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Electronic Supplementary Information (ESI)

Exploring the meaning of sugar configuration in a supramolecular environment: Comparison of six octyl glycoside micelles by ITC and NMR spectroscopy

Jörn Schmidt-Lassen and Thisbe K. Lindhorst*

Contents

1. General methods used in synthesis

Commercially available starting materials and reagents were used without further purification. Reactions requiring dry conditions were performed under an atmosphere of nitrogen using oven-dried glassware. Dichloromethane was dried over CaH_2 and methanol over magnesium. Solvents were purified by distillation prior to use. Reaction monitoring was performed by TLC on silica gel F_{254} (Merck) or RP-18 (Merck) plates, detection was achieved by UV light and/or by treatment of the plates with 10 % sulfuric acid in EtOH, or with molybdophosphoric acid solution (1.5 g molybdophosphoric acid in 40 mL sulphuric acid and 500 mL water/EtOH), or with cerium sulfate solution (5 g cerium (IV) sulfate and 12.5 g molybdophosphoric acid in 40 mL sulphuric acid and 500 mL water/EtOH) and subsequent heating. Flash chromatography was performed on Merck silica gel 60 (0.040–0.063 mm).
For NMR spectroscopy, Bruker DRX 500 or AV 600 instruments were used. Chemical shifts (δ) were calibrated relative to the internal solvent. For complete assignment the following two-dimensional NMR techniques were used: $^1H–^1H$ COSY, $^1H–^{13}C$ HSQC and $^1H–^{13}C$ HMBC. ESI-MS measurements were performed on a Mariner instrument (ESI-ToF 5280 Applied Biosystems), MALDI-ToF mass spectra were recorded with a Bruker Biflex III instrument with 19 kV acceleration voltage and an ionization laser at 337 nm; 4-chloro-α-cyanocinnamic acid (Cl-CCA) was used as a matrix. Optical rotation values were measured on a Perkin-Elmer 241 polarimeter (10 cm cells, sodium D-line: 589 nm) and are averaged from five measurements. Elemental analyses were carried out with a EuroEA Elemental Analyzer from EuroVector. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. For sample preparation a Golden Gate-diamond-ATR unit with a saphire stamp was used.

2. General synthetic procedures

2.A Glycosylation using the trichloroacetimidate method[1,2]

The glycosyl acceptor (1-octanol, 1-2.1 eq.) and the corresponding glycosyl trichloroacetimidate[3–5] (1-1.2 eq.) were dried at least 1 h under vacuum. The reactants were dissolved in anhydrous dichloromethane (1 mL / g glycosyl donor) under nitrogen atmosphere. After adding molecular sieves (4 Å, 500 mg) the solution was cooled to 0 °C and $BF_3 \cdot Et_2O$ (1.7-4.5 eq.) was added dropwise over a period of 30 min. After stirring for 30 min at 0 °C the reaction mixture was stirred overnight at ambient temperature. The reaction mixture was washed with satd. $NaHCO_3$ and water. The aqueous phase was extracted with dichloromethane (three times). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography.

2.B *O*-acetyl deprotection according to Zemplén and Pacsu[6]

The protected *O*-glycoside was dissolved in anhydrous methanol and a freshly prepared solution of sodium methoxide (1 M solution in methanol, 200 µL) was added. The mixture was stirred overnight at ambient temperature, neutralized with Amberlite IR120 (H), filtered and the solvents were evaporated to dryness. The substrate was dissolved in water and subjected to lyophilization.

2.C Fischer glycosylation with acetyl chloride[7]

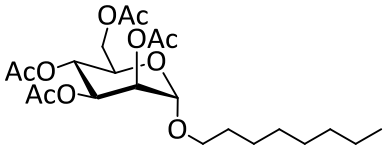
The glycosyl acceptor (1-octanol, 32 eq.) was used as solvent and cooled to 0 °C. Acetyl chloride (2.5 eq.) was added and the solution was stirred at 0 °C for 1 h. The monosaccharide was added in portions and the reaction mixture was stirred at 85 °C for 4.5 h. After cooling to room temperature the mixture was neutralized with Na_2CO_3 and filtered over Celite. The residue was washed with ethyl acetate. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography.

2.D General procedure for *O*-acetylation with acetic anhydride in pyridine

The compound for *O*-acetylation was dissolved in pyridine (10 mL / g) and acetic anhydride was added dropwise. The reaction mixture was stirred at ambient temperature overnight. Then the solvent was evaporated to dryness. The residue was codestilled with toluene three times. The resulting crude product was purified by silica gel chromatography.

3. Synthetic procedures and analytical data

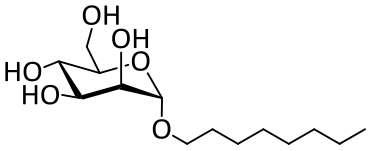
Octyl (2,3,4,6-tetra-*O*-acetyl)-α-D-mannopyranoside



According to the general procedure 2.A, 1-octanol (680 mL, 4.32 mmol), mannosyl trichloroacetimidate[4] (2.55 g, 5.19 mmol, 1.2 eq.) and $BF_3{\cdot}Et_2O$ (3.10 mL, 19.4 mmol, 4.5 eq) were allowed to react in dichloromethane (25 mL). The crude product was purified by silica gel chromatography (cylcohexane / ethyl acetate, 2:1) yielding the acetylated 1,2-*trans* glucoside (916 mg, 1.99 mmol, 46 %).as colourless oil.

R*f*: 0.43 (cyclohexane / ethyl acetate, 2:1); $[\alpha]_D^{20}$ = + 44.9 (*c* = 1.1, CH_2Cl_2);
^{1}H-NMR (500 MHz, DMSO-d_6): δ = 5.14-5.04 (m, 3 H, H-2, H-3, H-4), 5.18 (d, 1 H, $^3J_{1,2}$ = 1.4 Hz, H-1), 4.17 (dd, 1 H, $^3J_{5,6a}$ = 5.5 Hz, $^2J_{6a,6b}$ = 12.2 Hz, H-6a), 4.05 (dd, 1 H, $^3J_{5,6b}$ = 2.5 Hz, $^2J_{6a,6b}$ = 12.2 Hz, H-6b), 3.95-97 (m, 1 H, H-5), 3.62 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.7 Hz, Man-OC<u>H</u>H),3.47 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.7 Hz, Man-OCH<u>H</u>), 2.10, 2.02, 2.02, 1.94 (each s, each 3 H, 4 $COCH_3$), 1.63-1.49 (m, 2 H, Man-$OCH_2C\underline{H}_2$), 1.36-1.20 (m, 10 H, 5 CH_2), 0.85 (dd~t, 3 H, ^3J = 6.9 Hz, CH_3) ppm; **^{13}C-NMR** (125 MHz, DMSO-d_6): δ = 170.5, 170.1, 170.1, 170.0 (4 $\underline{C}OCH_3$), 97.0 (C-1), 69.3, 69.2 (C-2, C-3), 68.4 (C-5), 67.9 (Man-$O\underline{C}H_2$), 66.0 (C-4), 62.6 (C-6), 31.7 (CH_2), 29.1 (Man-$OCH_2\underline{C}H_2$), 29.1, 29.1, 26.0, 22.5 (4 CH_2), 21.1, 20.9, 20.9, 20.9 (4 $CO\underline{C}H_3$), 14.4 (CH_3) ppm; **ESI MS**: calcd. for $C_{22}H_{36}O_{10}$: *m/z* = 483.220 $[M+Na]^+$; found: *m/z* = 483.223 $[M+Na]^+$; **IR** (ATR): $\tilde{\nu}$ = 2928, 2857, 1745, 1369, 1216, 1135, 1082, 1044, 977, 600 cm^{-1}.

Octyl α-D-mannopyranoside (1)[8,9]

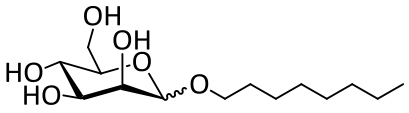


Deprotection of Octyl (2,3,4,6-tetra-*O*-acetyl)-α-D-mannopyranoside (3.94 g, 8.55 mmol) was achieved according general procedure 2.B in methanol (20 mL) yielding title compound **1** (2.29 g, 7.84 mmol, 92 %) as an amorphous white lyophilisate.

