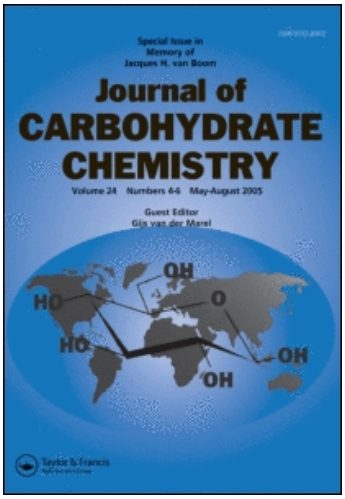

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An Improved Synthetic Procedure for the Preparation of *N*-Acyl (2-aminoethyl)-β-d-glycopyranoside Lipids and Characterization of Their Mesogenic Properties

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An Improved Synthetic Procedure for the Preparation of *N*-Acyl (2-aminoethyl)-β-D-glycopyranoside Lipids and Characterization of Their Mesogenic Properties

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A modified synthetic procedure was used for the synthesis of *N*-acyl (2-aminoethyl) glycosides bearing lactose, maltose, and melibiose carbohydrate headgroups and different acyl chains. The lipid glycosides were prepared in gram scale and investigated for their liquid crystalline properties. It was found that the polar spacer suppresses polymorphism, and the resulting simplified phase behavior was found in the pure state upon heating, as well as for the lyotropic phases

Keywords Liquid crystals, Amphiphiles, Glycolipids

INTRODUCTION

N-Acyl aminoethyl lactosides have gained interest as possible substitutes for ceramides in the investigation of enzymatic reactions.[1] Other kinds of spacer between the carbohydrate headgroup and the lipophilic tail have also been used as substitutes for ceramides[2] or for the preparation of biological active liposomes.[3] Nevertheless, the synthesis of homologs series of *N*-acyl aminoethyl disaccharides with variation of the sugar and the acyl chain has not been

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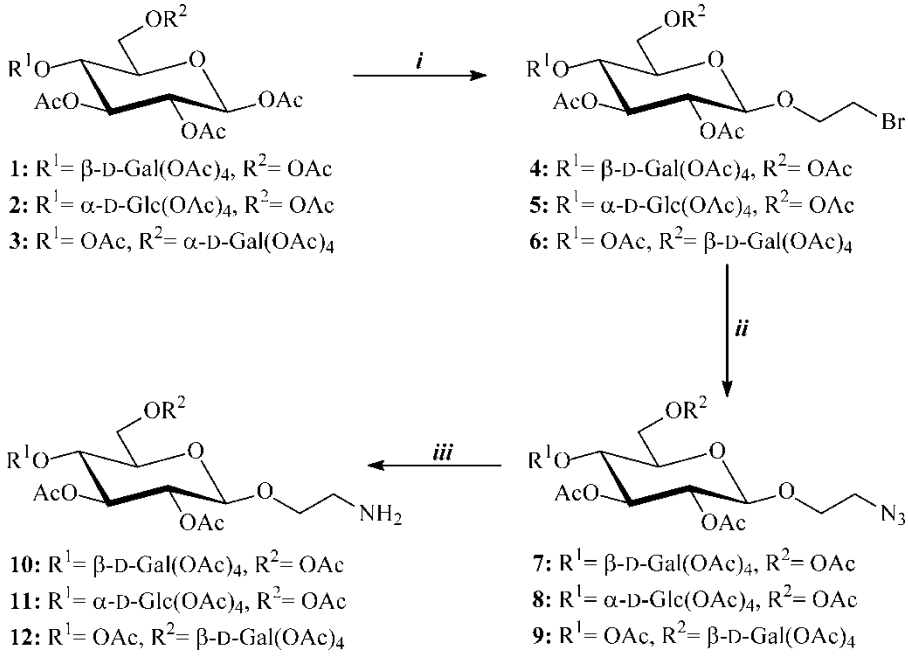
reported yet. Also, a characterization of their liquid crystalline properties in the pure state (thermotropic) and upon the addition of water (lyotropic) cannot be found, despite the fact that such information can explain possible biological functions of these lipids.[4–7] Liquid crystalline properties of n-alkyl glycosides, on the other hand, are well known for many compounds.[8] Disaccharides with alkyl chain length of 12 to 18 carbon atoms show a complex phase behavior, which depends on the structure of the carbohydrate headgroup.[9]

RESULTS AND DISCUSSION

Synthesis

A few *N*-acyl aminoethyl β-lactosides were first synthesized by Miura et al.,[10] bearing fatty acid chains with a chain length of 8, 12, 16, and 20 carbon atoms. Peracetylated lactose was condensed with Fmoc-protected ethanolamine in the route described there. After removal of the Fmoc group the amino group was acylated with octanoyl, dodecanoyl, hexadecanoyl, and eicosanoyl chloride. Deprotection gave the products in 22% to 30% overall yield. Although these yields are considerably good, they synthesized only amounts of about 300 mg. For a closer physical and biological characterization amounts of several grams are often necessary. Therefore, we used another route for the synthesis of different *N*-acyl (2-aminoethyl) glycosides that can easily be upscaled (Sch. 1 and 2).

