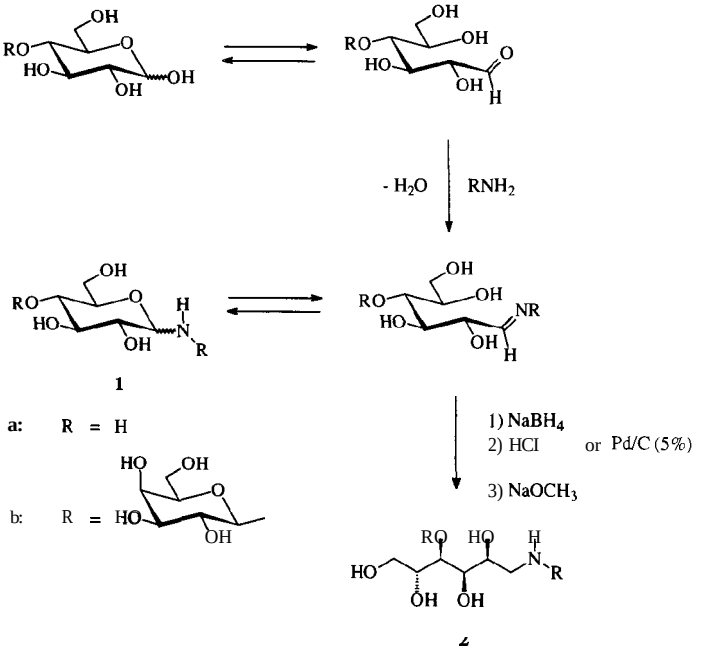
Chapter 2

Synthesis and Physical Properties of *N*-Acyl,*N*-alkyl-β-D-aldosylamines and *N*-Acyl,*N*-alkyl-1-amino-1-deoxy-D-alditols

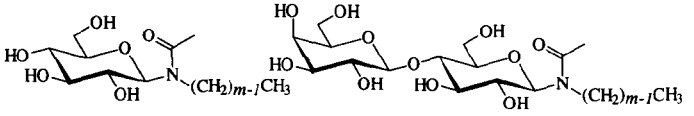
2.1 Introduction

As noted in Chapter 1, we have prepared several homologous series of carbohydrate-derived surfactants in which the alkyl chain is linked through an N-acylated amine bond (Figure 1). The carbohydrate, in our case either D-glucose or D-lactose, is first allowed to react with n-octyl-, decyl, or dodecylamine (Scheme 1), leading to *N*-alkyl-α,β-D-gluco-pyranosylamines and *N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amines. These *N*-alkyl-α,β-D-aldosylamines can be reduced to the *N*-alkyl-1-amino-1-deoxy-D-alditols.



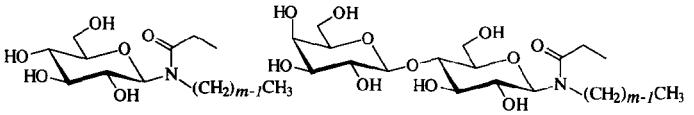
Scheme 1. The formation of *N*-alkyl-α,β-D-glucopyranosylamines (1a), N-alkyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amines (1b), N-alkyl-1-amino-1-deoxy-D-glucitols (2a), and *N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols (2b).

Acylation of the *N*-alkyl-α,β-D-aldosylamines and *N*-alkyl-1-amino-1-deoxy-D-alditols gave the compounds displayed in Figure 1. With these acylated compounds, we can easily vary the carbohydrate headgroup, the length of the acyl group and the length of the alkyl chain. The opportunity of introducing small structural changes should provide us with insights into the structure-property relationships, which are relevant for designing tailor-made materials.



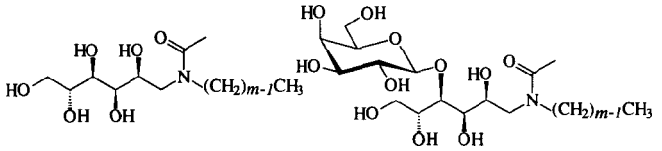
m = 8: NC_2nC_8 glucose
m = 10: NC_2nC_{10} glucose
m = 12: NC_2nC_{12} glucose

m = 8: NC_2nC_8 lactose
m = 10: NC_2nC_{10} lactose
m = 12: NC_2nC_{12} lactose



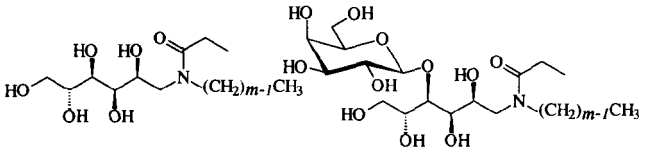
m = 8: NC_3nC_8 glucose
m = 10 NC_3nC_{10} glucose
m = 12: NC_3nC_{12} glucose

m = 8: NC_3nC_8 lactose
m = 10: NC_3nC_{10} lactose
m = 12: NC_3nC_{12} lactose



m = 8: NC_2nC_8 glucitol
m = 10: NC_2nC_{10} glucitol
m = 12: NC_2nC_{12} glucitol

m = 8: NC_2nC_8 lactitol
m = 10: NC_2nC_{10} lactitol
m = 12: NC_2nC_{12} lactitol



m = 8: NC_3nC_8 glucitol
m = 10: NC_3nC_{10} glucitol
m = 12: NC_3nC_{12} glucitol

m = 8: NC_3nC_8 lactitol
m = 10: NC_3nC_{10} lactitol
m = 12: NC_3nC_{12} lactitol

Figure 1. Structures and abbreviated names of the compounds synthesized.

2.2 Historical background

About a century ago, in 1893, Lobry de Bmyn reacted methanolic ammonia with glucose and obtained β-D-glucopyranosylamine.[1] At that time, the structure of the compound was not known. Other researchers, like Irvine[2] in 1913, not only used ammonia, but also performed reactions with ethylamine. About twenty years later, in 1934, Votoček[3] reported reactions of a number of monosaccharides with alkylamines (methyl to heptylamine) and solved their structure. The *N*-alkyl-α,β-D-glucopyranosylamines descibed in this thesis (the n-octyl, decyl, and dodecyl derivatives) were synthesized by Pigman et *al.*[4] in 1951, together with the lactose derivative *N*-dodecyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amine.

