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Improved synthesis of glycosylamines and a straightforward preparation of *N*-acylglycosylamines as carbohydrate-based detergents

André Lubineau *, Jacques Augé [1], Bruno Drouillat

Institut de Chimie Moléculaire, Laboratoire de Chimie Organique Multifonctionnelle, CNRS UA 462, Université de Paris-Sud, F-91405 Orsay, France

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Abstract

D-Glucose, D-galactose, lactose, cellobiose, and maltose yield quantitatively the corresponding glycosylamine when treated at 42°C for 36 h with a commercial aqueous solution of ammonia in the presence of one equivalent of ammonium hydrogen carbonate. After lyophilisation, the residue (i.e., the pure glucosylamine) was dissolved in a mixture of ethanol and water, and treated with acyl chlorides to afford in a few minutes *N*-acylglucosylamines. Micellar properties of these amphiphilic derivatives were determined.

Keywords: Glycosylamines; *N*-Acylglycosylamines; Non-ionic detergents; Carbohydrate-based detergents; Surfactants

1. Introduction

The reaction of ammonia or primary amines with sugars yields glycosylamines. These compounds are not stable. In slightly acidic or neutral aqueous solution, they show a striking sensitivity to hydrolysis. Unlike glycosylamines, their acyl derivatives are stable compounds. Owing to the great interest in sugar surfactants over the last decade [1], we expected that *N*-acylglycosylamines might be good candidates as detergents. Plusquellec et al. prepared *N*-acylglycosylamines from crystalline glycosylamines using 3-acyl (or alkoxycarbonyl)-5-methyl-1,3,4-thiadiazole-2 (3*H*)-thiones or 2-acylthio-5-methyl-1,3,4-thia-

* Corresponding author.

[1] Present adress: Laboratoire des Réactivités Spécifiques, Université de Cergy-Pontoise, EA 1389, F-95806 Cergy-Pontoise, France.

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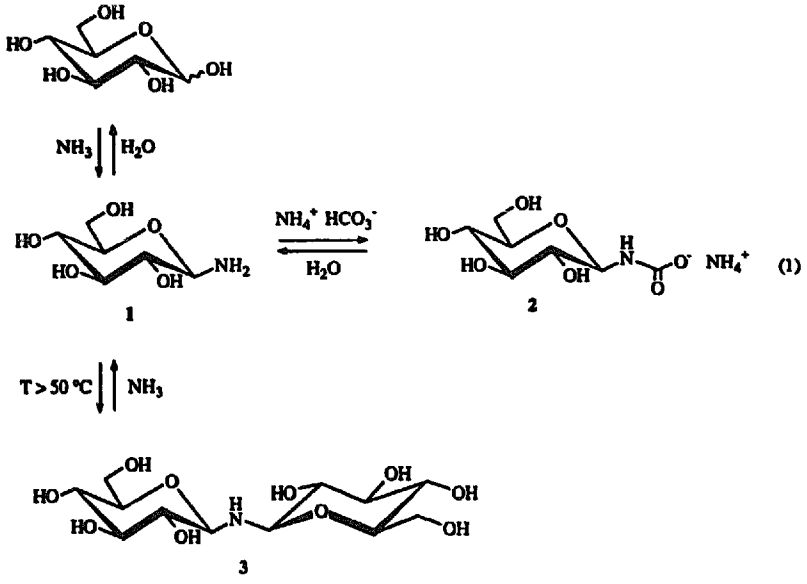
Table 1
Influence of the ammonium hydrogen carbonate concentration upon the percentage of D-glucosylcarbamate in the reaction with 0.2 M *D*-glucose (temperature 42°C, time 16 h)

$HCO_3^-NH_4^+$ (M)	1	2	3	4	5	6	7
D-Glucosycarbamate (%)	17	49	61	72	79	93	100

diazoles as acylating agents in dimethylformamide [2,3]. We now report an alternative strategy for a convenient access to *N*-acylglycosylamines, together with the micellar properties of these detergents.

