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New carbohydrate amphiphiles I. Synthesis

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The synthesis and characterization of two groups of new amphiphilic carbohydrates, 3,4,5-tris(alkoxy)-*N*-(1-deoxysorbitol-1-yl)benzamide and 3,4,5-tris(alkoxy)-*N*-(2-deoxyglucos-2-yl)benzamide are described. The phase behaviour was investigated by differential scanning calorimetry and thermo-optical analysis. All the investigated compounds exhibit thermotropic mesophases. Depending on the length of the alkyl chains, hexagonal columnar and cubic mesophases are obtained.

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1. Introduction

Numerous finite biological structures assemble themselves from their molecular components, e.g. collagen filaments, micro-tubuli, ribosomes, multi-enzyme complexes, cell membranes and viruses [1–4]. Formation of such complicated structures is based on rules and fundamental principles which control the growth of the molecular assemblies to finite sizes and defined geometrical shapes in the range between 1 and 100 nm.

Only recently have the principles of self-controlled growth become an issue of interest in materials research [5]. This is partially driven by scientific curiosity and partly by the growing interest in nanostructured materials. The assembly of supramolecular units of finite size represents a promising approach for the development of novel functional materials and thin films, complementary to lithographic techniques, which extend the size scale for structural engineering to even smaller dimensions. The potential of this approach can be seen with examples of supramolecular structures like rods, ribbons, helices, braids, tubuli and rolled up multilayered sheets with rather well defined widths, which have been observed for certain amphiphilic sugar molecules in aqueous solution [6–10]. Typical pictures can be found in reference [6], figure 2.4.

Because of the absence of the hydrophobic effect in organic solvents, the ability to form supramolecular structures is less pronounced in organic solvents [11] and we know only a few approaches towards the defined formation of small molecules into mesoscopic units in non-aqueous media [12–14].

The present work is an attempt to prepare well defined rod-like units, by association or aggregation of suitable small molecules, which can be used as components in macromolecular composites. Such composites can be formed if the units assemble in a solvent which is either a monomer or a reactive oligomer allowing polymerization in a second step with preservation of the supramolecular structure. In the case that the building block molecules of the self-assembled units carry polymerizable reactive groups, the structure can be fixed permanently by covalent links.

Carbohydrate amphiphiles are known to exhibit numerous forms of self-organization [15]; in particular several *N*-alkylgluconamide derivatives have been shown to give supramolecular aggregates in aqueous solutions [7, 8].

In a first approach we describe the synthesis and characterization of the non-polymerizable model compounds 3,4,5-tris(alkoxy)-*N*-(1-deoxysorbitol-1-yl)benzamides (**1**) and 3,4,5-tris(alkoxy)-*N*-(2-deoxyglucos-2-yl)benzamides (**2**) with three different alkoxy chains (cf. figure 1). The supramolecular aggregation and the embedding of the structures obtained into polymeric systems will be reported in a subsequent paper.

2. Results and discussion

An amphiphilic structure will result if long aliphatic chains are combined with a polar carbohydrate unit. Because of the high space requirement of three alkyl chains, the amphiphiles **1** and **2** are expected easily to form inverse associates or aggregates in non-polar environments. Furthermore, it is assumed that the wedge-shaped geometry of the molecules will favour the formation of cylindrical structures. Variation of the length of the alkyl chains allows tuning of the internal

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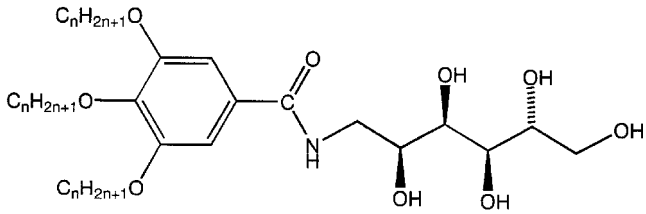

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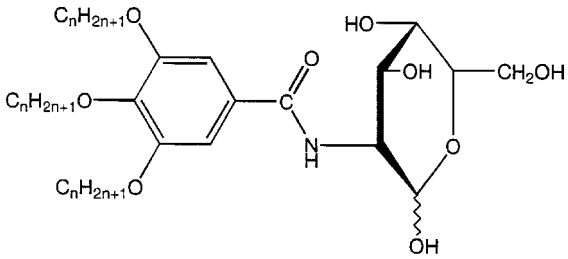

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Figure 1. Synthesized carbohydrate amphiphiles, **1**= 3,4,5-tris(alkoxy)-*N*-(1-deoxysorbitol-1-yl)benzamides (**1a**: $n=8$, **1b**: $n=12$, **1c**: $n=16$) and **2**=3,4,5-tris(alkoxy)-*N*-(2-deoxyglucos-2-yl)benzamides (**2a**: $n=8$, **2b**: $n=12$, **2c**: $n=16$).

