Electronic Supplementary Information

Synthesis and Biocompatibility Evaluation of Fluorinated, Single-tailed Glucopyranoside Surfactants

Xueshu Li,[a] Jaroslav Turánek,[b] Pavlína Knötigová,[b] Hana Kudláčková,[b] Josef Mašek,[b] D Brant Pennington,[c] Stephen E Rankin,[c] Barbara L Knutson[c] and Hans-Joachim Lehmler*[a]

[a] *Department of Occupational and Environmental Health, University of Iowa, Iowa City, IA, 52242, USA. Fax: 3193354290; Tel: 3193354211;* [b] *Veterinary Research Institute v.v.i., Department of Vaccinology and Immunotherapy, Brno, Czech Republic;* [c] *Chemicals and Materials Engineering Department, University of Kentucky, Lexington, KY, 40506, USA.*

CONTENT: Detailed characterization of compounds **6b**, **6c**, **6e**, **6f**, **7b**, **7c**, **7e**, **7f**, **8b**, **8c**, **8e**, **8f**, **9b**, **9c**, **9e** and **9f**.

11,11,12,12,13,13,14,14,15,15,16,16,16-Tridecafluorohexadecyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (6b): White solid; mp: 53-54 ºC; Yield, 53%; ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 1.1-1.4 (m, 12H, 6×CH_2), 1.57 (m, 4H, H-2′ and H-9′), 1.9-2.0 (m, 14H, 4×CH_3CO and H-10′), 3.45 (m, 1H, H-1′a), 3.68 (m, 1H, H-5), 3.86 (m, 1H, H-1′b), 4.12 (d, 1H, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.25 (dd,1H, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 4.7 Hz, H-6b), 4.47 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.97 (“t”, 1H, J ~ 8.4 Hz, H-2), 5.08 (“t”, 1H, J ~ 8.6 Hz, H-4), 5.16 (“t”, 1H, J ~ 8.4 Hz, H-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 20.1 (*C*-9′), 20.8 (4×*C*H_3CO), 25.9 (*C*-3′), 29.3-29.7 (*C*-2′, *C*-4′ to *C*-8′), 31.0 (t, J = 23 Hz, *C*-10′), 62.1 (C-6), 68.6 (C-4), 70.4 (C-1′), 71.5 (C-2), 71.9 (C-5), 73.0 (C-3), 101.0 (C-1), 169.5, 169.6, 170.5, 170.9 (4×*C*OCH$_3$). ^{19}F NMR δ/ppm (282 MHz, $CDCl_3$): -81.3 (CF_3), -114.9 (CF_2), -122.5 (CF_2), -123.4 (CF_2), -124.1 (CF_2), -126.7 (CF_2). Positive-ion ESI-MS peak at m/z 829 ([M+Na]$^+$).

11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Heptadecafluorooctadecyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (6c): White solid; mp: 75-76 ºC; Yield, 55%; ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 1.1-1.4 (m, 12H, 6×CH_2), 1.53 (m, 4H, H-2′ and H-9′), 1.9-2.1 (m, 14H, 4×CH_3CO and H-10′), 3.41 (m, 1H, H-1′a), 3.66 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.6, H-5), 3.83 (m, 1H, H-1′b), 4.09 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 2.4 Hz, H-6a), 4.24 (dd,1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 4.7 Hz, H-6b), 4.45 (d, 1H, J = 8.0 Hz, H-1), 4.95 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 5.05 (“t”, 1H, J ~ 9.6 Hz, H-4), 5.17 (“t”, 1H, J ~ 9.4 Hz, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 20.2 (*C*-9′), 20.7 (4×*C*H_3CO), 25.9 (*C*-3′), 29.2-29.6 (*C*-2′, *C*-4′ to *C*-8′), 30.9 (t, J = 21 Hz, *C*-10′), 62.1 (C-6), 68.6 (C-4), 70.4 (C-1′), 71.5 (C-2), 71.9 (C-5), 73.0 (C-3), 101.0 (C-1), 169.4,

169.5, 170.4, 170.8 (4×*C*OCH$_3$). ^{19}F NMR δ/ppm (282 MHz, CDCl$_3$): CDCl$_3$ -81.5 (CF$_3$), -115.1 (CF$_2$), -122.3 (3×CF$_2$), -123.3 (CF$_2$), -124.1 (CF$_2$), -126.7 (CF$_2$). Positive-ion ESI-MS peak at m/z 929 ([M+Na]$^+$).

