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Note

One-step synthesis of β-C-glycolipid derivatives from unprotected sugars

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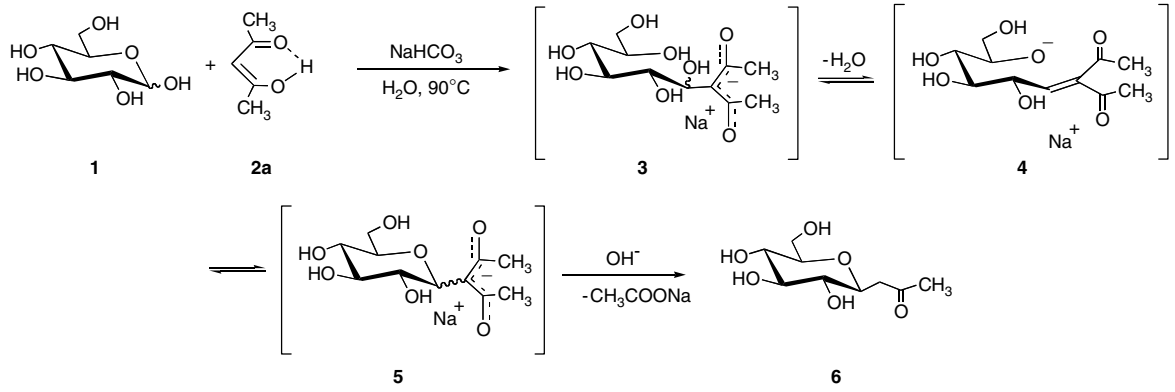
Abstract—Condensations of nonsymmetrical or symmetrical β-diketones and unprotected sugars in aq $NaHCO_3$ soln were explored. *C*-glucosyl and *C*-maltosyl derivatives bearing lipophilic residue of 8 or 11 carbon atoms were prepared efficiently using this one-step procedure. The amphiphilic properties of these compounds were demonstrated by measuring their CMC.

Keywords: *C*-glycosyl derivatives; C-glycolipids; Knoevenagel condensation

One-step synthesis of β-D-*C*-glycosylic ketones by condensation of pentan-2,4-dione with unprotected sugars in alkaline aq media has been recently explored in our laboratory[1]. Further studies on the use of other 1,3-dicarbonyl compounds as nucleophiles have been reported by Riemann et al.[2] The synthesis is based on Knoevenagel condensation between the carbanion of the β-diketone **2a** with the formyl group of the unprotected sugar **1** (Scheme 1). A β-elimination of water, followed by intramolecular Michael-type 1,4-addition gave the intermediate *C*-glycosyl derivative **5**. A retro-Claisen aldolisation with concomitant acetate elimination afforded a kinetic mixture of α- and β-pyranosyl and furanosyl derivatives (in which the α-furanosyl compound predominated), which upon further heating gave almost exclusively (>95%) the thermodynamic β-D



Scheme 1.

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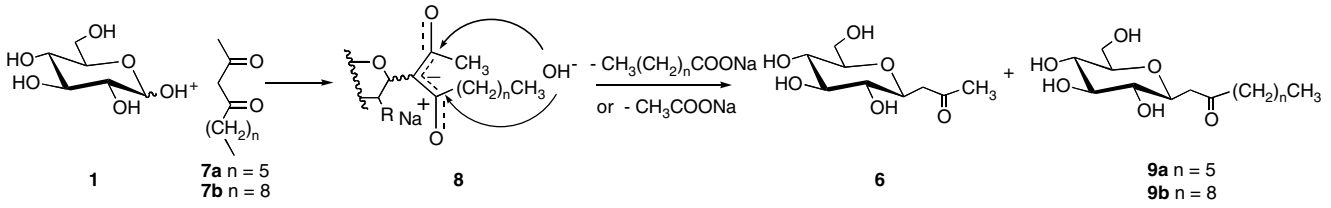
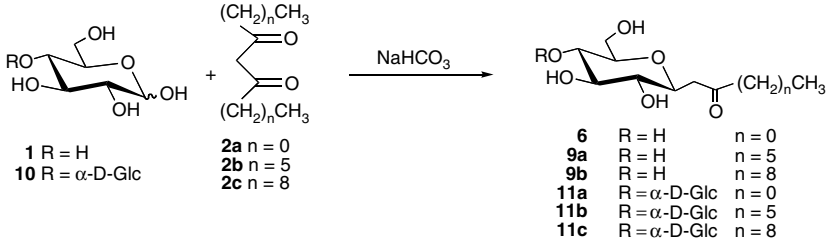


Scheme 2.