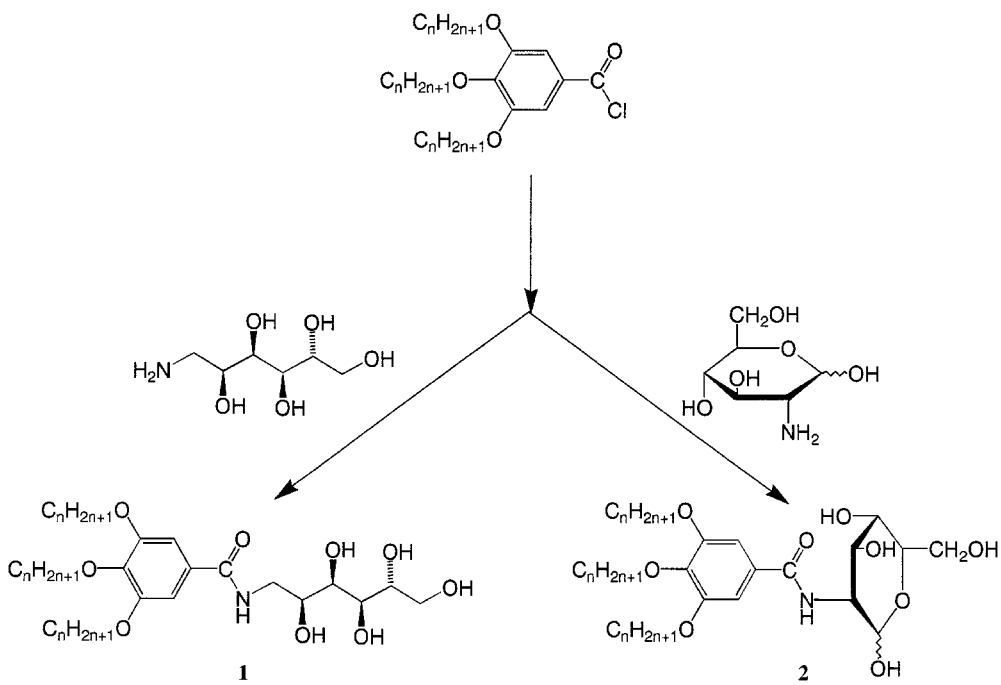
hydrophobic/hydrophilic balance which, in the first instance, determines the solubility and association behaviour of amphiphilic compounds [16–18]. Additionally, the association behaviour can be altered by variation of the carbohydrate head group. Sorbitylbenzamides **1** possess a more flexible, linear hexose group, while the glucosylbenzamides **2** contain a pyranose unit.

The carbohydrates were joined to the non-polar groups via amide linkages to avoid the formation of isomeric *O*-acylated products. In addition, the amide group forms relatively strong hydrogen bonds, which may enhance the self-organizing properties of the amphiphiles. Care was taken not to attach the carbohydrates at their anomeric carbon atoms, since the acetal-like character of such connections may facilitate hydrolytic or thermolytic bond cleavages.

Preparation of the sorbitylbenzamides **1** was accomplished by reacting 1-deoxy-1-aminosorbitol with the appropriate tris(alkoxy)benzoyl chloride [19] (cf. figure 2). 2-Deoxy-2-aminoglucosamine was prepared *in situ* by adding a stoichiometric amount of sodium methylate to a methanolic solution of 2-deoxy-2-aminoglucosamine hydrochloride. The glucosylbenzamides **2** were obtained by subsequent addition of the acid chloride to a supersaturated solution of 2-deoxy-2-aminoglucosamine (for details see experimental part).

Compounds **1** and **2** were synthesized with three different alkoxy substituents (**1a**, **2a**: $n=8$; **1b**, **2b**: $n=12$; **1c**, **2c**: $n=16$), cf. figure 3.