Synthesis involving reduction of the intermediate imine was patented in the United States in 1935.[5] The aim of this project was to develop a relatively simple practical method for the preparation of otherwise relatively inaccessible amino alcohols. The reduction was performed using a metal catalyst under pressure in a hydrogen atmosphere. Applications were mentioned, such as dye assistants, ingredients of wetting agents for viscose, and textile lubricants in mineral oil emulsions. Mitts *et al.*[6] also reduced some *N*-alkyl-α,β-D-glucopyranosylamines to the glucitol derivatives by hydrogenation in a Parr type bomb using Raney nickel (1944). He observed that the compounds, especially those from amines of intermediate molecular weight, lower the surface tension and are good wetting agents. Karrer *et al.*[7] described the catalytic reductive amination of carbohydrates with aliphatic arnines (the catalyst being nickel or palladium on carbon). Reductions can also be performed stoichiometrically. Hoagland,[8] for example, performed some reductive aminations with lactose using sodium cyanoborohydride in boiling methanol in the presence of a weak organic acid such as propionic or benzoic acid. He obtained the propionate or benzoate salts of the N-alkyl-4-0-(P-D-galactopyranosy1)-1-amino-1-deoxy-D-glucitols. Van Dam *et al.*[9] performed the reduction with $NaCNBH_3$ under alkaline conditions. Syntheses of 1-amino-1-deoxy-D-alditols by means of $NaBH_4$/$NaBH_3CN$ provide a useful alternative for the catalytic hydrogenation. The work-up procedure, however, is more laborious.

In 1990 and 1995, van Doren *et al.*[10-12] described the thennotropic and lyotropic liquid crystalline behavior of a number of *N*-alkyl-1-amino-1-deoxy-D-glucitols and *N*-acetyl,*N*-alkyl-1-amino-1-deoxy-D-glucitols.

In 1991 and 1992 Rico-Lattes *et al.*[13-15] patented the *N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols, *N*-acyl,*N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols, *N*-acyl,*N*-alkyl-β-D-glucopyranosylamines, and *N*-acyl,*N*-alkyl-[4-*O*-(β-D-galacto-pyranosyl)-β-D-glucopyranosyl]amines[16] and published a paper describing the syntheses and critical micelle concentrations of some *N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols. Later, they reported several NMR and X-ray diffraction studies on these compounds.[17-20] Some *N*-acetyl,*N*-alkyl-1-amino-1-deoxy-D-glucitols and *N*-acyl,*N*-alkyl-4-*O*-

(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols with long acyl chains (6 to 16 carbon atoms) were described by the same group in 1995 and 1997.[21,22]

Rico-Lattes *et al.*[22] showed some of these compounds can have potential pharmaceutical, biochemical, and medicinal applications. *N*-Nonyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitol showed promising behavior in the extraction of certain proteins from frog brain.[23] *N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols (with an optimum for the dodecyl analog) and *N*-hexadecanoyl,*N*-nonyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitol possess marked anti-HIV activity.[24,25] Patients with AIDS frequently develop infections due to filamentous fungi *(Aspergillus* series) for which there are few effective treatments. Particularly *N*-octadecanoyl,*N*-nonyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitol showed activity against *Aspergillus fumigatus*.[24] Rico-Lattes *et al.*[22] are currently optimizing the structures in order to maximize the ability to extract proteins and to obtain maximal antiviral and antifungal activities.

We prepared several series of these compounds (using slightly different routes) and investigated their thermodynamic properties with respect to micellization (Chapter 3) and their potential as co-surfactants in detergent systems (Chapter 4). This chapter elaborates the syntheses and purfications of the carbohydrate-derivedsurfactants.

2.3 Syntheses

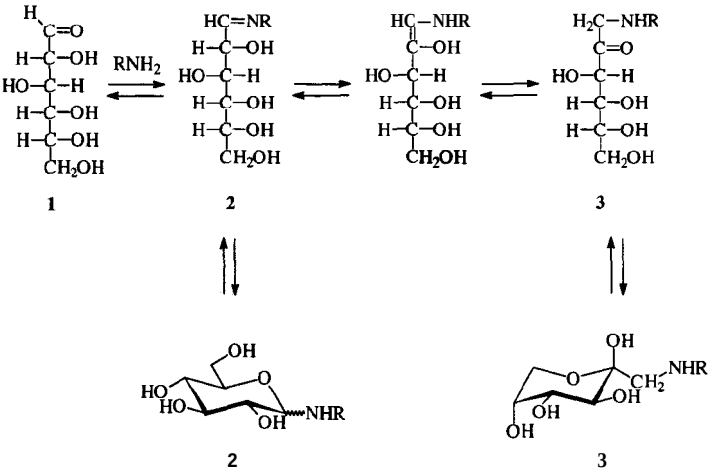
2.3.1 *N*-Alkyl-α,β-D-glucopyranosylamines and *N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amines

The reactions of D-glucose and D-lactose with alkylamines lead to the formation of N-alkyl-α,β-D-glucopyranosylamines and *N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]-amines. The compounds are mixtures of both a (minor product) and β (major product) anomers.

The *N*-alkyl-α,β-D-aldosylamines are unstable. They are susceptible to hydrolysis when dissolved in water and on heating, the solution becomes yellow and, after prolonged heating, brown. This color change is due to the Amadori rearrangement of the aldosylamines.[26,27]

The Amadori rearrangement (Scheme 2) is the transformation of the aldosylamine (a Schiff base) into the more stable 1-amino-1-deoxy-2-ketose.[26,27] This initial rearrangement leads to a whole chain of reactions, called the Maillard reaction.[27] At high temperature, such as during food preparation (*e.g.* roasting or baking), Maillard reactions of amino acids or proteins with sugars give rise to the characteristic appearance and aroma of baked and roasted food.[28] The Maillard reaction is favored at pH 4-7 and at temperatures > 50°C.[28] Although the reaction mixture in our case was alkaline (pH 10-11), the solutions became yellow if the thermal

conditions were too severe.



Scheme 2. Mechanism of the formation of an Amadori product (3) from glucose (1) via glucosylamine (2).