Scheme 3.

(equatorial) *C*-pyranosyl derivative **6** as shown by ^{1}H and ^{13}C NMR spectra.

In order to prepare carbohydrate-based amphiphiles by this straightforward methodology,[†] we envisaged the use of nonsymmetrical ketones **7a** and **7b** (Scheme 2) in the condensation assuming that the acetate elimination from the intermediate **8** should be favoured towards the elimination of the longer chain carboxylate residue affording C-glycolipids **9a** or **9b** rather than propanone *C*-glycosyl derivative **6**.

Hence, diketones **7a**[4] and **7b**[5] were prepared by Claisen condensation of ethyl acetate and octan-2-one or undecan-2-one, respectively, in the presence of sodium hydride as already described for similar compounds.[6] Glucose was treated with decan-2,4-dione (**7a**) (1.5 equiv) or tridecan-2,4-dione (**7b**) (1.5 equiv) and $NaHCO_3$ (1.5 equiv) in water at 90 °C. The reaction of glucose with **7a** gave, in these conditions after 48 h, **6** and **9a** in a 1:2 ratio, as judged by ^{13}C NMR, with 56% total yield, whereas the reaction with the less soluble **7b** lead to a complex mixture from which no major product could be isolated, which certainly results from self-condensation of dione in the organic phase. The two *C*-glycosyl compounds **6** and **9a** were separated by C-18 flash chromatography and the structure of **9a** was established by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum notably exhibited a large coupling constant for the H-1′ signal ($J_{1',2'}$ 9.3 Hz), indicating a trans-diaxial orientation of the C-1′ and C-2′ hydrogen atoms as expected for β-D configured pyranose moiety adopting a $^{4}C_{1}$ conformation. Use of a cosolvent which should favour the condensation by making the long-chain diketones more soluble was then envisaged and we were pleased to observe, in both cases, a clean reaction (94% with **7a** and 90% with **7b**) after one night using 4:1 EtOH–water as the solvent, the stoichiometry of the starting materials being unchanged (diketone 1.5 equiv, base 1.5 equiv). Unfortunately in these new conditions, **7a** gave a 1:1 mixture of the two *C*-glycosyl compounds **6** and **9a**. Likewise, **7b** gave **6** and **9b** in the same 1:1 ratio, as judged by ^{13}C NMR analysis of the crude mixtures. Nevertheless, we were able in these conditions to obtain pure **6** and **9b** in 47% and 43% yields, respectively, by flash chromatography and the structure of **9b** was established by ^{1}H NMR spectroscopy. As, under these conditions, no selectivity in the elimination of sodium acetate rather than sodium heptanoate or sodium decanoate has been obtained, we decided to use the symmetrical β-diketones **2** (Scheme 3). Hence, **2b**[7] and **2c**[8] were prepared by a Claisen condensation between 2-octanone or 2-decanone with methyl heptanoate or ethyl undecanoate, respectively. The reactions of these symmetrical diketones (1.5 equiv) with glucose in 4:1 EtOH–water as the solvent and $NaHCO_3$ (1.5 equiv) as the base were carried out. After one night of reflux, the reactions were complete (TLC analysis) and the C-glycolipid **9a** was isolated in 75% yield whereas the less soluble diketone **2c** gave **9b** in 52% yield. Then we tried to perform the reaction with D-maltose. To compare the reactivity, the disaccharide was allowed to react first with pentandione and $NaHCO_3$ in refluxing water overnight. Compound **11a** was obtained in 91% yield. The long-chain diketones **2b** was then engaged in this condensation in 4:1 EtOH–water as the solvent in the conditions used for glucose derivatives (**2b** 1.5 equiv, $NaHCO_3$ 1.5 equiv, 90 °C, 18 h). We isolated the C-disaccharide **11b** (40%) along with the C-monosaccharide **9a** (30%), which came from the degradation of either maltose or **11b** or both in the conditions of the reaction. Indeed,

[†] Part of this work has been patented.[3]

Table 1. CMC for C-glycolipids (25 °C)