12,12,13,13,14,14,15,15,16,16,17,17,17-Tridecafluoroheptadecyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (6e): White solid; mp: 61-62 ºC; Yield, 46%; ^{1}H NMR (400 MHz, CDCl$_3$): δ/ppm 1.1-1.4 (m, 14H, 7×C*H*$_2$), 1.56 (m, 4H, H-2´ and H-10´), 1.9-2.1 (m, 14H, 4×C*H*$_3$CO and H-11´), 3.46 (m, 1H, H-1´a), 3.67 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.6, H-5), 3.84 (m, 1H, H-1´b), 4.11 (m, 1H, H-6a), 4.25 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 4.8 Hz, H-6b), 4.47 (d, 1H, *J* = 8.0 Hz, H-1), 4.96 (dd, 1H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.06 (“t”, 1H, *J* ~ 9.7 Hz, H-4), 5.19 (“t”, 1H, J ~ 9.4 Hz, H-3). ^{13}C NMR (100 MHz, CDCl$_3$) δ/ppm 20.4 (*C*-10´), 20.7-20.8 (4×*C*H$_3$CO), 26.0 (*C*-3´), 29.3-29.7 (C-2´, C-4´ to C-9´), 31.2 (t, *J* = 22 Hz, *C*-11´), 62.4 (C-6), 69.0 (C-4), 70.3 (C-1´), 71.8 (C-2), 72.1 (C-5), 73.2 (C-3), 101.1 (C-1), 169.3, 169.5, 170.4, 170.7 (4×*C*OCH$_3$). ^{19}F NMR (282 MHz, CDCl$_3$): δ/ppm -81.3 (CF$_3$), -114.9 (CF$_2$), -122.5 (CF$_2$), -123.4 (CF$_2$), -124.1(CF$_2$), -126.7 (CF$_2$). Positive-ion ESI-MS peak at m/z 843 ([M+Na]$^+$).

12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluorononadecyl-2,3,4,6-tetra-O-acetyl-D-glucopyranoside (6f): White solid; mp: 76-77 ºC; Yield, 52 %; ^{1}H NMR (300 MHz, CDCl$_3$): δ/ppm 1.2-1.4 (m, 14H, -(C*H*$_2$)$_7$-), 1.60 (m, 4H, H-2´ and H-10´), 1.9-2.1 (m, 14H, 4×C*H*$_3$CO and H-11´), 3.47 (m, 1H, H-1´a), 3.70 (m, 1H, H-5), 3.86 (m, 1H, H-1´b), 4.0-4.14 (“d”, 1H, H-6a), 4.26 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 4.5 Hz, H-6b), 4.48 (d, 1H, *J* = 7.9 Hz, H-1), 4.98 (“t”, 1H, *J* ~ 8.5 Hz, H-2), 5.08 (“t”, 1H, *J*

~ 9.6 Hz, H-4), 5.20 ("t", 1H, J ~ 9.6 Hz, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 20.3 (CH_2-10′), 20.8-20.9 (4×CH_3CO), 26.0 (C-3′), 29.3-29.7 (7×CH_2, 2′, 4′-9′), 31.1 (t, J = 22 Hz, C-11′), 62.2 (C-6), 68.7 (C-4), 70.4 (C-1′), 71.6 (C-2), 71.9 (C-5), 73.1 (C-3), 101.1 (C-1), 169.5, 169.6, 170.5, 170.9 (4×$COCH_3$). ^{19}F NMR (282 MHz, $CDCl_3$): δ/ppm -81.3 (CF_3), -114.9 (CF_2), -122.5 (3×CF_2), -123.4 (CF_2), -124.1 (CF_2), -126.7 (CF_2). Positive-ion ESI-MS peak at m/z 943 ($[M+Na]^+$).

Hexadecyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (7b) [6]

White solid; mp: 67-68 ºC (Lit.: 70-73.5[1,2] ºC, 90-92 ºC[3]); Yield, 49%; ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 0.88 (t, 3H, J = 7.0 Hz, H-16′), 1.1-1.4 (m, 26H, 13×CH_2), 1.57 (m, 2H, H-2′), 1.9-2.1 (4×s, 12H, 4×CH_3CO), 3.48 (dt, 1H, $J_{1'a,1'b}$ = 9.4 Hz, $J_{1'a,2'}$ = 6.7 Hz, H-1′a), 3.70 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.7, H-5), 3.87 (dt, 1H, $J_{1'a,1'b}$ = 9.4 Hz, $J_{1'b,2'}$ = 6.7 Hz, H-1′b), 4.13 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, $J_{6a,5}$ = 2.5 Hz, H-6a), 4.26 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 4.7 Hz, H-6b), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.98 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.09 ("t", 1H, J ~ 9.7 Hz, H-4), 5.21 ("t", 1H, J ~ 9.5 Hz, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 14.3 (C-16′), 20.8-20.9 (4×CH_3CO), 22.9 (C-15′), 26.1 (C-3′), 29.5-29.9 (C-2′, C-4′ to C-13′), 32.1 (C-14′), 62.2 (C-6), 68.7 (C-4), 70.5 (C-1′), 71.6 (C-2), 71.9 (C-5), 73.0 (C-3), 101.0 (C-1), 169.5, 169.6, 170.5, 170.9 (4×$COCH_3$). Positive-ion ESI-MS peak at m/z 595 ($[M+Na]^+$).

Octadecyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (7c)

White solid; mp: 76-77 ºC (Lit.: 78-79.5 ºC[1]) Yield, 48%; ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 0.88 (t, 3H, J = 7.0 Hz, H-18′), 1.1-1.4 (m, 30H, 15×CH_2), 1.56 (m, 2H, H-2′),

2.0-2.1 (4×s, 12H, 4×C*H*$_3$CO), 3.47 (dt, 1H, $J_{1'a,1'b}$ = 9.5 Hz, $J_{1'a,2'}$ = 6.7 Hz, H-1´a), 3.69 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.8, H-5), 3.85 (dt, 1H, $J_{1'a,1'b}$ = 9.5 Hz, $J_{1'b,2'}$ = 6.7 Hz, H-1´b), 4.13 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, $J_{6a,5}$ = 2.5 Hz, H-6a), 4.25 (dd,1H, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 4.8 Hz, H-6b), 4.48 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.97 (dd, 1H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.08 ("t", 1H, J ~ 9.8 Hz, H-4), 5.20 ("t", 1H, J ~ 9.4 Hz, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 14.3 (*C*-18´), 20.8-20.9 (4×*C*H$_3$CO), 22.9 (*C*-17´), 26.1 (*C*-3´), 29.6-29.9 (C-2´, C-4´ to C-15´), 32.2 (*C*-16´), 62.3 (C-6), 68.9 (C-4), 70.5 (C-1´), 71.7 (C-2), 72.1 (C-5), 73.2 (C-3), 101.1 (C-1), 169.4, 169.6, 170.5, 170.8 (4×*C*OCH$_3$). Positive-ion ESI-MS peak at m/z 623 ([M+Na]$^+$).