In case of the *N*-alkyl-α,β-D-glucopyranosylamines, methanol was preferred as the reaction medium over ethanol. Small residual amounts of glucose dissolve better in methanol and thus precipitate less easily than from ethanol. As the product precipitated from the reaction mixture, co-precipitation of glucose was not desirable. The *N*-alkyl-α,β-D-glucopyranosylamines were crystallized from methanol and yielded white crystals. The yields increased with increasing chain length. Integration of the anomeric proton signal in 'H-NMR (CD_3OD) showed that about 90% of each glucosylamine exists in the β-configuration and about 10% in the a-configuration.

In an initial attempt to synthesize the *N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amines, the same route was used as for the glucose derivatives. However, large quantities of methanol had to be used and it was difficult to remove small amounts of residual lactose. Therefore, we used the method developed by Erickson,[13,29] in which a water-i-propanol mixture is the solvent. The disaccharide derivatives also displayed coloration upon prolonged heating, but the process is slower than for the monosaccharide derivatives. The products were finally crystallized from ethanol and isolated as white crystals.

Integration of the anomeric proton signal in 'H-NMR (DMSO-d_6) showed that about 75% of each lactosylamine exists in the β-configuration and about 25% in the a-configuration. This ratio is in agreement with the values found by Rico-Lattes *et al.*.[17]

2.3.2 *N*-Alkyl-1-amino-1-deoxy-D-glucitols and *N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols

N-alkyl-α,β-D-aldosylamines can be reduced to alditol derivatives with $NaBH_4$[10,13,30] or $NaCNBH_3$,[8,9,31] or with metal catalysts, *e.g.*, palladium on carbon[14,30,32] or Raney nickel,[14] which is more attractive for large-scale synthesis. *N*-alkyl-1-amino-1-deoxy-D-alditols are not susceptible to hydrolysis and also more stable to heat than *N*-alkyl-α,β-D-aldosylamines.

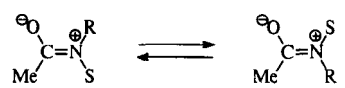
N-alkyl-α,β-D-glucopyranosylamines were reduced to glucitol derivatives with either $NaBH_4$[10] or with palladium on carbon (Scheme 1) in a Parr apparatus under hydrogen pressure. The products crystallized from ethanol.

N-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols can be synthesized via the same routes. Since the disaccharide is less prone to the Maillard reaction, the reaction temperature can be higher than that used for the monosaccharide. Purification by crystallization was more troublesome than for the glucitol derivatives. A wide range of organic solvents and mixtures of solvents (for example, ethanol, methanol, and mixtures of these alcohols with acetonitrile or acetone, 2-propanol, and water/acetone mixtures) were used in attempts to crystallize the compounds. The surfactants solidified in a mixture of methanol/acetonitrile (about 4 : 1) in the form of "structured gels".

2.4 Acylation

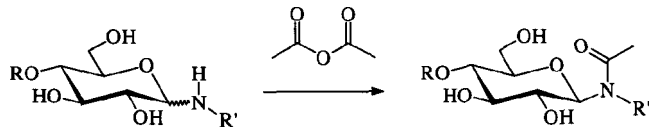
Since *N*-alkyl-α,β-D-aldosylamines and *N*-alkyl-1-amino-1-deoxy-D-alditols contain a secondary amino functionality there is a danger of formation of N-nitrosoamines, which are suspected to be carcinogenic. Acylation of the amine functionality (Scheme 3) eliminates the potential risk of nitrosoamine formation and also increases the solubility of the products in water.

Before acylation, *N*-alkyl-α,β-D-aldosylamines are a mixture of α- and β-anomers. The equilibrium between α- and β-configuration is still present when the compounds react with an acid anhydride to form *N*-acyl,*N*-alkyl-β-D-aldosylamines. *N*-acyl,*N*-alkyl-D-aldosylamines exist exclusively as the β-anomers as confirmed by the large coupling constants of the E-, *Z*-

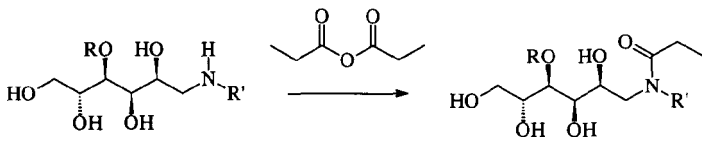


E-conformer **Z-conformer**

Scheme 4. E, *Z* conformers of the amide bond (S = sugar).

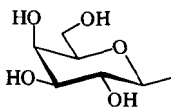


a and β anomers **1** **exclusively β configuration**



2

a: R = H

b: R = 

R' = n-alkyl

Scheme 3. Acylation of the *N*-alkyl-α,β-D-aldosylamines and *N*-alkyl-1-amino-1-deoxy-D-alditols. Formation of *N*-acyl,*N*-alkyl-β-D-glucopyranosylamines (1a), *N*-acyl,*N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]amines (1b), N-acyl,*N*-alkyl-1-amino-1-deoxy-D-glucitols (2a), and *N*-acyl,*N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols (2b).

conformers (Scheme 4) of the amide functionality (**6** 4.92 and 5.46 ppm, $^3J_{HH}$ = 8-9 Hz). Thus formation of the β-anomer of the *N*-acyl,*N*-alkyl-β-D-aldosylamines is kinetically favored. As the reaction proceeds, the equilibrium between a- and β-anomers of the *N*-alkyl-α,β-D-aldosylamine is maintained and N-alkyl-a-D-aldosylamine is transformed into the β-anomer which reacts with the anhydride leading to a β-configuration of the *N*-acyl,*N*-alkyl-D-aldosylamines. According to calculations performed by Rico-Lattes *et al.*[18] the β-configuration of *N*-acyl,*N*-alkyl-D-aldosylamines is also favored thermodynamically.