2. Results and discussion

Synthesis of glycosylamines.—Glycosylamines can be prepared by reacting the corresponding reducing sugars in a methanolic solution of ammonia [4,5]. The yields of crystalline products are, however, rather low and the method is time consuming and requires large quantities of methanol. The interesting methodology, introduced by Kochetkov and co-workers for amino sugars [6] and successfully applied to various mono- and di-saccharides [7–12], requires a large quantity of ammonium hydrogen carbonate, which could be a major drawback for an industrial development since elimination of the salt may be problematic. We turned our attention to the use of a commercial aqueous solution of ammonia, despite rather pessimistic literature allegations [13]. When 0.2 M D-glucose was treated with aqueous 16 M ammonia at 42°C, the reaction went to completion after 2 days. D-Glucosylamine was formed, along with impurities, as evidenced by ^{13}C NMR spectroscopy. This result was rather encouraging and prompted us to perform the reaction by adding a small quantity of ammonium hydrogen carbonate. Progress of the reaction was monitored by analysing the anomeric region of the ^{13}C NMR spectrum of the mixture. The anomeric carbon of D-glucose gave two signals at 96.05 (β) and 92.23 (α) ppm, whereas D-glucosylamine (**1**) was identified by its C-1 resonance at 85.19 ppm (β). The anomeric carbon of D-glucosylcarbamate (**2**) and di-D-glucosylamine (**3**) at 83.21 (β) and 88.17 (β) ppm, respectively, could be detected in some spectra. The formation of di-D-glucosylamine was obviated by performing the reaction at moderate temperature (<50°C) when using D-glucose at a concentration <0.5 M. In fact, di-D-glycosylamine could be prepared by heating at reflux a solution of D-glucosylamine in methanol [14]. The presence of D-glucosylcarbamate is a consequence of the presence of ammonium hydrogen carbonate as suggested previously [7,10]. We found that, when performing the reaction at 42°C with 0.2 M D-glucose, the ratio of D-glucosylcarbamate in the mixture was increased from 17 to 100% (Table 1) when the ammonium hydrogen carbonate concentration was increased from 1 to 7 M (saturation). Since the equilibrium (1) (Scheme 1) could be totally shifted by evaporation, lyophilisation, or dilution, we anticipated that the percentage of D-glucosylcarbamate in the reaction is not a determining feature. For this reason we use the term "quantitatively" when the reaction leads only to D-glucosylamine or to D-glucosylcarbamate as a precursor. The best conditions for the formation of D-glucosylamine, in terms of temperature and concentration of the reactants were obtained [15] when 0.2 M glucose



Scheme 1.

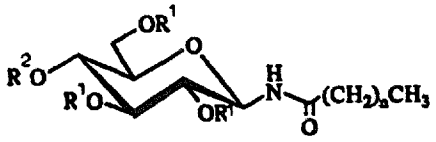
was allowed to react at 42°C with 16 M ammonia yielding quantitatively D-glucosylamine after 36 h. Only a small amount of D-glucosylcarbamate (< 8%) was detected in the mixture after 36 h.

Our methodology was applied to other mono- and di-saccharides. Thus a quantitative yield of D-galactosylamine, lactosylamine, cellobiosylamine, and maltosylamine was obtained when the corresponding reducing sugars (0.2 M) and 0.2 M ammonium hydrogen carbonate were dissolved in aqueous 16 M ammonia, and the mixture was allowed to stand at 42°C for 36 h (Table 2).

Synthesis of N-*acylglycosylamines.*—Taking advantage of the greater nucleophilicity of the nitrogen atom in unsubstituted glycosylamines, we first investigated the reaction of acetic anhydride with freeze-dried D-glucosylamine in water. The reaction was immediate at 0°C and afforded *N*-acetyl-β-D-glucopyranosylamine [16], which was further acetylated (Ac_2O, CH_3CO_2Na, 100°C) to yield the crystalline peracetylated D-glucosylamine (**4**; 78% from D-glucose). This method was scaled up to 100 g of D-glucose without loss of yield. An alternative method consisted in the direct acetylation of D-glucosylamine with acetic anhydride–pyridine (77% from D-glucose). Compound **4** turned out to be an excellent bleaching booster for detergents [17].

