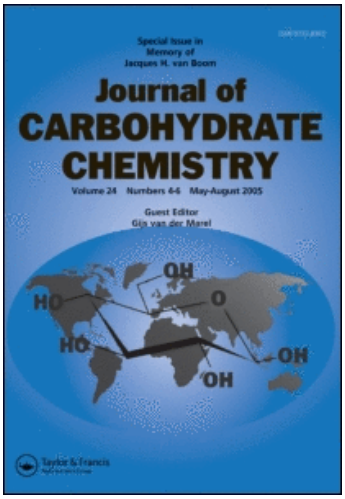

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GLYCOSYLHYDRAZIDES, A NEW CLASS OF SUGAR SURFACTANT. PREPARATION AND AMPHIPHILIC PROPERTIES OF 1-GLYCOSYL-2-ACYLHYDRAZINES

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ABSTRACT

The synthesis and the amphiphilic properties of 1-glycosyl-2-acylhydrazines are described. This new class of surfactants, referred to as glycosylhydrazides, is easily available from a reducing sugar and hydrazides without protection. Seven hydrazides having an alkyl chain of up to fourteen carbon atoms, are coupled with glucose giving 1-glucosyl-2-acylhydrazines in good yields; 1-maltosyl-2-octanoylhydrazine, as a typical disaccharide-based surfactant, is prepared as well. Critical micellar concentrations of these surfactants range from 0.04 to 252 mM.

INTRODUCTION

Glycosylated derivatives with a long chain extension are of great interest because of their use in areas such as extraction and purification processes of membrane proteins,[1,2] molecular recognition in glycobiology[3] or immunology.[4] In addition, among these additives, alkylpolyglycosides or acylated glycosamines exhibit well established amphiphilic properties, which allow their use in industry as surfactants.[5]

In the elaboration of glycoconjugates, the key step is usually the creation of an anomeric bond between oligosaccharides and the aglycone moiety. A similar stategy, based on anomeric chemistry, can be adopted in the synthesis of carbohydrate-based detergents. Thus glycosylamines are both precursors of glycosyl conjugates[6] and sugar surfactants.[7]

Coupling between hydrazide reagents and various oligosaccharides was recently developed for carbohydrate recognition studies.[8] The synthesis of sugar amphiphiles we describe herein is based on the reaction of a reducing sugar and hydrophobic acylhydrazines or, alternatively, on the reaction of glucosylhydrazine and hydrophobic acid derivatives. The surfactant properties of these amphiphilic molecules are reported as well.

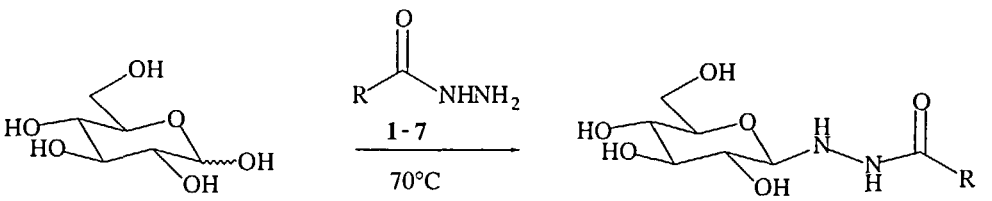
RESULTS AND DISCUSSION

The isomerism of saccharide hydrazones in solution is well documented.[9,10] Saccharide hydrazones in hydrazine solution exist mainly as the acyclic isomer, whereas, after removal of the hydrazine and redissolution in water, isomerization occurs to give glycosylhydrazines.[9]

Reaction between reducing sugars and acylhydrazines

We first prepared acylhydrazines by coupling hydrazine and the corresponding esters in ethanol. These hydrazides (**1-7**) are well known and those with high molecular weight could be directly obtained in a crystalline form from the solvent.[11]

The condensation between glucose and acylhydrazines **1-4** was performed in methanol at 65 °C and led, after a chromatographic step, to crystalline glucosylhydrazides in yields ranging from 70 to 98% (Scheme 1). Thin-layer chromatography first revealed the formation of an acyclic glucosylacylhydrazone which was progressively transformed into a cyclic glycosylacylhydrazine. When an acyclic glucosylacylhydrazone is isolated in water,



8-14

$R = (CH_2)_nCH_3$ from n = 0 to n = 12, n being an even number

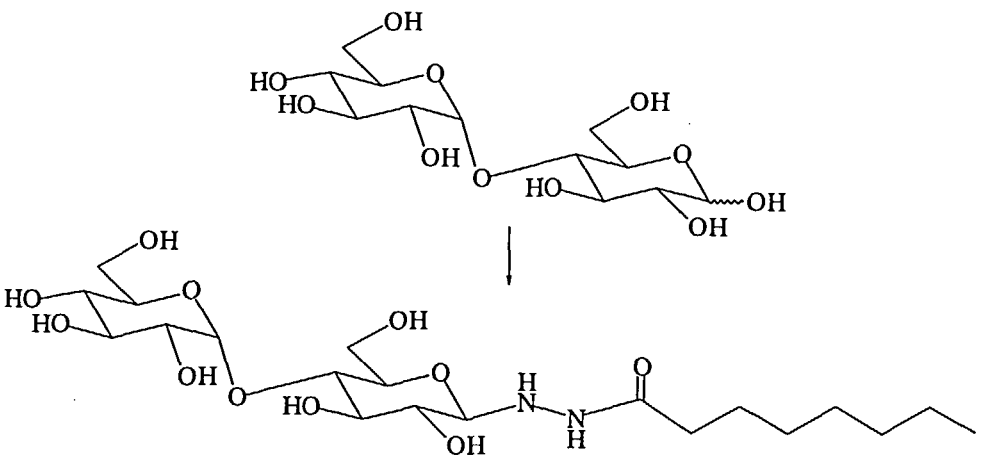
Scheme 1

an equilibrium towards the cyclic glycosylacylhydrazine slowly occurs at room temperature, indicating that the cyclic form is the more stable isomer.

