Synthesis, Structural Analysis, and Properties of *N*-Alkylglucosyl(meth)acrylamides: New Reactive Sugar Surfactants

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Received August 11, 1997

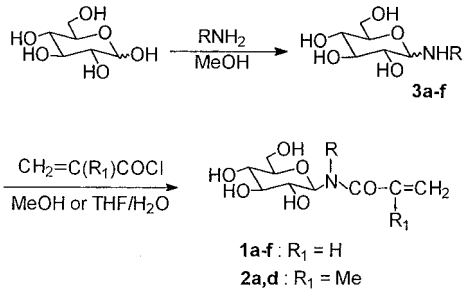
New reactive-surfactants, *N*-alkylglucosylacrylamides and *N*-alkylglucosylmethacrylamides, are easily prepared in two steps from glucose without protection. The complete structural analysis of these compounds by 1D and 2D NMR spectroscopy shows the existence of a rotational isomerism that is strongly dependent on the steric hindrance of the carbonyl substituent: whatever the alkyl chain length, both endo and exo rotamers are observed for *N*-alkylglucosylacrylamides **1** while the endo rotamer is the sole species observed in the case of *N*-alkylglucosylmethacrylamides **2**. For acrylamido derivatives **1**, the exo−endo equilibrium is solvent-dependent: the endo isomer is favored in polar nonaqueous solvents (endo−exo isomeric ratio $R = 70/30$) while the equilibrium is shifted toward the exo rotamer in protic acidic medium ($R = 50/50$ in water and 80/20 in acidic medium). An intramolecular hydrogen bond is assumed to be responsible for the increased stability of the endo rotamer. Furthermore, for tetra-*O*-acetylated derivatives the exo rotamer becomes favored in aprotic solvents. Surface tension measurements demonstrate that *N*-octyl- to -tetradecyl-substituted compounds **1** and **2** are surfactants with critical micelle concentrations ranging from 1.2×10^{-2} to 1.7×10^{-5} mol/L.

Introduction

Supramolecular assemblies and aqueous surfactant aggregates can enhance chemical rates, particularly in the case of functionalized aggregates.[1] Moreover, the microenvironment provided by the aggregates can affect the selectivity, and some enantioselective reactions have been described in chiral surfactant aggregates.[2] Nevertheless, the search for more effective systems requires the design of new functionalized surfactants with specific, fitted, properties.[2a]

We have chosen to develop a general, short synthetic pathway to various functionalized surfactants starting from a common reactive-surfactant precursor. This "surfactant synthon" includes moieties that permit the covalent binding to various molecular structures, thus leading to an array of elaborate surfactants with additional functionalities or to amphiphilic macromolecules. One of the main expected outcomes of this approach is the rational control of the aggregation properties of the resulting compound by the structure of the starting reactive surfactant.

Scheme 1



a: R=C_8H_{17}; **b**: R=$C_{10}H_{21}$; **c**; R=$C_{12}H_{25}$; **d**: R=$C_{14}H_{29}$; **e**: R=$C_{18}H_{37}$; **f**: R=$(CH_2)_4Ph$

We present here the synthesis, the structural characterization, and the surfactant behavior of a new family of chiral reactive surfactants derived from glucose, of general formula **1** and **2** (Scheme 1). Numerous complex amphiphilic molecules are readily available, in one step, from these precursors since the (meth)acrylamido substituent can act as a polymerizable group as well as a Michael acceptor. For example, amphiphilic polymers have been obtained by radical polymerization of compounds **1** and **2**,[3a] and surfactant cage molecules are readily accessible by nucleophilic addition of azacrowns (e.g., tetraazacyclotetradecane) to acrylamido compounds **1**.[3b] Finally, these compounds have been found to be successful for direct glucosylation of amino−latex particles.[3c]

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S0022-3263(97)01486-2 CCC: $15.00
Published on Web 01/22/1998

Table 1. ^{13}C NMR Data (75 MHz) of Compounds 1a and 2a in DMSO-d_6[a]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
2a	87.54	69.91	79.18	69.86	77.81	61.12	172.78	140.44	114.81	40.51
1aA	82.17	69.91	79.31	70.00	77.67	61.17	166.09	128.98	128.14	42.26
1aB	86.39	70.43	78.97	69.80	77.49	61.06	166.76	129.68	126.59	42.26

[a] Chemical shifts δ in ppm. Assignments made from DEPT and 2D $^{13}C-^{1}H$ NMR spectra. The atoms are numbered as shown in Scheme 2 and Figure 3.

Results and Discussion

1. Synthesis of *N*-Alkylglucosyl(meth)acrylamides 1 and 2. The glucosylamides **1** and **2** are obtained in two steps from D-glucose (Scheme 1). In the first step, glucose is reacted with the corresponding alkylamine according to the previously described procedures.[4] The resulting alkylglucosylamines **3** have been purified by recrystallization in ethanol and characterized by NMR spectroscopy. Their ^{13}C and ^{1}H NMR spectra show the presence of the two α and β anomers in DMSO solutions.[5]

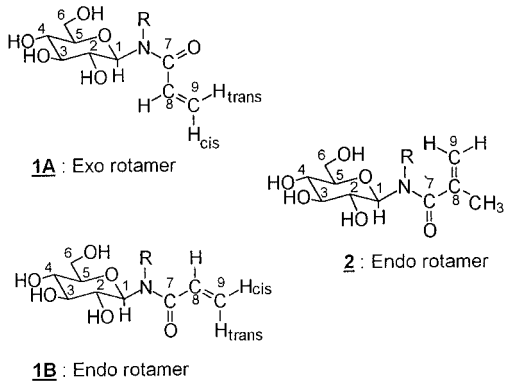
Compounds **1** and **2** are obtained in a second step by amidification of the alkylglucosylamines **3**. Selective formation of amides from amino alcohols can be achieved using specific acylating reagents[6] or by performing the reactions directly with an excess of acyl chloride in the presence of water.[7] We have found that selective (meth)acryloylation of alkylglucosylamines **3** can indeed be achieved using the latter procedure. These reactions can also be performed in pure methanol in the presence of a lower excess (2 equiv) of acyl chloride since methanol competes with primary and secondary alcohols but does not hydrolyze the acyl chloride.

Thus, the alkylglucosylamine **3** is reacted with 2 equiv (or 4−5 equiv) of acryloyl or methacryloyl chloride in the presence of sodium carbonate in methanol (or in THF−water). TLC monitoring of the reaction shows that the amide **1** or **2** is formed first (within 10 min to 1 h depending on the alkyl chain length of the starting glucosylamine and on the solvent). Bis- and poly(meth)acryloylated side products are formed in a second step and observed for longer reaction times. The crude product **1** or **2** is isolated by extraction with ethyl acetate and purified by column chromatography on silica gel. The reaction yields range from 50% to 60%. The purity of compounds **1** and **2** is demonstrated by HPLC analysis.

2. Structural Characterization of Compounds 1 and 2. *N*-Alkylglucosyl(meth)acrylamides **1** and **2** have been characterized by IR, NMR, and mass spectrometry. The mass spectra (CI, NH_3) are in agreement with the proposed structures with base peaks corresponding to the quasimolecular ($M - H^+$) ions. The IR spectra show the conjugated amide I and C=C stretching bands (1650 and 1610 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of compounds **2a** and **2d** in DMSO-d_6 are in agreement with the specific methacryloylation of the nitrogen atom. The ^{13}C NMR spectra (Table 1, Figure 1) show the following characteristic signals: CH_3, ethylenic sp^2, and CO carbon nuclei of the methacryloyl substituent (at 20, 115, 140, and 172 ppm, respectively), CH_2 linked to nitrogen at 40 ppm (compared to 46 ppm for the starting glucosylamine **3**), and glucopyranosyl carbon nuclei (61−88 ppm). The glucopyranosyl carbon C_2 is shielded compared to the starting glucosylamine **3** ($\Delta\delta \sim 3-4$ ppm) as already observed for other glucosylamides.[8,9]

Scheme 2



The single resonance observed for carbon C_1 demonstrates that only one isomer is present in DMSO solution. The β configuration of compounds **2a** and **2d** is clearly established by the ^{1}H NMR spectra, which demonstrate the axial position of the anomeric proton H_1: its chemical shift (4.7 ppm) is close to those described for secondary β-glucosylamides[6c,7b,10] displaying a characteristic axial−axial coupling constant with the H_2 nucleus ($^{3}J_{H_1-H_2} = 9$ Hz).[11] Moreover, the other ^{1}H signals are in agreement with the proposed structure (see the Experimental Section). It is worth noticing that the α-anomer has not been detected either during the acylation or during the treatment. As already observed for other glucosylamines,[6−10] the acylation leads selectively to the β-glucosylamide probably via α/β mutarotation.

Owing to the restricted rotation around the amide C−N bond, the absence of doubling of ^{1}H and ^{13}C resonances demonstrates that only one rotational isomer exists in DMSO solution. Furthermore, the glucopyranosyl ^{1}H and ^{13}C resonances of compounds **2** are close to those of secondary β-glucosylamides where the anti conformation of the amide C−N bond has been demonstrated by the trans H_1-NH coupling constant.[10] One can thus propose that the endo isomer (with the glucose ring cis to the carbonyl oxygen atom, Scheme 2) is the sole rotational isomer in solution. Moreover, as already described for other *N*,*N*-disubstituted methacrylamides, the α,β-unsaturated methacryloyl group is expected to adopt predominantly the s-trans conformation (Scheme 2).[12]

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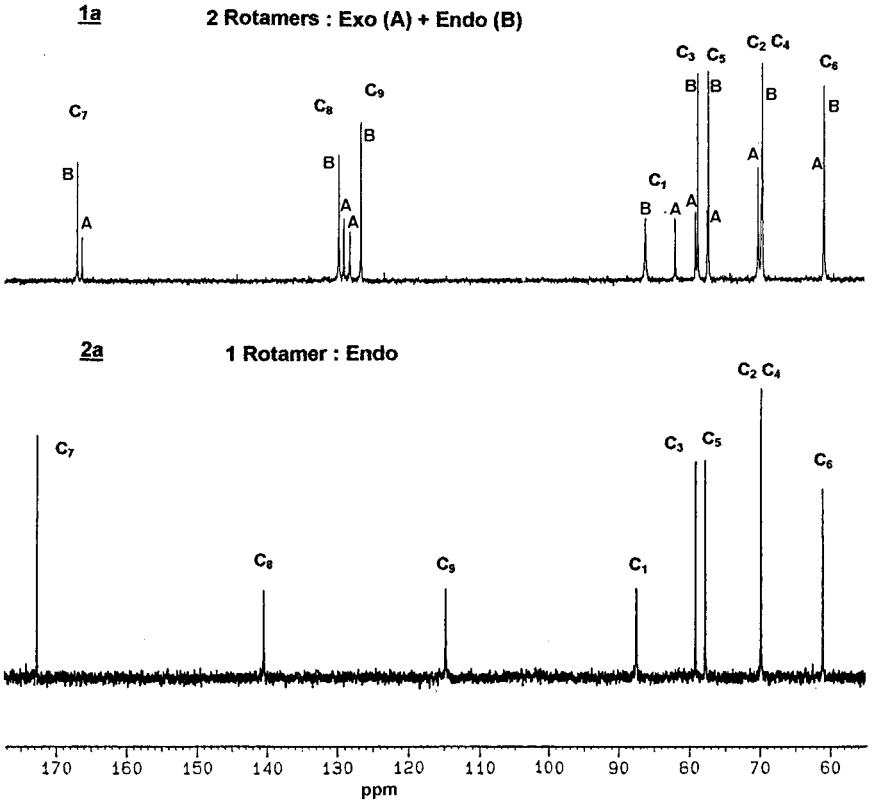

Figure 1. ^{13}C NMR Spectra (75 MHz) of *1a* (top) and *2a* (bottom) in DMSO-d_6, from 60 to 175 ppm.