R*f*: 0.50 (ethyl acetate / methanol, 6:1); $[\alpha]_D^{20}$ = +65.3 (*c* = 1.0, MeOH);
^{1}H-NMR (500 MHz, MeOH-d_4): δ = 4.73 (d, 1 H, $^3J_{1,2}$ = 1.7 Hz, H-1), 3.82 (dd, 1 H, $^3J_{5,6a}$ = 2.4 Hz, $^2J_{6a,6b}$ = 11.7 Hz, H-6a), 3.78 (dd, 1 H, $^3J_{1,2}$ = 1.7 Hz, $^3J_{2,3}$ = 3.4 Hz, H-2), 3.73 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.5 Hz, $^2J_{CH,CH}$ = 9.6 Hz, Man-OC<u>H</u>H), 3.68 (dd, 1 H, $^3J_{3,4}$ = 3.4 Hz, $^3J_{3,4}$ = 9.4 Hz, H-3), 3.70 (dd,

1 H, $^{3}J_{5,6b}$ = 5.8 Hz, $^{2}J_{6a,6b}$ = 11.7 Hz, H-6b), 3.61 (dd∼t, 1 H, $^{3}J_{3,4} = {}^{3}J_{4,5}$ = 9.5 Hz, H-4), 3.51 (ddd, 1 H, $^{3}J_{5,6a}$ = 2.4 Hz, $^{3}J_{5,6b}$ = 5.8 Hz, $^{3}J_{4,5}$ = 9.5 Hz, H-5), 3.41 (dt, 1 H, $^{3}J_{\underline{C}H,CH2}$ = 6.5 Hz, $^{2}J_{CH,\underline{C}H}$ = 9.6 Hz, Man-OCH<u>H</u>), 1.70-1.48 (m, 2 H, Man-OCH$_2$C<u>H</u>$_2$), 1.47-1.08 (m, 10 H, 5 CH$_2$), 0.90 (dd∼t, 3 H, ^{3}J = 6.9 Hz, CH$_3$) ppm; **^{13}C-NMR** (125 MHz, MeOH-d$_4$): δ = 101.6 (C-1), 74.6 (C-5), 72.7 (C-3), 72.3 (C-2), 68.7 (C-4), 68.6 (Man-O<u>C</u>H$_2$), 62.5 (C-6), 33.0 (CH$_2$), 30.6 (Man-OCH$_2$<u>C</u>H$_2$), 30.5, 30.4, 27.4, 23.7 (4 CH$_2$), 14.4 (CH$_3$) ppm; **ESI MS**: calcd. for $C_{14}H_{28}O_6$: *m/z* = 315.1778 [M+Na]$^+$; found m/z = 315.1726 [M+Na]$^+$; **EA**: calcd. for $C_{14}H_{28}O_6 \cdot 0.1\ CH_3OH$ (M = 295.57 g·mol^{-1}): C 57.29, H 9.69; found: C 57.36, H 9.88; **IR** (ATR): $\tilde{\nu}$ = 3345, 2913, 2850, 1467, 1416, 1355, 1140, 1084, 1063, 1009, 885, 812 cm^{-1}.

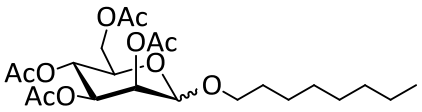
Octyl α,β-D-mannopyranoside (1, 2)



According to the general procedure 2.C, 1-octanol (232 g, 178 mmol, 32 eq.), acetyl chloride (10.0 mL, 138 mmol, 2.5 eq.) and D-mannose (10.0 g, 55.5 mmol) were allowed to react. The crude product was purified by silica gel chromatography (ethyl acetate / methanol, 10:1) and a following second silica gel chromatography (ethyl acetate / methanol, 30:1) yielding an anomeric mixture of **1** and **2** (12.6 g; 43.1 mmol, 78 %) as light yellow foam.

R$_f$: 0.37 (ethyl acetate / methanol, 10:1); anomeric ratio according to ^{1}H-NMR (500 MHz, DMSO-d$_6$): α:β = 95:5; detailed analytical data are described for the pure anomers, **1** and **2**.

Octyl (2,3,4,6-tetra-*O*-acetyl)-α- and -β-D-mannopyranoside[10]



According to general procedure 2.C, octyl α,β-D-mannopyranoside (**1**, **2**) (6.21 g, 21.3 mmol) was dissolved in pyridine (65 mL) and acetic anhydride (20.1 mL, 213 mmol, 10 eq.) was added. The crude product was purified by silica gel chromatography (cyclohexane / ethyl acetate, 4:1) and a second silica gel chromatography (Et$_2$O / PE (30-60), 1:1) for separation of the anomeric mixture yielding the pure α-anomer (8.98 g, 19.5 mmol, 92 %) and β-anomer (406 mg, 881 µmol, 4 %) as colourless oils.

Anomeric ratio according to ^{1}H-NMR (500 MHz, DMSO-d$_6$): α:β = 95:5.

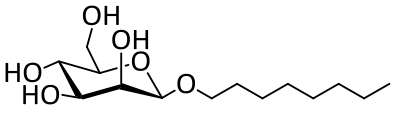
α-anomer: R$_f$: 0.32 (Et$_2$O / PE (30-60), 1:1); $[\alpha]_D^{20}$ = + 44.9 (*c* = 1.1, CH$_2$Cl$_2$);

^{1}H-NMR (500 MHz, DMSO-d_6): δ = 5.14-5.04 (m, 3 H, H-2, H-3, H-4), 5.18 (d, 1 H, $^3J_{1,2}$ = 1.4 Hz, H-1), 4.17 (dd, 1 H, $^3J_{5,6a}$ = 5.5 Hz, $^2J_{6a,6b}$ = 12.2 Hz, H-6a), 4.05 (dd, 1 H, $^3J_{5,6b}$ = 2.5 Hz, $^2J_{6a,6b}$ = 12.2 Hz, H-6b), 3.95-97 (m, 1 H, H-5), 3.62 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.7 Hz, Man-OC<u>H</u>H),3.47 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.7 Hz, Man-OCH<u>H</u>), 2.10, 2.02, 2.02, 1.94 (je s, je 3 H, 4 $COCH_3$), 1.63-1.49 (m, 2 H, Man-$OCH_2C\underline{H}_2$), 1.36-1.20 (m, 10 H, 5 CH_2), 0.85 (dd~t, 3 H, ^3J = 6.9 Hz, CH_3) ppm; **^{13}C-NMR** (125 MHz, DMSO-d_6): δ = 170.5, 170.1, 170.1, 170.0 (4 $\underline{C}OCH_3$), 97.0 (C-1), 69.3, 69.2 (C-2, C-3), 68.4 (C-5), 67.9 (Man-$O\underline{C}H_2$), 66.0 (C-4), 62.6 (C-6), 31.7 (CH_2), 29.1 (Man-$OCH_2\underline{C}H_2$), 29.1, 29.1, 26.0, 22.5 (4 CH_2), 21.1, 20.9, 20.9, 20.9 (4 $CO\underline{C}H_3$), 14.4 (CH_3) ppm; **^{13}C-NMR-gated-decoupled** (125 MHz, DMSO-d_6): δ = 97.0 ($J_{C\text{-}1,H\text{-}1}$ = 173.4 Hz, C-1) ppm; **ESI MS**: calcd. for $C_{22}H_{36}O_{10}$: *m/z* = 483.220 $[M+Na]^+$; found: *m/z* = 483.223 $[M+Na]^+$; **IR** (ATR): $\tilde{\nu}$ = 2928, 2857, 1745, 1369, 1216, 1135, 1082, 1044, 977, 600 cm^{-1}.

β-anomer: R_f: 0.23 (Et_2O / PE (30-60), 1:1); $[\alpha]_D^{20}$ = -33.0 (*c* = 1.1, $CHCl_3$);

^{1}H-NMR (500 MHz, DMSO-d_6): δ = 5.27 (dd, 1 H, $^3J_{1,2}$ = 1.0 Hz,$^3J_{2,3}$ = 3.5 Hz, H-2), 5.18 (dd, 1 H, $^3J_{2,3}$ = 3.5 Hz,$^3J_{3,4}$ = 10.0 Hz, H-3), 4.99 (dd~t, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 10.0 Hz, H-4), 4.93 (d, 1 H, $^3J_{1,2}$ = 1.0 Hz, H-1), 4.17 (dd, 1 H, $^3J_{5,6a}$ = 5.6 Hz, $^2J_{6a,6b}$ = 12.2 Hz, H-6a), 4.00 (dd, 1 H, $^3J_{5,6b}$ = 2.6 Hz, $^2J_{6a,6b}$ = 12.2 Hz, H-6b), 3.84 (ddd, 1 H, $^3J_{5,6b}$ = 2.6 Hz, $^3J_{5,6a}$ = 5.6 Hz, $^3J_{4,5}$ = 10.0 Hz, H-5), 3.67 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.7 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Man-OC<u>H</u>H),3.47 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.7 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Man-OCH<u>H</u>), 2.09, 2.02, 2.01, 1.92 (each s, each 3 H, 4 $COCH_3$), 1.52-1.43 (m, 2 H, Man-$OCH_2C\underline{H}_2$), 1.30-1.20 (m, 10 H, 5 CH_2), 0.85 (dd~t, 3 H, ^3J = 7.0 Hz, CH_3) ppm; **^{13}C-NMR** (125 MHz, DMSO-d_6): δ = 170.0, 169.8, 169.5, 169.4 (4 $\underline{C}OCH_3$), 97.6 ($J_{C\text{-}1,H1}$ = 162.1 Hz, C-1), 71.0 (C-5), 70.4 (C-3), 68.9 (Man-$O\underline{C}H_2$), 68.7 (C-2), 65.9 (C-4), 62.5 (C-6), 31.2 (CH_2), 28.8 (Man-$OCH_2\underline{C}H_2$), 28.6, 28.6, 25.3, 22.0 (4 CH_2), 20.5, 20.5, 20.5, 20.3 (4 $CO\underline{C}H_3$), 13.9 (CH_3) ppm; **^{13}C-NMR-gated-decoupled** (125 MHz, DMSO-d_6): δ = 97.6 ($J_{C\text{-}1,H\text{-}1}$ = 162.1 Hz, C-1) ppm; **ESI MS**: calcd. for $C_{22}H_{36}O_{10}$: *m/z* = 483.2201 $[M+Na]^+$; found: *m/z* = 483.2225 $[M+Na]^+$; **IR** (ATR): $\tilde{\nu}$ = 2956, 2928, 2857, 1747, 1731, 1372, 1228, 1212, 1177, 1072, 1044, 978, 592 cm^{-1}.