With the acylhydrazines **5-7** the reaction, carried out in dimethylformamide at 70 °C, directly afforded crystalline glucosylhydrazides without the chromatographic step (Scheme 1). The NMR spectrum of glucosylacetylhydrazine **8** was consistent with the recently reported data.[12] The ^{1}H NMR spectra of the glucosylhydrazides **9-14** displayed doublets at 3.9 ppm in D_2O or 4.6 ppm in C_5D_5N, which were diagnostic of the presence of the cyclic form of the sugar moiety. The vicinal coupling constants between pyranose protons $J_{2',3'}$, $J_{3',4'}$ and $J_{4',5'}$ ranging from 8.5 to 9 Hz confirmed our interpretation. Besides, the β-configuration of the glucosylhydrazides was assigned based on the value of $J_{1',2'}$ coupling constant near to 9 Hz. A general feature of these molecules is that the hydrazido nitrogen bonded to the acyl group is sp^2 hybridized, and, like amide nitrogens, has a significant double-bond character due to overlap of p orbitals with the carbonyl carbon. This phenomenon was particularly studied in the glycosylamide series.[13] Two isomers referred as *cis* and *trans* isomers were generally detected;[12,13] similarly, the NMR spectra of the glucosylhydrazides revealed sometimes the existence of a minor (< 5%) β-pyranosyl isomer in equilibrium with the major one.

In order to prove the reaction is not limited to monosaccharides, coupling between the dissaccharide maltose and octanoylhydrazine was performed under similar conditions to afford 1-(β-maltosyl)-2-octanoylhydrazine **15** in 55% yield (Scheme 2).

All the glycosylhydrazides were purified in a crystalline form.

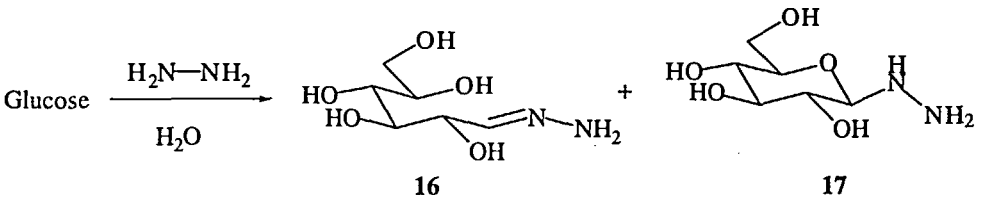


15

Scheme 2

Reaction between glucosylhydrazine and activated acid derivatives

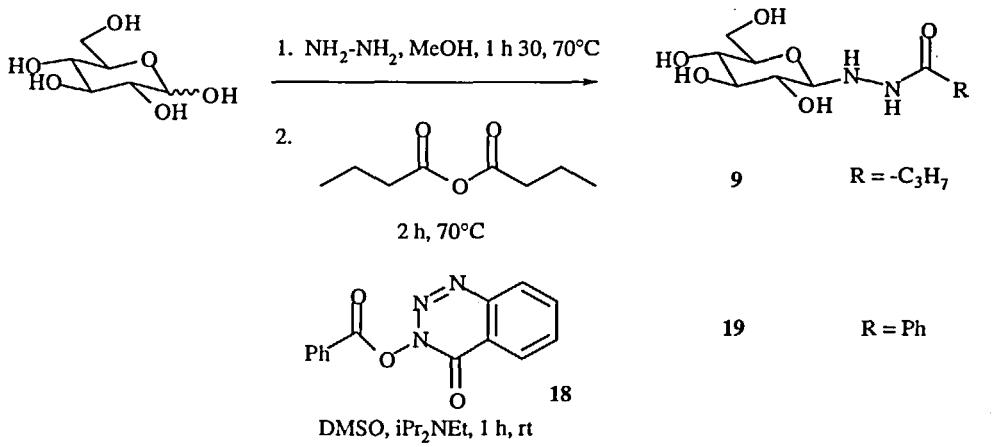
Hydrazine monohydrate was allowed to react with glucose in water for 1.5 h at 70 °C (Scheme 3).



16 17

Scheme 3

Progress of the reaction was monitored by analysing the anomeric region of the ^{13}C NMR spectrum of the mixture. The sp^2 carbon of the acyclic glucosylhydrazone **16** gave a signal at 147.5 ppm (66%), whereas the anomeric carbon of the cyclic glucosylhydrazine **17** was detected at 92 ppm (34%). Such a mixture was concentrated giving essentially glucosylhydrazine,[9] which was then allowed to react with butanoic anhydride in methanol at 70 °C in the presence of sodium bicarbonate to afford 1-(β-glucosyl)-2-butanoylhydrazine **9** in 58% yield (Scheme 4). Alternatively, the anhydride could be replaced by a carboxylic acid activated by 3-hydroxy-1,2,3-benzotriazin-4(*3H*)-one (Dhbt-OH). As an example, coupling of glycosylhydrazine with 3-benzoyloxy-1,2,3-benzotriazin-4(*3H*)-one **18** in DMSO in the presence of an amine gave the glucosylbenzoylhydrazide **19** (Scheme 4).