NMR spectra of the acylated carbohydrate-derived surfactants show that for *N*-acyl,*N*-alkyl-1-amino-1-deoxy-D-alditols, the ratio of the E-, Z-conformers is 1 : 1. For *N*-acyl,*N*-alkyl-β-D-aldosylamines Rico-Lattes *et al.*[18] also found a conformer ratio of 1 : 1 (DMSO-d,). However, we found ratios of about **15** : **85** for *N*-acyl,*N*-alkyl-β-D-glucopyranosylamines and 25 : 75 for *N*-acyl,*N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]amines (CD_3OD). The Z-conformer probably predominates due to possible hydrogen-bond formation

of the primary hydroxyl group of the glucopyranosyl part of the headgroup and the oxygen of the carbonyl functionality (Figure 2).[33] In the case of the reduced carbohydrate headgroups, the glucopyranosyl ring is not intact and the primary hydroxyl group is not available for hydrogen bond formation with the carbonyl oxygen. Indeed, the *E/Z* ratio is now 1 : 1.

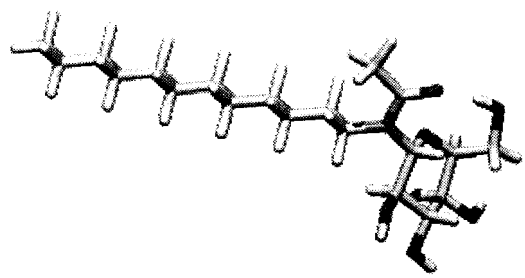


Figure 2. Frame model of the *Z*-conformer of *N*-acetyl,*N*-dodecyl-β-D-glucopyranosylamine (CHARMM program). Hydrogen-bond formation between the hydroxyl group of the primary alcohol functionality of the glucopyranoside headgroup and the carbonyl of the amide functionality is anticipated. Hydrogen-bond formation between C_6-OH and the oxygen in the ring is also possible.

Acylations were performed using acetic anhydride or propionic anhydride. The reactions proceeded quantitatively but during the work-up procedure some product was lost, leading to isolated yields in the range of 85-95%. The purity of the crude product was about 95%, which would suffice for many industrial applications. However, examination of the structure-property relationships require higher purities. The purification of these compounds from 95% purity to the point of satisfactory elemental analyses proved to be a challenge. Column chromatography did not lead to satisfactory results. On a silica gel column a mixture of chloroform and methanol could be used as the eluent, but the amount of methanol required (at least 10%) considerably deactivated the column material. Moreover, the yields were low (30-50%).[15] Other column materials (aluminium oxide, anion and cation exchangers[M]) did not lead to pure compounds.

For large scale syntheses, column chromatography is not desirable and crystallizations are favored. Although crystallization was not easy for the majority of the synthesized compounds, we nevertheless succeeded in finding reasonable to good solvents for crystallization and obtained satisfactory elemental analyses.

Glucose derivatives (*N*-acyl,*N*-alkyl-β-D-glucopyranosylamines) gave the most severe

purification problems. Crude products were slightly yellow. In acetonitrile the yellow impurity precipitated first, and the pure product could be obtained from the clear supernatant. The products were very hygroscopic.

Lactose derivatives (*N*-acyl,*N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]-amines) formed "geolids" from ethanol. The word geolid indicates intermediate structures between a gel and a solid. The precipitates had the appearance of a gel, but they could be separated from the solution by filtration; the geolid remained on the Biichner funnel as a waxy solid. The compounds were then freeze-dried to provide white fluffy solids, which contain one mole of water per mole of product.

The only compounds which did not have crystallization problems were glucitol derivatives (*N*-acyl,*N*-alkyl-1-amino-1-deoxy-D-glucitols). Depending on chain length, they formed nice crystals from ethanol/ether, ethyl acetate, or acetonitrile.

Lactitol derivatives (*N*-acyl,*N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols) were dissolved in methanol. Acetonitrile was added just to the point of precipitation. Upon evaporation, the lactitol derivatives formed white solidified material, the closest physical description is "pimples".

2.5 Physical properties

Melting points of the compounds were determined using differential scanning calorimetry (DSC), Table 1. *N*-acyl,*N*-alkyl-β-D-glucopyranosylamines were very hygroscopic and their melting points could not be determined. No melting peaks were observed either for the fluffy, freeze-dried *N*-acyl,*N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]amines.

C_{10} and C_{12} chain analogs exhibit enantiotropic liquid-crystalline behavior and thus show both "melting" peaks and clearing peaks in a heating run. This phenomenon is described in the next section.

The relatively large difference between the clearing points obtained upon heating and cooling in the cases of NC_2nC_{10} lactitol, NC_3nC_{10} lactitol, and NC_3nC_{12} lactitol (the abbreviations are explained in Figure 1) may indicate initiation of the decomposition of these compounds.

Table 1. Melting points and clearing points of *N*-acyl,*N*-alkyl-1-amino-1-deoxy-D-glucitols,[10] *N*-acyl,*N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols, and *N*-acyl,*N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]amines.

Compound	mp (°C)	AH (kJ mol^{-1})	cp (°C)	AH (kJ mol^{-1})
NC_2nC_8 glucitol	51.3-59.6	24.1		
NC_2nC_{10} glucitol	56.8-62.6	28.2	77.6 (75.5)	0.7 (-1.0)
NC_2nC_{12} glucitol	62.1-66.2	36.2	119.8 (118.6)	1.2 (-1.1)
NC_3nC_8 glucitol	94.0-96.1	47.5		
NC_3nC_{10} glucitol	87.0-88.6	39.0	- (21.9)	(-0.6)
NC_3nC_{12} glucitol	92.4-98.1	63.0	- (66.4)	(-1.1)
NC_2nC_8 lactitol	[a]			
NC_2nC_{10} lactitol	54.9-62.3	22.7	132 (115.4)	0.8 (-0.2)
NC_2nC_{12} lactitol	–50-59.6	25.7	182.3 (168.3)	0.7 (-0.2)
NC_3nC_8 lactitol	93.5-100.9	30.7		
NC_3nC_{10} lactitol	89.9-95.8	37.2	138.8 (134.2)	1.0 (-1.0)
NC_3nC_{12} lactitol	57.4-91.4[b]	[c]	181.9 (160.7)	1.6 (-0.8)
NC_2nC_{12} lactose	[d]	[d]	140.3 (137.7)	0.3 (-0.3)
NC_3nC_{12} lactose	[d]	[d]	145.9 (143.4)	1.2 (-1.3)

[a] The compound was solid, but not very structured. [b] Two broad peaks. [c] Could not be detected. [d] The freeze-dried *N*-acyl,*N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]amines did not show melting peaks in the DSC.