C-glycosyl derivative	CMC (mM)
9b	40
11b	12
11c	1.4

after 6 h in refluxing soln of $NaHCO_3$ in 4:1 EtOH–water, maltose was partly decomposed into glucose and **11b** partly into **9a**, in both cases together with unidentified products. This degradation increased dramatically after 24 h. Considering these results, we decided to stop the condensation between maltose and **2b** after 5 h and in these conditions, **11b** was obtained in 65% isolated yield, the amount of **9a** being limited to 20%. The same procedure applied to the reaction between maltose and the less reactive diketone **2c** produced **11c** in only 16% yield in 5 h whereas a longer reaction time (12 h) gave rise only to a slightly increased 20% yield. Assuming that these poor results were probably due to the low solubility of **2c** and the decomposition of maltose during the reaction, we changed the protocol of the reaction by adding dropwise the aq ethanolic soln of maltose to a refluxing soln of diketone **2c** in pure ethanol in the presence of $NaHCO_3$. This allowed us to obtain, after chromatography, compound **11c** in 30% and **9b** in 13% isolated yields.

The critical micelle concentration (CMC), that is the concentration of free amphiphiles in equilibrium with micelles in soln, was determined for each synthesised C-glycolipid. Colorimetry measurements using Coomassie Brillant blue G (CBBG) as a chromogenic probe[9] were performed at 620 nm with various concentrations of **9a**, **9b**, **11b** and **11c**. Critical micelle concentrations of these compounds are reported in Table 1. No change in the absorbance of the CBBG reagent in the presence of **9a** in aq soln was detected within the solubility limit whereas, in every other case, a sharp visible change in the colour of the assay occurred at the CMC from grey-blue to sky-blue when the concentration was increased.

In conclusion, we described here a straightforward synthesis of β-C-glycolipid derivatives based on the condensation of symmetrical long chain β-diketone and unprotected sugars in a basic aq medium. This method allowed us to prepare glucose and maltose derivatives bearing C-linked hydrophobic residue of 8 or 11 carbon atoms. These amphiphile molecules have CMC between 1 and 40 mM.

1. Experimental

1.1. General methods

Flash column chromatography was performed on Silica Gel 60A C.C. (6–35 μm, SDS) or on Lichroprep RP-18 (25–40 μm, E. Merck). Reactions were monitored by TLC on Silica Gel 60 F_{254} with detection by charring with sulfuric acid. Melting points were determined with a Buchi B 545 capillary apparatus and are uncorrected. Optical rotations were determined using a Jasco DIP-370 digital polarimeter. NMR spectra were recorded at room temperature at 250 or 400 MHz (^1H) and 62.5 MHz (^{13}C) with Bruker spectrometers. Mass spectrometry was recorded on a MAT 95S instrument. Elemental analyses were performed at the CNRS Microanalytical Laboratory (Gif sur Yvette, France). Absorbances were measured with a Varian (Cary 1) spectrophotometer. Infrared spectra were recorded with a Bruker IFS 66 spectrometer.

1.2. 1-*C*-(β-D-Glucopyranosyl)octan-2-one (9a)

To a soln of D-glucose (4.5 g, 25 mmol) in EtOH–water (4:1, 70 mL) were added $NaHCO_3$ (3.11 g, 37 mmol) and pentadecan-7,9-dione (**2b**) (8.9 g, 37 mmol). The suspension was stirred at 90 °C for one night, then cooled to rt and treated with Dowex 50 X-8 200 H^+ to reach pH 2. The resin was filtered and EtOH was evaporated. The aq soln was washed with Et_2O and concentrated. Flash chromatography of the residue (step gradient from 95:5 to 1:1 EtOAc–*i*PrOH) afforded **9a** (5.4 g, 75%) as a white powder; mp 53 °C; $[\alpha]_D^{27}$ −1.3° (*c* 1.0, MeOH); IR (KBr) *v* 3210, 2878, 2851, 1700 cm^{-1}; ^1H NMR (CD_3OD, 250 MHz): δ 3.78 (dd, 1H, $J_{6'a,6'b}$ 12.0, $J_{5',6'a}$ 2.5 Hz, H-6′a), 3.66 (dt, 1H, $J_{1',2'} = J_{1',1a}$ 9.0, $J_{1',1b}$ 3.0 Hz, H-1′), 3.62 (dd, 1H, $J_{5',6'b}$ 5.0 Hz, H-6′b), 3.34 (dd, 1H, $J_{2',3'} = J_{3',4'}$ 9.0 Hz, H-3′), 3.28 (dd, 1H, $J_{4',5'}$ 9.0 Hz, H-4′), 3.21 (ddd, 1H, H-5′), 3.06 (dd, 1H, H-2′), 2.85 (dd, 1H, $J_{1a,1b}$ 16.0 Hz, H-1b), 2.58 (dd, 1H, H-1a), 2.53 (t, 2H, *J* 7.0 Hz, H-3a, H-3b), 1.62–1.49 (m, 2H, CH_2), 1.35–1.25 (m, 6H, $3CH_2$), 0.93–0.87 (m, 3H, CH_3); ^{13}C NMR (CD_3OD, 62.9 MHz): δ 212.1, 81.5, 79.5, 77.2, 75.0, 71.6, 62.7, 46.4, 44.1, 32.7, 29.9, 24.4, 23.5, 14.4. Anal. Calcd for $C_{14}H_{26}O_6$: C, 57.91; H, 9.03; O, 33.06. Found: C, 57.61; H, 9.13; O, 33.11.