Table 2
Chemical shift of the anomeric carbon for various glycosylamines and glycosylcarbamates

Sugar	Glycosylamine	Glycosylcarbamate
D-Glucose	85.19	83.21
D-Galactose	85.78	83.77
Lactose	85.17	83.20
Cellobiose	85.19	83.21
Maltose	85.19	83.21



4	$R^1 = R^2 = Ac$	$n = 0$
5	$R^1 = R^2 = H$	$n = 6$
6	$R^1 = R^2 = H$	$n = 8$
7	$R^1 = R^2 = H$	$n = 10$
8	$R^1 = R^2 = H$	$n = 12$
9	$R^1 = H, R^2 =$ α-D-Glc	$n = 6$
10	$R^1 = H, R^2 =$ α-D-Glc	$n = 8$
11	$R^1 = H, R^2 =$ α-D-Glc	$n = 10$
12	$R^1 = H, R^2 =$ α-D-Glc	$n = 12$

In order to attach the lipophilic chain to the glycosylamine, we used an acyl chloride rather than an acyl anhydride which, from a stoichiometric point of view, would have resulted in a loss of reagent. Two methods, both using a mixture of water and ethanol as solvent, were investigated. In the first one (*A*), the acyl chloride was used in excess at 0°C in the presence of sodium carbonate. In this case, pure *N*-acyl derivatives could only be obtained after chromatography of the mixture. The compounds eluted first were a mixture of the fatty acid and amide, resulting from the hydrolysis and aminolysis of the acyl chloride. The compound eluted second was identified as the pure *N*-acylglycosylamine, as evidenced by spectroscopic data and elementary analysis. This method provided *N*-octanoyl-, *N*-decanoyl-, *N*-lauroyl-, and *N*-myristoyl-β-D-glucopyranosylamine along with *N*-octanoyl-, *N*-decanoyl-, *N*-lauroyl-, and *N*-myristoyl-β-maltosylamine in 50–56% yield.

In the second method (*B*), the glycosylamine was used in excess, both as reactant and base. The low cost of the sugar as compared to the acyl chloride, should make the method extremely advantageous for industrial applications. Furthermore, the methodology did not require a chromatographic step, since the excess of sugar could be eliminated in the aqueous phase, after the extraction of the product. The reaction occurred at 0°C in a mixture of ethanol and water. The purification of the glycosylamides was carried out after extraction and crystallisation from ethanol and the yield in *N*-octanoyl-, *N*-decanoyl-, *N*-lauroyl-, and *N*-myristoyl-β-D-glucopyranosylamine was ca. 40%.

Amphiphilic properties of N-*acylglycosylamines*.—The concentration of free amphiphiles in equilibrium with micelles in solution, known as the critical micelle concentration (CMC) is a key property for the design of detergents. The micellisation is detected by marked changes in properties such as surface tension, refractive index, and light scattering. Other methods for CMC measurements include fluorescence or absorption of solubilized dyes. Colorimetry measurements using Coomassie Brilliant blue G (CBBG) as a chromogenic probe [18] were performed at 620 nm with various concentrations of octyl-β-D-glucopyranoside (OG) as reference, *N*-octanoyl-β-D-glucosylamine (NOG), *N*-decanoyl-β-D-glucosylamine (NDG), *N*-octanoyl-β-maltosylamine (NOM), *N*-decanoyl-β-maltosylamine (NDM), and *N*-lauroyl-β-maltosylamine (NLM) (Figs. 1–3). Critical micelle concentrations of these detergents are reported in Table 3. No change in the absorbance of the CBBG reagent in the presence of NDG and NLM in aqueous solution

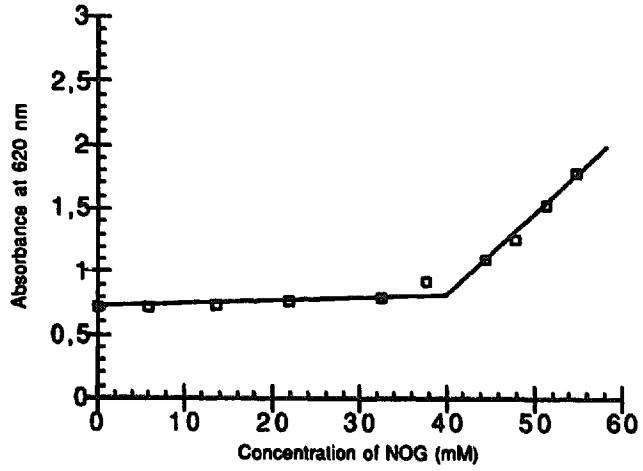


Fig. 1. Absorbance at 620 nm versus concentration of *N*-octanoyl-β-D-glucosylamine