Table 2. ^1H NMR (300 MHz) Data of Compound 1a in DMSO-d_6[a]

	1aB	1aA
H_1	4.76 ppm, d, $^3J_{H_1-H_2} = 7.4$ Hz	5.38 ppm, d, $^3J_{H_1-H_2} = 8.7$ Hz
H_2	3.27 ppm	3.22 ppm
H_3	3.24 ppm	3.16 ppm
H_4	3.09 ppm	
H_5	3.25 ppm	
H_{6a}	3.40 ppm, ddd, $^3J = 2.2$, 5.5 Hz, $^2J = 11.9$ Hz	
H_{6b}	3.66 ppm, ddd, $^3J = 6.0$, 5.5 Hz, $^2J = 11.9$ Hz	
H_8	6.69 ppm, dd, $^3J = 17$, 11 Hz	
H_{9cis}	5.75 ppm, dd, $^3J = 11$ Hz, $^2J = 2.5$ Hz	5.65 ppm, dd, $^3J = 11$ Hz, $^2J = 2.5$ Hz
H_{9trans}	6.20 ppm, dd, $^3J = 17$ Hz, $^2J = 2.5$ Hz	6.08 ppm, dd, $^3J = 17$ Hz, $^2J = 2.5$ Hz
H_{10}	3.25 ppm (broad)	
H_{11}	1.52 ppm (broad)	
OH_2	5.20 ppm, d, $^3J = 5$ Hz	4.98 ppm, db, $^3J = 5$ Hz
OH_3	5.13 ppm, d, $^3J = 4$ Hz	5.09 ppm, d, $^3J = 4$ Hz
OH_4	5.03 ppm, d, $^3J = 5$ Hz	
OH_6	4.48 ppm, tb, $^3J = 5.6$ Hz	

[a] Assignments made from 2D $^{13}C-^1H$, $^1H-^1H$ (COSY), *J*-resolved spectra. The atoms are numbered as shown in Scheme 2 and Figure 3.

The ^1H and ^{13}C NMR spectra of compounds **1a**−**f** in DMSO-d_6 are more complicated since they exhibit a doubling of some resonances, mainly for the glucose ring and the acryloyl substituent, with a relative intensity 70/30 indicating the presence of two species **1A** (∼30%) and **1B** (∼70%) in solution whatever the alkyl chain length (Tables 1 and 2, Figures 1 and 2). This doubling of ^1H and ^{13}C resonances demonstrates the existence of two rotational isomers **1A** and **1B** in solution. Spectral assignments have been performed using 2D $^{13}C-^1H$ and $^1H-^1H$ (COSY) NMR spectra; the coupling constants have been determined from a $^1H-^1H$ *J*-resolved spectrum. The spectroscopic data and spectra of compound **1a** are used to illustrate the following structural discussion.

The ^{13}C and ^1H NMR data of the major species **1B** are close to those of compounds **2**. The ^{13}C signals of species **1A** only slightly differ from **1B** for the glucose nuclei and the acryloyl substituent ($\Delta\delta \approx 0.1-1.5$ ppm), the main difference being observed for C_1 nuclei (86.4 ppm for **1aB** and 82.2 ppm for **1aA**, Figures 1 and 2, Table 1). The ^1H NMR spectra of compounds **1** show two sets of signals for terminal ethylenic protons H_9**A** and H_9**B** and two well-separated resonances for H_1**A** and H_1**B** nuclei: the H_1**B** chemical shift is very close to those observed for compounds **2** (4.76 ppm for **1aB** and 4.68 ppm for **2a**,

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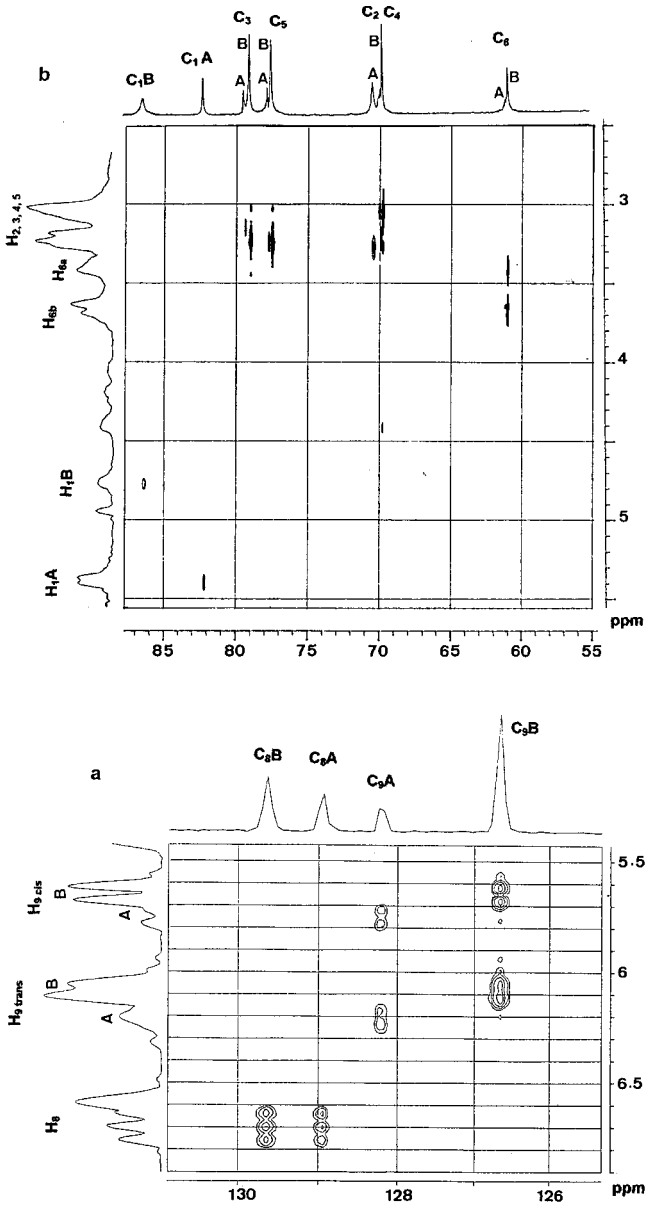

Figure 2. 2D Heteronuclear ^{13}C-^{1}H NMR Spectrum of *1a* in DMSO-d_6 a (bottom): Ethylenic region (125 to 130 ppm − 5.5 to 6.9 ppm) b (top): Glucose region (55 to 90 ppm − 3.0 to 5.5 ppm)

respectively, Figure 2, Table 2). On the other hand, the H_1 nucleus of species **1A** is deshielded (5.38 ppm): the characteristic trans coupling constant with H_2 (8.7 Hz) confirms the β-structure of species **1A**. Molecular modeling shows that in the exo rotamer (with the glucose ring anti to the carbonyl oxygen atom, Scheme 2) the anomeric proton H_1 and the carbonyl group are close together (∼2.7 Å) and that H_1 lies in the deshielding area of the carbonyl, in agreement with the high value of the observed low-field resonance of H_1**A** (Figure 3). The deshielding of proton nuclei trans to the oxygen atom is indeed well-known for *N*-methylamides.[13]

Therefore, *N*-alkylglucosylacrylamides **1** exist in DMSO solution as two rotamers in equilibrium: an exo isomer **1A** and an endo isomer **1B** (Scheme 2). The existence of two rotamers has already been observed for other tertiary glucosylamides such as *N*-alkyl-*N*-alkanoylglucosylamines but without structural assignments.[9,14] *N*-alkyl-*N*-acryloylglucosylamines **1a**−**f** behave like other *N*,*N*-dialkyl-substituted tertiary amides, including disubstituted acrylamides,[15] for which the ratio of the two rotamers usually depends on steric repulsions between the substituents and favors the conformation where the bulkiest substituent is cis to the carbonyl oxygen atom.[13,15,16] Accordingly, for compounds **1a**−**f**, the exo (A)−endo (B) rotamer ratio is almost constant (∼30/70) whatever the alkyl chain length.

On the other hand, for *N*-alkylglucosylmethacrylamides **2**, steric repulsions between the methyl group on C_8 and the glucose ring destabilize the exo rotamer so that the endo rotamer is the sole rotational isomer observed in solution in DMSO as well as in other usual solvents including protic solvents such as methanol and water. Such an effect of the steric hindrance of the C═O substituent has been described for other tertiary amides.[13,16a]

3. Study of the Endo−Exo Isomer Equilibrium of *N*-Alkylglucosylacrylamides 1a−f. 3.1. NOESY. The NOESY spectrum of *N*-octylglucosylacrylamide (**1a**) in DMSO-d_6 (Figure 4) clearly shows correlation peaks between the anomeric protons H_1**A** and H_1**B** and between the ethylenic protons H_9**A** (cis and trans) and H_9**B** (cis and trans) of the two rotamers A and B, thereby supporting a conformational equilibrium between the exo (A) and endo (B) rotamers.[17]

The NOESY spectrum also demonstrates the spatial proximity of the ethylenic H_8 nuclei with the anomeric proton H_1**A** or H_1**B**. Molecular models show indeed that H_8 and H_1 are close together in the exo rotamer A, with a minimal interatomic distance of about 1.9 Å, for an s-cis conformation of the acryloyl group. In addition, the absence of a correlation peak between H_9**A**(trans) and H_1**A** is also in agreement with an s-cis conformation of the acryloyl group (approximative minimal distances H_9-**A**(trans)-H_1**A**: about 1 and 4.5 Å, respectively, for s-trans and s-cis conformations of the acryloyl group). For the endo rotamer B, molecular models indicate that (i) whatever the conformation s-cis or s-trans of the acryloyl group, spatial interactions between the ethylenic protons (H_9**B** trans and cis) and the anomeric proton H_1**B** are not expected, and (ii) the ethylenic protons H_9**B** trans and the protons H_{10} and H_{11} of the alkyl chain are close together for a s-trans conformation of the acryloyl group (approximative minimal distances H_9**B**(trans)−H_{10} and H_9**B**(trans)−H_{11}: 1.3−2 Å) and far away for a s-cis conformation of the acryloyl group. The absence of correlation peaks with the alkyl-chain nuclei clearly demonstrates an s-cis conformation. Thus, the acryloyl group adopts an s-cis conformation in both the endo (B) and the exo (A) rotamers of *N*-alkyl-*N*-acryloylglucosyl-