Phase transitions of compounds **1** and **2** were investigated by differential scanning calorimetry (DSC) and thermo-optical analysis with crossed polarizers. The observed transition temperatures, as obtained from the



1 **2**

Figure 2. Synthetic scheme for the preparation of the carbohydrate amphiphiles **1** and **2**.

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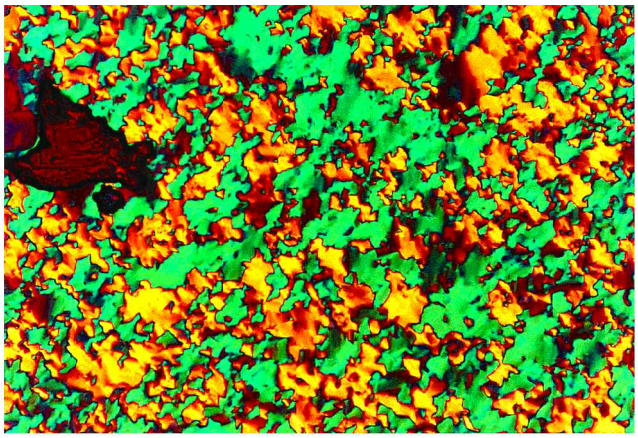
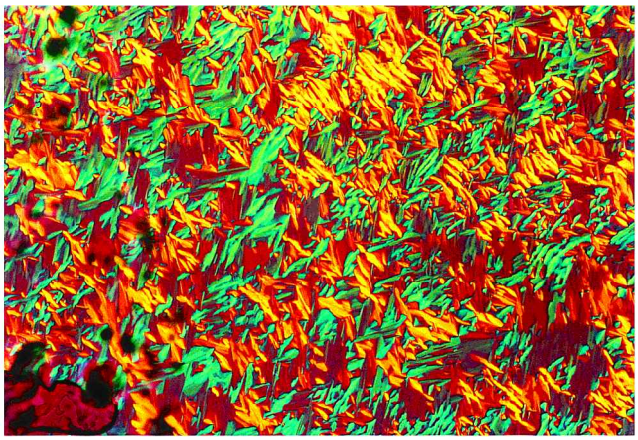


(*a*)



(*b*)

Figure 3. Optical micrographs, crossed polarizers, λ-plate inserted, magnification = 100 ×. (*a*) **1a**: $T = 20°C$, after cooling from 170°C; (*b*) **1a**: $T = 167°C$, heated from ambient temperature, after annealing for 1 hour.

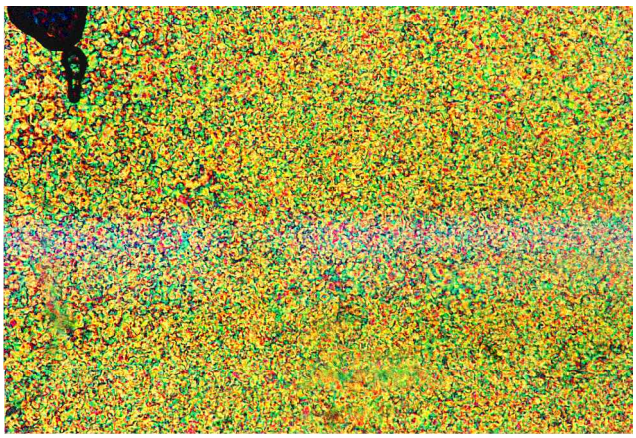
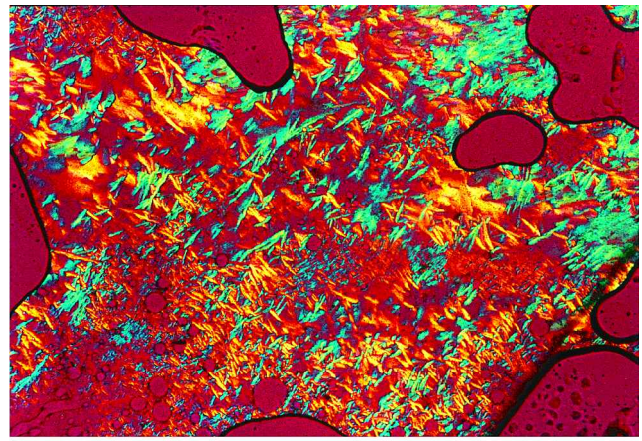
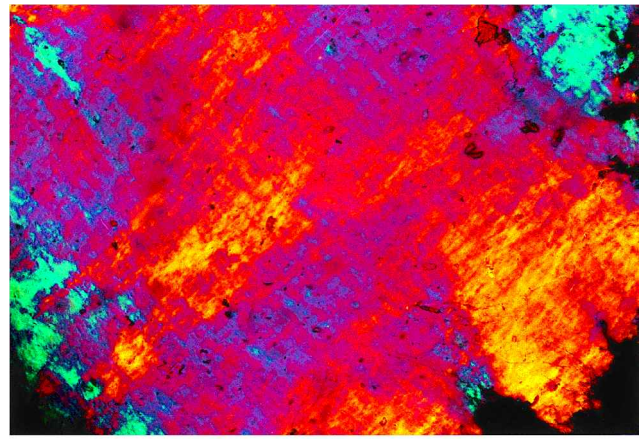