2.6 Liquid-crystalline behavior[35]

In the crystalline form, carbohydrate-derived surfactants are packed in bimolecular layers, with the sugar moieties arranged head-to-head and with fully interdigitized alkyl chains.[36] When the crystals are heated, the alkyl chains start to melt, whereas the carbohydrate sheets which are held together by hydrogen bonds remain intact. At this stage, the compound is in an intermediate phase (a mesophase) between the liquid and the crystalline phase. If heating is continued, the hydrogen bonds between the sheets break down and, at the clearing point, an isotropic liquid is formed. This thermal behavior is called thermotropic liquid crystalline behavior. Generally, clearing points are higher for longer chain lengths.

Mesophases formed by amphiphilic carbohydrate-derived liquid crystals fall into two main

categories: (1) compounds with one alkyl chain (generally with an n-hexyl chain or longer) form smectic A (S_A) phases; (2) compounds with two or more alkyl chains usually form hexagonal columnar phases.[10,37-40] The compounds we synthesized fall into the first category, because the second chain is very short (C, or C,): the compounds (generally with a chain containing 10 or 12 carbon atoms) display smectic A phases.[10,41] In the smectic (Greek for soap) phase the molecules are aligned more or less parallel and there is also some positional order of the molecules, resulting in a layered structure.

When a clearing point exists both upon heating and cooling, compounds are said to be enantiotropic. NC_3nC_{10} glucitol and NC_3nC_{12} glucitol are monotropic, and hence only show a mesophase upon cooling, due to supercooling of the isotropic phase.[42]

Carbohydrate-derived surfactants not only show liquid-crystalline behavior upon heating (thermotropic liquid-crystalline behavior), but also when a solvent is added (lyotropic liquid-crystalline behavior). The lyotropic mesophases displayed by these compounds are discussed in Chapter 3.

2.7 Conclusions

The synthetic routes we used to prepare carbohydrate-based surfactants are straightforward and have high yields. The final purifications from ~95% purity to satisfactory elemental analyses are rather troublesome, but we have found appropriate solvent mixtures to obtain high purities by crystallization. The syntheses are applicable on a large scale, especially when taking into account that for most industrial applications a 95% purity suffices. For industrial purposes, the palladium on carbon used to prepare the *N*-acyl,*N*-alkyl-1-aminoalditols can be replaced by the economically more attractive Raney nickel.

The syntheses are not restricted to glucose and lactose; other mono- (*e.g.* galactose) and disaccharides (such as maltose) can also be used.

2.8 Experimental

Materials. Starting materials and solvents were purchased from any of the large chemical suppliers.

General Methods. Quantitative thermal analyses were performed using a Perkin Elmer PC Series DSC 7 (heating rate 5 °C min^{-1}). Thennomicroscopy used a Mettler FP 800 system, the hot stage was mounted on a Nikon polarizing microscope.

Characterization. 'H- and ^{13}C-NMR spectra were run on a Varian VXR-300 spectrometer (300MHz),

or on a Varian Gemini spectrometer (200 Mhz). 2-D NMR and HETCOR spectra were recorded on a Varian Unity Plus spectrometer (500 MHz). Chemical shifts are denoted in units (ppm) and referenced to residual protons in deuterated solvents for ^{1}H-NMR (CD_3OD: 3.31 or DMSO-d_6: 2.50) and to solvent resonances for ^{13}C-NMR (CD_3OD: 49.00 or DMSO-d_6: 39.50), coupling constants are given in Hz. Elemental analyses were performed at the Microanalytical Department of this laboratory by Mr. H. Draaijer, Mr. J. Ebels, and Mr. J. Hommes.

N-Alkyl-α,β-D-glucopyranosylamines. D-Glucose (10 g, 56 mmol) and one mol equivalent of the appropriate alkylamine were stirred in methanol overnight. The product precipitated from the reaction mixture. The suspension was heated until a clear solution was obtained and subsequently cooled down slowly. The white crystals were filtered off and washed with cold methanol and acetone (to remove unreacted alkylamine). The yields were 61-79%. The products were crystallized from methanol (overall yields 42% (C_7), 50% (C_{10}), 68% (C_{12}), not optimized).

N-Dodecyl-α,β-D-glucopyranosylamine. ^{1}H-NMR (COSY, CD_3OD, ppm): alkyl chain 0.89 (t, 3H, $^3J_{12\text{-}11} = 7.0$). 1.29 (bs, 18H), 1.47-1.52 (m, 2H), 2.64 (m, H_{1A}), 2.90 (m, H_{1B}), sugar moiety 3.06 (t (dd), H_{1B}, $^3J_{2\text{-}1} = {}^3J_{2\text{-}3} = 8.7$), 3.23 (m, H_5, $^3J_{5\text{-}6A} = 2.3$, $^3J_{5\text{-}6B} = 5.3$), 3.28 (t (dd), H_4, $^3J_{4\text{-}3} = {}^3J_{4\text{-}5} = 8.7$), 3.35 (t (dd), H_3, $^3J_{3\text{-}2} = {}^3J_{3\text{-}5} = 8.7$). 3.66 (dd, H_{6B}, $^2J_{6B\text{-}6A} = 11.7$, $^3J_{6B\text{-}5} = 5.3$), 3.82 (d, H_1, β product, $^3J_{1\text{-}2} = 8.7$), 3.83 (dd, H_{6A}, $^2J_{6A\text{-}6B} = 11.7$, $^3J_{6A\text{-}5} = 2.3$), 4.48 (d, H_1, α product, $^3J_{1\text{-}2} = 4.8$), 4.71 (s, 4O<u>H</u>). ^{13}C-NMR (CD_3OD, ppm): alkyl chain 14.38 (C_{12}), 23.67 (C_{11}), 28.38 (C_3), 30.40, 30.64, 30.69, 30.73, 31.13 (C_2, C_4-C_9), 33.02 (C_{10}), 47.19 (C_1), sugar moiety 63.02 (C_6), 71.95, 74.98, 78.90, 78.98 (C_2-C_5), 91.89 (C_1, β product).