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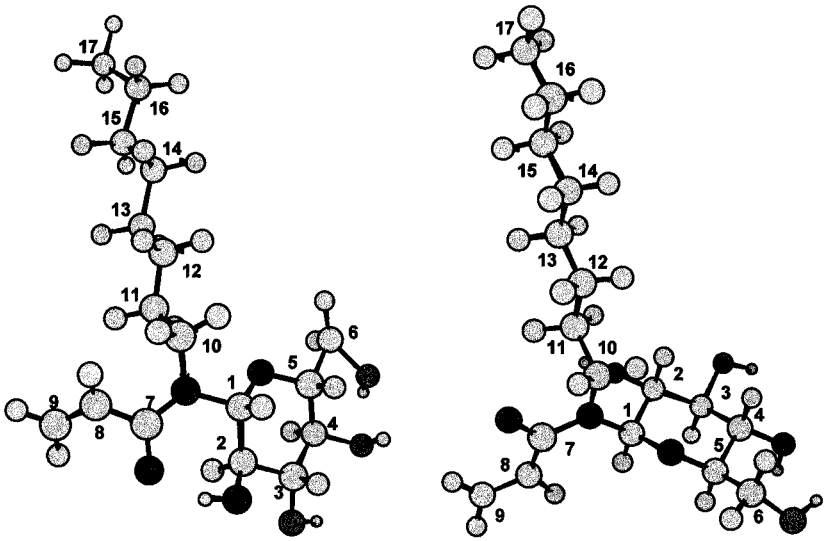


Figure 3. Molecular models of both endo and exo rotamers of *N*-(*β*-D-glucopyranosyl)-*N*-octyl-acrylamide *1a*.

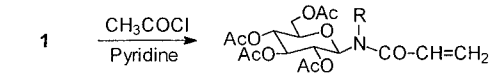
amines **1**. The preferred s-cis conformation of acrylamides is well-documented.[12]

3.2. Influence of the Solvent: Evidence for Intramolecular Hydrogen Bonding in the Endo Isomer B. ^{1}H and ^{13}C NMR spectra of compounds **1a**−**f** recorded in various solvents such as pyridine, DMSO, and methanol show that the exo/endo (A/B) isomer ratio remains almost constant (from 25/75 to 35/65). Temperature-dependent ^{1}H NMR spectra of compound **1a** in deuterated methanol show that the exo/endo (A/B) ratio is only slightly increased from 30/70 to 40/60 when the temperature is lowered from +35 to −40 °C and remains almost constant (30/70) above 0 °C. Unfortunately, experiments cannot be performed at higher temperatures since polymerization occurs above 40−50 °C.

On the other hand, in water, the exo/endo (A/B) ratio increases to 50/50, demonstrating that the amount of endo isomer is significantly decreased in protic medium. The A/B ratio in water is not concentration-dependent and remains almost constant below and above the critical micelle concentration (vide infra), thus indicating that micellization does not shift the exo-endo equilibrium. Moreover, the addition of 2 equiv of trifluoroacetic acid to **1a** in D_2O gives rise to a significant increase of the exo/endo ratio (A/B) from 50/50 in pure water to 80/20 in the presence of acid (Figure 5).

This variation of the exo/endo (A/B) ratio, leading to the predominance of the exo (A) rotamer in protic acidic medium, can be explained by the existence of a strong intramolecular hydrogen bond in the endo (B) rotamer, between the glucopyranosyl hydroxyl group OH_2 and the oxygen of the amide group, in polar aprotic and poorly protic solvents. The splitting of the OH_2 resonance in DMSO (4.98 and 5.20 ppm, respectively, for OH_2A and OH_2B) and the higher chemical shift for the endo rotamer (B) confirm this assumption. Furthermore, molecular models of the endo (B) rotamer show that the oxygen of the carbonyl group is very close to the hydroxyl substituent of the glucose carbon C_2 (approximative minimal distance OH_2/O═C ≈ 0.7 Å, Figure 3). This intramolecular hydrogen bond between the carbonyl group and the hydroxyl substituent OH_2 may thus well be responsible for the increased stability of the endo rotamer B in polar aprotic and poorly protic solvents.

Scheme 3



1a: R=C_8H_{17} **4a**: R=C_8H_{17}

1f: R=$(CH_2)_4Ph$ **4f**: R=$(CH_2)_4Ph$

To further check this hypothesis, the tetra-*O*-acetylated compounds **4a** and **4f** have been synthesized (Scheme 3) and characterized by 1D and 2D homo and heteronuclear NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of acetylated compounds **4a** and **4f** show for both derivatives the presence of the exo (A) and endo (B) rotamers, easily identified by their anomeric protons (H_1**A** and H_1**B**, respectively, at 5.95 and 5.53 ppm in CD_3OD for **4a**), with an exo/endo isomer ratio of 50/50 in methanol and 70/30 in chloroform. Therefore, when hydrogen bonding cannot take place, the exo/endo equilibrium is shifted toward the exo isomer (A) even with a much bulkier tetra-*O*-acetylglucopyranosyl substituent.

An intramolecular hydrogen bond may thus account for the predominance of the sterically unfavored endo (B) rotamer for *N*-alkylglucosylacrylamides **1a**−**f** in polar aprotic and poorly protic solvents.[18]

4. Surfactant Properties. *N*-Alkylglucosyl(meth)-acrylamides **1** and **2** are fairly soluble in water for alkyl chain lengths up to 14 carbon atoms; the octadecyl derivative **1e** is the only water-insoluble compound. Moreover, surprisingly, the solubility in water does not vary significantly with the alkyl chain length: about 3 × 10^{-2} mol/L for the octyl derivative **1a** and 1 × 10^{-2} mol/L for the tetradecyl derivative **1d**. It is noteworthy that our glucosyl(meth)acrylamides **1** and **2** are much more water-soluble than classical alkyl glucosides and thioglucosides.[19,20]

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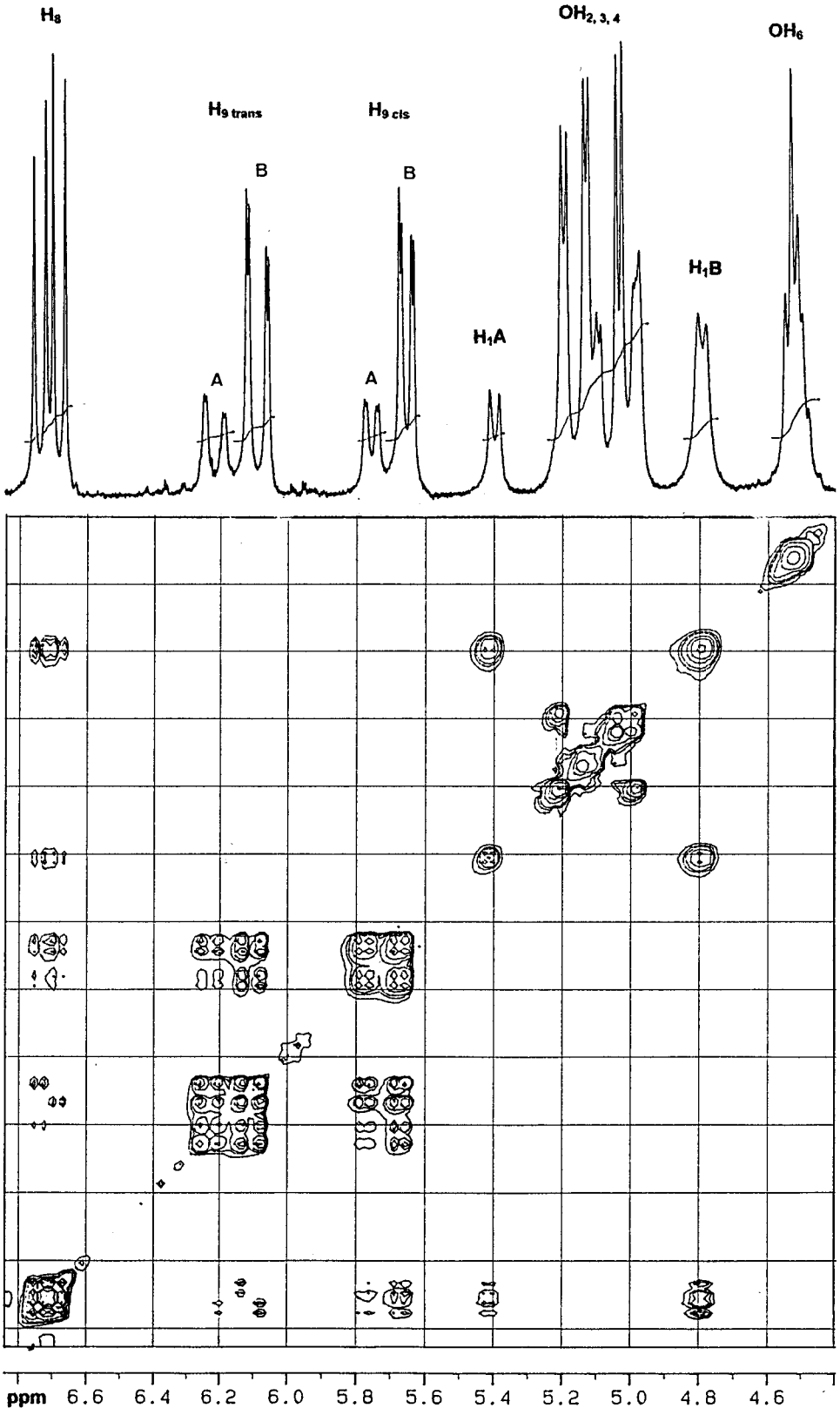

Figure 4. NOESY Spectrum (DMSO-d_6, 300 MHz, mixing time: 0.9s) of *1a*, from 4.4 to 6.8 ppm.