Figure 5. Optical micrograph, crossed polarizers, showing the broken texture of a long chained compound **1** (**1c**: $T = 20°C$, after annealing for 23 hours, λ-plate inserted, magnification = 100 ×).



(*a*)



(*b*)

Figure 6. Optical micrographs, crossed polarizers, λ-plate inserted, magnification = 100 ×. (*a*) **2a**: $T = 107°C$, after cooling from 140°C; (*b*) **2c**: $T = 91°C$, after annealing for 23 hours.

first heating runs on the solvent-precipitated samples, are summarized in the table. All compounds investigated can be supercooled very easily. In fact the observed phase sequence depended strongly on the thermal history of the samples. All compounds started to decompose above 180°C.

At room temperature, the solvent-precipitated carbohydrate amides **1** and **2** were white powders. X-ray powder diffraction measurements, using a Guinier camera, indicated a mesomorphic, partially disordered structure. The scattering diagrams showed a reflection around $2\Theta = 12°$ and a weak halo with a maximum near $2\Theta = 20$–$24°$. This is typical for mesophases without three dimensional long range order. Phase type and lattice geometry could not be determined from these preliminary data, since no measurements were done below $2\Theta = 8°$ [20].

The presence of a mesophase could also be observed

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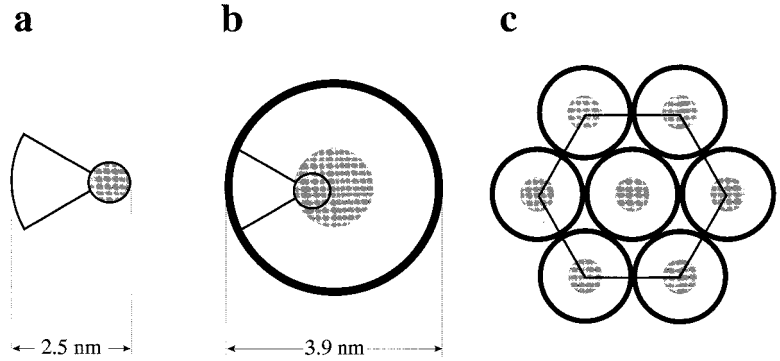

Figure 4. Proposed structural model for the columnar hexagonal disordered (Col_{hd}) mesophase of **1a** and **2a**. (*a*) Schematic representation of a carbohydrate amphiphile with octyloxy chains; (*b*) proposed head to head arrangement with head group overlapping in a column cross section; (*c*) hexagonal arrangement of the columns (view on the 11-plane).

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by applying pressure to the methanol-precipitated white powders, placed between two glass plates. The compounds sintered and gave an opaque–transparent glass. Between crossed polarizers a broken, non-specific texture was found for all compounds **1**.

At room temperature, the 3,4,5-tris(octyloxy)-*N*-(1-deoxysorbitol-1-yl)benzamide (**1a**) exhibited a mosaic-like texture (cf. figure 3 (*a*)). The compound transformed at 78°C ($\Delta H = 46\,kJ\,mol^{-1}$) into a second mesophase showing a 'needle' texture (cf. figure 3 (*b*)) which is typical for columnar phases. Upon raising the temperature further, **1a** became isotropic at 167°C.