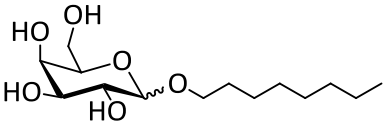
Octyl β-D-mannopyranoside (2)[10,11]



Deprotection of octyl (2,3,4,6-tetra-*O*-acetyl)-β-D-mannopyranoside (750 mg, 1.63 mmol) was achieved according to general procedure 2.B in methanol (10 mL) yielding title compound **2** (442 mg (1.51 mmol, 92 %) as an amorphous white lyophilisate.

R*f*: 0.44 (ethyl acetate / methanol, 6:1); $[\alpha]_D^{20}$ = - 49.6 (*c* = 0.9, MeOH);
^{1}H-NMR (500 MHz, DMSO-d$_6$): δ = 4.70 (d, 1 H, ^3J = 5.1 Hz, OH), 4.51 (d, 1 H, ^3J = 6.0 Hz, OH), 4.40 (t, 1 H, ^3J = 6.0 Hz, OH), 4.33 (d, 1 H, $^3J_{1,2}$ = 0.7 Hz, H-1), 4.24 (d, 1 H, ^3J = 5.0 Hz, OH), 3.75 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.8 Hz, $^2J_{CH,CH}$ = 9.6 Hz, Man-OC$\underline{H}$H), 3.67 (ddd, 1 H, $^3J_{5,6a}$ = 2.2 Hz, $^3J_{6a,OH}$ = 6.0 Hz, $^2J_{6a,6b}$ = 11.6 Hz, H-6a), 3.60 (m$_c$, 1 H, H-2), 3.44 (m$_c$, 1 H, H-6b), 3.31-3.19 (m, 2 H, H-3, H-4), 3.40 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.8 Hz, $^2J_{CH,CH}$ = 9.6 Hz, Man-OCH$\underline{H}$), 3.00 (ddd, 1 H, $^3J_{5,6a}$ = 2.2 Hz, $^3J_{5,6b}$ = 6.4 Hz, $^3J_{4,5}$ = 8.8 Hz, H-5), 1.57-1.44 (m, 2 H, Man-OCH$_2$C$\underline{H}_2$), 1.33-1.19 (m, 10 H, 5 CH$_2$), 0.85 (dd∼t, 3 H, ^3J = 7.0 Hz, CH$_3$) ppm; **^{13}C-NMR** (125 MHz, DMSO-d$_6$): δ = 100.2 (C-1), 77.5 (C-5), 73.7 (C-3/4), 70.6 (C-2), 68.4 (Man-O$\underline{C}$H$_2$), 67.2 (C-3/4), 61.4 (C-6), 31.2 (CH$_2$), 29.2 (Man-OCH$_2\underline{C}$H$_2$), 28.9, 28.7, 25.6, 22.1 (4 CH$_2$), 14.4 (CH$_3$) ppm; **^{13}C-NMR-gated-decoupled** (125 MHz, DMSO-d$_6$): δ = 100.2 ($J_{C\text{-}1,H\text{-}1}$ = 155.7 Hz, C-1) ppm; **ESI MS**: calcd. for $C_{14}H_{28}O_6$: m/z = 315.1778 $[M+Na]^+$; found: m/z = 315.1783 $[M+Na]^+$; **EA**: calcd. for $C_{14}H_{28}O_6$ (M = 292.37 g·mol^{-1}): C 57.51, H 9.65; found: C 57.90, H 9.79; **IR** (ATR): $\tilde{\nu}$ = 3460, 3188, 2916, 2851, 1377, 1185, 1153, 1140, 1056, 1015, 946, 796, 721, 528 cm^{-1}.

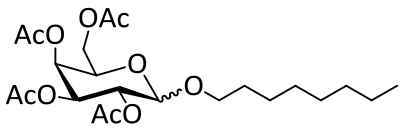
Octyl α,β-D-galactopyranoside (3, 4)



According to the general procedure 2.C, 1-octanol (45.9 g, 353 mmol, 32 eq.), acetyl chloride (2.00 mL, 27.7 mmol, 2.5 eq.) and D-galactose (2.00 g, 11.1 mmol) were allowed to react. The crude product was purified by silica gel chromatography (ethyl acetate / methanol, 10:1) yielding an anomeric mixture of **1** and **2** (1.76 g, 6.02 mmol, 54 %) as light yellow solid.

R*f* $_{(α)}$ = 0.23; **R*f*** $_{(β)}$ = 0.14 (ethyl acetate / methanol, 10:1); anomeric ratio according to ^{1}H-NMR (500 MHz, MeOH-d$_4$): α:β = 3:1. Detailed analytical data are described for the pure anomers, **3** and **4**.

Octyl (2,3,4,6-tetra-*O*-acetyl)-α- and -β-D-galactopyranoside[12]



According to general procedure 2.C, octyl α,β-D-galactopyranoside (**3**, **4**) (1.76 g, 6.02 mmol) was dissolved in pyridine (20 mL) and acetic anhydride (5.69 mL, 60.2 mmol, 10 eq.) was added. For separation of the anomeric mixture the crude product was purified by silica gel chromatography (cyclohexane / ethyl acetate, 4:1) yielding the pure α-anomer (1.61 g, 3.49 mmol, 58 %) and β-anomer (340 mg, 738 µmol, 12 %) as colourless oils.

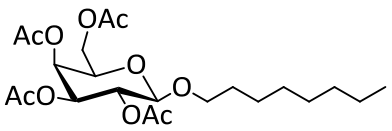
α-anomer: R_f: 0.20 (cyclohexane / ethyl acetate, 4:1); $[\alpha]_D^{20}$ = + 126.4 (*c* = 1.0, MeOH);

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.48 (dd, 1 H, $^3J_{3,4}$ = 3.4 Hz, $^3J_{4,5}$ = 1.2 Hz, H-4), 5.36 (m_c, 1 H, H-3), 5.15-5.06 (m, 2 H, H-1, H-2), 4.22 (m_c, 1 H, H-5), 4.11 (dd, 1 H, $^3J_{5,6a}$ = 6.1 Hz, $^2J_{6a,6b}$ = 11.2 Hz, H-6a), 4.08 (dd, 1 H, $^3J_{5,6b}$ = 7.0 Hz, $^2J_{6a,6b}$ = 11.2 Hz, H-6b), 3.68 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Gal-OC<u>H</u>H), 3.42 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Gal-OCH<u>H</u>), 2.14, 2.07, 2.04, 1.99 (each s, each 3 H, 4 $COCH_3$), 1.63-1.54 (m, 2 H, Gal-$OCH_2C\underline{H}_2$), 1.38-1.22 (m, 10 H, 5 CH_2), 0.89 (dd∼t, 3 H, ^3J = 7.0 Hz, CH_3) ppm; **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 170.4, 170.4, 170.3, 170.0 (4 $\underline{C}OCH_3$), 96.1 (C-1), 68.7 (Gal-$O\underline{C}H_2$), 68.3 (C-2), 68.2 (C-4), 67.7 (C-3), 66.2 (C-5), 61.8 (C-6), 31.8 (CH_2), 29.3 (Gal-$OCH_2\underline{C}H_2$), 29.3, 26.1, 22.6, 21.0 (4 CH_2), 20.7, 20.6, 20.6, 20.6, (4 $CO\underline{C}H_3$), 14.1 (CH_3) ppm; **ESI MS**: calcd. for $C_{22}H_{36}O_{10}$: *m/z* = 483.220 $[M+Na]^+$; found; *m/z* = 483.226 $[M+Na]^+$; **IR** (ATR): $\tilde{\nu}$ = 2928, 2857, 1744, 1370, 1041, 599 cm^{-1}.

β-anomer: R_f: 0.14 (cyclohexane / ethyl acetate, 4:1); $[\alpha]_D^{20}$ = - 12.3 (*c* = 1.2, MeOH);

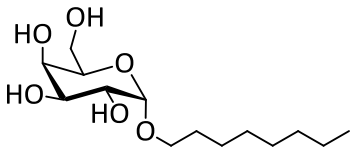
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.38 (dd, 1 H, $^3J_{4,5}$ = 1.1 Hz,$^3J_{3,4}$ = 3.5 Hz, H-4), 5.20 (dd, 1 H, $^3J_{1,2}$ = 8.0 Hz,$^3J_{2,3}$ = 10.5 Hz, H-2), 5.02 (dd, 1 H, $^3J_{3,4}$ = 3.5 Hz,$^3J_{2,3}$ = 10.5 Hz, H-3), 4.46 (d, 1 H, $^3J_{1,2}$ = 8.0 Hz, H-1), 4.19 (dd, 1 H, $^3J_{5,6a}$ = 6.4 Hz, $^2J_{6a,6b}$ = 11.2 Hz, H-6a), 4.13 (dd, 1 H, $^3J_{5,6b}$ = 7.0 Hz, $^2J_{6a,6b}$ = 11.2 Hz, H-6b), 3.93-3.85 (m, 1 H, Gal-OC<u>H</u>H), 3.90 (ddd∼td, 1 H, $^3J_{4,5}$ = 1.1 Hz, $^3J_{5,6a}$ = 6.4 Hz, H-5), 3.47 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.9 Hz, $^2J_{CH,CH}$ = 9.6 Hz, Gal-OCH<u>H</u>), 2.15, 2.05, 2.04, 1.98 (each s, each 3 H, 4 $COCH_3$), 1.70-1.50 (m, 2 H, Gal-$OCH_2C\underline{H}_2$), 1.41-1.19 (m, 10 H, 5 CH_2), 0.88 (dd∼t, 3 H, ^3J = 7.0 Hz, CH_3) ppm; **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 170.4, 170.3, 170.2, 169.4 (4 $\underline{C}OCH_3$), 101.4 (C-1), 71.0 (C-3), 70.6 (C-5), 70.3 (Gal-$O\underline{C}H_2$), 69.0 (C-2), 67.1 (C-4), 61.3 (C-6), 31.8 (CH_2), 29.4 (Gal-$OCH_2\underline{C}H_2$), 29.3, 29.2, 25.8, 22.6 (4 CH_2), 20.7, 20.7, 20.7, 20.6 (4 $CO\underline{C}H_3$), 14.1 (CH_3) ppm; **ESI MS**: calcd. for $C_{22}H_{36}O_{10}$: *m/z* = 483.2201 $[M+Na]^+$; found: *m/z* = 483.2188 $[M+Na]^+$; **IR** (ATR): $\tilde{\nu}$ = 3326, 2927, 2855, 1379, 1145, 1070, 1053, 1015, 982, 919 cm^{-1}.