Surface tension measurements of aqueous solutions at 25 °C demonstrate that *N*-alkylglucosyl(meth)acrylamides **1a**−**d** and **2a,d** are surfactants (Figure 6). The parameters derived from these measurements are given in Table 3. On the other hand, for the butylphenyl derivative **1f**, no micelle formation could be observed up to its solubility limit (5×10^{-2} mol/L). It behaves rather like a hydrotrope owing to the polarity of the aromatic nucleus.[21]

The critical micelle concentrations (cmc) of compounds **1a**−**d** and **2a,d** decrease with the alkyl chain length. Log(cmc) displays a linear dependence on the number of

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Table 3. Values Obtained from Surface Tension Measurements for Compounds 1 and 2[a]

		cmc (mol/L)	Γ (mmol/m^2)	a_s (Å^2)	γ_{cmc} (mN/m)
1a	R = C_8H_{17}	$(1.2 \pm 0.2) \times 10^{-2}$	2.5 ± 0.2	67 ± 4	35.5
1b	R = $C_{10}H_{21}$	$(1.2 \pm 0.1) \times 10^{-3}$	3.1 ± 0.1	53 ± 2	33.5
1c	R = $C_{12}H_{25}$	$(1.4 \pm 0.1) \times 10^{-4}$	3.5 ± 0.1	47 ± 2	32.2
1d	R = $C_{14}H_{29}$	$(3.0 \pm 0.1) \times 10^{-5}$	4.2 ± 0.2	39 ± 3	31.8
2a	R = C_8H_{17}	$(8.0 \pm 0.5) \times 10^{-3}$	2.7 ± 0.5	60 ± 5	34.0
2d	R = $C_{14}H_{29}$	$(1.7 \pm 0.3) \times 10^{-5}$	4.4 ± 0.5	38 ± 4	33.5
alkylglucosides[19]	R = C_8H_{17}	2.5×10^{-2} (1.9×10^{-2})[b]	3.9	42 (43)[c]	30.1
	R = $C_{10}H_{21}$	2.2×10^{-3}	3.5	47 (43)[c]	27.7
	R = $C_{12}H_{25}$	1.9×10^{-4}	4.6	36	39.4

[a] The superficial excess Γ and the area per headgroup a_s are calculated below the cmc from the Gibbs adsorption isotherm: $d\gamma = -\Gamma RTdLnC$. γ_{cmc} is the superficial tension above the cmc. [b] From ref 22. [c] From ref 24.

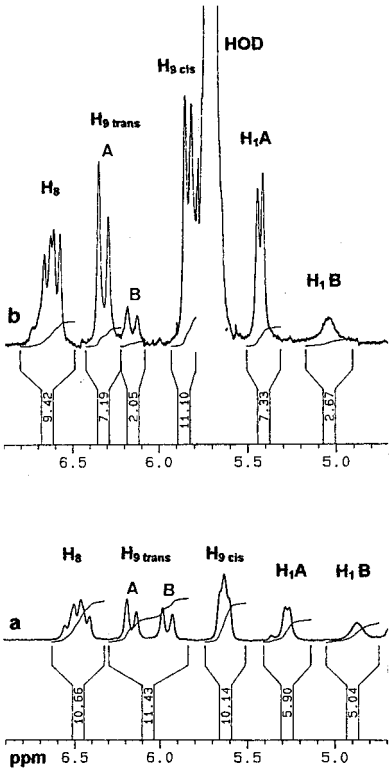

Figure 5. ^{1}H NMR Spectra (300 MHz) of *1a*, from 4.7 to 6.9 ppm a (bottom): in D_2O b (top): in D_2O + 2eq.TFA

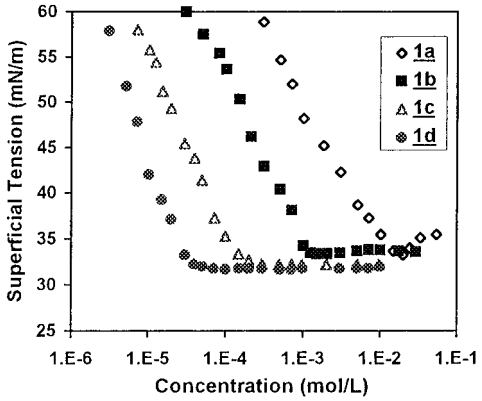

Figure 6. Air−water interfacial tension γ vs concentration for surfactants *1a−d* at 25 °C.

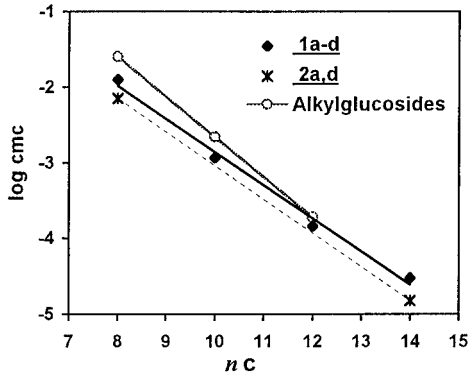

Figure 7. log cmc (mol/L) versus number of carbon atoms *n*C of the alkyl substituent. **1a−d**: log(cmc **1**) ≈ 1.51 − 0.44n_C; **2a,d**: log(cmc **2**) ≈ 1.45 − 0.45n_C; alkylglucosides:[19] log(cmc) ≈ 2.64 − 0.53n_C.

carbon atoms in the aliphatic chain n_c. It follows the Klevens equation, log(cmc) = $a - bn_C$, as with classical nonionic surfactants such as alkylglucosides[19] and alkylthioglucosides[20] (Figure 7). Nevertheless, the smaller values of the intercept and gradient obtained for compounds **1** and **2** as well as the lower cmc values of compounds **1a−c** and **2a** compared to the homologous alkylglucosides[19,22] may be due to a weak contribution of the (meth)acryloyl substituent to the free energy of micellization. Furthermore, the lower cmc of methacryloyl compounds **2a** and **2d** compared to their acryloyl homologs **1a** and **1d** clearly indicates that the methyl group has a hydrophobic contribution.

The area per headgroup a_s for compounds **1a−d** and **2a,d**, evaluated using the Gibbs adsorption isotherm, ranges from 67 to 38 Å^2. It decreases when the alkyl chain length is increased, probably because of increasing chain−chain interactions in the monolayer.[25] The location of the (meth)acryloyl group at the interface[23] may account for the high values of a_s for compounds **1a−c** and **2a** compared to those reported for alkyl glucosides.[19,24]

Conclusion

N-Alkylglucosyl(meth)acrylamides, new polymerizable and Michael acceptor surfactants, are conveniently prepared in two steps from glucose. The structural analysis demonstrates the existence of a rotational isomerism that is strongly dependent on the steric hindrance of the unsaturated substituent: both endo and exo isomers are observed for the acrylamido derivatives while the endo

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rotamer is the sole species observed in the case of *N*-alkylglucosylmethacrylamides. The influence of the protic medium on the *N*-alkylglucosylacrylamides endo−exo equilibrium and the comparison with their acetylated derivatives suggest that an intramolecular hydrogen bond may be responsible for the increased stability of the endo rotamer. The surfactant properties of *N*-octyl- to -tetradecyl-substituted glucosyl(meth)acrylamides are similar to usual sugar-based surfactants. Furthermore, their fairly high solubility in water suggests that they may have valuable biological applications.[20] The synthetic applications of these new reactive sugar-based surfactants **1a**−**d** and **2a,d** for the preparation of functionalized, chiral surfactants are currently being studied.

Experimental Section

General Methods. All unspecified reagents were from commercial resources. The IR spectra were recorded using a FTIR apparatus. The NMR spectra were obtained on a Bruker AM300 spectrometer, ^{1}H (300 MHz) and ^{13}C (75.5 MHz). Mass spectra in the chemical ionization mode (CI, reactant gas NH_3) were obtained by direct introduction; for electrospray the samples were diluted in CH_3CN/HCO_2H 1% in water (50/50). Elemental analyses have been obtained from the "Service Central d'Analyse" (CNRS, Vernaison, France). HPLC analyses were carried out in both the normal mode [method A, silica column (15 cm), eluent: methanol/water 80/20, 1.5 mL·min^{-1}, UV detection 235 nm] and the reverse mode [method B, RP18 column (15 cm), eluent: dichloromethane/methanol 96/4, 2 mL·min^{-1}, UV detection 230 nm]. Capacity factor: $k' = (t_r - t_0)/t_0$. TLC on silica plates (Merck 60F$_{254}$); indicators: I, UV 254 nm; II, sulfuric acid (20% in ethanol); III, ninhydrine (0.2% in ethanol). Molecular models were obtained using CS Chem3D software, MM2-minimized energy. Surface tension was measured using a Krüss K10 tensiometer and Pt du Nouy ring, thermostated at 25 °C. The aqueous solutions were prepared using ultrapure water (MilliQ, resistivity > 18 MΩ) and previously freeze-dried compounds. The concentration of residual ions, measured by capillary electrophoresis, was always very low (<0.05 mol per mol surfactant).

***N*-Alkyl-D-glucopyranosylamines 3a−f.** *N*-Octyl-D-glucopyranosylamine (**3a**), *N*-decyl-D-glucopyranosylamine (**3b**), *N*-dodecyl-D-glucopyranosylamine (**3c**), *N*-tetradecyl-D-glucopyranosylamine (**3d**), *N*-octadecyl-D-glucopyranosylamine (**3e**), and *N*-butyl-4-phenyl-D-glucopyranosylamine (**3f**) were prepared by reaction of D-glucose with the corresponding alkylamine (stoichiometric amount) in methanol at 60−65 °C, according to the previously described procedures.[4] **3a**, **3b**, **3c**, **3d**, and **3e** were purified by repeated recrystallization in absolute ethanol until the melting point remained constant (usually three recrystallizations). **3f** was recrystallized twice from EtOH/H$_2$O (9/1).