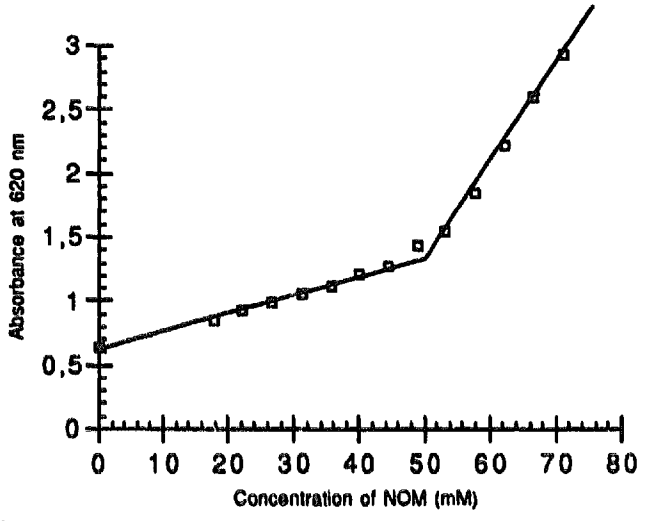


Fig. 2. Absorbance at 620 nm versus concentration of *N*-octanoyl-β-maltosylamine

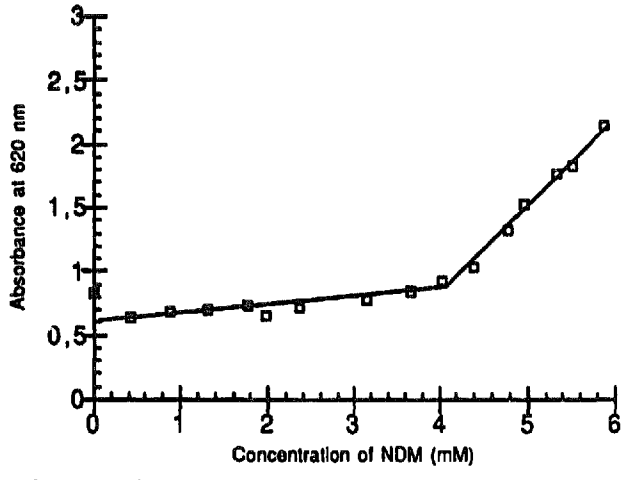


Fig. 3. Absorbance at 620 nm versus concentration of *N*-decanoyl-β-maltosylamine

was detected within the solubility limit. It must be noted that, in every 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.

Table 3
CMC (mM) for *N*-acylglycosylamines

Detergent	CMC (mM)	Reported CMC (mM)
OG	17	19 [20], 25 [21]
NOG	40	
NOM	51	
NDM	4.1	

3. Experimental

General methods.—Melting points (uncorrected) were determined on a Reichert hot-stage apparatus. Optical rotations were determined at 20°C using a Jasco DIP-370 digital polarimeter. ^1H and ^{13}C NMR spectra were recorded at 200, 250, or 400 MHz (^1H) and 50, 62.5, or 100 MHz (^{13}C) with a Bruker spectrometer; ^1H and ^{13}C NMR spectra of the compounds dissolved in organic solvents are reported in ppm relative to Me_4Si; for compounds in water, acetone was the internal standard at 2.225 and 30.5 ppm, respectively. Ultraviolet-visible spectra were recorded with a Varian (Cary 1) spectrophotometer. Infrared spectra were recorded with a Bruker IFS 66 spectrometer; the spectra are reported in cm^{-1}. Elemental analyses were performed by the Service Central de Microanalyse du CNRS.

General procedures for the synthesis of glycosylamines.—To an aqueous solution of the reducing sugar (0.2 M) containing NH_4HCO_3 (0.2 M), commercial aq NH_3 (16 M) was added. This solution was heated during 36 h at 42°C, concentrated to half volume, and then freeze-dried.

N-*Acetyl-2,3,4,6-tetra*-O-*acetyl*-β-D-*glucopyranosylamine* (**4**).—Freeze-dried D-glucosylamine, prepared from D-glucose (1 g, 5.55 mmol) as described above, was dissolved with $NaHCO_3$ (4.7 g, 55 mmol) in water (40 mL). Acetic anhydride (1.1 mL, 11.2 mmol) was then added dropwise at 0°C. After evaporation to dryness, NaOAc (0.5 g, 6.1 mmol) and Ac_2O (9 mL, 91 mmol) were added and heated at 100°C. After 2 h, the mixture was extracted with CH_2Cl_2 (50 mL), washed with satd $NaHCO_3$, and the residue recrystallised from ether to afford **4** (1.6 g, 78%); mp 161°C, $[\alpha]_D^{20}$ +17°(*c* 0.97, $CHCl_3$); lit. [5] mp 163°C, $[\alpha]_D^{20}$ +17°($CHCl_3$).

