an excess of diazomethane in dry ether. The mixture was filtered and the filtrate was concentrated to dryness. Preparative TLC using ethyl acetate – pentane (1:3) as eluent yielded **2e** (51 mg, 50 %) as a syrup with $[\alpha]_D^{23}$ + 46.6° (*c* 1.3, chloroform). Anal. $C_{56}H_{62}O_{11}$: C, H. $^{13}$C NMR (67.89 MHz, $CDCl_3$): 104.6 ppm (C-1); 96.7 (C-1′); 60.6 (4′-*O*-methyl; 56.9 (1-*O*-methyl). Other signals: 84.8; 82.4; 82.0; 79.5; 79.2; 75.4; 74.6 (2 carbons); 73.9; 73.5; 73.4; 73.3; 72.5; 71.1; 69.2; 68.4.

*Methyl 4′-O-methyl-β-maltoside* (**2a**). To a solution of **2e** (30 mg, 0.033 mmol) in methanol (10 ml) and acetic acid (2 ml) was added 5 % palladium-on-carbon (10 mg). The mixture was stirred under 1 atm hydrogen pressure for 16 h. The catalyst was filtered off and washed with methanol. The filtrate and washings were combined and concentrated, and water (5 ml) was added and co-evaporated twice to remove acetic acid. This yielded **2a** (10 mg, 0.027 mmol, 82 %) as a syrup. $^1$H NMR (270 MHz, $D_2O$): δ 5.39 (H-1′); 3.22 (H-4′); 3.70 (H-5′); 3.85 (H-6a′); 4.39 (H-1); 3.29 (H-2); 3.92 (H-6a); 3.57, 3.56 (OMe). $^{13}$C NMR (67.89 MHz, $D_2O$): 100.3 ppm (C-1′); 72.5 (C-2′, C-3′); 79.9 (C-4′); 73.5 (C-5′); 61.1 (C-6′); 103.9 (C-1); 73.8 (C-2); 77.1 (C-3); 77.6 (C-4); 75.4 (C-5); 61.5 (C-6); 59.5, 58.0 (OMe).

*Methyl 2,3,6,2′,3′,4′-hexa-O-acetyl-β-maltoside* (**3c**). A solution of methyl 2,3,6,2′,3′-penta-*O*-acetyl-4′,6′-*O*-benzylidene-β-maltoside (1.0 g, 1.53 mmol) in acetic acid (20 ml) and water (5 ml) was heated on a steam-bath for 1 h. The mixture was evaporated, and water (25 ml) was added and co-evaporated four times to remove acetic acid. The residue (crude methyl 2,3,6,2′,3′-penta-*O*-acetyl-β-maltoside) was dissolved in pyridine (20 ml) and trityl chloride (2 g, 7.18 mmol) was added. The mixture was left at 30 °C for 4 d. Acetic anhydride (10 ml) was added and the mixture was left for 16 h at room temperature. Conventional work-up yielded crude methyl 2,3,6,2′,3′,4′-hexa-*O*-acetyl-6′-*O*-triphenylmethyl-β-maltoside together with triphenylcarbinol. The mixture was dissolved in

acetic acid (50 ml) and water (25 ml), and the solution was heated on a steam-bath for 1 h and filtered after cooling. The filtrate was washed with pentane (25 ml). The acetic acid – water phase was concentrated, and ethanol (10 ml) was added and co-evaporated three times to remove traces of acetic acid. From the resulting syrup, **3c** (529 mg, 57 %) could be crystallized from ethanol (m.p. 181–183 °C). Recrystallization from ethanol gave **3c** with m.p. 186–187 °C and $[\alpha]_D^{23}$ + 66.7° (*c* 1.3, chloroform). Lit.[6] m.p. 187–190 °C and $[\alpha]_D$ + 49° (*c* 0.7, chloroform). $^{13}$C NMR (67.89 MHz, $CDCl_3$): 95.6 ppm (C-1′); 70.3 (C-2′); 72.2 (C-3′); 75.5 (C-4′); 72.5 (C-5′); 62.8 (C-6′); 101.2 (C-1); 72.2 (C-2, C-3); 75.5 (C-4); 72.5 (C-5); 62.8 (C-6); 57.0 (OMe).