N-alkyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amines were prepared according to Erickson's procedure.[29,13] The appropriate alkylamine (100 mmol) was dissolved in 2-propanol (200 mL) and added to a stirred solution of D-lactose (60 mmol) in water (100 mL). After a while the solution became turbid. After 48 hours, the suspension was heated at 60 °C for 30 min, and a clear solution was obtained. The solvents were evaporated under reduced pressure. In order to remove all the water, the residue was taken up twice in ethanol and the solvents were re-evaporated, finally the compounds were dried under vacuum. The (slightly yellow) solids were dissolved in ethanol, filtered over celite and were then allowed to crystallize. The white crystals were washed with ethanol and ether (to remove residual amine). The yields averaged 68%, and were not optimized.

N-Octyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amine. ^{1}H-NMR (DMSO-d_6, ppm): alkyl chain 0.85 (t, 3H, $^3J_{8\text{-}7} = 6.7$), 1.24 (bs, 10H), 1.40 (m, 2H), 2.19 (bs, 1H), 2.48 (m, H_{1A}, falls partly under the DMSO-d_6 signal), 2.77 (m, H_{1B}), sugar moiety 2.92 (m, H_1), 3.13-3.64 (m, H_3-H_6, $H_{2'}$-$H_{6'}$), 3.70 (d, H_1, β product, $^3J_{1\text{-}2} = 8.5$), 4.19 (d, $H_{1'}$, $^3J_{1'\text{-}2'} = 7.0$), 4.28 (d, H_1, α product, $^3J_{1\text{-}2} = 4.8$). 4.30-5.11 (various peaks, 7O<u>H</u>). ^{13}C-NMR (DMSO-d_6, ppm): alkyl chain 14.31 (C_7), 22.45 (C_{11}), 27.17 (C_3), 29.08, 29.36, 30.28 (C_2, C_4, C_5), 31.64 (C_6), 45.95 (C_1), sugar moiety 60.71 (C_6), 61.21 ($C_{6'}$), 68.46 ($C_{4'}$), 70.89 ($C_{5'}$), 73.54 (C_2, $C_{3'}$), 75.81 ($C_{5'}$), 75.89 (C_5), 75.94 (C_3), 81.75 (C_4), 86.80 ($C_{1'}$, α product), 90.96 ($C_{1'}$, β product), 104.18 ($C_{2'}$).

N-Alkyl-1-amino-1-deoxy-D-glucitols. D-Glucose (7 g, 39 mmol), the appropriate alkylamine (2 molar equivalents), and 0.75 g Pd/C (5 %) in ethanol (75 mL) were stirred in a Parr apparatus under hydrogen pressure (60 bar) at 40°C overnight. Subsequently, the carbon was filtered off and the ethanol was evaporated under reduced pressure. The white solid was crystallized twice from ethanol (overall yield ca. 76%). Reductive amination with sodium borohydride has been described in literature."

N-Octyl-1-amino-1-deoxy-D-glucitol. ^{1}H-NMR (COSY, CD_3OD, ppm): 0.90 (t, 3H, $^3J_{8,7}$ = 6.9), 1.33 (bs, 10H), 1.52 (m, 2H), 2.60 (m, 2H), sugar moiety 2.71-2.79 (m, 2H), 3.64 (m, H_5, H_{6B}), 3.71 (m, H_4), 3.78 (m, H_3, H_{6A}), 3.87 (m, H_2), 4.59 (s, 5OH). ^{13}C-NMR (HETCOR, CD_3OD, ppm): alkyl chain 14.12 (C_8), 23.42 (C_7), 28.19, 30.10, 30.36 (C_3, C_4, C_5), 32.73 (C_6), 50.51 (C,), sugar moiety 52.34 (C_1), 64.87 (C_6), 72.61 (C_2, C,), 72.72 (C,), 72.96 (C_4).

N-Alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols. Lactose (5 g, 14 mmol), the appropriate alkylamine (2 molar equivalents), and 0.75 g Pd/C (5 %) in ethanol (50 mL) were stirred in a Parr apparatus under hydrogen pressure (80 bar, the reaction does also proceed when the pressure is reduced to 20 bar) at 70°C overnight. The catalyst was filtered off and the ethanol was evaporated under reduced pressure. The white solid was stirred in ether to remove excess alkylamine and then extracted continuously to remove residual alkylamine (average yields ca. 88%).

N-Dodecyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols. ^{1}H-NMR (CD_3OD, ppm): alkyl chain 0.89 (t, 3H, $^3J_{12-11}$= 7.0), 1.29 (bs, 18H), 1.53 (m, 2H), 2.54-2.79 (m, 2H), sugar moiety 2.54-2.79 (m, 2H), 3.47-3.89 (m, H_3-H_6, $H_{2'}$-$H_{6'}$), 4.02 (m, H,), 4.44 (d, $H_{1'}$, $^3J_{1'-2'}$ = 7.3), 4.83 (s, 8OH). ^{13}C-NMR (CD_3OD, ppm): alkyl chain 14.35 (C_{12}), 23.62 (C_{11}), 28.38 (C_3), 30.35, 30.47, 30.60, 30.65, 30.69 (C_2, C_4-C_9), 32.98 (C_{10}), 50.81 (C_1) sugar moiety 53.87 (C,), 62.73 (C_6), 63.83 (C,.), 70.61, 71.60, 72.83, 72.99, 74.87, 77.15, 82.13 (C_{2-5}, $C_{2'-5'}$) 105.31 (C,.).

Acylation, general prodedure. Acetic anhydride or propionic anhydride (1.5 molar equivalents) was added to the *N*-alkyl-α,β-D-glucopyranosylamines, *N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-α,β-D-glucopyranosyl]amines, *N*-alkyl-1-amino-1-deoxy-D-glucitols, and the *N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols, respectively, in ethanol and stirred overnight. The solution was neutralized with Dowex OH', filtered and the ethanol was removed by evaporation under reduced pressure. Yields of the crude products ranged from 85-95%. The compounds were purified by crystallization.

N-Acyl,*N*-alkyl-β-D-glucopyranosylamines were dissolved in a small amount of acetone and hexane was added to the point of precipitation. The products separated out from acetonelhexane as slightly yellow oils. The yellow impurities (not detectable by ^{1}H-NMR) were also the first to crystallize from acetonitrile. The supernatant was decanted and allowed to crystallize. The products precipitated as white oils/gels which became solid after drying. The glucopyranosylamines were solid but were very hygroscopic and therefore stock solutions were prepared for this type of compounds. Purified yields

ranged from 41-53%.