WAXS diffractograms of **1a** at $T = 100$°C showed three reflections at $d_{10} = 3{\cdot}35$ nm, $d_{11} = 1{\cdot}97$ nm and $d_{20} = 1{\cdot}72$ nm, indicating a two dimensional hexagonal order. The lattice spacing was determined as $a_{hex} = 3{\cdot}9$ nm. Since in the mid-angle region ($2\Theta = 10$–$30°$) no sharp reflections were found, the mesophase type must be columnar hexagonal disordered (Col_{hd}). The column diameter $d_{col} = a_{hex}$ can be correlated to the molecular dimensions assuming that the molecules assemble via association of the carbohydrate head groups, stabilized by hydrogen bonds (cf. figure 4). The number of molecules per column cross-section was estimated to be $(6 \pm 0{\cdot}6)$ if the average vertical distance between two molecules inside a column was assumed to be 0·5–0·6 nm and the density of the compound was taken to be $1{\cdot}0 \pm 0{\cdot}1\,g\,cm^{-3}$.

Compounds **1b** and **1c** showed an interesting polymorphism, exhibiting up to three consecutive mesophases. All transition temperatures, as obtained from the first DSC heating run, are summarized in the table. The phase above 92°C (**1b**) and 67°C (**1c**), respectively, was an optically isotropic phase with a very high viscosity, which did not show fluid properties. If the samples were sheared between two glass slides, the phase showed stress-induced birefringence. The interference colours vanished after release of the shear stress. Upon heating, the viscosity decreased abruptly at a definite temperature (**1b**: $T = 235$°C, **1c**: $T = 138$°C). These observations can be regarded as a first indication of the formation of a cubic mesophase.

Phase structures of the other mesophases could not be identified by optical investigations, since even after annealing for several hours only broken, non-specific textures were established (cf. figure 5). Detailed X-ray studies are being undertaken.

As the data in the table demonstrate, the phase sequences of the compounds **2** were similar to those of the amphiphiles **1**. Compound **2a** showed two consecutive mesophases, the second one being a Col_{hd} phase with a lattice spacing of $a_{hex} = 3{\cdot}8$ nm. It is assumed that the structural model proposed for the Col_{hd} phase of **1a** can be applied in this case too. The mesophase exhibited a broken mosaic/'needle'-like texture (cf. figure 6 (*a*)). Further polarizing microscopy studies were only of limited help because of the very high melt viscosity which prevented the formation of characteristic textures (figure 6 (*b*)).

Compounds **2b** and **2c** also seem to possess a cubic mesophase (**2b**: $T_{d1} = 113$°C, **2c**: $T_{d2} = 99$°C). If a sorbitylbenzamide **1** is compared with a glucosylbenzamide **2**

Table Transition temperatures and enthalpies for the solution-precipitated amphihilic compounds **1** and **2** as observed on the first heating run by DSC. Transition temperatures in °C, transition enthalpies in $kJ\,mol^{-1}$.

Compound	T_g	T_{d1}	ΔH_1	T_{d2}	ΔH_2	T_{iso}
1a[c]	—	78	46	—	—	167[a,b]
1b[d]	—	79	35	92	3	≈235[a,b]
1c[c]	—	57	63	67	8	≈138[a,b]
2a[c]	54	103	20	—	—	≈140[a,b]
2b[d]	72	113	21	—	—	≈194[a,b]
2c[d]	73	81	84	99	6	≈188[a,b]

[a] Data from thermo-optical analysis.
[b] Sample decomposes before isotropization.
[c] Heating rate = 5 K min^{-1}.
[d] Heating rate = 2 K min^{-1}.

with the same substituents, the phase sequence seems to be essentially the same.

3. Conclusion

A simple synthetic route was used to couple non-polar 3,4,5-tris(alkoxy)benzoyl chlorides with carbohydrate amines of high polarity via amide linkages, yielding two novel classes of carbohydrate amphiphiles. It was demonstrated that the sorbitylbenzamides (**1**) and glucosylbenzamides (**2**) show a complicated phase behaviour, including liquid crystalline phases of columnar and cubic types. Detailed X-ray investigations will be performed to identify the observed mesophases of these carbohydrate amphiphiles. The occurrence of different mesophases may be taken as an indicator of the ability of compounds **1** and **2** to form supramolecular structures.

Future work will investigate the suitability of the sorbityl- or glucosyl-benzamides as useful tools for the construction of supramolecular assemblies of limited size in organic solutions.