1.3. 1-*C*-(β-D-Glucopyranosyl)undecan-2-one (9b)

D-Glucose (4.1 g, 22.9 mmol) was treated with heneicosan-10,12-dione (**2c**) (11.1 g, 34.4 mmol) and $NaHCO_3$ (2.9 g, 34.4 mmol) as described for the preparation of **9a**. During the washing step with Et_2O, pure **9b** crystallised (1.8 g). Flash chromatography of the residue (step gradient from 95:5 to 1:1 EtOAc–*i*PrOH) obtained from the aq layer afforded 2.2 g of **9b**. (52% combined yield); mp 70–72 °C; $[\alpha]_D^{29}$ 0° (*c* 1.0, MeOH); IR (KBr) *v* 3368, 2920, 2850, 1709 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ 3.77 (dd, 1H, $J_{6'a,6'b}$ 12.0, $J_{5',6'a}$ 2.5 Hz, H-6′a), 3.66 (dt, 1H, $J_{1',2'} = J_{1',1a}$ 9.0, $J_{1',1b}$ 3.0 Hz, H-1′), 3.62 (dd, 1H, $J_{5',6'b}$ 5.0 Hz, H-6′b), 3.33 (dd, 1H, $J_{2',3'} = J_{3',4'}$ 8.5 Hz, H-3′), 3.28 (dd, 1H, $J_{4',5'}$ 9.0 Hz, H-4′), 3.21 (ddd, 1H, H-5′), 3.06 (dd, 1H, H-2′), 2.85 (dd, 1H, $J_{1a,1b}$ 16.0 Hz, H-1b),

2.58 (dd, 1H, H-1a), 2.53 (dt, 2H, J 7.0, 1.5 Hz, H-3a, H-3b), 1.62–1.49 (m, 2H, CH_2), 1.35–1.25 (m, 12H, 6 CH_2), 0.93–0.87 (m, 3H, CH_3); ^{13}C NMR (CD_3OD, 62.9 MHz): δ 212.1, 81.5, 79.5, 77.2, 75.0, 71.5, 62.6, 46.4, 44.1, 33.0, 30.6, 30.4, 30.2, 24.5, 23.7, 14.4. Anal. Calcd for $C_{17}H_{32}O_6$: C, 61.42; H, 9.70; O, 28.88. Found: C, 61.41; H, 9.91; O, 28.75.

1.4. 1-*C*-(β-D-Maltosyl)propan-2-one (11a)