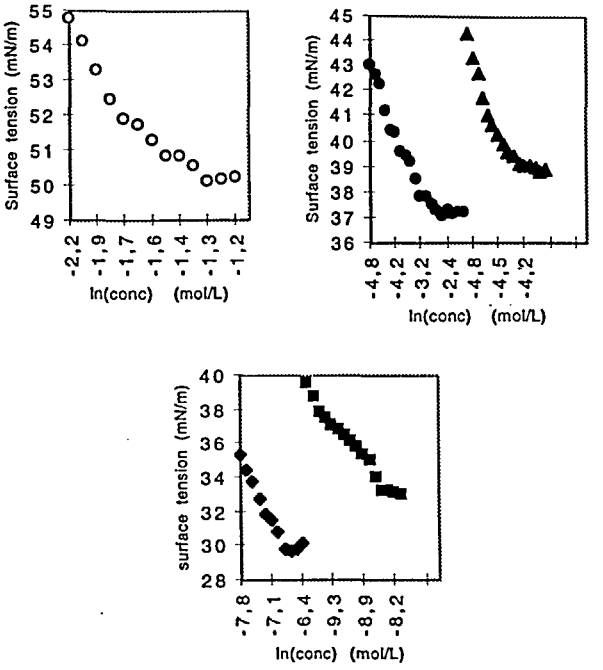


9 R = $-C_3H_7$

18

19 R = Ph

Scheme 4



o glucosylbutanoylhydrazide **9**, ● glucosylhexanoylhydrazide **10**, ▲ glucosyloctanoylhydrazide **11**, ◆ glucosyldecanoylhydrazide **12**, ■ glucosyldodecanoylhydrazide **13**

Figure 1. Surface tension vs concentration of surfactant

Amphiphilic properties of the glycosylhydrazides

Glucosylhydrazides are soluble in water for alkyl chains up to 14 carbon atoms. The critical micellar concentration (CMC) of compounds **9-15** was determined from surface tension versus concentration plots (Figure 1). For comparison, absorbance versus concentration plots for the glycosylhydrazides **8-15** in the presence of Coomassie Brilliant Blue G as a chromogenic probe[14] was shown in Figure 2. Unlike glycosylhydrazides **9-15**, the glucosylhydrazide **8** does not display interfacial properties, although there is a slope discontinuity in the absorbance vs concentartion curve for that compound. This is probably due to non-micellar aggregation.

Table 1 gives the amphiphilic properties of the glycosylhydrazides **9-15**. The CMC and the surface tension at the CMC (γ_{CMC}) were directly obtained at the slope discontinuity in the surface tension versus concentration plots. The surface excess concentration Γ and the area per headgroup a_s were calculated from the Gibbs adsorption equation relating

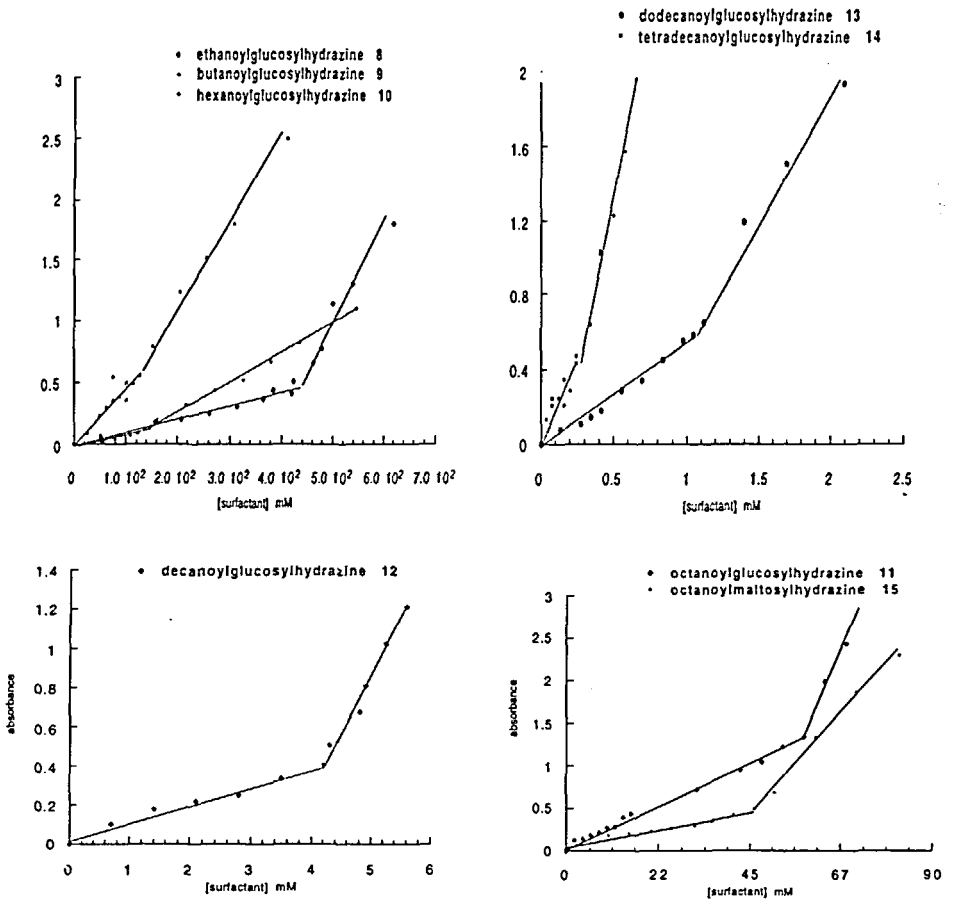


Figure 2. Absorbance vs concentration of surfactant

surface excess to surface tension and the chemical potential of the solute. If $\Delta G°_{mic}$ is the standard free energy change for the transfer of one mole of surfactant from solution to micellar phase, then