3a: 86% yield; mp 104−106 °C (lit.[4] mp 102 °C); MS (electrospray) *m*/*z* 292 (100, MH$^+$); ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 3H, CH$_3$, ^3J = 7 Hz), 1.25 (m, 10H, CH$_2$ alkyl), 1.38 (b, 2H, NCH$_2$*CH*$_2$), 2.13 (b, 1H, NH), 2.5 (mb, 1H, NC*H*$_a$), 2.75 (mb, 1H, NC*H*$_b$), 2.85 (m, 1H, H$_2$), 3.01 (m, 2H, H$_4$, H$_5$), 3.11 (m, 1H, H$_3$), 3.39 (m, 1H, H$_{6a}$), 3.62 (m, 1H, H$_{6b}$), 3.66 (d, 1Hβ, H$_1\beta$, $^3J_{H_1-H_2}$ = 7 Hz), 4.29 (d, 1Hα, H$_1\alpha$, $^3J_{H_1-H_2}$ = 5 Hz), 4.35 (t, 1H, OH$_6$, ^3J = 6 Hz), 4.45 (d, 1H, OH$_2$, ^3J = 4 Hz), 4.80 (d, 1H, OH$_3$, ^3J = 4.5 Hz), 4.84 (d, 1H, OH$_4$, ^3J = 4.5 Hz); ^{13}C NMR (DMSO-d_6) δ 13.90 (CH$_3$), 22.03, 26.78, 28.67, 28.96, 29.90 and 31.21 (CH$_2$ alkyl), 45.48 (N*C*H$_2$), 61.31 (C$_6$), 70.46 (C$_4$), 73.44 (C$_2$), 77.37 (C$_5$), 77.55 (C$_3$), 86.92 (C$_1\alpha$), 90.72 (C$_1\beta$). Isomeric ratio: α/β = 20/80. **3b**: 65% yield; mp 103 °C (lit.[4] mp 103−104 °C); ^{1}H NMR (DMSO-d_6) δ 0.84 (t, 3H, CH$_3$, ^3J = 7 Hz), 1.24 (m, 14H, CH$_2$ alkyl), 1.35 (b, 2H, NCH$_2$*CH*$_2$), 2.16 (b, 1H, NH), 2.49 (mb, 1H, NC*H*$_2$), 2.82 (mb, 1H, H$_2$), 3.00 (m, 2H, H$_4$, H$_5$), 3.10 (m, 1H, H$_3$), 3.37 (m, 1H, H$_{6a}$), 3.62 (m, 1H,H$_{6b}$), 3.65 (d, 1Hβ, H$_1\beta$, $^3J_{H_1-H_2}$ = 7 Hz), 4.3 (b, 1Hα, H$_1\alpha$), 4.35 (t, 1H, OH$_6$, ^3J = 6 Hz), 4.44 (d, 1H, OH$_2$, ^3J = 4 Hz), 4.79 (d, 1H, OH$_3$, ^3J = 3 Hz), 4.83 (d, 1H, OH$_4$, ^3J = 4.5 Hz); ^{13}C NMR (DMSO-d_6) δ 13.19 (CH$_3$), 22.09, 26.85, 28.73, 29.10, 29.96 and 31.30 (CH$_2$ alkyl), 45.55 (N*C*H$_2$), 61.13 and 61.36 (C$_6\alpha$ and β), 70.50, 70.65, 70.90, 71.57, 73.47, 73.71, 77.40 and 77.56 (C$_2$, C$_3$, C$_4$, C$_5$, α and β), 86.91 (C$_1\alpha$), 90.76 (C$_1\beta$). Isomeric ratio: α/β = 20/80. **3c**: 60% yield; mp 106 °C (lit.[4] mp 105.5 °C); ^{1}H NMR (DMSO-d_6) δ 0.84 (t, 3H, CH$_3$, ^3J = 7 Hz), 1.23 (m, 18H, CH$_2$ alkyl), 1.37 (b, 2H, NCH$_2$*CH*$_2$), 2.17 (b, 1H, NH), 2.48 (mb, 1H, NC*H*$_2$), 2.81 (mb, 1H, H$_2$), 3.00 (m, 2H, H$_4$, H$_5$), 3.10 (m, 1H, H$_3$), 3.39 (m, 1H, H$_{6a}$), 3.55 (m, 1H, H$_{6b}$), 3.62 (d, 1Hβ, H$_1\beta$, $^3J_{H_1-H_2}$ = 7 Hz), 4.28 (b, 1Hα, H$_1\alpha$), 4.33 (t, 1H, OH$_6$, ^3J = 6 Hz), 4.44 (d, 1H, OH$_2$, ^3J = 4 Hz), 4.79 (d, 1H, OH$_3$, ^3J = 3 Hz), 4.83 (d, 1H, OH$_4$, ^3J = 4.5 Hz); ^{13}C NMR (DMSO-d_6) δ 13.91 (CH$_3$), 22.11, 26.87, 28.73, 29.03, 29.09, 29.11, 29.59, 29.98, and 31.31 (CH$_2$ alkyl), 45.48 and 45.92 (NCH$_2$ α and β), 61.37 (C$_6$), 70.65 and 70.93 (C$_4$ α and β), 73.49 and 73.72 (C$_2$ α and β), 77.43 (C$_5$), 77.59 (C$_3$), 86.92 (C$_1\alpha$), 90.79 (C$_1\beta$). Isomeric ratio: α/β = 20/80. **3d**: 78% yield; mp 107−109 °C; ^{1}H NMR (DMSO-d_6) δ 0.84 (t, 3H, CH$_3$, ^3J = 7 Hz), 1.23 (m, 10H, CH$_2$ alkyl), 1.38 (b, 2H, NCH$_2$*CH*$_2$), 2.50 (mb, 1H, NC*H*$_2$), 2.82 (mb, 1H, H$_2$), 3.02 (m, 2H, H$_4$, H$_5$), 3.12 (m, 1H, H$_3$), 3.34 (m, 1H, H$_{6a}$), 3.58 (m, 1H, H$_{6b}$), 3.63 (d, 1Hβ, H$_1\beta$, $^3J_{H_1-H_2}$ = 8 Hz), 4.30 (b, 1Hα, H$_1\alpha$), 4.33 (t, 1H, OH$_6$, ^3J = 6 Hz), 4.46 (d, 1H, OH$_2$, ^3J = 4 Hz), 4.81 (b, 1H, OH$_3$), 4.84 (d, 1H, OH$_4$, ^3J = 4.5 Hz); ^{13}C NMR (DMSO-d_6) δ 13.96 (CH$_3$), 22.08, 26.85, 28.70, 29.00, 29.05, 29.08, 29.57, 29.98, and 31.28 (CH$_2$ alkyl), 45.55 and 45.91 (NCH$_2$ α and β), 61.37 (C$_6$), 70.67 and 70.95 (C$_4$ α and β), 73.51 and 73.71 (C$_2$ α and β), 77.44 (C$_5$), 77.61 (C$_3$), 86.91 (C$_1\alpha$), 90.79 (C$_1\beta$). Isomeric ratio: α/β = 20/80. **3e**: 78% yield; mp 104 °C (lit.[4] 103.5 °C); ^{13}C NMR (C$_5$D$_5$N, 22.5 MHz) δ 14.31 (CH$_3$), 22.95 (CH$_2$ alkyl), 27.75 (CH$_2$ alkyl), 29.67 (CH$_2$ alkyl), 30.02 (CH$_2$ alkyl), 31.02 (CH$_2$ alkyl), 32.19 (CH$_2$ alkyl), 46.63 (CH$_2$N, β), 47.12 (CH$_2$N, α), 62.96 (C$_6$ β), 63.18 (C$_6$ α), 71.90 (C$_4$ β), 72.52 (C$_4$ α), 75.01 (C$_2$ β), 75.66 (C$_2$ α), 79.02 (C$_3$, C$_5$), 88.50 (C$_1$ α), 92.05 (C$_1$ β). Isomeric ratio: α/β = 20/80. **3f**: 41% yield; mp 64−66 °C; IR (KBr, ν cm^{-1}) 3420, 3325, and 3257 (OH, NH), 3026, 2999, 2950−2830, 1650 and 1500 (νC=C); ^{1}H NMR (DMSO-d_6) δ 1.45−1.38 (m, 2H, NCH$_2$*CH*$_2$), 1.64−1.54 (m, 2H, *CH*$_2$CH$_2$Ph), 2.18 (bp, 1H, N−H), 2.59−2.53 (m, 3H, NC*H*$_a$ and *CH*$_2$Ph), 2.89−2.77 (m, 2H, H$_2$, and NC*H*$_b$), 3.00 (m, 2H, H$_4$, H$_5$), 3.13−3.08 (m, 1H, H$_3$), 3.42−3.38 (m, 1H, H$_{6b}$), 3.67−3.62 (m, 2H, H$_1\beta$, H$_{6a}$), 4.30 (d, 1Hα, H$_1\alpha$, J = 5.5 Hz), 4.36 (dd, 1H, OH$_6$, J = 5.5, 5.9 Hz), 4.45 (d, 1H, OH$_2$, J = 4.0 Hz), 4.80 (d, 1H, OH$_4$, J = 4.4 Hz), 4.83 (d, 1H, OH$_3$, J = 4.8 Hz), 7.25−7.13 (m, 5H, ArH); ^{13}C NMR (DMSO-d_6) δ 28.96 (NCH$_2$*C*H$_2$ or *C*H$_2$CH$_2$Ph, β), 28.07 and 29.38 (NCH$_2$*C*H$_2$ and *C*H$_2$CH$_2$Ph, α), 29.79 (NCH$_2$*C*H$_2$ or *C*H$_2$CH$_2$Ph, β), 35.26 (*C*H$_2$Ph, α), 35.32 (*C*H$_2$Ph, β), 45.53 (N*C*H$_2$, β), 45.89 (N*C*H$_2$, α), 61.39 (C$_6\alpha$), 61.63 (C$_6\beta$), 70.94, 71.23, 71.83, and 73.72 (C$_2\alpha$, C$_3\alpha$, C$_4\alpha$, C$_5\alpha$), 70.75, 73.94, 77.66 and 77.82 (C$_2\beta$, C$_3\beta$, C$_4\beta$, C$_5\beta$), 87.13 (C$_1\alpha$), 90.98 (C$_1\beta$), 125.75, 128.40 and 128.49 (C$_{Ar}$), 142.52 (C$_{ipso}$). Isomeric ratio: α/β = 20/80. Anal. Calcd for C$_{16}$H$_{25}$O$_5$N·H$_2$O: C, 58.34; H, 8.26; N, 4.25. Found: C, 58.48; H, 8.67; N, 4.31.

***N*-(β-D-Glucopyranosyl)-*N*-octylacrylamide (1a).** Sodium carbonate (6.63 g, 62.5 mmol) was added to a solution of **3a** (7 g, 24 mmol) in 100 mL of methanol containing 100 ppm of sodium nitrite (radical inhibitor). The resulting mixture was cooled to 0 °C with an ice bath, and 3.9 mL (48 mmol) of acryloyl chloride was added dropwise via a dropping funnel in 5 min. The ice bath was then removed. The reaction mixture was stirred for 25 min at room temperature (TLC analysis) and then poured into 100 mL of water. After removal of methanol under reduced pressure, the crude product was extracted with ethyl acetate (6 × 50 mL). The combined organic phases were washed with a saturated solution of sodium bicarbonate (3 × 50 mL) and brine (3 × 50 mL), dried over magnesium sulfate, and concentrated under vacuum (about 100 ppm of di-*tert*-butylphenol was added before concentration). Crude **1a** (8 g, 95%) as a viscous oil was thus obtained. **1a** was purified by column chromatography on silica gel using an elution gradient starting with dichloromethane followed by dichloromethane−methanol 90/10. A second column, using the same eluent system, was almost always necessary in order to obtain a product free of impurity according to the TLC analysis: yield of purification 52%