Heptadecyl 2,3,4,6-tetra-O-acetyl- β-D-glucopyranoside (7e): White solid; mp: 75-76 ºC; Yield, 50 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 0.88 (t, 3H, J = 7.0 Hz, H-17´), 1.2-1.3 (m, 28H, 14×C*H*$_2$), 1.56 (m, 2H, H-2´), 2.0-2.1 (4×s, 12H, 4×C*H*$_3$CO), 3.48 (dt, 1H, $J_{1'a,1'b}$ = 9.7 Hz, $J_{1'a,2'}$ = 6.7 Hz, H-1´a), 3.68 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 2.6 Hz, $J_{5,6b}$ = 4.8, H-5), 3.86 (dt, 1H, $J_{1'a,1'b}$ = 9.7 Hz, $J_{1'a,2'}$ = 6.7 Hz, H-1´b), 4.14 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, $J_{6a,5}$ = 2.5 Hz, H-6a), 4.26 (dd,1H, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 4.8 Hz, H-6b), 4.49 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.98 (dd, 1H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.08 ("t", 1H, J ~ 9.7 Hz, H-4), 5.21 ("t", 1H, J ~ 9.5 Hz, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 14.3 (C-17´), 20.8-21.0 (4×*C*H$_3$CO), 22.9 (C-16´), 26.0 (C-3´), 29.5-29.9 (C-2´, C-4´ to C-14´), 32.2 (C-15´), 62.2 (C-6), 68.7 (C-4), 70.5 (C-1´), 71.6 (C-2), 72.0 (C-5), 73.1 (C-3), 101.1 (C-1), 169.5, 169.6, 170.5, 170.9 (4×*C*OCH$_3$). Positive-ion ESI-MS peak at m/z 609 ([M+Na]$^+$).

Nonadecyl 2,3,4,6-tetra-O-acetyl-(α+β)-D-glucopyranoside (7f): White solid; mp: 69-71ºC (1:4 mixture of the α- and β-anomer); Yield, 52%; ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 0.8-0.9 (t, 3H, J = 7.0 Hz, H-19´), 1.1-1.4 (m, 32H, 16×CH_2), 1.60 (m, 2H, CH_2-2´), 1.9-2.2 (m, 12H, 4×CH_3CO), 3.48 (m, 1H, H-1´αa and H-1´βa), 3.6-3.7 (m, H-1´bα and H-5β), 3.83 (m, H-1´bβ), 3.9-4.2 (m, H-4α, H-5α, H-6aβ), 4.2-4.3 (m, H-6aα, H-6bβ), 4.45 (d, $J_{1,2}$ = 7.9 Hz, H-1β), 4.81 (d, H-6bα), 4.9-5.1 (m, H-2α, H-3α, H-2β, H-4β), 5.15 (t, J ~ 9.5 Hz, H-3β), 5.43 (t, J = 9.4 Hz, H-1α). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm typical signal of α and β-anomer: 95.7 (C-1α), 100.9 (C-1β). Positive-ion ESI-MS peak at m/z 637 ($[M+Na]^+$).

11,11,12,12,13,13,14,14,15,15,16,16,16-Tridecafluorohexadecyl-β-D-glucopyranoside (8b): White solid; mp: 70-72 ºC; mp(DSC): 68.87±0.57 ºC, 161.92±1.08 ºC; Yield, 93%; ^{1}H NMR (300 MHz, CD_3OD): δ/ppm 1.3-1.5 (m, 12H, 6×CH_2), 1.6-1.7 (m, 4H, H-2´ and H-9´), 2.15 (m, 2H, H-10´), 3.20 (“t”, 1H, J ~ 8.1 Hz, H-2), 3.2-3.4 (m, 3H, H-3, H-4 and H-5), 3.57 (m, 1H, H-1´a), 3.66 (dd, 1H, $J_{6a,6b}$ = 11.9 Hz, $J_{5,6a}$ = 5.0 Hz, H-6a), 3.8-4.0 (m, 2H, H-6b and H-1´b), 4.28 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1). ^{13}C NMR (75 MHz, CD_3OD) δ/ppm 21.4 (*C*-9´), 27.3 (*C*-3´), 30.3-30.9 (*C*-2´, *C*-4´ to *C*-8´), 31.9 (t, J = 22 Hz, *C*-10´), 62.9 (C-6), 71.0 (*C*-1´), 71.7 (C-4), 75.2 (C-2), 78.0 (C-5), 78.2 (C-3), 104.5 (C-1). ^{19}F NMR (282 MHz, CD_3OD) δ/ppm -80.7 (CF_3), -113.8 (CF_2), -121.3 (CF_2), -122.3 (CF_2), 122.9 (CF_2), 125.7 (CF_2). Anal. calcd. for $C_{22}H_{31}F_{13}O_6$: C 41.39, H 4.89. Found: C 41.15, H 4.74. HR-MS of $[M+Na]^+$ m/z: Calcd. 661.1811, Found. 661.1811.