Octyl (2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranoside



According to the general procedure 2.A, 1-octanol (1.67 mL, 12.8 mmol, 2.1 eq.), galactosyl trichloroacetimidate[3] (3.04 g, 6.17 mmol) and $BF_3{\cdot}Et_2O$ (1.00 mL, 10.3 mmol, 1.7 eq.) were allowed to react in dichloromethane (30 mL). The crude product was purified by silica gel chromatography (cylcohexane / ethyl acetate, 2:1) yielding the acetylated 1,2-*trans* galactoside (1.58 g, 3.43 mmol, 55 %).as colourless oil. Detailed analytical data are described for the β-anomer in the procedure describing synthesis of octyl (2,3,4,6-tetra-*O*-acetyl)-α- and -β-D-galactopyranoside.

Octyl α-D-galactopyranoside (3)



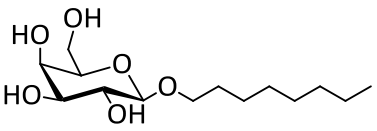
Deprotection of octyl (2,3,4,6-tetra-*O*-acetyl)-α-D-galactopyranoside (923 mg, 2.00 mmol) was achieved according to general procedure 2.B in methanol (10 mL) yielding title compound **3** (573 mg, 1.96 mmol, 98 %) as an amorphous white lyophilisate.

R_f: 0.55 (ethyl acetate / methanol, 6:1); $[\alpha]_D^{20}$ = - 135.9 (*c* = 1.1, MeOH);

^{1}H-NMR (500 MHz, MeOH-d_4): δ = 4.79 (d, 1 H, $^3J_{1,2}$ = 3.4 Hz, H-1), 3.89 (dd, 1 H, $^3J_{4,5}$ = 0.9 Hz, $^3J_{3,4}$ = 9.1 Hz, H-4), 3.80 (td, 1 H, $^3J_{4,5}$ = 0.9 Hz, $^3J_{5,6}$ = 9.1 Hz, H-5), 3.76 (dd, 1 H, $^3J_{1,2}$ = 3.4 Hz, $^3J_{2,3}$ = 10.1 Hz, H-2), 3.74 (m_c, 1 H, H-3), 3.73 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Gal-OC<u>H</u>H), 3.69 (m_c, 2 H, H-6a, H-6b), 3.44 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Gal-OCH<u>H</u>), 1.63 (mc, 2 H, Gal-OCH$_2$C<u>H</u>$_2$), 1.45-1.23 (m, 10 H, 5 CH_2), 0.89 (dd∼t, 3 H, ^3J = 7.0 Hz, CH_3) ppm;

^{13}C-NMR (125 MHz, MeOH-d_4): δ = 100.3 (C-1), 72.3 (C-5), 71.6 (C-3), 71.1 (C-4), 70.3 (C-2), 69.2 (Gal-O<u>C</u>H$_2$), 62.7 (C-6), 33.0 (CH_2), 30.6 (Gal-OCH$_2$<u>C</u>H$_2$), 30.6, 30.4, 27.3, 23.7 (CH_2), 14.1 (CH_3) ppm; **ESI MS**: calcd. for $C_{14}H_{28}O_6$: *m/z* = 315.178 $[M+Na]^+$; found: *m/z* = 315.182 $[M+Na]^+$; **EA**: calcd. for $C_{14}H_{28}O_6 \cdot 0.1\ H_2O \cdot 0.1\ CH_3OH$ (M = 297.34 g·mol^{-1}): C 56.95, H 9.69; found: C : C 56.93, H 9.68; **IR** (ATR): $\tilde{\nu}$ = 3373, 2920, 2854, 1407, 1150, 1063, 1047, 971, 882, 827, 762, 723, 668 cm^{-1}.

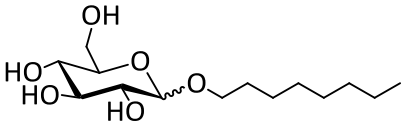
Octyl β-D-galactopyranoside (4)[8,13]



Deprotection of octyl (2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranoside (1.58 g, 3.43 mmol) was achieved according to general procedure 2.B in methanol (20 mL) yielding title compound **4** (871 mg, 2.98 mmol, 87 %) as an amorphous white lyophilisate.

R*f*: 0.58 (ethyl acetate / methanol, 6:1); $[\alpha]_D^{20}$ = - 16.8 (*c* = 1.1, MeOH); **^{1}H-NMR** (500 MHz, MeOH-d_4): δ = 4.20 (d, 1 H, $^3J_{1,2}$ = 7.5 Hz, H-1), 3.89 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.9 Hz, $^2J_{CH,CH}$ = 9.5 Hz, Gal-OC<u>H</u>H), 3.83 (dd, 1 H, $^3J_{4,5}$ = 0.9 Hz, $^3J_{3,4}$ = 3.3 Hz, H-4), 3.75 (dd, 1 H, $^3J_{5,6a}$ = 6.6 Hz, $^2J_{6a,6b}$ = 11.3 Hz, H-6a), 3.73 (dd, 1 H, $^3J_{5,6b}$ = 5.6 Hz, $^2J_{6a,6b}$ = 11.3 Hz, H-6b), 3.54 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.9 Hz, $^2J_{CH,CH}$ = 9.5 Hz, Gal-OCH<u>H</u>), 3.51-3.47 (m, 2 H, H-2, H-5), 3.45 (dd, 1 H, $^3J_{3,4}$ = 3.3 Hz, $^3J_{2,3}$ = 9.7 Hz, H-3), 1.62 (m_c, 2 H, Gal-OCH$_2$C<u>H</u>$_2$), 1.44-1.21 (m, 10 H, 5 CH$_2$), 0.90 (dd∼t, 3 H, ^3J = 7.0 Hz, CH$_3$) ppm; **^{13}C-NMR** (125 MHz, MeOH-d_4): δ = 105.0 (C-1), 76.6 (C-5), 75.1 (C-3), 72.6 (C-2), 70.9 (Glc-O<u>C</u>H$_2$), 70.3 (C-4), 62.5 (C-6), 33.1 (CH$_2$), 30.9 (Gal-OCH$_2$<u>C</u>H$_2$), 30.6, 30.5, 27.2, 23.8 (4 CH$_2$), 14.5 (CH$_3$) ppm; **ESI MS**: calcd. for $C_{14}H_{28}O_6$: m/z = 315.178 $[M+Na]^+$; found m/z = 315.179 $[M+Na]^+$; **EA**: calcd. for $C_{14}H_{28}O_6 \cdot 0.3\ H_2O \cdot 0.2\ CH_3OH$ (M = 304.18 g·mol^{-1}): C 56.07, H 9.74; found: C 56.11, H 9.76; **IR** (ATR): $\tilde{\nu}$ = 3310, 2924, 2854, 1376, 1146, 1063, 981, 919, 856, 658 cm^{-1}.

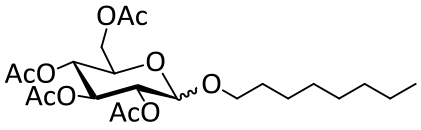
Octyl α,β-D-glucopyranoside (5, 6)



According to the general procedure 2.C, 1-octanol (45.9 g, 353 mmol, 32 eq.), acetyl chloride (2.00 mL, 27.7 mmol, 2.5 eq.) and D-glucose (2.00 g, 11.1 mmol) were allowed to react. The crude product was purified by silica gel chromatography (ethyl acetate / methanol, 10:1) yielding an anomeric mixture of **5** and **6** (2.31 g, 7.90 mmol, 71 %) as light yellow solid.

R*f* (α) = 0.34; **R*f*** (β) = 0.28 (ethyl acetate / methanol, 10:1); anomeric ratio according to ^{1}H-NMR (500 MHz, MeOH-d_4): α:β = 3:1. Detailed analytical data are described for the pure anomers, **5** and **6**.