(amorphous paste); TLC $R_f = 0.22$ (CH_2Cl_2/MeOH, 9/1); HPLC (method B) $k' = 0.9$; $[\alpha]^{20}_D = +16.7$ ($c = 1.5$, EtOAc); MS (CI, NH_3) m/z 346 (100, MH^+); IR (Nujol, ν cm^{-1}) 3500−3200 (OH), 1650 (CO, amide I), 1610 (C═C); ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 3H, CH_3, $^3J = 7$ Hz), 1.25 (m, 10H, H_{12-16}), 1.52 (b, 2H, H_{11}), 3.09 (m, 1H, H_4), 3.16 (m, 1H**A**, H_3), 3.21 (m, 1H**A**, H_2), 3.24 (m, 1H**B**, H_3), 3.25 (m, 1H, H_5), 3.25 (mb, 2H, H_{10}), 3.28 (m, 1H**B**, H_2), 3.40 (ddd, 1H, H_{6a}, $^3J = 2.2$ Hz, $^3J = 5.5$ Hz, $^2J = 11.9$ Hz), 3.66 (ddd, 1H, H_{6b}, $^3J = 6.0$, 5.5 Hz, $^2J = 11.9$ Hz), 4.48 (m, 1H, OH_6), 4.76 (d, 1H**B**, H_1**B**, $^3J_{H_1-H_2} = 7.4$ Hz), 4.98 (d, 1H**A**, OH_2**A**, $^3J = 5$ Hz), 5.03 (d, 1H, OH_4, $^3J = 5$ Hz), 5.09 (d, 1H**A**, OH_3**A**, $^3J = 4$ Hz), 5.13 (d, 1H**B**, OH_3**B**, $^3J = 4$ Hz), 5.20 (d, 1H**B**, OH_2**B**, $^3J = 5$ Hz), 5.38 (d, 1H**A**, H_1**A**, $^3J_{H_1-H_2} = 8.7$ Hz), 5.65 (dd, 1H**B**, H_{9cis}**B**, $^3J = 11$ Hz, $^2J = 2.5$ Hz), 5.75 (dd, 1H**A**, H_{9cis}**A**, $^3J = 11$ Hz, $^2J = 2.5$ Hz), 6.08 (dd, 1H**B**, H_{9trans}**B**, $^3J = 17$ Hz, $^2J = 2.5$ Hz), 6.20 (dd, 1H**A**, H_{9trans}**A**, $^3J = 17$ Hz, $^2J = 2.5$ Hz), 6.69 (dd, 1H, H_8, $^3J = 17$, 11 Hz); the exo (A)−endo (B) isomer ratio 27/73 was calculated from the integration curve of protons H_{9cis}**A**/H_{9cis}**B**, H_{9trans}**A**/H_{9trans}**B**, and H_1**A**/H_1**B**; ^{13}C NMR (DMSO-d_6) δ 13.90 (CH_3), 22.03 (CH_2 alkyl), 26.40 (CH_2 alkyl), 26.71 (CH_2 alkyl), 28.39 (C_{12}**B**), 28.62 (CH_2 alkyl), 28.71 (CH_2 alkyl), 30.70 (C_{12}**A**), 31.21 (CH_2 alkyl), 42.26 (C_{10}), 61.06 (C_6**B**), 61.17 (C_6**A**), 69.80 (C_4**B**), 69.91 (C_2**A**), 70.00 (C_4**A**), 70.43 (C_2**B**), 77.49 (C_5**B**), 77.67 (C_5**A**), 78.97 (C_3**B**), 79.31 (C_3**A**), 82.17 (C_1**A**), 86.39 (C_1**B**), 126.59 (C_9**B**), 128.14 (C_9**A**), 128.98 (C_8**A**), 129.68 (C_8**B**), 166.09 (C_7**A**), 166.76 (C_7**B**). Anal. Calcd for $C_{17}H_{31}NO_6 \cdot 0.5H_2O$: C, 57.63; H, 9.04; N, 3.95; O, 29.38. Found: C, 57.51; H, 9.12; N, 3.98; O, 29.41.

***N*-(*β*-D-Glucopyranosyl)-*N*-decylacrylamide (1b)** was prepared using the procedure described above for **1a**: quantitative yield of crude **1b**, viscous oil; yield of purification (elution gradient CH_2Cl_2/MeOH) 70% (amorphous paste); TLC $R_f = 0.22$ (CH_2Cl_2/MeOH, 9/1); HPLC (method B) $k' = 1.6$); $[\alpha]^{20}_D = +14$ ($c = 2$, EtOAc); MS (CI, NH_3) m/z 374 (100, MH^+); IR (Nujol, ν cm^{-1}) 3500−3200 (OH), 1650 (CO, amide I), 1610 (C═C); ^{1}H NMR (D_2O) δ 0.87 (t, 3H, CH_3, $^3J = 7$ Hz), 1.28 (m, 18H, H_{12-20}), 1.62 (b, 2H, H_{11}), 3.0−3.60 (m, 6H, H_2, H_3, H_4, H_5, H_{10}), 3.67 (b, 1H, H_{6a}), 3.83 (db, 1H, H_{6b}, $J = 9$ Hz), 4.92 (b, 1H**B**, H_1**B**), 5.44 (db, 1H**A**, H_1**A**, $^3J_{H_1-H_2} = 8$ Hz), 5.76 (db, 1H, H_{9cis}, $J = 9.5$ Hz), 6.11 (d, 1H**B**, H_{9trans}**B**, $^3J = 17$ Hz), 6.32 (d, 1H**A**, H_{9trans}**A**, $^3J = 17$ Hz), 6.60 (dd, 1H, H_8, $^3J = 17$, 11 Hz); the exo (A)−endo (B) isomer ratio 50/50 was calculated from the integration curve of protons H_{9trans}**A**/H_{9trans}**B** and H_1**A**/H_1**B**; ^{13}C NMR (CD_3OD) δ 14.47 (CH_3), 23.64, 27.98, 28.30, 29.85, 30.37, 30.14, 30.62, 30.69, 32.09 and 32.97 (CH_2 alkyl), 43.33 (C_{10}**B** or **A**), 44.00 (C_{10}**A** or **B**), 62.79 (C_6), 71.03 (C_4**B** and C_2**A**), 71.58 (C_4**A**), 71.95 (C_2**B**), 79.06 (C_5), 80.16 (C_3), 84.47 (C_1**A**), 88.39 (C_1**B**), 127.91 (C_9**B**), 129.62 (C_9**A**), 129.70 (C_8**A**), 130.50 (C_8**B**), 169.77 (C_7**A**), 170.58 (C_7**B**). Anal. Calcd for $C_{19}H_{35}NO_6 \cdot 0.3H_2O$: C, 60.25; H, 9.41; N, 3.70; O, 26.64. Found: C, 60.19; H, 9.56; N, 3.67; O, 26.66.

***N*-(*β*-D-Glucopyranosyl)-*N*-dodecylacrylamide (1c)** was prepared using the procedure described above for **1a**: yield of crude **1c** 87%; viscous oil; yield of purification (elution gradient CH_2Cl_2/MeOH) 60% (amorphous paste); TLC $R_f = 0.22$ (CH_2Cl_2/MeOH, 9/1); HPLC (method B) $k' = 3.1$; $[\alpha]^{20}_D = +13.3$ ($c = 1.5$, EtOAc); MS (CI, NH_3) m/z 402 (100, MH^+); IR (Nujol, ν cm^{-1}) 3500−3200 (OH), 1650 (CO, amide I), 1610 (C═C); ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 3H, CH_3, $^3J = 7$ Hz), 1.25 (m, 18H, H_{12-20}), 1.52 (b, 2H, H_{11}), 3.09 (m, 1H, H_4), 3.20−3.30 (m, 3H, H_2, H_3, H_5), 3.25 (m, 2H, H_{10}), 3.40 (m, 1H, H_{6a}), 3.66 (ddd, 1H, H_{6b}, $^3J = 6.0$ Hz, $^3J = 4.5$ Hz, $^2J = 11.5$ Hz), 4.47 (m, 1H, OH_6), 4.76 (d, 1H**B**, H_1**B**, $^3J_{H_1-H_2} = 7.2$ Hz), 4.94 (d, 1H**A**, OH_2**A**, $^3J = 5$ Hz), 4.99 (d, 1H, OH_4, $^3J = 5$ Hz), 5.07 (db, 1H**A**, OH_3**A**, $^3J = 5$ Hz), 5.07 (db, 1H**B**, OH_3**B**, $^3J = 5$ Hz), 5.16 (d, 1H**B**, OH_2**B,** $^3J = 5$ Hz), 5.38 (d, 1H**A**, H_1**A**, $^3J_{H_1-H_2} = 8.5$ Hz), 5.65 (dd, 1H**B**, H_{9cis}**B**, $^3J = 11$ Hz, $^2J = 2.2$ Hz), 5.75 (dd, 1H**A**, H_{9cis}**A**, $^3J = 10$ Hz, $^2J = 2$ Hz), 6.08 (dd, 1H**B**, H_{9trans}**B**, $^3J = 16.9$ Hz, $^2J = 2.2$ Hz), 6.20 (dd, 1H**A**, H_{9trans}**A**, $^3J = 16$ Hz, $^2J = 2$ Hz), 6.69 (dd, 1H, H_8, $^3J = 17$, 10.5 Hz); the exo (A)−endo (B) isomer ratio 30/70 is calculated from the integration curve of protons H_{9cis}**A**/H_{9cis}**B**, H_{9trans}**A**/H_{9trans}**B**, and H_1**A**/H_1**B**; ^{13}C NMR (DMSO-d_6) δ 13.90 (CH_3), 22.04 (CH_2 alkyl), 26.41 (CH_2 alkyl**A**), 26.73 (CH_2 alkyl**B**), 28.42 (CH_2 alkyl), 28.66 (CH_2 alkyl), 28.77 (CH_2 alkyl), 28.99 (CH_2 alkyl), 30.72 (CH_2 alkyl**A**), 31.25 (CH_2 alkyl**B**), 41.00 (b, C_{10}**A**), 42.26 (C_{10}**B**), 61.06 (C_6**B**), 61.17 (C_6**A**), 69.81 (C_4**B**), 69.91 (C_2**A**), 70.02 (C_4**A**), 70.43 (C_2**B**), 77.49 (C_5**B**), 77.69 (C_5**A**), 78.99 (C_3**B**), 79.33 (C_3**A**), 82.17 (C_1**A**), 86.40 (C_1**B**), 126.58 (C_9**B**), 128.10 (C_9**A**), 128.99 (C_8**A**), 129.70 (C_8**B**), 166.08 (C_7**A**), 166.74 (C_7**B**). Anal. Calcd for $C_{21}H_{39}NO_6 \cdot 0.3H_2O$: C, 62.01; H, 9.74; N, 3.44; O, 24.80. Found: C, 61.95; H, 9.85; N, 3.41; O, 24.83.