$$\Delta G°_{mic} = RT \ln x_{CMC} = 2.3\ RT\ (\log CMC - \log w)$$

where x_{CMC} is the mole fraction of monomers and where w = 55.4. A logarithmic decrease of CMC and therefore a linear decrease of $\Delta G°_{mic}$ with the number n_C of carbon atoms of the hydrophobic chain is observed (Figure 3) as usual for nonionic surfactants.[15-18] The contribution for each aliphatic carbon $\Delta G(CH_2)$ is averaged to -2.13 kJ.mol^{-1} which is somehow smaller than the usual value for non-ionic surfactants.[18]

Table 1. Values obtained from surface tension measurements for compounds **9**

n_C	Compound	CMC (mM)	γ_{CMC} (mN/m)	Γ (mmol/m^2)	a_S (Å^2)
4	**9**	252	50.2	2.44	68
6	**10**	23	37.1	2.65	62.5
8	**11**	13	38.9	4.03	41.1
10	**12**	1.2	24	3	55.3
12	**13**	0.22	32.7	2.43	68
14	**14**	0.04	36	-	-
8	**15**	3.55	23.7	4.75	35

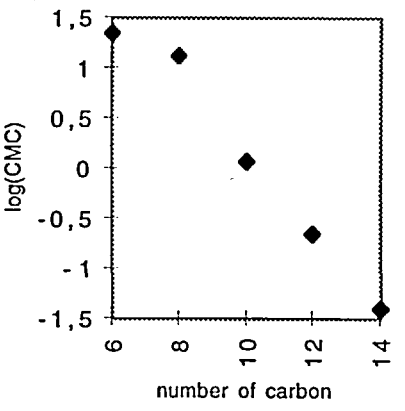


Figure 3. log(cmc) versus hydrophobic chain length n_c

The CMC values for compounds **11-13** and the interfacial surface values for compounds **11-12** are similar to the corresponding values for alkylglucosides (Table 2). More surprising is the behavior of glucosylhydrazide **9**. The slope discontinuity in both surface tension and absorbance versus concentration plots argues in favor of the formation of micelles at concentration above 250 mM. The linearity in the function log(CMC) = f (n_C) for n_C ranging from 4 to 14 corroborates this feature. Such a high CMC value was previously mentioned in the case of another surfactant which does not carry a long chain alkyl; thus a value of 600 mM was recently reported for the CMC value of trimethyl-*p*-vinylbenzylammonium chloride.[19]

Table 2. Compared amphiphilic properties of glucosylhydrazides and alkylglucosides

n_C	glucosylhydrazide CMC (mM)	alkylglucoside CMC (mM) [a]	glucosylhydrazide a_S (Å^2)	alkylglucoside a_S (Å^2) [a]
8	13	25	41.1	42
10	1.2	2.2	53.3	47
12	0.22	0.19	68	36

a. Ref 17

EXPERIMENTAL

General Methods. TLC was run on silica plates in 1-butanol-acetic acid-water (5:3:2 v/v) and compounds were revealed by spraying with 10% sulfuric acid in ethanol. Preparative flash column chromatographies were carried out using SDS silica gel 60 (6-35μ). New compounds were purified after recrystallisation either from methanol, ethanol or water and analysed by High Resolution Mass Spectrometry in the chemical ionization mode (CI, reactant CH_4) or FAB$^+$ with direct introduction. Mps were measured on an oil bath Büchi 530 apparatus. Optical rotations were recorded on a Perkin Elmer 241 apparatus; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. NMR spectra were measured on a Brucker Avance DPX 250 MHz spectrometer (250 MHz for ^{1}H and 62.5 MHz for ^{13}C). Chemical shifts were expressed in parts per million downfield from TMS; J values are given in Hz. IR spectra were recorded using FTIR Perkin Elmer 1600. Surface tension was measured using a Langmuir Blodgett trough (NIMA type 611) at room temperature.

Preparation of acylhydrazines.[11] As a typical experiment, hydrazine monohydrate (10 g, 58 mmol) was added to a solution of ethyl tetradecanoate (16.13 g, 63 mmol) dissolved in ethanol (120 mL). The solution was stirred at 70 °C for 3 hours and concentrated under vacuum. The crystalline compound was washed with cyclohexane (3x20 mL). Filtration yielded tetradecanoylhydrazine **7** (14.17 g, 93%). For compounds **1-3**, ethanol was removed by distillation after which crystallisation occurred. The crystals were washed with cyclohexane and filtered off.

Ethanoylhydrazine (1). Oil; bp_{40} 130 °C (lit.,[11] mp 67 °C); IR (KBr) 3250-3550 (NH), 2800-2900 (CH), 1618 (CO, hydrazide); ^{1}H NMR ($CDCl_3$) δ 0.55 (s, 3H, CH_3), 2.8 (br, 2 H, NH_2), 7.2 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 20.99 (CH_3), 171.43 (C=O, hydrazide).

Butanoylhydrazine (2). Mp 54-55 °C (lit.,[11] 44 °C); IR (KBr) 3250-3550 (NH), 2800-2900 (CH), 1618 (CO, hydrazide); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, CH_3), 1.55 (m, 2H, CH_3-CH_2), 2.05 (t, 2H, CH_2), 3.85 (br, 2H, NH_2), 7.3 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 14.33 (CH_3), 19.55, 36.99 (CH_2), 174.59 (C=O, hydrazide).