11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Heptadecafluorooctadecyl-β-D-glucopyranoside (8c): White solid; mp: 106-108 ºC; mp(DSC): 109.15±1.38 ºC, 183.14±0.50 ºC; Yield, 96%; ^{1}H NMR (400 MHz, CD_3OD): δ/ppm 1.3-1.4 (m, 12H, 6×CH_2), 1.6-1.7 (m, 4H, H-2´ and H-9´), 2.17 (m, 2H, H-10´), 3.21 (t, 1H, J ~ 8.1 Hz, H-2), 3.3-3.4 (m, 3H, H-3, H-4 and H-5), 3.58 (m, 1H, H-1´a), 3.72 (dd, 1H, $J_{6a,6b}$ = 11.8 Hz, $J_{5,6a}$ = 5.1 Hz, H-6a), 3.8-4.0 (m, 2H, H-6b and H-1´b), 4.28 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1). ^{13}C NMR (75 MHz, CD_3OD) δ/ppm 21.3 (C-9´), 27.1 (C-3´), 30.1-30.9 (C-2´, C-4´ to C-8´), 31.9 (t, J = 22 Hz, C-10´), 62.9 (C-6), 70.9 (*C*-1´), 71.8 (C-4), 75.2 (C-2), 77.9 (C-5), 78.3 (C-3), 104.4 (C-1). ^{19}F NMR (282 MHz, CD_3OD) δ/ppm -81.4 (CF_3), -114.9 (CF_2), -122.3 (3×CF_2), -123.3 (CF_2), -124.4 (CF_2), -126.7 (CF_2). Anal. calcd. for $C_{24}H_{31}F_{17}O_6$: C 39.03, H 4.23. Found: C 39.31, H 4.28. HR-MS of $[M+Na]^+$ m/z: Calcd. 761.1747, Found. 761.1760.

12,12,13,13,14,14,15,15,16,16,17,17,17-Tridecafluoroheptadecyl-β-D-glucopyranoside (8e): White solid; mp: 106-107 ºC; mp(DSC): 110.12±0.19 ºC, 182.56±0.11 ºC; Yield, 95%; ^{1}H NMR (400 MHz, CD_3OD): δ/ppm 1.3-1.5 (m, 14H, 7×CH_2), 1.6-1.7 (m, 4H, H-2´ and H-10´), 2.18 (m, 2H, H-11´), 3.23 (“t”, 1H, J ~ 8 Hz, H-2), 3.3-3.4 (m, 3H, H-3, H-4 and H-5), 3.59 (m, 1H, H-1´a), 3.70 (dd, 1H, $J_{6a,6b}$ = 11.9 Hz, $J_{5,6b}$ = 5.2 Hz, H-6a), 3.8-4.0 (m, 2H, H-6b and H-1´b), 4.31 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1). ^{13}C NMR (100 MHz, CD_3OD) δ/ppm 21.3 (*C*-10´), 27.1 (*C*-3´), 30.1-30.9 (*C*-2´, *C*-4´ to *C*-9´), 31.9 (t, J = 22 Hz, *C*-11´), 62.9 (C-6), 70.9 (*C*-1´), 71.9 (C-4), 75.2 (C-2), 77.9 (C-5), 78.3 (C-3), 104.5 (C-1). ^{19}F NMR (282 MHz, CD_3OD) δ/ppm -81.3 (CF_3), -114.9 (CF_2), -122.5 (CF_2), -

123.4 (CF_2), -124.1 (CF_2), -126.7 (CF_2). Anal. calcd. for $C_{23}H_{33}F_{13}O_6$: C 42.34, H 5.10. Found: C 42.29, H 5.03. HR-MS of $[M+Na]^+$ m/z: Calcd. 675.1967, Found. 675.1961.