*Methyl 2,3,6,2′,3′,4′-hexa*-O-*acetyl-6′*-O-*methyl-β-maltoside* (**3b**). To a solution of **3c** (150 mg, 0.24 mmol) in dichloromethane (15 ml) was added 2 drops of boron trifluoride etherate and an excess of diazomethane in dry ether, and the solution was left for 1 h. The mixture was filtered and the filtrate was concentrated. The residue was purified by preparative TLC by elution with diethyl ether. This gave **3b** (112 mg, 75 %), which crystallized spontaneously; m.p. 160–165 °C. Recrystallization from ethanol gave **3b** with m.p. 162–163 °C and $[\alpha]_D^{23}$ + 53.5° (*c* 1.1, chloroform). Anal. $C_{26}H_{38}O_{17}$: C, H. $^{13}$C NMR (67.89 MHz, $CDCl_3$): 95.5 ppm (C-1′); 70.2 (C-2′); 69.5 (C-3′); 68.8 (C-4′); 70.2 (C-5′); 69.7 (C-6′); 101.2 (C-1); 72.2 (C-2, C-3); 75.6 (C-4); 72.4 (C-5); 62.9 (C-6); 59.6, 57.0 (OMe).

*Methyl 6′*-O-*methyl-β-maltoside* (**3a**). De-*O*-acetylation of **3b** (50 mg, 0.080 mmol) with 0.1 % sodium methoxide in methanol (10 ml) yielded **3a** (21 mg, 71 %) as a syrup. $^1$H NMR (270 MHz, $D_2O$): δ 5.49 (H-1′); 3.57 (H-2′); 3.67 (H-3′); 3.42 (H-4′); 3.80 (H-5′); 4.39 (H-1); 3.29 (H-2); 3.58, 3.41 (OMe). $^{13}$C NMR (67.89 MHz, $D_2O$): 100.4 ppm (C-1′); 72.5 (C-2′); 73.6 (C-3′); 70.2 (C-4′); 72.2 (C-5′); 71.1 (C-6′); 104.0 (C-1); 73.8 (C-2); 77.1 (C-3); 77.8 (C-4); 75.3 (C-5); 61.5 (C-6); 59.5, 58.0 (OMe).

*Methyl 4*-O-*(α-D-glucopyranosyl)-β-D-allopyranoside* (**4a**). Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-allopyranoside (**4b**)[4] was de-*O*-acetylated as described above to give **4a** as a syrup (15 mg, 90 %). $^{13}$C NMR (125.77 MHz, $D_2O$): 96.1 ppm (C-1′); 72.4 (C-2′); 74.2 (C-3′); 70.6 (C-4′); 74.0 (C-5′); 61.7 (C-6′); 102.4 (C-1); 71.4 (C-2); 68.0 (C-3); 71.9 (C-4); 73.5 (C-5); 62.3 (C-6); $^1$H NMR (500 MHz, $D_2O$): δ 5.14 (H-1′); 3.59 (H-2′); 3.71 (H-3′); 3.44 (H-4′); 3.66 (H-5′); 3.85 (H-6a′); 3.76 (H-6b′); 4.67 (H-1); 3.45 (H-2); 4.43 (H-3); 3.78 (H-4); 3.95 (H-5); 3.93, 3.73 (H-6a, H-6b part of an ABX system).