General procedures for the synthesis of N-*acyl*-β-D-*glucopyranosylamines* (**5–8**).—*Method A.* Freeze-dried D-glucosylamine, obtained from D-glucose (1 g, 5.55 mmol) was dissolved in 3:1 EtOH–H_2O (8 mL). Then Na_2CO_3 (0.4 g, 6.48 mmol) was added and the mixture was cooled to 0°C before the addition of the acyl chloride (22.24 mmol). The reaction was immediate. The mixture was purified on silica gel (1:9 MeOH–CH_2Cl_2) to afford the following compounds.

N-*Octanoyl*-β-D-*glucopyranosylamine* (**5**).—Yield 0.936 g (55%); mp (EtOH) 173–176°C; $[\alpha]_D^{20}$ +5° (*c* 1.1, H_2O); lit. [2] mp 177–178°C; IR (KBr): ν 1633, 2853, 2911, 3325, 3455; ^1H NMR (250 MHz, D_2O): δ 0.83 (t, 3 H, *J* 7 Hz, CH_2CH_3), 1.27 [m, 8 H, $(CH_2)_4CH_3$], 1.61 (m, 2 H, CH_2CH_2CONH), 2.32 (t, 2 H, *J* 7.5 Hz, CH_2CH_2CONH), 3.39 (m, 2 H, H-2 and H-4), 3.52 (m, 2 H, H-3 and H-5), 3.71 (dd, 1 H, $J_{6a,6b}$ 12, $J_{5,6a}$ 5 Hz, H-6a), 3.87 (d, 1 H, H-6b), 4.94 (d, 1 H, *J* 9 Hz, H-1); ^{13}C NMR (50 MHz, D_2O): δ

13.68 (CH_3), 22.12, 25.37, 28.40, 31.22, and 36.07 [(CH_2)$_6$$CH_3$], 60.87 (C-6), 69.55, 72.04, 76.82, and 77.81 (C-2,3,4,5), 79.51 (C-1), 215.47 (NHCO). Anal. Calcd for $C_{14}H_{27}NO_6$: C, 55.07; H, 8.91; N, 4.59. Found: C, 55.59; H, 9.39; N, 4.42.

N-*Decanoyl-β-*D-*glucopyranosylamine* (**6**).—Yield 1.04 g (56%); mp (EtOH) 183–185°C; $[\alpha]_D^{20}$ −1°(*c* 1, C_5H_5N); lit. [2] mp 185–187°C; lit. [19] $[\alpha]_D^{15}$ +4° (C_5H_5N); IR (KBr): *ν* 1632, 2852, 2911, 3325, and 3441; ^{1}H NMR (400 MHz, C_5D_5N): *δ* 0.83 (t, 3 H, *J* 7 Hz, CH_2CH_3), 1.13 [m, 10 H, (CH_2)$_5$$CH_3$], 1.31 (quintuplet, 2 H, *J* 7.5 Hz, $CH_2CH_2CH_2CONH$), 1.81 (quintuplet, 2 H, *J* 7 Hz, CH_2CH_2CONH), 2.48 (t, 2 H, *J* 7.5 Hz, CH_2CH_2CONH), 4.04 (m, 1 H, H-5), 4.12 (dd, 1 H, $J_{1,2}$ 9, $J_{2,3}$ 8 Hz, H-2), 4.28 (m, 2 H, H-3 and H-4), 4.37 (dd, 1 H, $J_{6a,6b}$ 12, $J_{5,6a}$ 4.5 Hz, H-6a), 4.48 (dd, 1 H, $J_{5,6b}$ 2 Hz, H-6b), 6.03 (dd, 1 H, $J_{1,2}=J_{1,NH}=9$ Hz, H-1), 9.64 (d, 1 H, NH); ^{13}C NMR (100 MHz, C_5D_5N): *δ* 14.25 (CH_3), 22.87, 25.96, 29.49, 29.71, 32.03, and 36.88 [(CH_2)$_8$$CH_3$], 62.65 (C-6), 71.72, 74.63, 79.74, and 80.04 (C-2,3,4,5), 81.30 (C-1), 173.97 (NHCO). Anal. Calcd for $C_{16}H_{31}NO_6$: C, 57.64; H, 9.37; N, 4.20. Found: C, 57.34; H, 9.13; N, 4.16.