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4. Experimental

4.1. *Methods*

For thermo-optical analysis a Zeiss AXIOSKOP polarizing microscope equipped with a Mettler FP 82 hot stage and the photoautomat Mettler FP 80, was used. DSC measurements were performed using a Perkin-Elmer DSC 7 unit. Infrared spectra were taken from a Bruker IFS 66V-Spectrophotometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (50·4 MHz) spectra were recorded on a Bruker AC200 spectrometer, using tetramethylsilane as internal standard. Thin layer chromatography (TLC) was performed with petrolethes: dichlormethane mixtures on Merck KG-60/F254 TLC-plates, with detection by illuminating with UV light (254 nm) or using iodine vapour. For WAXS measurements, a Guinier camera (Huber) was used; the X-ray radiation (Cu-$K_{\alpha 1}$) came from a Philips PW 1120 X-ray generator, equipped with a SiO_2 monochromator. Elemental analyses were performed by the microanalytical laboratory of the University of Ulm.

4.2. *Materials*

4.2.1. *3,4,5-Tris(alkyloxy)benzoyl chloride*

This was prepared as described in the literature [19]. 1-Amino-1-deoxy-D-sorbitol (Merck, 96%), 2-amino-2-deoxy-D-glucose (Aldrich, 98%) and triethylamine (Fluka, >98%) were used as received; solvents (technical grade) were purified by standard procedures.

4.2.2. *3,4,5-Tris(alkoxy)-N-(1-deoxysorbitol-1-yl)benzamides* (**1**)

To a well stirred solution of 1·45 g (8 mmol) of 1-amino-1-deoxy-D-sorbitol and 0·76 g (7·5 mmol) of triethylamine in 100 ml of methanol was slowly added a solution of 7·5 mmol of 3,4,5-tris(alkoxy)benzoyl chloride in 200 ml of dry tetrahydrofuran at ambient temperature; stirring was continued for 30 min after completing the addition. The solvent was removed under reduced pressure; the residue was extracted with water to remove the excess of the D-sorbitol and subsequently stirred with 200 ml of methanol until a clear solution was obtained (2–3 days). The pure product precipitated after storing the solution in the refrigerator.

4.2.3. *3,4,5-Tris(octyloxy)-N-(1-deoxysorbitol-1-yl)benzamide* (**1a**)

Yield: 3·4 g (73%) of white product, decomposition at 170°C, purity >95% (^{1}H NMR), TLC: single spot. Elemental analysis for $C_{37}H_{67}NO_9$ (669·9 g mol^{-1}): C 66·0, H 10·0, N 2·3, O 21·8 wt%; calc. C 66·3, H 10·1, N 2·1, O 21·5 wt%. ^{1}H NMR (THF-d8, δ/ppm): 0·88 (t, 9H, $-CH_3$), 1·36 (m, 24H, $(-CH_2)_4$), 1·54 (m, 6H, γ-CH_2), 1·77 (m, 6H, β-CH_2), 3·12 (s, 5H, CH*OH*), 3·63 (t, 6H, α-CH_2), 4·00 (m, 13H, C*H*OH), 4·98 (d, 2H, CH_2OH), 7·22 (s, 2H, H–C2, H–C6), 8·20 (s, 1H, –NH). ^{13}C NMR (THF-d8, δ/ppm): 14·36 (–CH 3), 23·38 (Cβ3/5), 26·97 (Cβ4), 29·87–32·28 (C alkyl), 56·00 (Ca), 62·12 (Cf), 69·03–72·94 (b–e, α3/5, α4), 92·35 (C2, C6), 107·13 (C1), 129·78 (C4), 140·77 (C3), 167·00 (C7). IR (KBr-pellet, ν/cm^{-1}): 3364, 2955, 2917, 2872, 2851, 1637, 1581, 1546, 1500, 1468, 1427, 1386, 1340, 1231, 1120, 1052, 761, 712.

4.2.4. *3,4,5-Tris(dodecyloxy)-N-(1-deoxysorbitol-1-yl)-benzamide* (**1b**)