*2,3-Di*-O-*acetyl-1,6-anhydro-4-O-(2,3,4,6-tetra*-O-*acetyl-α-D-galactopyranosyl)-β-D-glucopyranose* (**6**). To a solution of 125 mg (0.22 mmol) of 2′,3′,4′, 2,3 hexa-*O*-acetyl-1,6-anhydro-β-lactose (**5**)[8] in 5 ml of hot chlorobenzene was added 34 µl (0.67 mmol) of bromine and the mixture was heated under reflux for 1½ h over a heat lamp (250 W) with exclusion of moisture. The dark brown solution was cooled to room temperature, washed with 10 % (*w/w*) aqueous sodium thiosulfate (2×15 ml) and saturated sodium hydrogen carbonate (2×15 ml), dried (magnesium sulfate), filtered through charcoal and concentrated. The resulting mixture was purified by preparative TLC, eluting with ethyl acetate–hexane (2:1). The slowest-moving fraction gave 37 mg (30 %) of starting material (**5**). The next fraction gave 25 mg (20 %) of the title compound **6**, which was characterized through its $^1$H NMR spectrum. $^1$H NMR (500 MHz, $CDCl_3$): δ 5.33 (H-1′); 5.10 (H-2′); 5.42 (H-3′); 5.49 (H-4′); 4.56 (H-5′); 4.16 (H-6a′); 4.05 (H-6b′); 5.46 (H-1, $J_{12}$ = 3.6 Hz); 4.79 (H-2); 4.58 (H-3); 3.56 (H-4); 4.75 (H-5); 3.97 (H-6a); 3.88 (H-6b).

*Methyl 2,3,6-tri*-O-*acetyl-4*-O-*(2,3,4,6-tetra*-O-*acetyl-α-D-galactopyranosyl-β-D-glucopyranoside* (**7b**). To a solution of **6** (40 mg, 0.07 mmol) in acetic anhydride (5 ml) was added 2 drops of conc. $H_2SO_4$, and after 5 min stirring the solution was poured into water (40 ml) and stirred for 2½ h. The mixture was extracted 3 times with dichloromethane, and the combined organic phases were washed with water and saturated sodium hydrogen carbonate solution, dried and concentrated. The residue was dissolved in dichloromethane (10 ml) and hydrogen bromide in acetic acid (6 ml) was added. After 50 min at room temperature the mixture was diluted with cold dichloromethane (20 ml), washed with ice-water and saturated sodium hydrogen carbonate, dried and concentrated. To the resulting glycosyl

bromide in dichloromethane (10 ml) was added dry methanol (10 ml) and silver carbonate (220 mg, 0.75 mmol), and the mixture was stirred overnight in the dark. The silver salts were removed by filtration through charcoal, and washed with methanol and dichloromethane. The combined filtrate was evaporated and purified by preparative TLC by elution with ethyl acetate–hexane (1:1). The main fraction gave 21 mg (47 %) of methyl 4′-epi-hepta-*O*-acetyl-β-maltoside (**7**), which crystallized from ethanol with m.p. 145–146 °C and $[\alpha]_D^{22}$ + 61.0° (*c* 0.7; chloroform). Anal. $C_{27}H_{38}O_{18}$: C, H. $^{13}$C NMR (125.77 MHz, $CDCl_3$): 95.9 ppm (C-1′); 66.8, 67.2, 67.2, 67.6 (C-2′, C-3′, C-4′, C-5′); 61.3 (C-6′); 101.0 (C-1); 72,1, 72,2, 72,6 (C-2, C-3, C-5); 75.4 (C-4); 62.9 (C-6); $^1$H NMR (500 MHz, $CDCl_3$): δ 5.45 (H-1′); 5.13 (H-2′); 5.25 (H-3′); 5.44 (H-4′); 4.20 (H-5′); 4.09, 4.04 (H-6a′, H-6b′); 4.45 (H-1); 4.82 (H-2); 5.23 (H-3); 4.00 (H-4); 3.67 (H-5); 4.50, 4.23 (H-6a, H-6b).

*Methyl 4-*O*-(α-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**7a**). Treatment of 13 mg of methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-glucopyranoside (**7b**) with 0.5 ml of 0.1 % sodium methoxide in dry methanol (5 ml) overnight gave 5 mg (65 %) of **7b** as a syrup. $^{13}$C NMR (125.77 MHz, $D_2O$): 100.7 ppm (C-1′); 69.6 (C-2′); 70.1 (C-3′); 70.0 (C-4′); 72.6 (C-5′); 62.0 (C-6′); 103.9 (C-1); 73.8 (C-2); 77.0 (C-3); 77.8 (C-4); 75.4 (C-5); 61.6 (C-6); $^1$H NMR (500 MHz, $D_2O$): δ 5.42 (H-1′, $J_{12}$ = 3.6 Hz); 3.83, 3.89 (H-2′, H-3′ AB system); 4.01 (H-4′); 4.01 (H-5′); 3.75 (H-6a′, H-6b′ AB system); 4.40 (H-1, $J_{12}$ = 8.0 Hz); 3.31 (H-2); 3.78 (H-3); 3.63 (H-4); 3.60 (H-5); 3.80 (H-6a); 3.97 (H-6b).

*Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranosyl)-β-*D*-glucopyranoside* (**8**). To a mixture of methyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[9] (255 mg, 0.55 mmol), silver trifluoromethanesulfonate (205 mg, 0.8 mmol), tetramethylurea (0.096 ml, 0.8 mmol) and 4 Å molecular sieves in dry dichloromethane cooled to −20 °C was added a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (326 mg, 0.79 mmol) in dichloromethane (5 ml). The mixture was protected from light and stirred under nitrogen for 2 h. The reaction mixture was diluted with dichloromethane (25 ml) and filtered into ice-water and sodium hydrogen carbonate. The organic phase was washed with water, dried (magnesium sulfate) and concentrated to yield a syrup (540 mg) which wasa purified by preparative TLC by elution with ethyl acetate–pentane (1:2). The slower-moving fraction gave **8** (107 mg, 0.13 mmol, 25 %), as a syrup, characterized by 500 MHz $^1$H and $^{13}$C NMR spectra. $^1$H NMR (500 MHz, $CDCl_3$): δ 5.40 (H-1′, $J_{12}$ = 2 Hz), 5.28 (H-2′); 5.24 (H-3′); 5.20 (H-4′); 3.97 (H-5′); 4.17 (H6a′); 3.88 (H-6b′); 4.35 (H-1, $J_{12}$ = 8.0 Hz); 3.54 (H-2); 3.67 (H-3); 3.80 (H-4); 3.53 (H-5); 3.81 (H-6a); 3.73 (H-6b). $^{13}$C NMR (500 MHz, $CDCl_3$): 97.4 ppm (C-1′); 62.1 (C-6′); 104.4 (C-1); 65.5 (C-6); 56.9 ($OCH_3$); unassigned: 84.1, 82.0, 75.3, 74.7, 74.2, 74.0, 73.3, 69.2, 69.1, 69.0, 68.9. The faster- moving fraction gave the aglycone (143 mg, 56 %).

*Methyl-4-*O*-(α-*D*-mannopyranosyl)-β-*D*-glucopyranoside* (**9**). To a solution of **8** (107 mg, 0.13 mmol) in methanol (10 ml) and acetic acid (1 ml) was added 5 % palladium-on-carbon (40 mg). The mixture was stirred for 16 h under 1 atm hydrogen pressure and then diluted with methanol (25 ml). The catalyst was filtered off and washed with methanol. Concentration of the filtrate to dryness yielded a syrup (80 mg). The product was de-*O*-acetylated with 0.1 % sodium methoxide in methanol (8 ml). The solution was neutralized with solid carbon dioxide, and the sodium ions were removed by stirring with Amberlite IRC-50($H^+$) ion-exchange resin Filtration through activated carbon and concentration gave **9** (32 mg, 69 %). $^1$H NMR (500 MHz, $D_2O$): δ 5.25 (H-1′, $J_{12}$ = 1.8 Hz); 4.03 (H-2′);3.78 (H-3′); 3.66 (H-4′); 3.67 (H-5); 3.86 (H-6a′); 3.73 (H-6b′); 4.34 (H-1, $J_{12}$ = 8.6 Hz); 3.26 (H-2); 3.64 (H-3); 3.59 (H-4); 3.52 (H-5); 3.91 (H-6a); 3.75 (H-6b). $^{13}$C NMR (500 MHz, $D_2O$): 102.1 ppm (C-1′); 71.1 (C-2′); 71.1 (C-3′); 67.4 (C-4′); 74.5 (C-5′); 61.7 (C-6′); 103.9 (C-1); 74.0 (C-2) 77.1 (C-3); 77.0 (C-4); 75.4 (C-5); 61.6 (C-6); 58.1 (OMe).

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