Hexanoylhydrazine (3). Mp 72 °C (lit.,[11] 73.1-74 °C); IR (KBr) 3200-3500 (NH), 2800-2900 (CH), 1619 (CO, hydrazide); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, CH_3), 1.25 (m, 4H, $(CH_2)_2$), 1.55 (m, 2H, CH_2), 2.1 (t, 2H, CH_2), 3.8 (br, 2H, NH_2), 7.1 (br, 1H, NH); 14.26 (CH_3), 22.71, 25.57, 31.79, 34.89 (4 CH_2), 174.50 (C=O, hydrazide).

Octanoylhydrazine (4). Mp 88-89 °C (lit.,[11] 88.8-89.6 °C); IR (KBr) 3300-3500 (NH), 2800-2900 (CH), 1619 (CO, hydrazide); ^{1}H NMR ($CDCl_3$) δ 0.7 (t, 3H, CH_3), 1.2 (m, 8H, $(CH_2)_4$), 1.6 (m, 2H, CH_2), 2 (t, 2H, CH_2), 3.7 (br, 2H, NH_2), 6.8 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 14.26 (CH_3), 22.99, 25.91, 29.36, 29.63, 32.06, 34.98 (6 CH_2), 174.48 (C=O, hydrazide).

Decanoylhydrazine (5). Mp 98-99 °C (lit.,[11] 98.5-99.1 °C); IR (KBr) 3300-3500 (NH), 2800-2900 (CH), 1619 (CO, hydrazide); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, CH_3), 1.3 (m, 14H, $(CH_2)_7$), 1.65 (m, 2H, CH_2), 2.15 (t, 2H, CH_2), 3.9 (br, 2H, NH_2), 6.8 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 14.76 (CH_3), 23.32, 26.18, 29.95, 30.09, 32.51, 35.26 (CH_2), 174.73 (C=O, hydrazide).

Dodecanoylhydrazine (6). Mp 103 °C (lit.,[11] 104.7-105.5 °C); IR (KBr) 3300-3500 (NH), 2800-2900 (CH), 1619 (CO, hydrazide); ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3H, CH_3), 1.25 (m, 16H, $(CH_2)_8$), 1.7 (m, 2H, CH_2), 2.15 (t, 2H, CH_2), 3.9 (br, 2H, NH_2), 6.8 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ 14.51 (CH_3), 23.08, 25.91, 29.70, 29.86, 29.99, 32.30, 35.00 (CH_2), 174.44 (C=O, hydrazide).

Tetradecanoylhydrazine (7). Mp 109 °C (lit.,[11] 112.2-112.4 °C); IR (KBr) 3300-3300 (NH), 2800-2900 (CH), 1629 (CO, hydrazide); ^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3H, CH_3), 1.25 (m, 20H, $(CH_2)_{10}$), 155 (m, 2H, CH_2), 2.1 (t, 2H, CH_2), 3.7 (s, 2H, NH_2), 6.7 (s, 1H, NH).

Preparation of 2-acyl-1-glycosylhydrazines 8, 9, 10 and 11. Typically, butanoylhydrazine (4 g, 39.21 mmol) was added to a solution of glucose (6.41 g, 35.65 mmol) dissolved in methanol (36 mL). The solution was heated at 70 °C for one day. After monitoring of the reaction by TLC, the mixture was concentrated to dryness and the residue was chromatographed [dichloromethane-methanol (4:1 v/v)] to give compound **9** (8.497 g, 91%).

2-Ethanoyl-1-β-D-glucopyranosylhydrazine (8). Mp 86-88 °C (from EtOH); $[\alpha]_D^{30}$ -16 (*c* 1.22 in EtOH); IR ν (KBr) 3200-3500 (OH), 2800-2900 (CH), 1654 (CO, hydrazide); ^{1}H NMR (D_2O) δ 1.85 (s, 3H, CH_3), 3.2 (dd, 1H, $J_{1',2'}$ 9, $J_{2',3'}$ 9, 2'-H), 3.3 (dd, 1H, $J_{3',4'}$ 8.6, $J_{4',5'}$ 8.6, 4'- H), 3.32 (m, 1H, 5'-H), 3.43 (dd, 1H, 3'-H), 3.62

(dd, 1H, $J_{5',6''}$ 5.3, $J_{6',6''}$ 12.2, 6''-H), 3.82 (dd, 1H, $J_{5',6'}$ 1.7, 6'-H), 3.99 (d, 1H, 1'-H); ^{1}H NMR (D_2O) δ 21.57 (CH_3), 62.52 (C-6'), 71.21, 72.21, 77.88, 78.53 (C-2', -3', -4' and -5'), 91.26 (C-1'), 174.99 (CO, hydrazide). HRMS (CI, MH^+) Calcd for $C_8H_{17}O_6N_2$ 237.1086. Found 237.1090.

Anal. Calcd for $C_8H_{16}O_6N_2$+ H_2O: C, 37.78; H, 7.14. Found: C, 37.78; H, 7.30.