Yield: 5·5 g (82%) of white product, decomposition at 210°C, purity >95% (^{1}H NMR), TLC: single spot. Elemental analysis for $C_{48}H_{91}NO_9$ (838·3 g mol^{-1}): C 70·3, H 11·0, N 1·9, O 16·8 wt%; calc. C 70·2, H 10·2, N 1·7, O 17·2 wt%. ^{1}H NMR (THF-d8, δ/ppm): 0·90 (t, 9H, $-CH_3$), 1·36 (m, 48H, $(-CH_2)_4$), 1·52 (m, 6H, γ-CH_2), 1·74 (m, 6H, β-CH_2), 3·13 (s, 5H, CH*OH*), 3·59 (t, 6H, α-CH_2), 4·00 (m, 13H, C*H*OH), 5·13 (d, 2H, CH_2OH), 7·22 (s, 2H, H–C2, H–C6), 8·18 (s, 1H, –NH). ^{13}C NMR (THF-d8, δ/ppm): 14·40 ($-CH_3$), 23·46 (Cβ3/5), 27·08 (Cβ4), 30·25–32·78 (C Alkyl), 56·08 (Ca), 62·93 (Cf), 69·61–73·42 (b–e, α3/5, α4), 92·54 (C2, C6), 107·02 (C1), 130·23 (C4), 141·77 (C3), 167·89 (C7). IR (KBr-pellet, ν/cm^{-1}) 3367, 2955, 2920, 2872, 2850, 1635, 1581, 1546, 1501, 1468, 1427, 1389, 1340, 1236, 1120, 1093, 760, 722.

4.2.5. *3,4,5-Tris(hexadecyloxy)-N-(1-deoxysorbitol-1-yl)-benzamide* (**1c**)

Yield: 6·3 g (78%) of white product, decomposition at 210°C, purity >95% (^{1}H NMR), TLC: single spot. Elemental analysis for $C_{61}H_{115}NO_9$ (1006·6 g mol^{-1}): C 72·2, H 11·3, N 1·8, O 14·7 wt%; calc. C 72·8, H 11·5, N 1·4, O 14·3 wt%. ^{1}H NMR (THF-d8, δ/ppm): 0·90 (t,

9H, $-CH_3$), 1·32 (m, 72H, $(-CHO_2)_{12}$), 1·56 (m, 6H, γ-CH_2), 1·81 (m, 6H, β-CH_2), 3·21 (s, 5H, CH*OH*), 3·62 (t, 6H, α-CH_2), 4·00 (m, 13H, C*H*OH) 5·09 (d, 2H, CH_2OH), 7·21 (s, 2H, H–C2, H–C6), 8·51 (s, 1H, –NH). ^{13}C NMR (THF-d8, δ/ppm): 14·72 ($-CH_3$), 24·36 (Cβ3/5), 27·95 (Cβ4), 30·89–34·21 (C alkyl), 56·76 (Ca), 64·02 (Cf), 69·82–75·04 (b–e, α3/5, α4), 93·78 (C2, C6), 108·64 (C1), 132·42 (C4), 142·96 (C3), 167·99 (C7). IR (KBr-pellet, ν/cm^{-1}): 3363, 2955, 2917, 2872, 2850, 1638, 1581, 1545, 1499, 1469, 1426, 1385, 1340, 1230, 1122, 1035, 763, 720, 619.

4.2.6. *3,4,5-Tris(alkoxy)-N-(2-deoxyglucos-2-yl)benzamides* (**2**)

Following the literature [21], a solution of 0·43 g (8 mmol) of sodium methylate in 100 ml of methanol was poured into a well stirred solution of 1·73 g (8 mmol) of D-2-amino-2-deoxyglucose in 100 ml of methanol and stirred for 15 min. Then 0·76 g (7·5 mmol) of triethylamine was added and finally a solution of 3,4,5-tris(alkoxy)benzoyl chloride in 200 ml tetrahydrofuran was slowly added at ambient temperature. Reaction was carried out and isolation of the product achieved as described for the synthesis of 3,4,5-tris(alkoxy)benzoylglucamides (**1**).

4.2.7. *3,4,5-Tris(octyloxy)-N-(2-deoxyglucos-2-yl)benzamide* (**2a**)