To a soln of D-maltose (0.5 g, 1.4 mmol) in water (5 mL) was added pentan-2,4-dione (**2a**) (167 mg, 1.7 mmol) and $NaHCO_3$ (175 mg, 2.1 mmol). The mixture was stirred at 90 °C for one night, then cooled to rt and treated with Dowex 50 X-8 200 H^+ to reach pH 2. The resin was filtered and the aq soln was washed with Et_2O and concentrated. Flash chromatography of the residue (step gradient from 9:1 to 1:1 CH_2Cl_2–MeOH) afforded **11a** (485 mg, 91%) as a colourless syrup; $[\alpha]_D^{27}$ +82° (c 1.0, MeOH); IR (KBR); ν 3380, 2925, 2853, 1703 cm^{-1}; ^1H NMR (CD_3OD, 250 MHz): δ 5.15 (d, 1H, $J_{1'',2''}$ 4.0 Hz, H-1″), 3.85–3.75 (m, 3H, H-6″a, H-6′a, H-6′b), 3.72–3.60 (m, 3H, H-5″, H-6″b, H-1′), 3.61 (dd, 1H, $J_{2'',3''} = J_{3'',4''}$ 9.5 Hz, H-3″), 3.59 (dd, 1H, $J_{2',3'} = J_{3',4'}$ 9.0 Hz, H-3′), 3.50 (dd, 1H, $J_{4',5'}$ 9.5 Hz, H-4′), 3.44 (dd, 1H, H-2″), 3.34–3.28 (m, 1H, H-5′), 3.25 (dd, 1H, $J_{4'',5''}$ 10.0 Hz, H-4″), 3.11 (dd, 1H, $J_{1',2'}$ 9.0 Hz, H-2′), 2.88 (dd, 1H, $J_{1a,1b}$ 16.0, $J_{1',1b}$ 3.0 Hz, H-1b), 2.60 (dd, 1H, $J_{1',1a}$ 9.0 Hz, H-1a), 2.20 (s, 3H, CH_3); ^{13}C NMR (CD_3OD, 62.9 MHz): δ 210. 1, 102.8, 81.3, 80.2, 79.3, 77.1, 75.0, 74.6, 74.1, 71.4, 62.6, 62.1, 46.9, 30.6. Anal. Calcd for $C_{15}H_{26}O_{11}$0.7 H_2O: C, 45.61; H, 6.99; O, 47.39. Found: C, 45.62; H, 6.87; O, 47.59; HRESIMS: m/z calcd for $C_{15}H_{26}O_{11}Na$ 405.1372; found 405.1377.

1.5. 1-*C*-(β-D-Maltosyl)octan-2-one (11b)

D-Maltose (2.0 g, 5.5 mmol) was treated with pentadecan-7,9-dione (**2b**) (2.0 g, 8.3 mmol) and $NaHCO_3$ (0.7 g, 8.3 mmol) as described for the preparation of **9a** for 5 h. Flash chromatography of the residue (step gradient from 95:5 to 6:4 EtOAc–MeOH) afforded at first **11a** (0.3 g, 18%) and secondly **11b** (1.6 g, 65%) as a colourless syrup; $[\alpha]_D^{29}$ +71° (c 1.0, MeOH); IR (KBr); ν 3432, 2926, 2856, 1710 cm^{-1}; ^1H NMR (CD_3OD, 250 MHz): δ 5.15 (d, 1H, $J_{1'',2''}$ 4.0 Hz, H-1″), 3.81 (dd, 1H, $J_{6''a,6''b}$ 11.0, $J_{5'',6''a}$ 1.5 Hz, H-6″a), 3.76 (d, 2H, $J_{5',6'}$ 3.0 Hz, H-6′a, H-6′b), 3.72–3.60 (m, 3H, H-5″, H-6″b, H-1′), 3.61 (dd, 1H, $J_{2'',3''} = J_{3'',4''}$ 9.5 Hz, H-3″), 3.59 (dd, 1H, $J_{2',3'} = J_{3',4'}$ 9.0 Hz, H-3′), 3.51 (dd, 1H, $J_{4',5'}$ 9.5 Hz, H-4′), 3.43 (dd, 1H, H-2″), 3.29 (dt, 1H, $J_{4'',5''}$ 10.0 Hz, H-5″), 3.25 (dd, 1H, H-4″), 3.12 (dd, 1H, $J_{1',2'}$ 9.0 Hz, H-2′), 2.83 (dd, 1H, $J_{1a,1b}$ 16.0, $J_{1',1b}$ 3.0 Hz, H-1b), 2.59 (dd, 1H, $J_{1',1a}$ 9.0 Hz, H-1a), 2.52 (t, 2H, J 7.0 Hz, H-3a, H-3b), 1.62–1.49 (m, 2H, CH_2), 1.35–1.25 (m, 6H, 3CH_2), 0.93–0.87 (m, 3H, CH_3); ^{13}C NMR (CD_3OD, 62.9 MHz): δ 212.1, 102.8, 81.3, 80.1, 79.3, 77.2, 75.0, 74.7, 74.1, 71.4, 62.7, 62.1, 46.2, 44.2, 32.8, 29.9, 24.4, 23.6, 14.4. Anal. Calcd for $C_{20}H_{36}O_{11}$0.5 H_2O: C, 52.05; H, 8.08; O, 39.87. Found: C, 52.13; H, 8.00; O, 39.85; HRESIMS: m/z calcd for $C_{20}H_{36}O_{11}Na$ 475.2155; found 475.2162.