Octyl (2,3,4,6-tetra-*O*-acetyl)-α- and -β-D-glucopyranoside[14]



According to general procedure 2.C, octyl α,β-D-glucopyranoside (**5**, **6**) (2.31 g, 7.90 mmol) was dissolved in pyridine (23 mL) and acetic anhydride (7.47 mL, 79.0 mmol, 10 eq.) was added. For separation of the anomeric mixture the crude product was purified by silica gel chromatography (cyclohexane / ethyl acetate, 4:1) yielding the pure α-anomer (1.91 g, 4.15 mmol, 53 %) and β-anomer (490 mg (1.06 mmol, 13 %) as colourless oils.

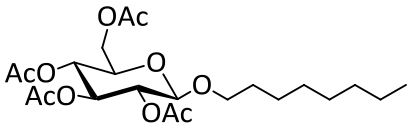
α-anomer: R_f: 0.21 (cyclohexane / ethyl acetate, 4:1); $[\alpha]_D^{20}$ = + 35.1 (*c* = 0.9, $CHCl_3$);

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.48 (dd∼t, 1 H, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.8 Hz, H-3), 5.06 (d, 1 H, $^3J_{1,2}$ = 3.8 Hz, H-1), 5.05 (dd∼t, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.8 Hz, H-4), 4.85 (dd, 1 H, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.8 Hz, H-2), 4.26 (dd, 1 H, $^3J_{5,6a}$ = 4.6 Hz, $^2J_{6a,6b}$ = 12.3 Hz, H-6a), 4.02 (dd, 1 H, $^3J_{5,6b}$ = 2.3 Hz, $^2J_{6a,6b}$ = 12.3 Hz, H-6b), 4.02 (ddd, 1 H, $^3J_{5,6b}$ = 2.3 Hz, $^3J_{5,6a}$ = 4.6 Hz, $^3J_{4,5}$ = 9.8 Hz, H-5), 3.67 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Glc-OC<u>H</u>H), 3.42 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.8 Hz, Glc-OCH<u>H</u>), 2.09, 2.06, 2.03, 2.01 (each s, each 3 H, 4 $COCH_3$), 1.64-1.55 (m, 2 H, Glc-$OCH_2C\underline{H}_2$), 1.39-1.20 (m, 10 H, 5 CH_2), 0.89 (dd∼t, 3 H, ^3J = 6.8 Hz, CH_3) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 170.7, 170.2, 170.1, 169.9 (4 $\underline{C}OCH_3$), 95.6 (C-1), 70.9 (C-2), 70.3 (C-3), 68.8 (Glc-$O\underline{C}H_2$), 68.7 (C-4), 67.1 (C-5), 62.0 (C-6), 31.8 (CH_2), 29.3 (Glc-$OCH_2\underline{C}H_2$), 29.2, 26.9, 26.0, 22.6 (4 CH_2), 20.7, 20.7, 20.6, 20.6, (4 $CO\underline{C}H_3$), 14.1 (CH_3) ppm; **ESI MS**: calcd. for $C_{22}H_{36}O_{10}$: m/z = 483.220 $[M+Na]^+$; found: *m/z* = 483.226 $[M+Na]^+$.

β-anomer: R_f: 0.14 (cyclohexane / ethyl acetate, 4:1); $[\alpha]_D^{20}$ = - 15.1 (*c* = 0.8, $CHCl_3$);

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.20 (dd∼t, 1 H, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.7 Hz, H-3), 5.09 (dd∼t, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.7 Hz, H-4), 4.98 (dd, 1 H, $^3J_{1,2}$ = 8.0 Hz,$^3J_{2,3}$ = 9.7 Hz, H-2), 4.49 (d, 1 H, $^3J_{1,2}$ = 8.0 Hz, H-1), 4.26 (dd, 1 H, $^3J_{5,6a}$ = 4.8 Hz, $^2J_{6a,6b}$ = 12.3 Hz, H-6a), 4.14 (dd, 1 H, $^3J_{5,6b}$ = 2.5 Hz, $^2J_{6a,6b}$ = 12.3 Hz, H-6b), 3.87 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.6 Hz, Glc-OC<u>H</u>H), 3.69 (ddd, 1 H, $^3J_{5,6b}$ = 2.5 Hz, $^3J_{5,6a}$ = 4.8 Hz, $^3J_{4,5}$ = 9.7 Hz, H-5), 3.47 (dt, 1 H, $^3J_{\underline{C}H,CH2}$ = 6.6 Hz, $^2J_{CH,CH}$ = 9.6 Hz, Glc-OCH<u>H</u>), 2.08, 2.04, 2.02, 2.00 (each s, each 3 H, 4 $COCH_3$), 1.69-1.49 (m, 2 H, Glc-$OCH_2C\underline{H}_2$), 1.38-1.17 (m, 10 H, 5 CH_2), 0.88 (dd∼t, 3 H, ^3J = 7.0 Hz, CH_3) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 170.7, 170.3, 169.4, 169.3 (4 $\underline{C}OCH_3$), 100.8 (C-1), 72.9 (C-3), 71.8 (C-5), 71.4 (C-2), 70.2 (Glc-$O\underline{C}H_2$), 68.5 (C-4), 62.0 (C-6), 31.8 (CH_2), 29.4 (Glc-$OCH_2\underline{C}H_2$), 29.3, 29.2, 25.8, 22.6 (4 CH_2), 20.7, 20.6, 20.6, 20.6 (4 $CO\underline{C}H_3$), 14.1 (CH_3) ppm; **ESI MS**: calcd. for $C_{22}H_{36}O_{10}$: m/z = 483.2201 $[M+Na]^+$; found: *m/z* = 483.2346 $[M+Na]^+$.

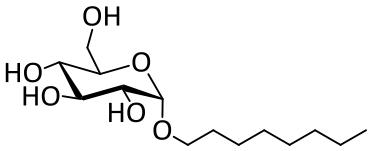
Octyl (2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranoside



According to the general procedure 2.A, 1-octanol (1.32 mL, 10.1 mmol, 2.1 eq.), glucosyl trichloroacetimidate[5] (2.39 g, 4.85 mmol) and $BF_3{\cdot}Et_2O$ (800 µL, 8.10 mmol, 1.7 eq) were allowed to react in anhydrous dichloromethane (25 mL). The crude product was purified by silica gel chromatography (cylcohexane / ethyl acetate, 2:1) yielding the acetylated 1,2-*trans* glucoside (1.06 g, 2.30 mmol, 47 %) as colourless oil.

Detailed analytical data are described for the β-anomer in the procedure describing synthesis octyl (2,3,4,6-tetra-*O*-acetyl)-α- and -β-D-glucopyranoside.

Octyl α-D-glucopyranoside (5)[8]

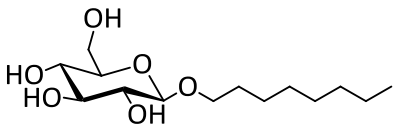


Deprotection of octyl (2,3,4,6-tetra-*O*-acetyl)-α-D-glucopyranoside (580 mg, 1.26 mmol) was achieved according to general procedure 2.B in methanol (8 mL) yielding title compound **5** (336 mg, 1.15 mmol, 92 %) as an amorphous white lyophilisate.

R_f: 0.56 (ethyl acetate / methanol, 6:1); $[\alpha]_D^{20}$ = +117.4 (*c* = 0.98, MeOH);

^{1}H-NMR (500 MHz, MeOH-d_4): δ = 4.79 (d, 1 H, $^3J_{1,2}$ = 3.8 Hz, H-1), 5.05 (dd, 1 H, $^3J_{5,6a}$ = 2.4 Hz, $^2J_{6a,6b}$ = 11.8 Hz, H-6a), 3.76 (dt, 1 H, $^3J_{CH,CH2}$ = 6.7 Hz, $^2J_{CH,CH}$ = 9.7 Hz, Glc-OC<u>H</u>H), 3.70 (dd, 1 H, $^3J_{5,6b}$ = 5.5 Hz, $^2J_{6a,6b}$ = 11.8 Hz, H-6b), 3.66 (dd∼t, 1 H, $^3J_{2,3}$ $^3J_{3,4}$ = 9.3 Hz, H-3), 3.60 (ddd, 1 H, $^3J_{5,6a}$ = 2.4 Hz, $^3J_{5,6b}$ = 5.5 Hz, $^3J_{4,5}$ = 9.9 Hz, H-5), 3.47 (dt, 1 H, $^3J_{CH,CH2}$ = 6.7 Hz, $^2J_{CH,CH}$ = 9.7 Hz, Glc-OCH<u>H</u>), 3.41 (dd, 1 H, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.3 Hz, H-2), 3.32 (dd, 1 H, $^3J_{3,4}$ = 9.3 Hz, $^3J_{4,5}$ = 9.9 Hz, H-4), 1.67 (m_c, 2 H, Glc-OCH$_2$C<u>H</u>$_2$), 1.49-1.26 (m, 10 H, 5 CH_2), 0.93 (dd∼t, 3 H, ^3J = 7.0 Hz, CH_3) ppm; **^{13}C-NMR** (125 MHz, MeOH-d_4): δ = 100.1 (C-1), 75.1 (C-3), 73.6 (C-5), 73.6 (C-2), 71.8 (C-4), 69.1 (Glc-O<u>C</u>H$_2$), 62.7 (C-6), 33.0 (CH_2), 30.6 (Glc-OCH$_2$<u>C</u>H$_2$), 30.6, 30.4, 27.3, 23.7 (4 CH_2), 14.4 (CH_3) ppm; **ESI MS**: calcd. for $C_{14}H_{28}O_6$: *m/z* = 315.178 $[M+Na]^+$; found: *m/z* = 315.178 $[M+Na]^+$; **EA**: calcd. for $C_{14}H_{28}O_6 \cdot 0.4\ H_2O$ (M = 304.18 g·mol^{-1}): C 56.13, H 9.69; found: C 56.14, H 9.45; **IR** (ATR): $\tilde{\nu}$ = 3365, 2923, 1409, 1146, 1088, 1027, 1004, 915, 852, 767, 726, 524 cm^{-1}.