Yield: 6·3 g (79%) of white product, decomposition at 170°C, purity >95% (^{1}H NMR), TLC: single spot. Elemental analysis for $C_{37}H_{65}O_8$ (651·9 g mol^{-1}): C 67·4, H 10·2, N 2·1, O 20·4 wt%; calc. C 68·2, H 10·0, N 2·2, O 19·6 wt%. ^{1}H NMR (THF-d8, δ/ppm): 0·87 (t 9H, $-CH_3$), 1·31 (m, 24H, $(-CH_2)_4$), 1·42 (m, 6H, γ-CH_2), 1·67 (m, 6H, β-CH_2), 3·04 (s, 4H, CH*OH*), 3·42 (t, 6H, α-CH_2), 3·98 (m, 13H, C*H*OH), 5·05 (d, 2H, CH_2OH), 6·98 (s, 2H, H–C2, H–C6), 7·99 (s, 1H, –NH). ^{13}C NMR (THF-d8, δ/ppm): 13·98 (–CH 3), 22·86 (Cβ3/5), 25·98 (Cβ4), 29·76–32·02 (C alkyl), 54·89 (Ca), 61·35 (Cf), 67·47–71·53 (b–e, α3/5, α4), 90·61 (C2, C6), 105·77 (C1), 129·36 (C4), 139·03 (C3), 165·28 (C7). IR (KBr-pellet, ν/cm^{-1}): 3376, 2957, 2925, 2855, 1638, 1582, 1542, 1498, 1468, 1426, 1342, 1229, 1115, 1081, 1042, 783, 650.

4.2.8. *3,4,5-Tris(dodecyloxy)-N-(2-deoxyglucos-2-yl)-benzamide* (**2b**)

Yield: 4·5 g (68%) of white product, decomposition at 175°C, purity >95% (^{1}H NMR), TLC: single spot. Elemental analysis for $C_{49}H_{89}NO_8$ (820·2 g mol^{-1}): C 69·5, H 10·8, N 1·9, O 17·8 wt%; calc. C 71·8, H 10·9, N 1·7, O 15·6 wt%. ^{1}H NMR (THF-d8, δ/ppm): 0·89 (t, 9H, $-CH_3$), 1·31 (m, 48H, $(-CH_2)_8$), 1·47 (m, 6H, γ-CH_2), 1·71 (m, 6H, β-CH_2), 3·09 (s, 4H, CH*OH*), 3·52 (t, 6H, α-CH_2), 4·98 (m, 13H, C*H*OH), 5·07 (d, 2H, CH_2OH), 7·24 (s, 2H, H–C2, H–C6), 8·21 (s, 1H, –NH). ^{13}C NMR (THF-d8, δ/ppm): 14·36 ($-CH_3$), 24·14 (Cβ3/5), 27·16 (Cβ4), 31·25–33·46 (C Alkyl), 56·38 (Ca), 63·82 (Cf), 69·92–73·52 (b–e, α3/5, α4), 91·74 (C2, C6), 107·02 (C1), 129·74 (C4), 140·05 (C3), 166·98 (C7). IR (KBr-pellet, ν/cm^{-1}): 3388, 2956, 2921, 2872, 2851, 1635, 1582, 1543, 1500, 1468, 1427, 1342, 1230, 1118, 1036, 850, 763, 721.

4.2.9. *3,4,5-Tris(hexadecyloxy)-N-(2-deoxyglucos-2-yl)-benzamide* (**2c**)

Yield: 4·5 g (84%) of white product, decomposition at 183°C, purity >95% (^{1}H NMR), TLC: single spot. Elemental analysis for $C_{61}H_{113}NO_8$ (988·6 g mol^{-1}): C 71·6, H 11·2, N 1·7, O 15·5 wt%; calc. C 73·1, H 11·3, N 1·4, O 14·2 wt%. ^{1}H NMR (THF-d8, δ/ppm): 0·89 (t, 9H, $-CH_3$), 1·351 (m, 48H, $(-CH_2)_8$), 1·52 (m, 6H, γ-CH_2), 1·78 (m, 6H, β-CH_2), 3·21 (s, 4H, CH*OH*), 3·99 (t, 6H, α-CH_2), 5·12 (m, 13H, C*H*OH), 5·23 (d, 2H, CH_2OH), 7·38 (s, 2H, H–C2, H–C6), 8·19 (s, 1H, –NH). ^{13}C NMR (THF-d8, δ/ppm): 14·41 ($-CH_3$), 24·36 (Cβ3/5), 27·19 (Cβ4), 31·79–34·06 (C Alkyl), 56·78 (Ca), 63·92 (Cf), 69·99–74·31 (b–e, α3/5, α4), 91·79 (C2, C6), 107·15 (C1), 130·17 (C4), 140·35 (C3), 166·99 (C7). IR (KBr-pellet, ν/cm^{-1}): 3364, 2956, 2917, 2873, 2850, 1627, 1583, 1543, 1501, 1469, 1427, 1344, 1229, 1122, 1059, 737, 720.

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