2-Butanoyl-1-β-D-glucopyranosylhydrazine (9). Mp 94-95 °C (from EtOH); $[\alpha]_D^{30}$ -14 (*c* 1.05 in EtOH); IR (KBr) 3200-3500 (OH), 2800-2900 (CH), 1654 (CO, hydrazide); ^{1}H NMR (D_2O) δ 0.8 (t, 3H, CH_3), 1.5 (s, 2H, CH_2), 2.1 (t, 2H, CH_2), 3.17 (dd, 1H, $J_{1',2'}$ 9, $J_{2',3'}$ 9, 2'-H), 3.3 (m, 2H, 4'-H and 5'-H), 3.4 (dd, 1H, $J_{3',4'}$ 8.8, 3'-H), 3.6 (dd, 1H, $J_{5',6''}$ 5.45, $J_{6',6''}$ 12.2, 6''-H), 3.78 (dd, 1H, $J_{5',6'}$ 2, 6'-H), 3.97 (d, 1H, 1'-H); ^{13}C NMR (D_2O) δ 12.32 (CH_3), 18.51 (CH_2), 35.30 (CH_2), 60.59 (C-6'), 69.59, 70.32, 75.95, 76.61 (C-2', -3', -4' and -5'), 89.40 (C-1'), 176.05 (C=O, hydrazide). HRMS (CI, MH^+) Calcd for $C_{10}H_{21}O_6N_2$ 265.1399. Found 265.1398.

Anal. Calcd for $C_{10}H_{20}O_6N_2$+ H_2O: C, 42.53; H, 7.86; N, 9.92. Found: C, 42.15; H, 8.03; N, 9.89.

2-Hexanoyl-1-β-D-glucopyranosylhydrazine (10). Mp 88-92 °C (from EtOH); $[\alpha]_D^{30}$ -13 (*c* 1.53 in EtOH); IR (KBr) 3200-3500 (OH), 2800-2900 (CH), 1647 (CO, hydrazide); ^{1}H NMR (C_5D_5N) δ 0.6 (t, 3H, CH_3), 1.1 (m, 4H, $(CH_2)_2$), 1.55 (m, 2H, CH_2), 2.2 (t, 2H, CH_2), 3.82 (ddd, 1H, $J_{4',5'}$ 9, $J_{5',6'}$ 2.4, $J_{5',6''}$ 5.5, 5'-H), 3.92 (dd, 1H, $J_{1',2'}$ 8.8, $J_{2',3'}$ 8.8, 2'-H), 4.05 (dd, 1H, $J_{3',4'}$ 8.8, 4'-H), 4.15 (dd, 1H, 3'-H), 4.17 (dd, 1H, $J_{6',6''}$ 11.6, 6''-H), 4.39 (dd, 1H, 6'-H), 4.54 (1H, d, 1'-H); ^{13}C NMR (C_5D_5N) δ) 14.47 (CH_3), 22.99, 26.19, 32.05, 34.95 (CH_2), 63.38 (C-6'), 72.36, 73.04, 78.96, 80.30 (C-2', -3', -4' and -5'), 93.17 (C-1'), 174.15 (C=O, hydrazide). HRMS (CI, MH^+) Calcd for $C_{12}H_{25}O_6N_2$ 293.1712. Found 293.1714.

Anal. Calcd for $C_{12}H_{24}O_6N_2$+ H_2O: C, 46.42; H, 8.45; N, 9.03. Found: C, 46.35; H, 8.49; N, 9.17.

2-Octanoyl-1-β-D-glucopyranosylhydrazine (11). Mp 99-100 °C (from H_2O); $[\alpha]_D^{30}$ -13 (*c* 0.91 in EtOH); IR (KBr) 3200-3500 (OH), 2800-2900 (CH), 1654 (CO, hydrazide); ^{1}H NMR (C_5D_5N) δ 0.8 (t, 3H, CH_3), 1.2 (m, 8H, $(CH_2)_4$), 1.7 (m, 2H, CH_2), 2.3 (t, 2H, CH_2), 3.94 (ddd, 1H, $J_{4',5'}$ 8.3, $J_{5',6'}$ 2.1, $J_{5',6''}$ 5.5, 5'-H), 4.02 (dd, 1H, $J_{1',2'}$ 8.8, $J_{2',3'}$ 8.8, 2'-H), 4.13 (dd, 1H, $J_{3',4'}$ 8.8, 4'-H), 4.26 (dd, 1H, 3'-H), 4.27 (dd, 1H, $J_{6',6''}$ 11.5, 6''-H), 4.5 (dd, 1H, 6'-H), 4.64 (d, 1H, 1'-H); ^{13}C NMR (C_5D_5N) 14.79 (CH_3), 22.77, 26.09, 29.19, 29.23, 31.83, 34.65 (CH_2), 62.83 (C-6'), 71.79, 72.54, 78.44, 79.72 (C-2', -3', -4' and -5'), 92.59 (C-1'), 173.77 (C=O, hydrazide). HRMS (CI, MH^+) Calcd for $C_{14}H_{29}O_6N_2$ 321.2025. Found 321.2018.

Anal. Calcd for $C_{14}H_{28}O_6N_2$+ H_2O: C, 49.74; H, 8.94; N, 8.28. Found: C, 49.73; H, 8.14; N, 8.32.

Preparation of 2-acyl-1-glycosylhydrazines 12, 13, 14 and 15. Glucose (2.013 g, 11.18 mmol) was suspended in dimethylformamide (11.2 mL) and heated at 70 °C. Dodecanoylhydrazine (2.51 g, 11.74 mmol) was then added and the suspension was stirred for three days. After cooling, precipitation occurred. Compound **13** was then recrystallised from ethanol, yielding 4.06 g (92%).