Octyl β-D-glucopyranoside (6)[15]



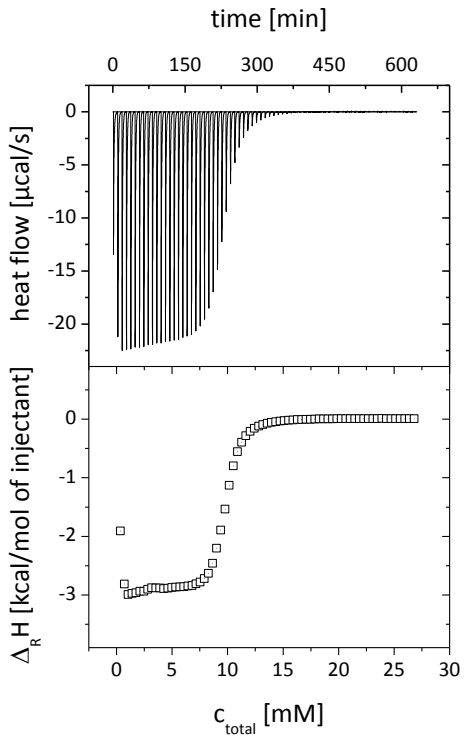
Deprotection of octyl (2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranoside (1.06 mg, 2.30 mmol) was achieved according to general procedure 2.B in methanol (15 mL) yielding title compound **6** (611 mg, 2.09 mmol, 91 %) as an amorphous white lyophilisate.

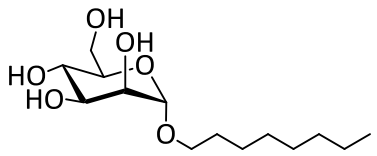
R_f: 0.40 (ethyl acetate / methanol, 6:1); $[\alpha]_D^{20}$ = - 23.4 (*c* = 1.0, MeOH); **^{1}H-NMR** (500 MHz, MeOH-d_4): δ = 4.25 (d, 1 H, $^3J_{1,2}$ = 7.9 Hz, H-1), 3.90 (dt, 1 H, $^3J_{CH,CH2}$ = 6.9 Hz, $^2J_{CH,CH}$ = 9.5 Hz, Glc-OC<u>H</u>H), 3.86 (dd, 1 H, $^3J_{5,6a}$ = 2.0 Hz, $^2J_{6a,6b}$ = 11.9 Hz, H-6a), 3.67 (dd, 1 H, $^3J_{5,6b}$ = 5.4 Hz, $^2J_{6a,6b}$ = 11.9 Hz, H-6b), 3.53 (dt, 1 H, $^3J_{CH,CH2}$ = 6.9 Hz, $^2J_{CH,CH}$ = 9.5 Hz, Glc-OCH<u>H</u>), 3.35 (dd∼t, 1 H, $^3J_{2,3}$ = $^3J_{3,4}$ =9.0 Hz, H-3), 3.30-3.22 (m, 2 H, H-4, H-5), 3.17 (dd, 1 H, $^3J_{1,2}$ = 7.9 Hz, $^3J_{2,3}$ = 9.0 Hz, H-2), 1.62 (m_c, 2 H, Glc-OCH$_2$C<u>H</u>$_2$), 1.44-1.23 26 (m, 10 H, 5 CH$_2$), 0.90 (dd∼t, 3 H, ^3J = 7.0 Hz, CH$_3$) ppm; **^{13}C-NMR** (125 MHz, MeOH-d_4): δ = 104.4 (C-1), 78.2 (C-3), 77.9 (C-5), 75.2 (C-2), 71.7 (C-4), 70.9 (Glc-O<u>C</u>H$_2$), 62.8 (C-6), 33.0 (CH$_2$), 30.8 (Glc-OCH$_2$<u>C</u>H$_2$), 30.6, 30.5, 27.5, 23.8 (4 CH$_2$), 14.5 (CH$_3$) ppm; **ESI MS**: calcd. for $C_{14}H_{28}O_6$: m/z = 315.178 $[M+Na]^+$; found: *m/z* = 315.179 $[M+Na]^+$; **EA**: calcd. for $C_{14}H_{28}O_6 \cdot 0.3\ H_2O$ (M = 297.77 g·mol^{-1}): C 56.47, H 9.68; found: C 56.35, H 9.46.

4. ITC measurements

The ITC data reported in the main manuscript are averaged values from three independent ITC measurements with standard deviations (SD).

4.1 ITC titration curves of homo-glycomicelles





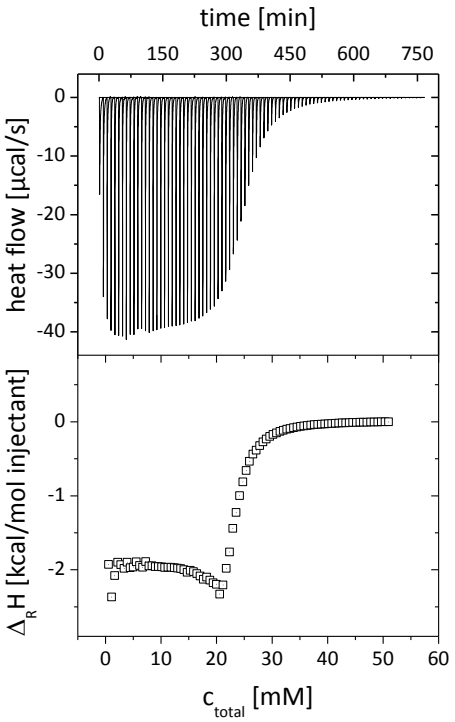
1

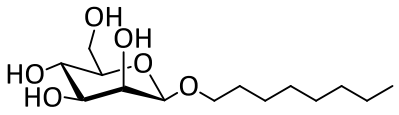
c = 123 mmol·L^{-1}

70 aliquots a 4 µL

cmc = 9.8 mM

Figure S1: Representative ITC curve of octyl α-D-mannopyranoside (**1**) to determine the *cmc* and ΔH°$_{demic}$ in water at 25°C.





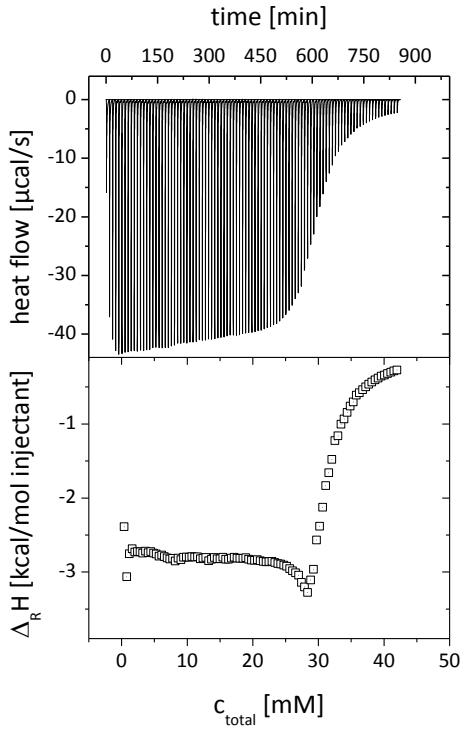
2

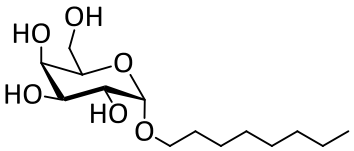
c = 259 mmol·L^{-1}

85 aliquots a 3 µL

cmc = 22.9 mM

Figure S2: Representative ITC curve of octyl β-D-mannopyranoside (**2**) to determine the *cmc* and ΔH°$_{demic}$ in water at 25°C.





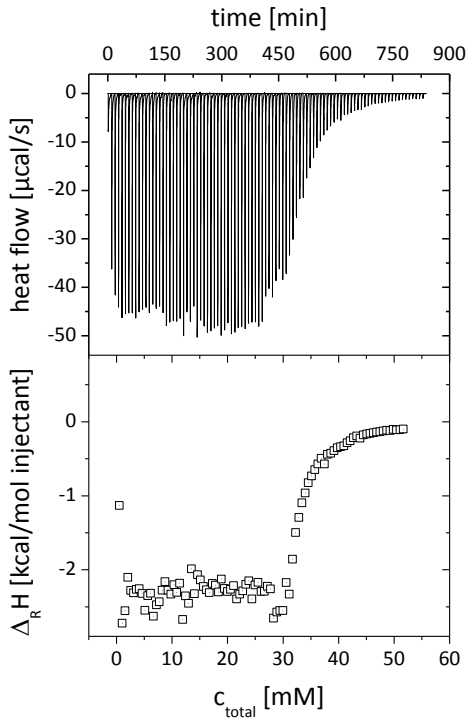
3

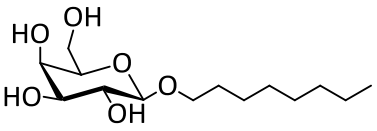
c = 189 mmol·L^{-1}

95 aliquots a 3 µL

cmc = 29.7 mM

Figure S3: Representative ITC curve of octyl α-D-galactopyranoside (**3**) to determine the *cmc* and ΔH°$_{demic}$ in water at 25°C.