***N*-Propionyl-*N*-octyl-β-D-glucopyranosylamine (NC_3nC_8 glucose).** ^{1}H-NMR (CD_3OD, ppm): alkyl chain 0.89 (bt, 3H), 1.30 (bs, 10H), 1.61 (m, 2H), both H_1 fall under the sugar moiety, acyl group 1.11 (2t, 3H, $^3J_{3\text{-}2}$ = 7.3), 2.50 (2q, 2H, $^3J_{2\text{-}3}$ = 7.3). sugar moiety 3.25-3.89 (m, H_2-H_6, 8H, including $2H_1$ of the alkyl chain), 4.84 (d, H,, $^3J_{1\text{-}2}$ = 8.1), 5.45 (d, H_1, $^3J_{1\text{-}2}$ = 8.8), 4.91 (s, 4OH). ^{13}C-NMR (CD_3OD, ppm): alkyl chain 14.42 (C_8), 23.67 (C_7), 28.18 (C_3), 28.37, 29.94, 30.41 (C,, C_4, C,), 32.98 (C_6), 42.94, 44.82 (C,), acyl group 9.82 (C,), 27.64 (C,), 177.68 (C,), sugar moiety 62.93 (C_6), 71.41, 71.98, 79.24, 80.37 (C_2-C_5), 84.40, 88.02 (C_1).

***N*-Acyl,*N*-alkyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]amines** were crystallized from ethanol. The compounds formed "geolids" (*vide* supra) from ethanol. The compounds were freeze-dried and they formed white fluffy solids which contains one mol of water per mol of product. Yields were in the range 51- 60%. The products contain one mol of water per mol of compound.

***N*-Propionyl,*N*-decyl-[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]amine (NC_3nC_{10} lactose).** ^{1}H-NMR (COSY, CD_3OD), ppm): alkyl chain 0.90 (t, 3H, $^3J_{10\text{-}9}$ = 7.1), 1.29 (bs, 14H), 1.62 (m, 2H), 3.27, 3.42 (2m, H_{1A}, H_{1B}), acyl group 1.11 (2t, 3H, $^3J_{3\text{-}2}$ = 7.4), 2.48 (2q, 2H, $^3J_{2\text{-}3}$ = 7.4), sugar moiety 3.49-3.62 (m, H_2, H_3, H_5, H_2-H_5,), 3.71 (dd, $H_{6A'}$, $^2J_{6A'\text{-}6B'}$ = 11.4, $^3J_{6A'\text{-}5}$ = 4.3), 3.80 (dd, $H_{6B'}$, $^2J_{6B'\text{-}6A'}$ = 11.4, $^3J_{6B'\text{-}5'}$ = 7.4), 3.82-3.84 (m, $H_{4'}$, H_{6B}), 3.90 (dd, H_{6A}, $^2J_{6A\text{-}6B}$ = 12.1, $^3J_{6A\text{-}5HH}$ = 2.0), 4.38 (d, $H_{1'}$, $^3J_{1'\text{-}2'}$ = 7.8), 4.87 (s, 7OH), 4.92, 5.46 (2d, H_1 $^3J_{1\text{-}2}$ = 9.00 Hz). ^{13}C-NMR (HETCOR, CD_3OD, ppm): alkyl chain 14.42 (C_{10}), 23.67 (C_9), 27.78 (C,), 28.19, 28.40, 29.98, 30.28, 30.39, 30.45, 30.65, 30.75 (C_2, C_4-C_7), 33.01 (C_8), 42.92, 44.91 (C,), acyl chain 9.79, 9.88 (C,), 27.69, 27.75 (C,), 177.50, 178.13 (C,) sugar moiety 62.03, 62.13 (C_6), 62.50 ($C_{6'}$), 70.25 ($C_{4'}$), 71.16, 71.67 (C,), 72.49 ($C_{2'}$), 74.77 ($C_{3'}$), 77.06 ($C_{5'}$), 77.50, 77.64 (C_5), 78.75 (C,), 80.38 (C_4), 84.28, 87.80 (C,), 105.02 (C,.).

N-Acyl,*N*-alkyl-1-amino1-deoxy-D-glucitols were crystallized from ethanol-ether (NC_2nC_8 glucitol and NC_3nC_{12} glucitol, yields 78% and 86%, respectively), ethyl acetate (NC_2nC_{10} glucitol, yield 60%, NC_3nC_{10} glucitol, yield 84%), ethanol-ether and subsequently ethyl acetate (NC_2nC_{12} glucitol, yield 42%), or from acetonitrile(NC_3nC_8 glucitol, yield 73%).

***N*-Propionyl,*N*-decyl-1-amino-1-deoxy-D-glucitol (NC_3nC_{10} glucitol).** ^{1}H-NMR (COSY, CD_3OD, ppm): alkyl chain 0.90 (2t, 3H, $^3J_{10\text{-}9}$ = 6.9), 1.30 (bs, 14H), 1.55, 1.61 (2m, 2H), 3.26-3.60 (m, 2H), acyl group 1.11 (2t, 3H, $^3J_{3\text{-}2}$ = 7.3). 2.47 (m, 2H), sugar moiety 3.26-3.60 (m, H_1), 3.60-3.80 (m, H_3-H_6), 3.98 (m, H_2), 4.81 (s, 5OH). ^{13}C-NMR (HETCOR, CD_3OD, ppm): alkyl chain 14.44 (C,,), 23.67 (C_9), 27.83, 28.04 (C_3), 28.30, 29.71 (C,), 30.37, 30.38, 30.42, 30.52, 30.60, 30.63, 30.65, 30.69 (C_4-C_7), 32.98, 33.00 (C,), 47.41, 50.53 (C,), acyl group 10.07 (C_3), 27.11, 27.39 (C,), 177.12, 177.21 (C_1), sugar moiety 50.67, 51.36 (C_1), 64.67 (C_6), 71.07, 71.55, 72.64, 72.90, 73.02, 73.16, 73.51, 74.17 (C_2-C_5).