***N*-(*β*-D-Glucopyranosyl)-*N*-tetradecylacrylamide (1d)** was prepared using a modified procedure owing to the low solubility of **3d** in methanol. Typical procedure: 6.4 g (17 mmol) of **3d** was solubilized in 200 mL of THF at 50−60 °C. Sodium carbonate (27 g, 25.5 mmol) in 40 mL of water, 100 mg of sodium nitrite, and 40 mL of methanol were then added. The resulting mixture was cooled to 0 °C with an ice bath, and 9 mL (111 mmol) of acryloyl chloride was then added dropwise via a dropping funnel in 15 min. The reaction and treatment were then carried out using the procedure described above for **1a**: reaction time 2 h; quantitative yield of crude **1d**, viscous oil; yield of purification (elution gradient CH_2Cl_2/MeOH) 60% (amorphous paste); TLC $R_f = 0.22$ (CH_2Cl_2/MeOH, 9/1); HPLC (method B): $k' = 6.7$; $[\alpha]^{20}_D = +10.7$ ($c = 1.5$, CH_2Cl_2); MS (CI, NH_3) m/z 430 (100, MH^+); IR (Nujol, ν cm^{-1}) 3500−3200 (OH), 1650 (CO, amide I), 1610 (C═C); ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 3H, CH_3, $^3J = 7$ Hz), 1.25 (m, 18H, H_{12-20}), 1.52 (b, 2H, H_{11}), 3.05 (m, 1H, H_4), 3.20−3.30 (m, 3H, H_2, H_3, H_5), 3.25 (m, 2H, H_{10}), 3.40 (m, 1H, H_{6a}), 3.66 (db, 1H, H_{6b}, $^2J = 11$ Hz), 4.47 (b, 1H, OH_6), 4.76 (d, 1H**B**, H_1**B**, $^3J_{H_1-H_2} = 7$ Hz), 4.94 (b, OH), 4.99 (b, OH), 5.09 (b, OH), 5.16 (b, OH), 5.38 (d, 1H**A**, H_1**A**, $^3J_{H_1-H_2} = 8$ Hz), 5.64 (dd, 1H**B**, H_{9cis}**B**, $^3J = 10.5$ Hz, $^2J = 2$ Hz), 5.74 (d, 1H**A**, H_{9cis}**A**, $^3J = 10$ Hz), 6.07 (dd, 1H**B**, H_{9trans}**B**, $^3J = 17$ Hz, $^2J = 2$ Hz), 6.20 (d, 1H**A**, H_{9trans}**A**, $^3J = 16.5$ Hz), 6.68 (dd, 1H, H_8, $^3J = 17$, 10.5 Hz); the exo (A)−endo (B) isomer ratio 30/70 is calculated from the integration curve of protons H_{9cis}**A**/H_{9cis}**B**, H_{9trans}**A**/H_{9trans}**B**, and H_1**A**/H_1**B**; ^{13}C NMR (CD_3OD) δ 14.59 (CH_3), 23.78, 27.83, 28.15, 28.45, 30.01, 30.35, 30.56, 30.74, 30.81, 30.85, 30.86, 30.88, 30.89, 32.26 and 33.14 (CH_2 alkyl), 43.79 (C_{10}**B** or **A**), 44.73 (C_{10}**A** or **B**), 62.71 (C_6**A**), 62.94 (C_6**B**), 71.22 (C_4**B**), 71.38 (C_2**A**), 71.71 (C_4**A**), 72.09 (C_2**B**), 78.97 (C_5**B**), 79.15 (C_5**A**), 80.32 (C_3**A**), 80.61 (C_3**B**), 84.60 (C_1**A**), 88.55 (C_1**B**), 127.99 (C_9**A** and **B**), 129.79 (C_8**A**), 130.70 (C_8**B**), 169.88 (C_7**A**), 170.54 (C_7**B**). Anal. Calcd for $C_{23}H_{43}NO_6 \cdot 0.5H_2O$: C, 63.01; H, 10.05; N, 3.20; O, 23.74. Found: C, 63.08; H, 10.05; N, 3.28; O, 23.67.

***N*-(*β*-D-Glucopyranosyl)-*N*-octadecylacrylamide (1e)** was prepared using the procedure described above for **1d**: yield of crude **1e** 90%; viscous oil; yield of purification (elution gradient CH_2Cl_2/MeOH) 55% (white powder); mp 44−45 °C; TLC $R_f = 0.23$ (CH_2Cl_2/MeOH, 9/1); HPLC (method A) $k' = 5.8$; $[\alpha]^{20}_D = +7.9$ ($c = 1.1$, CH_2Cl_2); MS (CI, NH_3) m/z 486 (100, MH^+); IR (Nujol, ν cm^{-1}) 3500−3200 (OH), 1650 (CO, amide I), 1610 (C═C); ^{1}H NMR (DMSO-d_6) δ 0.88 (t, 3H, CH_3, $^3J = 7$ Hz), 1.25 (m, 18H, H_{12-20}), 1.54 (b, 2H, H_{11}), 3.08 (m, 1H, H_4), 3.20−3.30 (m, 3H, H_2, H_3, H_5), 3.25 (m, 2H, H_{10}), 3.40 (m, 1H, H_{6a}), 3.69 (ddd, 1H, H_{6b}, $^3J = 6.0$, 4.5 Hz, $^2J = 11$ Hz), 4.51 (m, 1H, OH_6), 4.78 (d, 1H**B**, H_1**B**, $^3J_{H_1-H_2} = 7.5$ Hz), 4.97 (b, 1H**A**, OH_2**A**), 5.03 (d, 1H, OH_4, $^3J = 4.5$ Hz), 5.08 (b, 1H**A**, OH_3**A**), 5.13 (b, 1H**B**, OH_3**B**), 5.20 (d, 1H**B**, OH_2**B**, $^3J = 4$ Hz), 5.40 (d, 1H**A**, H_1**A**, $^3J_{H_1-H_2} = 8.5$ Hz), 5.66 (dd, 1H**B**, H_{9cis}**B**, $^3J = 10.5$ Hz, $^2J = 2$ Hz), 5.77 (d, 1H**A**, H_{9cis}**A**, $^3J = 10$ Hz), 6.10 (dd, 1H**B**, H_{9trans}**B**, $^3J = 17$ Hz, $^2J = 2$ Hz), 6.22 (d, 1H**A**, H_{9trans}**A**, $^3J = 17$ Hz), 6.71 (dd, 1H, H_8, $^3J = 17$, 10.5 Hz); the exo (A)−endo (B) isomer ratio 28/72 is calculated from the integration curve of protons H_{9cis}**A**/H_{9cis}**B**, H_{9trans}**A**/H_{9trans}**B**, and H_1**A**/H_1**B**; ^{13}C NMR (C_5D_5N, 22.5 MHz) δ 14.10 (CH_3), 22.71 (CH_2 alkyl), 27.37 (CH_2 alkyl), 29.40 (CH_2 alkyl), 29.75 (CH_2 alkyl), 31.92 (CH_2 alkyl), 42.65 (C_{10}), 62.29 (C_6), 70.95 (C_4), 71.49 (C_2), 78.86 (C_5), 80.16 (C_3), 88.02 (C_1**B**), 126.55 (C_9), 130.20 (C_8), 168.22 (C_7). Anal. Calcd for $C_{23}H_{43}NO_6 \cdot 0.8H_2O$: C, 64.88; H, 10.53; N, 2.80; O, 21.79. Found: C, 64.81; H, 10.87; N, 2.97; O, 21.36.

***N*-(*β*-D-Glucopyranosyl)-*N*-(4-butyl-4-phenyl)-acrylamide (1f)** was prepared using the procedure described above for **1a**: quantitative yield of crude **1f**, viscous oil; purification by chromatography (elution: ethyl acetate followed by ethyl acetate/ethanol (95:5), two successive columns);

yield 40% (amorphous paste); TLC R_f = 0.5 (CH_2Cl_2/MeOH, 4/1); $[\alpha]^{25}_D$ = +11.00 (c = 1.5, CH_2Cl_2), the solution becomes turbid during the measurements; MS (electrospray) m/z 366 (100, M + H^+), 388 (20, M + Na^+); IR (KBr, ν cm^{-1}) 3377 (OH), 3026, 2939, 2870, 2832, 1645 (CO, amide I), 1606 (C=C); ^{1}H NMR (CD_3OD) δ 1.64 (m, 4H, H_{11}, H_{12}), 2.63 (m, 2H, H_{13}), 3.23−3.58 (m, 6H, H_2, H_3, H_4, H_5, H_{10}), 3.63 (dd, 1H, H_{6a}, ^3J = 5.5 Hz, ^2J = 12 Hz), 3.85 (d, 1H, H_{6b}, ^2J = 12 Hz), 4.87 (d, 1H, H_1**B**, ^3J = 8.5 Hz), 5.49 (d, 1H, H_1**A**, ^3J = 6.9 Hz), 5.70 (d, 1H, H_{9cis}**B**, ^3J = 11.2 Hz), 5.74 (d, 1H, H_{9cis}**A**, ^3J = 13.1 Hz), 6.15 (d, 1H, H_{9trans}**B**, ^3J = 17.0 Hz), 6.28 (d, 1H, H_{9trans}**A**, ^3J = 16.1 Hz), 6.64 (dd, H_8**A**, ^3J = 15.7, 11.1 Hz), 6.73 (dd, H_8**B**, ^3J = 17.0, 10.8 Hz), 7.13−7.24 (m, 5H, H_{14}); the exo (A)−endo (B) isomer ratio equals 27/75 and is calculated from the integration curve of protons H_{9trans}**A**/H_{9trans}**B**; ^{13}C NMR (CD_3OD) δ 29.50, 30.15 and 31.39 (C_{11}, C_{12}), 36.09 and 36.42 (C_{13}**A** and C_{13}**B**), 42.97 (C_{10}**A**), 44.32 (C_{10}**B**), 62.69 (C_6), 71.11, 71.44, 74.81 (C_2, C_4), 78.89 (C_3 or C_5), 80.05 (C_3 or C_5), 84.36 (C_1**A**), 88.27 (C_1**B**), 126.57, 126.72, 128.07, 129.17, 129.28, 129.45, 129.63, 129.80 and 130.36 (C_o, C_p, and C_m), 143.17 (C_{ipso}**A**), 143.55 (C_{ipso}**B**), 169.73 (C_7**A**), 170.38 (C_7**B**).

***N*-(β-D-Glucopyranosyl)-*N*-octylmethacrylamide (2a)** was prepared using the procedure described above for **1a** using methacryloyl chloride instead of acryloyl chloride; yield of crude **2a** 93%; viscous oil; yield of purification (elution gradient CH_2Cl_2/MeOH) 55% (amorphous paste); TLC R_f = 0.26 (CH_2Cl_2/MeOH, 9/1); $[\alpha]^{20}_D$ = +15.33 (c = 1.5, AcOEt); MS (CI, NH_3) m/z 360 (100, MH^+); IR (Nujol, ν cm^{-1}) 3500−3200 (OH), 1645 (CO, amide I), 1610 (C=C); ^{1}H NMR (DMSO-d_6) δ 0.87 (t, 3H, CH_3 chain, ^3J = 7 Hz), 1.25 (m, 10H, H_{12}−H_{16}), 1.52 (b, 2H, H_{11}), 1.86 (s, 3H, CH_3 metha), 3.01 (m, 1H, H_4), 3.15 (m, 1H, H_3), 3.2−3.5 (mb, 2H, H_2, H_{6b}, H_{10}), 3.66 (db, 1H, H_{6b}, ^2J = 11.5 Hz), 4.50 (b, 1H, OH_6), 4.68 (d, 1H, H_1, $^3J_{H_1-H_2}$ = 8.5 Hz), 5.00−5.30 (b, 3H, OH_2OH_4), 5.11 (s, 1H, H_{9cis}), 5.14 (s, 1H, H_{9trans}); ^{13}C NMR (DMSO-d_6) δ 13.90 (CH_3 alkyl), 20.48 (CH_3 metha), 22.04 (CH_2 alkyl), 26.68 (CH_2 alkyl), 28.24 (CH_2 alkyl), 28.62 (CH_2 alkyl), 31.21 (CH_2 alkyl), 40.47 (C_{10}), 61.09 (C_6), 69.88 (C_4 and C_2), 77.80 (C_5), 79.19 (C_3), 87.53 (C_1), 114.82 (C_9), 140.44 (C_8), 172.69 (C_7).