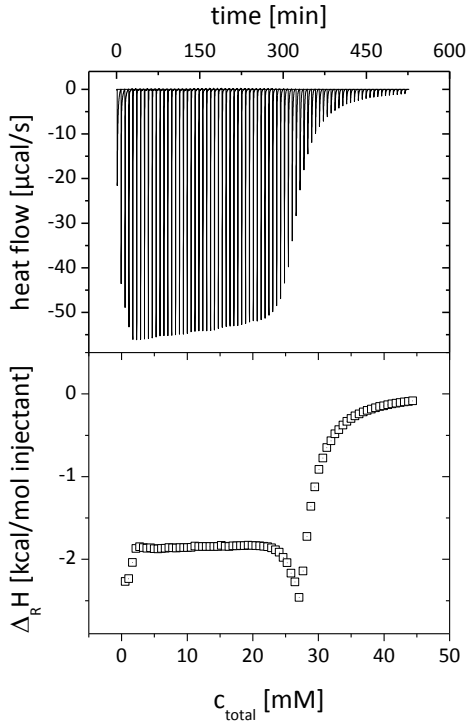
4

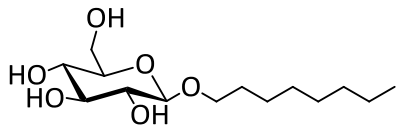
c = 238 mmol·L^{-1}

95 aliquots a 3 µL

cmc = 31.5 mM

Figure S4: Representative ITC curve of octyl β-D-galactopyranoside (**4**) to determine the *cmc* and ΔH°$_{demic}$ in water at 25°C.





6

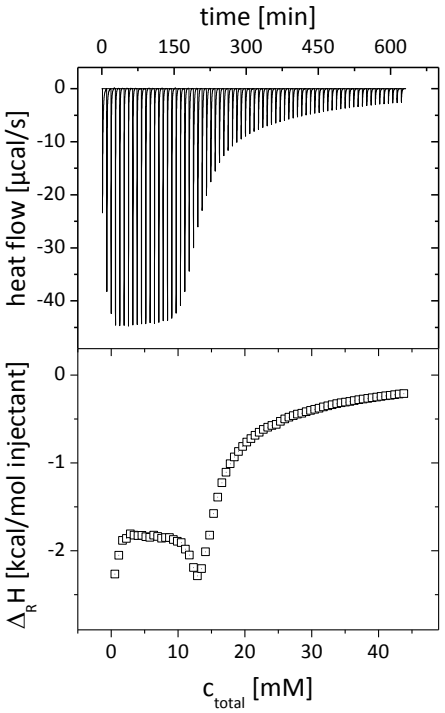
c = 258 mmol·L^{-1}

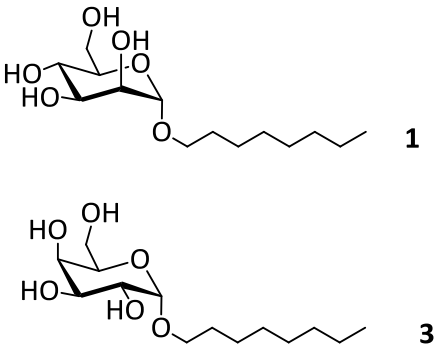
75 aliquots a 3 µL

cmc = 28.3 mM

Figure S5: Representative ITC curve of octyl β-D-glucopyranoside (**6**) to determine the *cmc* and ΔH°$_{demic}$ in water at 25°C.

4.2 ITC titration curves of hetero-glycomicelles



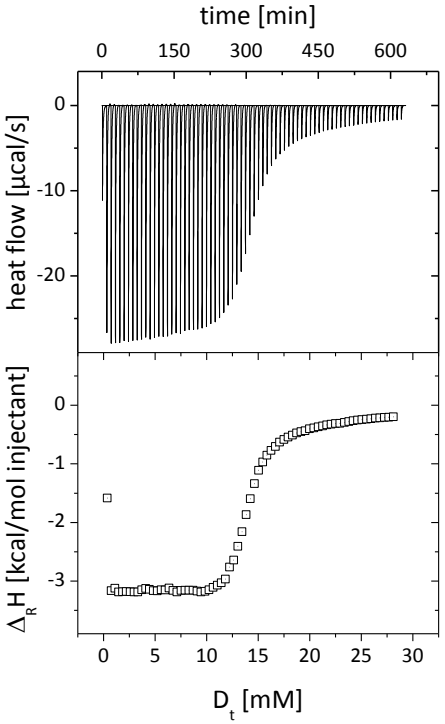


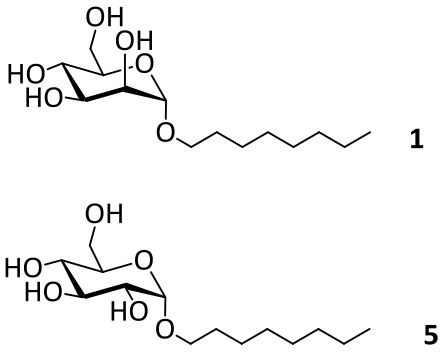
c = 201 mmol·L^{-1} (ratio 1:1)

70 aliquots a 4 µL

cmc = 15.4 mM

Figure S6: Representative ITC curve of a binary glycomicelle containing octyl α-D-mannopyranoside (**1**) and octyl α-D-galactopyranoside (**3**) to determine the *cmc* and $\Delta H°_{demic}$ in water at 25°C.



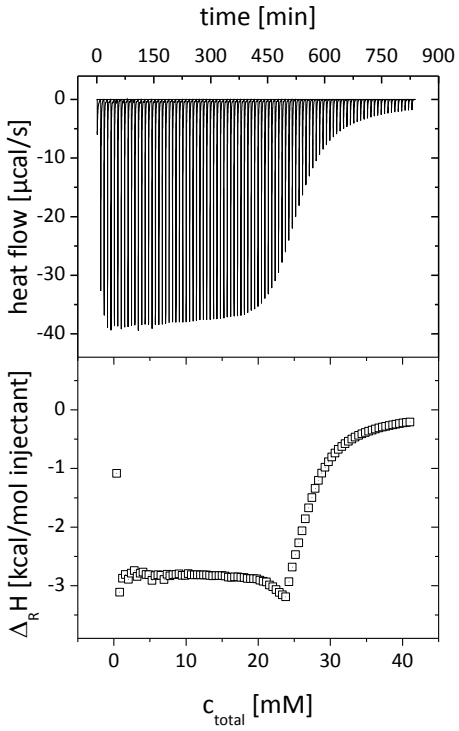


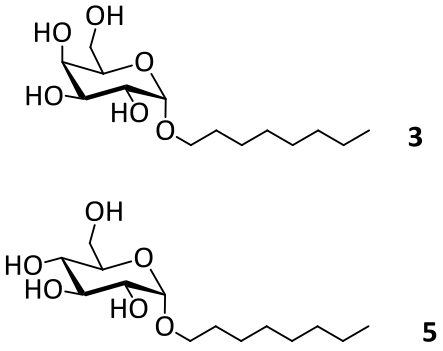
c = 129 mmol·L^{-1} (ratio 1:1)

70 aliquots a 4 µL

cmc = 13.8 mM

Figure S7: Representative ITC curve of a binary glycomicelle containing octyl α-D-mannopyranoside (**1**) and octyl α-D-glucopyranoside (**5**) to determine the *cmc* and $\Delta H°_{demic}$ in water at 25°C.



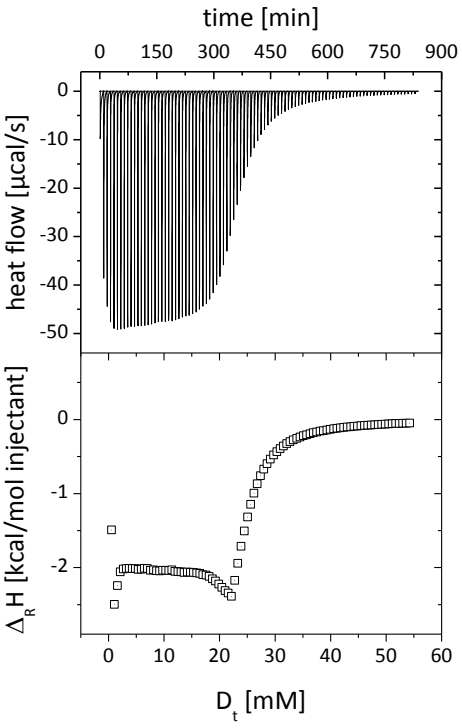


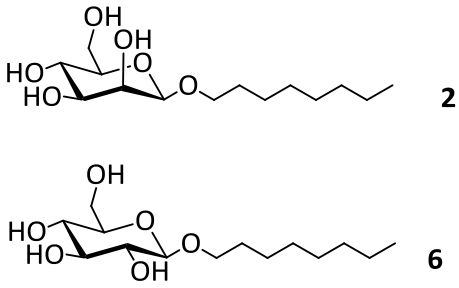
c = 189 mmol·L^{-1} (ratio 1:1)

95 aliquots a 3 µL

cmc = 25.6 mM

Figure S8: Representative ITC curve of a binary glycomicelle containing octyl α-D-galactopyranoside (**3**) and octyl α-D-glucopyranoside (**5**) to determine the *cmc* and $\Delta H°_{demic}$ in water at 25°C.