***N*-Acyl,*N*-alkyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols.** Acetic acid or propionic acid (1.5 mol equivalents) were added to the alkylated glucose or lactose derivatives and stirred overnight. The solution was neutralized with Dowex OH-, filtered and the ethanol was evaporated under reduced pressure. Crude yields 85-95%. The compounds were crystallized once or twice from methanol-acetonitrile mixtures, purified yields ranged from 58-76%.

***N*-Propionyl,*N*-decyl-4-*O*-(β-D-galactopyranosyl)-1-amino-1-deoxy-D-glucitols (NC_3nC_{10} lactitol).** ^{1}H-NMR (COSY, CD_3OD, ppm): alkyl chain 0.89 (t, 3H, $^3J_{10\text{-}9}$ = 6.5), 1.29 (bs, 14H), 1.55, 1.60 (2 n 2H), 3.18-3.50 (m, 2H), acyl chain 1.09, 1.12 (2q, 3H, $^3J_{3\text{-}2}$ = 7.3), 2.35-2.60 (m, 2H), sugar moiety 3.18-3.50 (m, H_1), 3.50-3.68 (m, $H_{,}$, $H_{3'}$, $H_{,}$), 3.68-3.79 (m, $H_{6'}$, H_6, $H_{4'}$), 3.79-3.97 (m, H_4, $H_{5'}$, H_5), 4.06, 4.08 (2m, H_2), 4.47 (2d, $H_{1'}$, $^3J_{1'\text{-}2'}$ = 7.8, $^3J_{1'\text{-}2'}$ = 7.3), 4.89 (s, 8O<u>H</u>). ^{13}C-NMR (HETCOR, CD_3OD) alkyl chain 14.41 (C,,), 23.67 (C,), 27.84 (C_3), 28.05, 28.29, 29.72, 30.41, 30.53, 30.61, 30.64, 30.68, 30.72 (C_2, $C_{4\text{-}7}$), 33.02 (C,), 47.37, 50.74 (C,), acyl chain 10.01 (C,), 27.13, 27.37 (C,), 177.04, 177.25 (C_1), sugar moiety 50.79, 51.62 (C_1), 62.46 (C,), 63.61 (C,.), 70.17, 70.25 (C,), 70.80, 70.87 (C,), 72.00, 72.03 (C,.), 72.86 ($C_{3'}$), 73.09 (C,.), 74.79, 74.81 (C,.), 77.08, 77.11 (C,), 83.25, 83.78 (C_4), 105.50, 105.75 (C,.).

N.B. The signals for the acetyl groups are positioned at: ^{1}H-NMR (CD_3OD): 2.11, 2.16 (2s, 3H), ^{13}C-NMR (CD_3OD): 21.34, 21.93 (C,), 173. 93, 174.21 (C,).

Table 2. Elemental analyses.

Compound	Formula	Calculated			Found		
		% C	% H	% N	% C	% H	% N
NC_2nC_8 glucose	$C_{16}H_{31}NO_6$	57.64	9.37	4.20	57.84	9.33	4.28
NC_3nC_8 glucose	$C_{17}H_{33}NO_6$	58.77	9.57	4.03	59.01	9.61	4.09
NC_2nC_{10} glucose	$C_{18}H_{35}NO_6$	59.81	9.76	3.87	60.00	9.88	3.92
NC_3nC_{10} glucose	$C_{19}H_{37}NO_6$	60.77	9.93	3.73	61.15	9.99	3.81
NC_2nC_{12} glucose	$C_{20}H_{39}NO_6$	61.67	10.09	3.60	61.86	10.12	3.66
NC_3nC_{12} glucose	$C_{21}H_{41}NO_6$	62.50	10.24	3.47	62.85	10.40	3.53
NC_2nC_8 lactose	$C_{22}H_{41}NO_{11}.H_2O$	51.43	8.44	2.73	51.51	8.40	2.73
NC_3nC_8 lactose	$C_{23}H_{43}NO_{11}.H_2O$	52.36	8.60	2.75	52.55	8.56	2.66
NC_2nC_{10} lactose	$C_{24}H_{45}NO_{11}.H_2O$	53.22	8.75	2.59	53.41	8.61	2.65
NC_3nC_{10} lactose	$C_{25}H_{47}NO_{11}.H_2O$	54.04	8.89	2.52	54.31	8.70	2.58
NC_2nC_{12} lactose	$C_{26}H_{49}NO_{11}.H_2O$	54.82	9.02	2.46	55.10	8.98	2.52
NC_3nC_{12} lactose	$C_{27}H_{51}NO_{11}.H_2O$	55.54	9.16	2.40	55.67	9.18	2.40
NC_2nC_8 glucitol	$C_{16}H_{33}NO_6$	57.29	9.92	4.18	57.32	9.85	4.22
NC_3nC_8 glucitol	$C_{17}H_{35}NO_6$	58.43	10.09	4.01	58.51	10.22	4.01
NC_2nC_{10} glucitol	$C_{18}H_{37}NO_6$	59.48	10.26	3.85	59.75	10.27	3.86
NC_3nC_{10} glucitol	$C_{19}H_{39}NO_6$	60.45	10.41	3.71	60.41	10.56	3.86
NC_2nC_{12} glucitol	$C_{20}H_{41}NO_6$	61.35	10.55	3.58	61.35	10.62	3.57
NC_3nC_{12} glucitol	$C_{21}H_{43}NO_6$	62.19	10.69	3.45	61.93	10.45	3.58
NC_2nC_8 lactitol	$C_{22}H_{43}NO_{11}$	53.11	8.71	2.81	53.14	8.66	2.84
NC_3nC_8 lactitol	$C_{23}H_{45}NO_{11}$	54.00	8.87	2.74	54.05	8.85	2.74
NC_2nC_{10} lactitol	$C_{24}H_{47}NO_{11}$	54.84	9.01	2.66	54.99	8.93	2.72
NC_3nC_{10} lactitol	$C_{25}H_{49}NO_{11}$	55.64	9.15	2.60	55.86	9.09	2.75
NC_2nC_{12} lactitol	$C_{26}H_{51}NO_{11}$	56.40	9.28	2.53	56.63	9.19	2.64
NC_3nC_{12} lactitol	$C_{27}H_{53}NO_{11}$	57.12	9.41	2.47	57.27	9.29	2.57

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