12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluorononadecyl-β-D-glucopyranoside (8f): White solid; mp: 117-118 ºC; mp(DSC): 115.51±1.99 ºC, 188.19±0.82 ºC; Yield, 96 %; ^{1}H NMR (400 MHz, CD_3OD): δ/ppm 1.3-1.4 (m, 14H, 7×C*H*$_2$), 1.5-1.7 (m, 4H, H-2´ and H-10´), 2.14 (m, 2H, H-11´), 3.17 ("t", 1H, J ~ 8.0 Hz, H-2), 3.2-3.4 (m, 3H, H-3, 4 and 5, overlapped with residue proton of CD_3OD), 3.55 (m, 1H, H-1´a), 3.67 (dd, 1H, $J_{6a,6b}$ = 11.9 Hz, $J_{5,6a}$ = 5.4 Hz, H-6a), 3.8-4.0 (m, 2H, H-6b and H-1´b), 4.25 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1). ^{13}C NMR (100 MHz, CD_3OD) δ/ppm 27.1 (C-3´), 30.1-30.9 (C-2´, C-4´ to C-9´), 63.0 (C-6), 71.0 (C-1´), 71.9 (C-4), 75.3 (C-2), 78.0 (C-5), 78.3 (C-3), 104.5 (C-1). ^{19}F NMR (282 MHz, CD_3OD) δ/ppm -81.0 (CF_3), -113.7 (CF_2), -121.4 (3×CF_2), -122.2 (CF_2), 122.9 (CF_2), 125.7 (CF_2). Anal. calcd. for $C_{25}H_{33}F_{17}O_6$: C 39.90, H 4.42. Found: C 40.12, H 4.50. HR-MS of $[M+Na]^+$ m/z: Calcd. 775.1903, Found. 775.1906.

Hexadecyl-β-D-glucopyranoside (9b): White powder; mp: 73-74 ºC (Lit.: 73-75 ºC[2]); mp(DSC): 68.43±1.07 ºC, 151.78±4.65 ºC; Yield, 97 %; ^{1}H NMR (300 MHz, CD_3OD): δ/ppm 0.90 (m, 3H, J = 6.9 Hz, H-16´), 1.3-1.4 (m, 26H, 13×CH_2), 1.62 (m, 2H, H-2´), 3.16 ("t", 1H, J ~ 8.7 Hz, H-2), 3.25-3.43 (m, 3H, H-3, 4 and 5, overlapped with residue proton of CD_3OD), 3.54 (m, 1H, H-1´a), 3.66 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 5.2 Hz, H-6a), 3.8-4.0 (m, 2H, H-6b and H-1´b), 4.24 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1). ^{13}C NMR (75 MHz, CD_3OD) δ/ppm 14.5 (C-16´), 23.7 (C-15´), 27.1 (C-3´), 30.4-30.9 (C-2´, C-4´ to C-

13′), 33.0 (C-14′), 62.9 (C-6), 71.0 (C-1′), 71.8 (C-4), 75.2 (C-2), 77.9 (C-5), 78.3 (C-3), 104.4 (C-1). Anal. calcd. for $C_{22}H_{44}O_6$: C 65.31, H 10.96. Found: C 65.61, H 10.96. HR-MS of $[M+Na]^+$ m/z: Calcd. 427.3036, Found. 427.3022.

Octadecyl-β-D-glucopyranoside (9c): White powder; mp: 82-83 ºC (Lit.: 120 ºC[13]); mp(DSC): 68.96±0.03 ºC, 84.06±0.10 ºC, 149.51±0.55 ºC (Lit.: transitions at 71.1, 86.6, 92.9 and 145.8 ºC[4]); Yield, 92 %; ^{1}H NMR (300 MHz, CD_3OD): δ/ppm 0.90 (m, 3H, J = 6.9 Hz, H-18′), 1.2-1.4 (m, 30H, 15×CH_2), 1.61 (m, 2H, H-2′), 3.12 (“t”, 1H, J ~ 8.1 Hz, H-2), 3.2-3.4 (m, 3H, H-3, 4 and 5, overlapped with residue proton of CD_3OD), 3.53 (m, 1H, H-1′a), 3.63 (dd, 1H, $J_{6a,6b}$ = 11.7 Hz, $J_{5,6a}$ = 4.2 Hz, H-6a), 3.7-3.9 (m, 2H, H-6b and H-1′b), 4.23 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1). ^{13}C NMR (75 MHz, CD_3OD) δ/ppm 14.7 (C-18′), 23.7 (C-17′), 27.1 (C-3′), 30.3-30.9 (C-2′, C-4′ to C-15′), 33.0 (C-16′), 62.9 (C-6), 70.7 (C-1′), 71.8 (C-4), 75.1 (C-2), 78.0 (C-5), 78.3 (C-3), 104.4 (C-1). Anal. calcd. for $C_{24}H_{48}O_6$: C 66.63, H 11.18. Found: C 66.46, H 11.18. HR-MS of $[M+Na]^+$ m/z: Calcd. 455.3373, Found. 455.3365.