***N*-(β-D-Glucopyranosyl)-*N*-tetradecylmethacrylamide (2d)** was prepared using the procedure described above for **1a** using methacryloyl chloride instead of acryloyl chloride; yield of crude **2d** 95%; viscous oil; yield of purification (elution gradient CH_2Cl_2/MeOH) 61% (amorphous paste); TLC R_f = 0.27 (CH_2Cl_2/MeOH, 9/1); $[\alpha]^{20}_D$ = +8.6 (c = 1.5, CH_2Cl_2); MS (CI, NH_3) m/z 360 (100, MH^+); IR (Nujol, ν cm^{-1}) 3500−3200 (OH), 1645 (CO, amide I), 1610 (C=C); ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 3H, CH_3 chain, ^3J = 7 Hz), 1.24 (m, 22H, H_{12}−H_{22}), 1.52 (b, 2H, H_{11}), 1.86 (s, 3H, CH_3 metha), 3.09 (m, 1H, H_4), 3.14 (m, 1H, H_3), 3.2−3.4 (mb, 2H, H_2, H_{6b}, H_{10}), 3.66 (d, 1H, H_{6b}, ^2J = 11.5 Hz)], 4.50 (b, 1H, OH_6), 4.68 (d, 1H, H_1, $^3J_{H_1-H_2}$ = 9 Hz), 5.00−5.20 (b, 3H, OH_2−OH_4), 5.11 (s, 1H, H_{9cis}), 5.14 (s, 1H, H_{9trans}); ^{13}C NMR (DMSO-d_6) δ 13.87 (CH_3 alkyl), 20.46 (CH_3 metha), 22.03 (CH_2 alkyl), 26.69 (CH_2 alkyl), 28.27 (CH_2 alkyl), 28.65 (CH_2 alkyl), 28.75 (CH_2 alkyl), 29.01 (CH_2 alkyl), 31.24 (CH_2 alkyl), 40.47 (C_{10}), 61.12 (C_6), 69.86 (C_4), 69.91 (C_2), 77.81 (C_5), 79.18 (C_3), 87.54 (C_1), 114.81 (C_9), 140.44 (C_8), 172.68 (C_7).

***N*-(β-D-(2,3,4,6-Tetra-*O*-acetylglucopyranosyl)-*N*-octylacrylamide (4a).** Acetyl chloride (5.6 mL, 78 mmol) was added dropwise via a dropping funnel to a solution of **1a** (2 g, 5.8 mmol) in 50 mL of pyridine cooled at 0 °C with an ice bath during the addition (addition time: 0.5 h). The reaction mixture was then stirred for 1 h at room temperature. After addition of 100 mL of ethyl acetate, the organic phase was washed with aqueous HCl (1 N, 5 × 50 mL) and a saturated solution of sodium bicarbonate (3 × 50 mL) and then dried over magnesium sulfate. After removal of the solvent under vacuum, crude **4a** (viscous oil) was chromatographed on silica gel (eluent: CH_2Cl_2/EtOAc 7/3): yield of pure **4a** 77%; TLC R_f = 0.74 (CH_2Cl_2/MeOH, 7/3); MS (electrospray) m/z 514.5 (100, MH^+); IR (film, ν cm^{-1}) 3025 (Csp_2H), 1751 (CO, ester), 1659 (CO, amide I), 1620 (C=C); ^{1}H NMR (CD_3OD) δ 0.91 (t, 3H, CH_3, ^3J = 7 Hz), 1.31 (m, 10H, H_{12-16}), 1.93 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 3.25 (mb, 2H, H_{10}), 4.02 (mb, 1H, H_5), 4.18 (dd, 1H, H_{6a}, ^3J = 2 Hz, ^2J = 12 Hz), 4.26 (dd, 1H, H_{6b}, ^3J = 7 Hz, ^2J = 12 Hz), 5.10 (t, 1H, H_4, ^3J = 9 Hz), 5.19 (t, 1H, H_2, ^3J = 9 Hz), 5.43 (t, 1H, H_3, ^3J = 9 Hz), 5.52 (db, 1H**B**, H_1**B**, $^3J_{H_1-H_2}$ = 9 Hz), 5.81 (m, 1H, H_{9cis}**A** + **B**, ^3J_A = ^3J_B = 11 Hz), 5.94 (db, 1H**A**, H_1**A**, $^3J_{H_1-H_2}$ = 9 Hz), 6.24 (d, 1H**B**, H_{9trans}**B**, ^3J = 17 Hz), 6.31 (d, 1H**A**, H_{9trans}**A**, ^3J = 16 Hz), 6.65 (dd, 1H**A**, H_8**A**, ^3J = 16, 11 Hz), 6.81 (dd, 1H**B**, H_8**B**, ^3J = 17, 11 Hz); the exo (A)−endo (B) isomer ratio 50/50 is calculated from the integration curve of protons H_8**A**/H_8**B**, H_{9trans}**A**/H_{9trans}**B**, and H_1**A**/H_1**B**; ^{13}C NMR (CD_3OD) δ 14.45 (CH_3 chain), 20.39 (CH_3CO), 20.45 (CH_3CO), 20.57 (CH_3CO), 20.68 (CH_3CO), 23.70 (CH_2 alkyl), 27.93 (CH_2 alkyl), 28.14 (CH_2 alkyl), 29.86 (C_{12}**B**), 30.32 (CH_2 alkyl), 32.49 (CH_2 alkyl), 32.95 (CH_2 alkyl), 43.6 (C_{10}**B** or **A**), 44.7 (C_{10}**A** or **B**), 62.79 (C_6**B** or **A**), 63.08 (C_6 **A** or **B**), 69.46 (C_4), 70.32 (C_2), 74.52 (C_5), 74.9 (C_3**B** or **A**), 75.3 (C_3**A** or **B**), 82.3 (C_1**A**), 85.55 (C_1**B**), 129.05 (C_8**B** or **A**), 129.17 (C_9**B** or **A**), 129.54 (C_8**A** or **B**), 130.04 (C_9**A** or **B**), 169.05 (C_7), 170.4 (CO), 171.2 (CO), 171.5 (CO), 172.0 (CO). Anal. Calcd for $C_{25}H_{39}NO_{10}$: C, 58.48; H, 7.60; N, 2.73; O, 31.19. Found: C, 58.22; H, 7.90; N, 2.66; O, 31.28.

***N*-(β-D-(2,3,4,6-Tetra-*O*-acetylglucopyranosyl)-*N*-(4-butyl-4-phenyl)acrylamide (4f)** was prepared from **1f** (2.6 g) using the procedure described above for **4a** and chromatographed eluting with hexane/EtOAc 2/1. Yield of pure **4f** 69.6% (2.64 g), white powder. An analytically pure sample (2.44 g, 64.3%) was obtained by diffusion of hexane in a CH_2Cl_2 solution of the product: TLC R_f = 0.57 (EtOAc); $[\alpha]^{25}_D$ = +12.55 (c = 1.5, EtOAc); MS (electrospray) m/z 534 (100, M + H^+), 551 (40), 556 (20, M + Na^+); IR (KBr, ν cm^{-1}) 1754 (CO ester), 1651 (CO, amide I), 1620 (C=C); ^{1}H NMR (CD_3OD) δ 1.61 (m, 4H, H_{11}, H_{12}), 1.91 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.62 (m, 2H, H_{13}), 3.15−3.52 (mb, 2H, H_{10}), 3.99 (mb, 1H, H_5), 4.13 (dd, 1H, H_{6a}, ^3J = 1.8 Hz, ^2J = 12.3 Hz), 4.21 (dd, 1H, H_{6b}, ^3J = 4.5 Hz, ^2J = 12.5 Hz), 5.09 (t, 1H, H_4, J = 9.7 Hz), 5.18 (mb, 1H, H_2), 5.40 (mb, 1H, H_3), 5.51 (mb, 1H, H_1**B**), 5.77 (dd, 2H, H_{9cis}**A** and **B**, ^3J_A = ^3J_B = 10.3 Hz, ^2J_A = ^2J_B = 2 Hz), 5.92 (d, 1H, H_1**A**, ^3J = 7 Hz), 6.24 (d, 1H, H_{9trans}**B**, ^3J = 16.9 Hz), 6.30 (d, 1H, H_{9trans}**A**, ^3J = 18 Hz), 6.57 (dd, 1H, H_8**A**, ^3J = 10.6, 15.4 Hz), 6.79 (dd, 1H, H_8**B**, ^3J = 10.6, 16.9 Hz), 7.12−7.28 (m, 5H, H_{Ar}); the exo (A)−endo (B) isomer ratio 50/50 is calculated from the integration curve of protons H_8**A**/H_8**B**, H_{9trans}**A**/H_{9trans}**B**, and H_1**A**/H_1**B**; ^{13}C NMR (CD_3OD) δ 20.40, 20.59 and 20.72 (CH_3), 29.51 (C_{11} or C_{12}), 30.01 (C_{11} or C_{12}), 31.89 (C_{11} or C_{12}), 36.28 (C_{13}**A** or **B**), 36.49 (C_{13}**A** or **B**), 43.23 and 44.43 (C_{10}**A** and **B**), 63.09 (C_6), 69.43 (C_4), 70.27 (C_2), 74.45 (C_3), 74.92 (C_5**A** or **B**), 75.19 (C_5**A** or **B**), 82.19 (C_1**A**), 85.50 (C_1**B**), 126.80 (C_{14}), 128.98 (C_8**A**), 129.36 (C_9**A** or **B**), 129.44 (C_{14} and C_8**B**), 130.42 (C_9**A** or **B**), 143.29 (C_{ipso}**A** or **B**), 143.61 (C_{ipso}**A** or **B**), 168.97 (CO), 170.66 (CO), 171.17 (CO), 171.46 (CO), 172.06 (CO). Anal. Calcd for $C_{27}H_{35}NO_{10}$: C, 60.78; H, 6.61; N, 2.62; O, 29.98. Found: C, 60.88; H, 6.67; N, 2.65; O, 29.86.

Acknowledgment. Solabia and ANRT are gratefully acknowledged for a grant to L.R. (Bourse CIFRE).

JO971486D