1.6. 1-*C*-(β-D-Maltosyl)undecan-2-one (11c)

To a soln of heneicosan-10,12-dione (**2c**) (2.0 g, 6.2 mmol) and $NaHCO_3$ (527 mg, 6.2 mmol) in EtOH (12 mL) at 90 °C was added dropwise a soln of D-maltose (1.5 g, 4.1 mmol) in EtOH–water (1:2.5, 12 mL) over a 4 h period. The mixture was stirred at 90 °C for one night, then cooled to rt and treated with Dowex 50 X-8 200 H^+ to reach pH 4. The resin was filtered and the solvents were evaporated. Flash chromatography of the residue (step gradient from 90:10 to 1:1 EtOAc–*i*PrOH) afforded at first **11a** (185 mg, 13%) and secondly **11c** (618 mg, 30%); mp 165 °C (water); $[\alpha]_D^{29}$ +59° (c 1.0, MeOH); IR (KBr); ν 3385, 2924, 2853, 1707 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz): δ 5.15 (d, 1H, $J_{1'',2''}$ 4.0 Hz, H-1″), 3.82 (dd, 1H, $J_{6''a,6''b}$ 11.0, $J_{5'',6''a}$ 1.5 Hz, H-6″a), 3.77 (d, 2H, $J_{5',6'}$ 3.0 Hz, H-6′a, H-6′b), 3.68 (ddd, 1H, $J_{5'',6''b}$ 5.5, $J_{4'',5''}$ 10.0 Hz, H-5″), 3.67 (dt, 1H, $J_{1',2'} = J_{1',1a}$ 9.0, $J_{1',1b}$ 3.0 Hz, H-1′), 3.65 (dd, 1H, H-6″b), 3.61 (dd, 1 H, $J_{2'',3''} = J_{3'',4''}$ 9.5 Hz, H-3″), 3.59 (dd, 1H, $J_{2',3'} = J_{3',4'}$ 9.0 Hz, H-3′), 3.52 (dd, 1H, $J_{4',5'}$ 9.5 Hz, H-4′), 3.44 (dd, 1H, H-2″), 3.30 (dt, 1H, H-5′), 3.26 (dd, 1H, H-4″), 3.12 (dd, 1H, H-2′), 2.83 (dd, 1H, $J_{1a,1b}$ 16.0 Hz, H-1b), 2.60 (dd, 1H, H-1a), 2.53 (dt, 2H, J 7.0, 1.5 Hz, H-3a, H-3b), 1.62–1.49 (m, 2H, CH_2), 1.35–1.25 (m, 12H, 6 CH_2), 0.93–0.87 (m, 3H, CH_3); ^{13}C NMR (CD_3OD, 62.9 MHz): δ 212.3, 102.8, 81.2, 80.0, 79.2, 77.1, 74.8, 74.6, 74.0, 71.4, 62.5, 62.0, 46.1, 44.1, 32.9, 30.5, 30.3, 30.1, 24.4, 23.6, 14.4. Anal. Calcd for $C_{23}H_{42}O_{11}$: C, 55.86; H, 8.56; O, 35.58. Found: C, 55.62; H, 8.43; O, 35.58; HRESIMS: m/z calcd for $C_{23}H_{42}O_{11}Na$ 517.2624; found 517.2622.

1.7. General procedure for the CMC measurements

The CBBG reagent (100 mg) was dissolved in 2:1 85% H_3PO_4–EtOH (150 mL) and the soln was adjusted to 250 mL with water. Aq solns of each *C*-glycosyl derivative (from 40 to 80 mM according to the water solubility) were prepared. Various quantities of *C*-glycosyl compound solns were adjusted to 0.8 mL with water, 0.2 mL of the CBBG reagent and 0.1 mL of 85% H_3PO_4 were then added, so that final detergent concentration was based on the total 1.1 mL volume. Absorbance was measured at 620 nm and at 25 °C. The CMC were de-

duced from the analysis of the curves obtained by plotting the absorbance versus the *C*-glycosyl derivative concentration.

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