2-Decanoyl-1-β-D-glucopyranosylhydrazine (12). Mp 98-100 °C (from H_2O); $[\alpha]_D^{30}$ -12 (*c* 0.96 in EtOH); IR (KBr) 3200-3500 (OH), 2800-2900 (CH), 1654 (CO, hydrazide); ^{1}H NMR (C_5D_5N) δ 0.9 (t, 3H, CH_3), 1.1-1.3 (s, 12H, $(CH_2)_6$), 1.7 (m, 2H, CH_2), 2.3 (t, 2H, CH_2), 3.92 (ddd, 1H, $J_{4',5'}$ 8.8, $J_{5',6'}$ 1.6, $J_{5',6''}$ 5.2, 5'-H), 4.02 (dd, 1H, $J_{1',2'}$ 8.7, $J_{2',3'}$ 8.7, 2'-H), 4.12 (dd, 1H, $J_{3',4'}$ 8.8, 4'-H), 4.28 (dd, 1H, 3'-H), 4.29 (dd, 1H, $J_{6',6''}$ 11.6, 6"-H), 4.5 (dd, 1H, 6'-H), 4.65 (d, 1H, 1'-H); ^{13}C NMR (C_5D_5N) 14.34 (CH_3), 22-34 (CH_2), 63.20 (C-6'), 72.19, 72.76, 78.76, 80.19 (C-2', -3', -4' and -5'), 93.00 (C-1), 173.95 (C=O, hydrazide). HRMS (CI, MH^+) Calcd for $C_{16}H_{33}O_6N_2$ 349.2338. Found 349.2337.

Anal. Calcd for $C_{16}H_{32}O_6N_2$+ H_2O: C, 52.43; H, 9.36. Found: C, 52.47; H, 9.68.

2-Dodecanoyl-1-β-D-glucopyranosylhydrazine (13). Mp 118-119 °C (from MeOH); $[\alpha]_D^{30}$ -11 (*c* 0.75 in EtOH); IR (KBr) 3200-3500 (OH), 2800-2900 (CH), 1654 (CO, hydrazide); ^{1}H NMR (C_5D_5N) 0.8 (t, 3H, CH_3), 1.1-1.3 (m, 16H, $(CH_2)_8$), 1.7 (m, 2H, CH_2), 2.3 (t, 2H, CH_2), 3.92 (ddd, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 1.8, $J_{5',6''}$ 6, 5'-H), 4.02 (dd, 1H, $J_{1',2'}$ 8.8, $J_{2',3'}$ 8.8, 2'-H), 4.14 (dd, 1H, $J_{3',4'}$ 8.8, 4'-H), 4.28 (dd, 1H, 3'-H), 4.29 (dd, 1H, $J_{6',6''}$ 11.5, 6"-H), 4.48 (dd, 1H, 6'-H), 4.65 (d, 1H, 1'-H), 5.1 (br, 1H, OH), 6.75 (br, 1H, NH-CO), 10.8 (br, 1H, NH-C-1'); ^{13}C NMR (C_5D_5N) 14.28 (CH_3), 22-34 (CH_2), 62.94 (C-6'), 71.90, 72.61, 78.57, 79.84 (C-2', -3', -4' and -5'), 92.64 (C-1'), 173.89 (C=O, hydrazide). HRMS (CI, MH^+) Calcd for $C_{18}H_{37}O_6N_2$ 377.2651. Found 377.2659.

Anal. Calcd for $C_{18}H_{36}O_6N_2$+ H_2O: C, 54.78; H, 9.74; N, 7.10 Found: C, 54.38; H, 9.80; N, 7.06.

2-Tetradecanoyl-1-β-D-glucopyranosylhydrazine (14). Mp 122-128 °C (from MeOH); $[\alpha]_D^{30}$ -11 (*c* 0.82 in EtOH); IR (KBr) 3200-3500 (OH), 2800-2900 (CH), 1654 (CO, hydrazide); ^{1}H NMR (C_5D_5N) δ 0.85 (t, 3H, CH_3), 1.1-1.3 (m, 20H,$(CH_2)_{10}$), 1.7 (m, 2H, CH_2), 2.3 (t, 2H, CH_2), 3.93 (ddd, 1H, $J_{4',5'}$ 8.6, $J_{5',6'}$ 2.4, $J_{5',6''}$ 5.6, 5'-H), 4.05 (dd, 1H, $J_{1',2'}$ 8.7, $J_{2',3'}$ 8.7, 2'-H), 4.18 (dd, 1H, $J_{3',4'}$ 8.8, 4'-H), 4.3 (m, 2H, 3'-H, 6"-H), 4.5 (dd, 1H, $J_{6',6''}$ 11.6, 6'-H), 4.67 (d, 1H, 1'-H), 6.4 (br, 1H, OH), 10.9 (br, 1H, NH-C-1'); ^{13}C NMR (C_5D_5N) 14.57 (CH_3), 22-34 (CH_2), 63.27 (C-6'), 72.24, 72.95, 78.89, 80.16 (C-2', -3', -4' and -5'), 93.08 (C-1'), 174 (C=O, hydrazide). HRMS (CI, MH^+) Calcd for $C_{20}H_{41}O_6N_2$ 405.2964. Found 405.2971.

Anal. Calcd for $C_{20}H_{40}O_6N_2$+ H_2O: C, 56.83; H, 10.02; N, 6.63 Found: C, 56.25; H, 10.16; N, 6.61.