N-*Lauroyl-β-*D-*glucopyranosylamine* (**7**).—Yield 1 g (51%); mp (EtOH) 178–184°C; $[\alpha]_D^{20}$ −1° (*c* 1, C_5H_5N); lit. [2] mp 183–187°C, lit. [19] mp 180–181°C, $[\alpha]_D$ +3° (C_5H_5N); IR (KBr): *ν* 1634, 2851, 2920, 3333, and 3432; ^{1}H NMR (400 MHz, C_5D_5N): *δ* 0.86 (t, 3 H, *J* 7 Hz, CH_2CH_3), 1.18 [m, 14 H, (CH_2)$_7$$CH_3$], 1.34 (quintuplet, 2 H, *J* 7.5 Hz, $CH_2CH_2CH_2CONH$), 1.82 (quintuplet, 2 H, *J* 7.5 Hz, CH_2CH_2CONH), 2.49 (t, 2 H, *J* 7.5 Hz, CH_2CH_2CONH), 4.06 (m, 1 H, H-5), 4.13 (dd, 1 H, $J_{1,2}$ 9, $J_{2,3}$ 8 Hz, H-2), 4.29 (m, 2 H, H-3 and H-4), 4.39 (dd, 1 H, $J_{6a,6b}$ 12, $J_{5,6a}$ 4.5 Hz, H-6a), 4.50 (d, 1 H, H-6b), 6.06 (dd, 1 H, $J_{1,2}=J_{1,NH}=9$ Hz, H-1), 9.67 (d, 1 H, NH); ^{13}C NMR (100 MHz, C_5D_5N): *δ* 14.27 (CH_3), 22.92, 25.98, 29.57, 29.76, 29.89, 32.11, and 36.90 [(CH_2)$_{10}$$CH_3$], 62.69 (C-6), 71.78, 74.67, 79.78, and 80.07 (C-2,3,4,5), 81.33 (C-1), 173.94 (NHCO). Anal. Calcd for $C_{18}H_{35}NO_6$: C, 59.83; H, 9.76; N, 3.88. Found: C, 59.90; H, 9.57; N, 4.05.

N-*Myristoyl-β-*D-*glucopyranosylamine* (**8**).—Yield 1.1 g (51%); mp (EtOH) 178–183°C; $[\alpha]_D^{20}$ −1° (*c* 1, C_5H_5N); lit. [2] mp 183–186°C, lit. [19] mp 176–178°C, $[\alpha]_D$ −3° (C_5H_5N); IR (KBr): *ν* 1633, 2850, 2919, 3327, and 3441; ^{1}H NMR (400 MHz, C_5D_5N): *δ* 0.86 (t, 3 H, *J* 7 Hz, CH_2CH_3), 1.19 [m, 18 H, (CH_2)$_9$$CH_3$], 1.32 (quintuplet, 2 H, *J* 7.5 Hz, $CH_2CH_2CH_2CONH$), 1.79 (quintuplet, 2 H, *J* 7,5 Hz, CH_2CH_2CONH), 2.46 (t, 2 H, *J* 7.5 Hz, CH_2CH_2CONH), 4.02 (m, 1 H, H-5), 4.09 (dd, 1 H, $J_{1,2}$ 9, $J_{2,3}$ 8 Hz, H-2), 4.24 (m, 2 H, H-3 and H-4), 4.33 (dd, 1 H, $J_{6a,6b}$ 12, $J_{5,6a}$ 4.5 Hz, H-6a), 4.45 (d, 1 H, H-6b), 5.99 (dd, 1 H, $J_{1,2}=J_{1,NH}=9$ Hz, H-1), 9.61 (d, 1 H, NH); ^{13}C NMR (100 MHz, C_5D_5N): *δ* 14.27 (CH_3), 22.94, 25.96, 29.61, 29.78, 29.93, 32.14, and 36.87 [(CH_2)$_{12}$$CH_3$], 62.68 (C-6), 71.75, 74.59, 79.70, and 79.99 (C-2,3,4,5), 81.27 (C-1), 173.94 (NHCO). Anal. Calcd for $C_{20}H_{39}NO_6$: C, 61.67; H, 10.09; N, 3.60. Found: C, 61.99; H, 9.81; N, 3.38.