Heptadecyl-β-D-glucopyranoside (9e): White powder; mp: 81-83 ºC; mp(DSC): 71.01±0.67ºC, 85.45±0.96 ºC, 149.53±0.18 ºC; Yield, 97 %; ^{1}H NMR (300 MHz, CD_3OD): δ/ppm 0.90 (m, 3H, J = 6.9 Hz, H-17′), 1.2-1.4 (m, 28H, 14×CH_2), 1.62 (m, 2H, H-2′), 3.15 (“t”, 1H, J ~ 8.3 Hz, H-2), 3.2-3.4 (m, 3H, H-3, 4 and 5, overlapped with residue proton of CD_3OD), 3.54 (m, 1H, H-1′a), 3.66 (dd, 1H, $J_{6a,6b}$ = 11.8 Hz, $J_{5,6a}$ = 5.3 Hz, H-6a), 3.8-4.0 (m, 2H, H-6b and H-1′b), 4.24 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1). ^{13}C NMR (75 MHz, CD_3OD) δ/ppm 14.6 (C-17′), 23.7 (C-16′), 27.1 (C-3′), 30.4-30.9 (2′, 4′~14′),

33.0 (C-15′), 62.9 (C-6), 71.0 (C-1′), 71.8 (C-4), 75.2 (C-2), 77.9 (C-5), 78.2 (C-3), 104.4 (C-1). Anal. calcd. for $C_{23}H_{46}O_6$: C 65.99, H 11.08. Found: C 65.93, H 11.05. HR-MS of $[M+Na]^+$ m/z: Calcd. 441.3192, Found. 441.3177.

Nonadecyl-β-D-glucopyranoside (9f): White powder; mp: 88-89 ºC; mp(DSC): 91.90±0.52 ºC, 145.49±0.07 ºC; Yield, 93 %; ^{1}H NMR (400 MHz, CD_3OD): δ/ppm 0.90 (t, 3H, J = 6.9 Hz, H-19′), 1.2-1.4 (m, 32H, 16×CH_2), 1.62 (m, 2H, H-2′), 3.17 (“t”, 1H, J ~ 7.8 Hz, H-2), 3.2-3.4 (m, 3H, H-3, 4 and 5, overlapped with residue proton signal of CD_3OD), 3.55 (m, 1H, H-1′a), 3.67 (dd, 1H, $J_{6a,6b}$ = 11.8 Hz, $J_{5,6a}$ = 5.5 Hz, H-6a), 3.8-3.9 (m, 2H, H-6b and H-1′b), 4.25 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1). ^{13}C NMR (100 MHz, CD_3OD) δ/ppm 14.4 (C-19′), 23.7 (C-18′), 27.1 (C-3′), 30.4-30.9 (C-2′, C-4′ to C-16′), 33.1 (C-17′), 63.0 (C-6), 71.0 (C-1′), 71.9 (C-4), 75.3 (C-2), 77.9 (C-5), 78.3 (C-3), 104.5 (C-1). Anal. calcd. for $C_{25}H_{50}O_6$: C 67.22, H 11.28. Found: C 67.45, H 11.41. HR-MS of $[M+Na]^+$ m/z: Calcd. 469.3505, Found. 469.35.9.

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