2-Octanoyl-1-β-D-maltosylhydrazine (15). Mp 98-100 °C (from EtOH); $[\alpha]_D^{30}$ -26 (*c* 0.95 in EtOH); IR (KBr) 3200-3500 (OH), 2800-2900 (CH), 1629 (CO, hydrazide); ^{1}H NMR (D_2O) δ 0.75 (t, 3H, CH_3), 1.1-1.3 (m, 8H, $(CH_2)_4$), 1.5 (m, 2H, CH_2), 2.2 (t, 2H, CH_2), 3.1-4 (m, 14H); ^{13}C NMR (D_2O) 14.06 (CH_3), 22-34 (CH_2), 61.02 (C-6',C-6"), 77-79 (C-2', -3', -4', -5', -2", -3" -4" and -5"), 90.35 (C-1'), 100.41 (C-1"), 176 (C=O, hydrazide). HRMS (CI, MH^+) Calcd for $C_{20}H_{39}O_{11}N_2$ 483.2553. Found 483.2558.

Anal. Calcd for $C_{20}H_{38}O_{11}N_2$+ H_2O: C, 47.98; H, 8.06; N, 5.60 Found: C, 47.97; H, 8.01; N, 5.76.

Reaction between glucosylhydrazine and activated acid derivatives.

2-Butanoyl-1-β-D-glucopyranosylhydrazine (9). Glucose (1 g, 5.55 mmol) was dissolved in methanol (11 mL). After addition of hydrazine monohydrate (296 mL, 6.1 mmol) the solution was stirred at 70 °C for 1 h 30. TLC of the reaction showed the formation of glucosylhydrazine in equilibrium with glucosylhydrazone. When glucose has totally disappeared, butanoic anhydride (2.895 g, 18.3 mmol) and sodium bicarbonate (1.536 g, 18.3 mmol) were added. After 2 h at 70 °C, the solution was filtered and washed with ethyl acetate (2x10 mL). After concentration under vacuum, flash chromatography in dichloromethane-methanol (4:1 v/v) yielded the title compound **9** (847 mg, 58%).

2-Benzoyl-1-β-D-glucopyranosylhydrazine (19). Benzoic acid (747 mg, 6.13 mmol) was dissolved in freshly distilled tetrahydrofuran (33 mL) and the solution was cooled at -35 °C. Dicyclohexylcarbodiimide (1.264 g, 6.13 mmol) was then added. After 10 min, Dhbt-OH (1 g, 6.13 mmol) was added and the mixture stirred at -35 °C for 3.5 h. The precipitate was filtered. After concentration, redissolution in THF (20 mL) and a second filtration through Celite, the resulting filtrate was concentrated to dryness. The residue was then purified by flash chromatography [cyclohexane-ethylacetate (4:1 v/v)] to afford 3-benzoyloxy-1,2,3-benzotriazin-4(3H)-one **18** (1,321 g, 81%) as a crystalline compound. Glucose (266 mg, 1.48 mmol) was treated with hydrazine monohydrate as previously described to give, after concentration, a mixture of glucosylhydrazine and glucosylhydrazone, which was dissolved in a mixture of dimethylsulphoxide (30 mL) and diisopropylethylamine (309 mL, 1.776 mmol). Compound **18** was then added to this solution and the resulting yellow solution was stirred for 1 hour at room temperature. Concentration under reduced pressure and flash chromatography in dichloromethane-methanol (9:1 v/v) yielded the title compound **19** (234 mg, 53%); mp 183-184 °C (from H_2O); $[\alpha]_D^{30}$ -35 (*c* 0.99 in MeOH); IR (KBr) 3200-3500 (OH), 2800-2900 (C-H), 1654 (CO, hydrazide); ^{1}H NMR (C_5D_5N) δ3.87 (ddd, 1H, $J_{4',5'}$ 9.1, $J_{5',6'}$ 2.7, $J_{5',6"}$ 5.8, 5'-H), 4.02 (dd, 1H, $J_{1',2'}$ 8.8, $J_{2',3'}$ 8.8, 2'-H), 4.07 (dd, 1H, $J_{3',4'}$ 8.7, 4'-H), 4.2 (m, 2H, 3'-H, 6"-H), 4.41 (dd, 1H, $J_{6',6"}$ 11.5, 6'-H), 4.69 (d, 1H, 1'-H), 7.2-7.5 (m, 5H, H_{arom}); ^{13}C

NMR (C_5D_5N) δ 62.99 (C-6'), 72.00, 72.97, 78.77, 79.89 (C-2', -3', -4' and -5'), 93.23 (C-1'), 128.18, 128.71, 131.72 (C_{arom}), 168.29 (C=O, hydrazide). HRMS (FAB, MNa^+) Calcd for $C_{13}H_{18}O_6N_2Na$ 321.1062. Found 321.1066.

Determination of the CMC. The CMC was determined using a Langmuir Blodgett trough. The aqueous solutions were prepared using ultrapure water (MilliQ). Aliquots were added to water (20 mL) and surface tension was measured after reequilibration of the surface i.e when the measured surface tension remainded constant with the time. In order to eliminate the effect of dilution, the same method was applied using aliquots of water. The CMC was obtained at the slope discontinuity in the corrected surface tension (γ) versus log(C) plots.

In another experiment, Coomassie Brillant Blue G (100 mg) was dissolved in phosphoric acid 85% (100 mL) and ethanol (50 mL). The solution was adjusted to 250 mL with purified water. The following mother solutions of surfactants were prepared in water (10 mL) : **8** (0.8 M), **9** (1.2 M), **10** (565 mM), **11** (117 mM), **12** (7.4 mM), **13** (1.6 mM), **14** (0.4 mM), **15** (112 mM). Absorbance was measured at 620 nm and at 25 °C for solutions containing phosphoric acid (0.1 mL), Coomassie Brillant Blue G solution (0.2 mL), surfactant solution (x mL) and water [(0.8-x) mL]. When micelles were formed, solutions became blue.

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