General procedures for the synthesis of N-*acyl-β-*D-*glucopyranosylamines* (**5–8**).—*Method B.* Freeze-dried D-glucosylamine, obtained from 4.82 g (26.8 mmol) of D-glucose was dissolved in 1:2 H_2O–EtOH (15 mL). The solution was cooled and acyl chloride (10.8 mmol) was added slowly at 0°C. The mixture was then diluted with water (100 mL) and extracted with the same volume of EtOAc (for compound **5**, 20% of EtOH was added in EtOAc). After evaporation of the solvent, the residue was taken up with boiled acetone (50 mL) and filtered off. The precipitate was recrystallised from EtOH to afford **5** (1.29 g,

40%), **6** (1.31 g, 39%), **7** (1.55 g, 40%), or **8** (1.57 g, 38%) according to the starting acyl chloride.

General procedures for the synthesis of N-*acyl-β-maltopyranosylamines* (**9–12**).—Freeze-dried maltosylamine, obtained from 0.5 g (1.39 mmol) of maltose according to our procedure (vide supra) was dissolved in 1:2 H_2O–EtOH (12 mL) (for the synthesis of **12**, maltosylamine was dissolved in hot MeOH). After cooling at 0°C, Na_2CO_3 (1.32 g, 12.4 mmol) and acyl chloride (6.9 mmol) were added. The mixture was then evaporated and purified on silica gel (3:7 MeOH–CH_2Cl_2) to afford the following compounds.

N-*Octanoyl-β-maltopyranosylamine* (**9**).—Yield 0.325 g (50%); mp 245°C; $[\alpha]_D^{20}$ +63° (*c* 1, C_5H_5N); IR (KBr): *ν* 1646, 2927, 3335, and 3470; ^{1}H NMR (250 MHz, D_2O): *δ* 0.85 (t, 3 H, *J* 6 Hz, CH_2CH_3), 1.28 [m, 8 H, $(CH_2)_4CH_3$], 1.61 (m, 2 H, CH_2CH_2CONH), 2.31 (t, 2 H, *J* 7 Hz, CH_2CONH), 3.41 (m, 2 H), 3.70 (m, 10 H), 4.95 (d, 1 H, $J_{1,2}$ 9 Hz, H-1), 5.42 (d, 1 H, $J_{1,2}$ 4 Hz, H-1′); ^{13}C NMR (62.5 MHz, D_2O): *δ* 13.62 (CH_3), 22.24, 25.24, 28.51, 28.52, 31.31, and 35.95 [$(CH_2)_6$], 60.56 and 60.60 (C-6 and C-6′), 69.38, 71.80, 72.78, 72.97, 76.23, 76.66, and 77.14 (C-2,3,4,5,2′,3′,4′,5′), 79.22 (C-1), 99.78 (C-1′), 178.12 (NHCO). Anal. Calcd for $C_{20}H_{37}NO_{11}$,1.5 H_2O: C, 48.48; H, 8.16; N, 2.83. Found: C, 48.48; H, 7.94 N, 2.72.

N-*Decanoyl-β-maltosylamine* (**10**).—Yield 0.333 g (45%); mp 245°C; $[\alpha]_D^{20}$ +62° (*c* 1, C_5H_5N); IR (KBr): *ν* 1668, 2851, 2919, and 3312; ^{1}H NMR (250 MHz, C_5D_5N): *δ* 0.83 (t, 3 H, *J* 7 Hz, CH_2CH_3), 1.20 [m, 12 H, $(CH_2)_6CH_3$], 1.80 (m, 2 H, CH_2CH_2CONH), 2.47 (t, 2 H, *J* 8 Hz, CH_2CONH), 3.90 (m, 1 H), 4.20 (m, 3 H), 4.40 (m, 5 H), 4.60 (m, 3 H), 5.96 (dd, 1 H, $J_{1,2}=J_{1,NH}=9$ Hz, H-1), 5.99 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1′), 9.70 (d, 1 H, NH); ^{13}C NMR (62.5 MHz, C_5D_5N): *δ* 14.25 (CH_3), 22.65, 25.73, 29.45, 29.46, 31.80, and 36.58 [$(CH_2)_8$], 61.48 and 62.46 (C-6 and C-6′), 71.67, 73.79, 74.20, 75.05, 75.20, 78.11, 78.89, and 80.78 (C-2,3,4,5,2′,3′,4′,5′), 80.94 (C-1), 102.79 (C-1′), 174 (NHCO).Anal. Calcd for $C_{22}H_{41}NO_{11}$: C, 53.30; H, 8.34; N, 2.83. Found: C, 52.84; H, 8.08; N, 2.91.