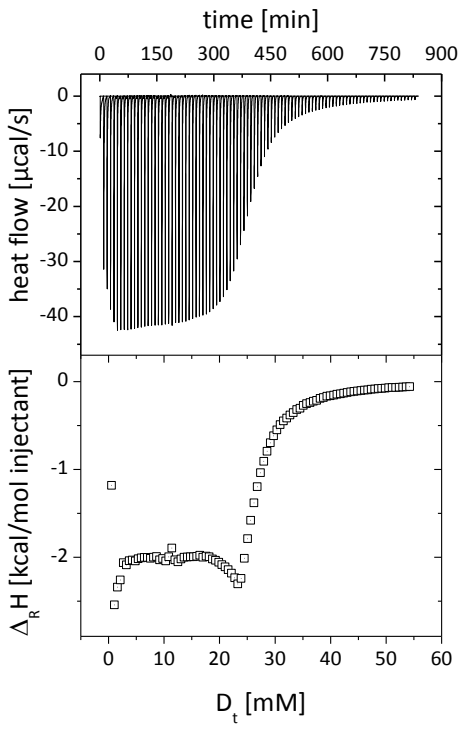


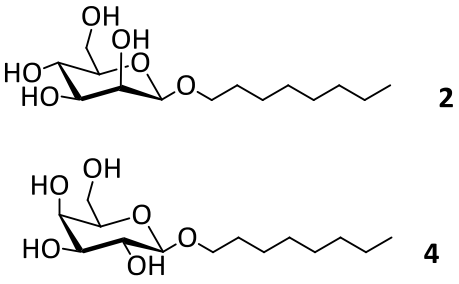
c = 250 mmol·L^{-1} (ratio 1:1)

95 aliquots a 3 µL

cmc = 23.3 mM

Figure S9: Representative ITC curve of a binary glycomicelle containing octyl β-D-mannopyranoside (**2**) and octyl β-D-glucopyranoside (**6**) to determine the *cmc* and $\Delta H°_{demic}$ in water at 25°C.



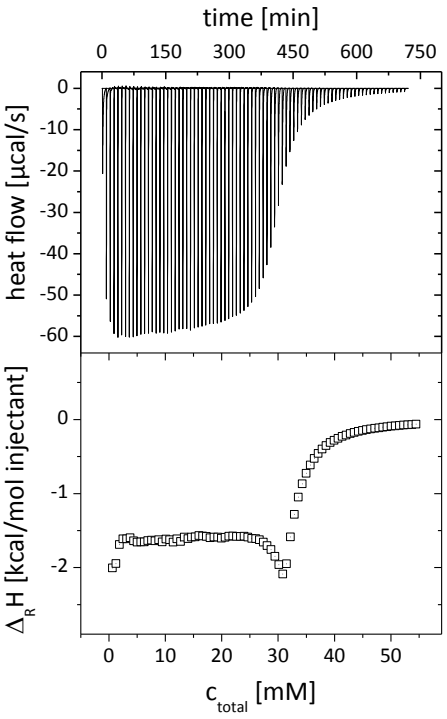


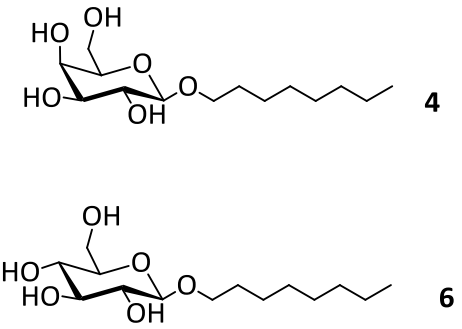
c = 250 mmol·L^{-1} (ratio 1:1)

95 aliquots a 3 µL

cmc = 24.5 mM

Figure S10: Representative ITC curve of a binary glycomicelle containing octyl β-D-mannopyranoside (**2**) and octyl β-D-galactopyranoside (**72**) to determine the *cmc* and ΔH°$_{demic}$ in water at 25°C.





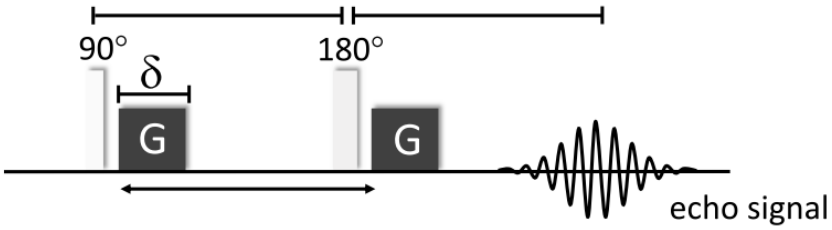
c = 238 mmol·L^{-1} (ratio 1:1)

95 aliquots a 3 µL

cmc = 31.5 mM

Figure S11: Representative ITC curve of a binary glycomicelle containing octyl β-D-galactopyranoside (**4**) and octyl β-D-glucopyranoside (**6**) to determine the *cmc* and ΔH°$_{demic}$ in water at 25°C.

5. DOSY NMR measurements



αOctylMan **1**		
c [mM]	δ [µs]	Δ [s]
2.5, 5, 7.5, 10, 15, 20	2000	0.15
40	2500	0.20
75, 100, 150, 250	3000	0.30

βOctylMan **2**		
c [mM]	δ [µs]	Δ [s]
10, 15, 17.5, 20	2000	0.15
22.5, 25, 30, 40	2500	0.20
75, 100, 150, 250	3000	0.30

Figure S12: Parameters employed for the pulsed gradient spin echo (PGSE) NMR experiment: duration time δ of the pulsed gradient G and time Δ (diffusion time) between the leading edges of the pulsed gradients. τ represents the first and the second period of the experiment.

For determination of the diffusion coefficients, four regions in the ^{1}H NMR spectra of the investigated compound were used (δ = 4.00-3.30, 1.65-1:37, 1.36-1.00, and 0.90-0.60 ppm).

5.1 Diffusion series of octyl α-D-mannopyranoside (1)

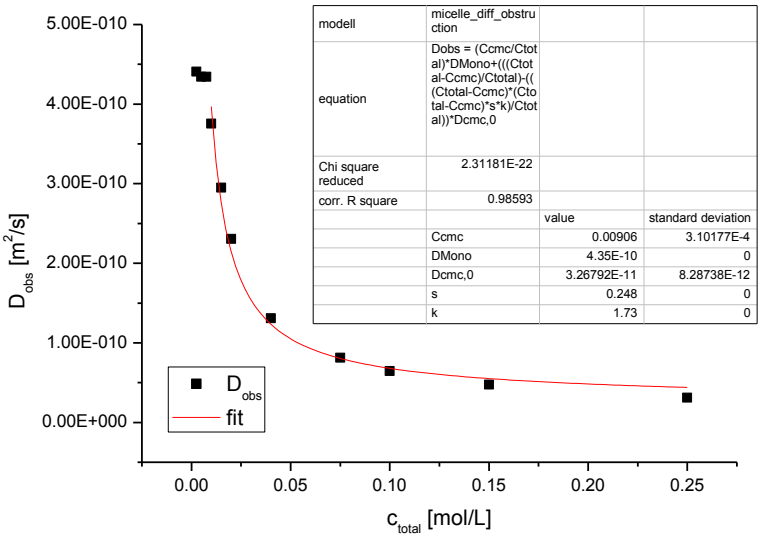


Figure S13: Experimentally determined diffusion coefficients of octyl α-D-mannopyranoside (**1**) and fit using equation (7). Density *d* of **1** was inserted as 1.18 g/cm^3.

5.2 Diffusion series of octyl β-D-mannopyranoside (2)

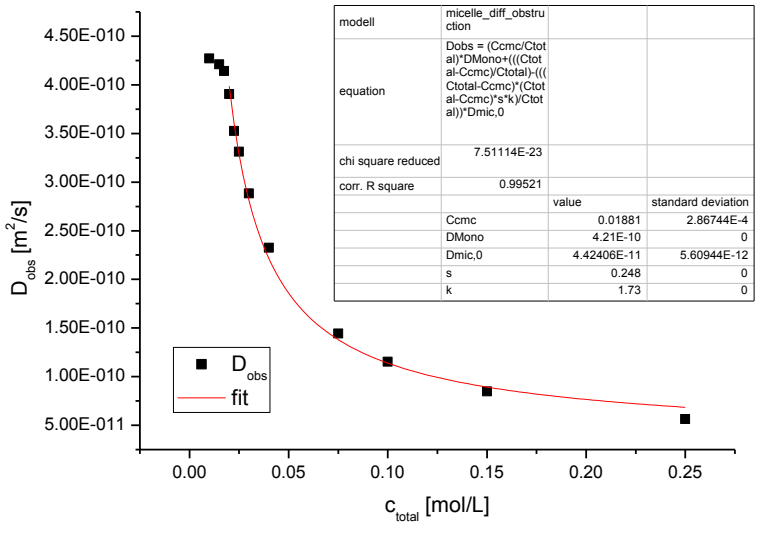


Figure S14: Experimentally determined diffusion coefficients of octyl β-D-mannopyranoside (**2**) and fit using equation (7). Density *d* of **2** was inserted as 1.18 g/cm^3.

6. References

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