N-*Lauroyl-β-maltosylamine* (**11**).—Yield 0.371 g (51%); mp 241°C; $[\alpha]_D^{20}$ +67° (*c* 1, C_5H_5N); IR (KBr): *ν* 1670, 2851, 2916, and 3316; ^{1}H NMR (250 MHz, C_5D_5N): *δ* 0.82 (t, 3 H, *J* 7 Hz, CH_2CH_3), 1.25 [m, 16 H, $(CH_2)_8CH_3$], 1.81 (m, 2 H, CH_2CH_2CONH), 2.47 (t, 2 H, *J* 8 Hz, CH_2CONH), 3.89 (m, 1 H), 4.18 (m, 3 H), 4.39 (m, 5 H), 4.60 (m, 3 H), 5.97 (dd, 1 H, $J_{1,2}=J_{1,NH}=9$ Hz, H-1), 5.99 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1′), 9.71 (d, 1 H, NH); ^{13}C NMR (62.5 MHz, C_5D_5N): *δ* 14.09 (CH_3), 22.70, 25.74, 29.51, 29.52, 29.53, 31.88, and 36.58 [$(CH_2)_{10}$], 61.47 and 62.45 (C-6 and C-6′), 71.64, 73.76, 74.16, 75.00, 75.16, 78.07, 78.85, and 80.76 (C-2,3,4,5,2′,3′,4′,5′), 80.92 (C-1), 102.75 (C-1′), 174 (NHCO). Anal. Calcd for $C_{24}H_{45}NO_{11}$: C, 55.04; H, 8.67; N, 2; 68. Found: C, 55.05; H, 8.37; N, 2.62.

N-*Myristoyl-β-maltosylamine* (**12**).—Yield 0.377 g (49%); mp 240°C; $[\alpha]_D^{20}$+62° (*c* 1, C_5H_5N); IR (KBr) *ν* 1670, 2850, 2915, and 3312; ^{1}H NMR (250 MHz, C_5D_5N): *δ* 0.80 (t, 3 H, *J* 7 Hz, CH_2CH_3), 1.18 [m, 20 H, $(CH_2)_{10}CH_3$], 1.75 (m, 2 H, CH_2CH_2CONH), 2.40 (t, 2 H, *J* 8 Hz, CH_2CONH), 3.80 (m, 1 H), 4.08 (m, 3 H), 4.32 (m, 5 H), 4.52 (m, 3 H), 5.90 (dd, 1 H, $J_{1,2}=J_{1,NH}=9$ Hz, H-1), 5.91 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1′), 9.65 (d, 1 H, NH); ^{13}C NMR (62.5 MHz, C_5D_5N): *δ* 14.03 (CH_3), 22.67, 25.69, 29.33, 29.49, 29.64, 31.84, and 36.56 [$(CH_2)_{12}$], 61.41 and 62.41 (C-6 and C-6′), 71.62, 73.81, 74.16, 75.00, 75.17, 78.05, 78.84, and 80.65 (C-2,3,4,5,2′,3′,4′,5′), 80.89 (C-1), 102.71 (C-1′), 173.74

(NHCO). Anal. Calcd for $C_{26}H_{49}NO_{11}$, H_2O: C, 54.83; H, 8.61; N, 2.46. Found: C, 54.62; H, 8.79; N, 2.65.

General procedures for the CMC measurements.—The CBBG reagent (100 mg) was dissolved in a mixture of 85% phosphoric acid and 50 mL of EtOH. The solution was adjusted to 250 mL with water. An aqueous solution of each detergent (from 4 to 100 mM according to the water solubility) was prepared. Various quantities of detergent solutions were adjusted to 0.8 mL with water; 0.2 mL of the CBBG reagent and 0.1 mL of 85% phosphoric acid were then added, so that final detergent concentration was based on the total 1.1 mL volume. Absorbance was measured at 620 mm.

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