Instead of Fmoc-protected ethanolamine, we condensed the peracetylated disaccharide with bromoethanol using boron trifluoride as Lewis acid according to procedures described before.[11] It is noteworthy to mention that in this case glycosylation at a temperature of 0°C gave considerably higher yields than at rt. After chromatographic purification the 2-bromoethyl glycosides were obtained in yields of 50% to 60%. Nucleophilic substitution of the bromine using sodium azide in *N*,*N*-dimethylformamide (DMF) afforded the corresponding azide in quantitative yields after workup, without further purification necessary. The 2-aminoethyl glycosides were prepared by reduction of the azide with hydrogen under catalysis of palladium on charcoal (10%). The azide was completely converted into the amine, as could be seen in TLC [1:3, light petroleum (b.p. 50–70°C): ethyl acetate], in which the educt spot of the starting material disappeared completely after 2 h and only one single spot that moved distinctly slower was detected. The amine was immediately reacted with the freshly distilled acyl chloride in DMF using a catalytic amount of pyridine according to the procedure of Masuda et al.[12] After stirring overnight TLC [1:2, light petroleum (b.p. 50–70°C): ethyl acetate] showed only three spots. Two moving far (R_f 0.7 and 0.8) possibly belong to the carbonic acid and some minor byproducts, and one spot (R_f 0.3) belongs



1: R^1= β-D-Gal(OAc)$_4$, R^2= OAc
2: R^1= α-D-Glc(OAc)$_4$, R^2= OAc
3: R^1= OAc, R^2= α-D-Gal(OAc)$_4$

4: R^1= β-D-Gal(OAc)$_4$, R^2= OAc
5: R^1= α-D-Glc(OAc)$_4$, R^2= OAc
6: R^1= OAc, R^2= β-D-Gal(OAc)$_4$

7: R^1= β-D-Gal(OAc)$_4$, R^2= OAc
8: R^1= α-D-Glc(OAc)$_4$, R^2= OAc
9: R^1= OAc, R^2= β-D-Gal(OAc)$_4$

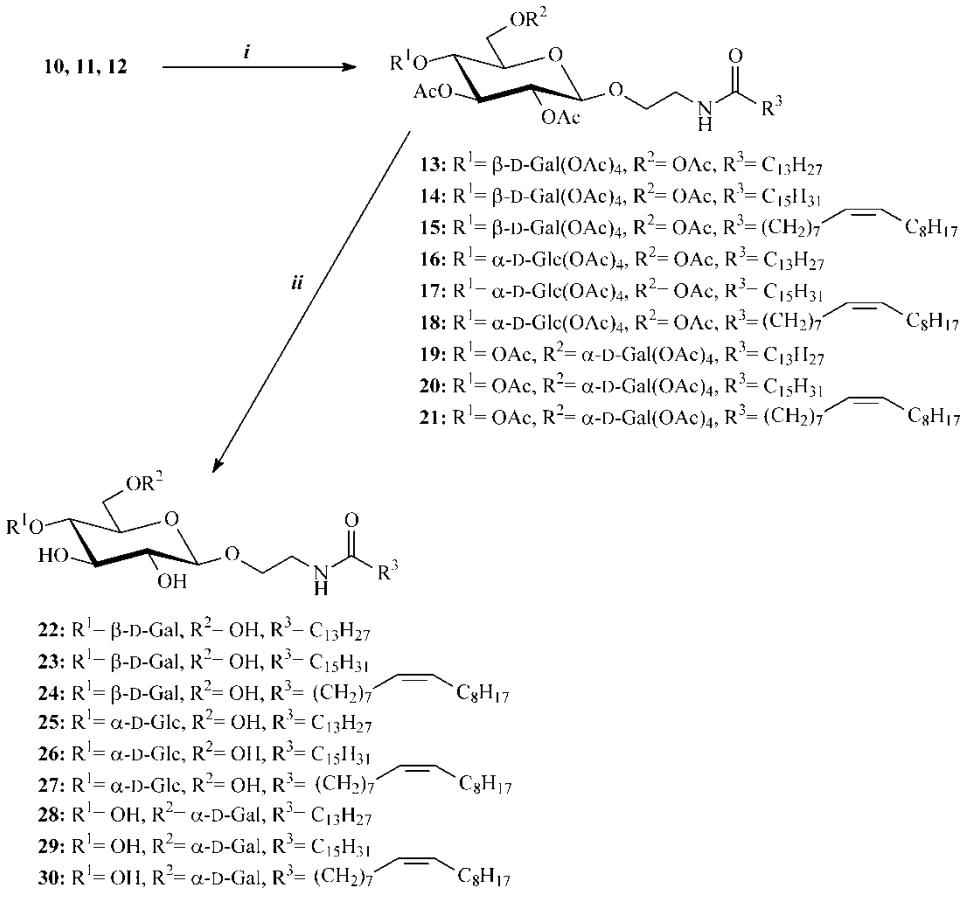
10: R^1= β-D-Gal(OAc)$_4$, R^2= OAc
11: R^1= α-D-Glc(OAc)$_4$, R^2= OAc
12: R^1= OAc, R^2= β-D-Gal(OAc)$_4$

Scheme 1: Synthesis of the precursors **10**, **11**, and **12**. Reagents and conditions: ***i***) $HO(CH_2)_2Br$, BF_3 * Et_2O, CH_2Cl_2 abs., 0°C, 2 h, rt, 18 h ***ii***) NaN_3, DMF, rt, 24 h; ***iii***) H_2, Pd/C 10%, MeOH abs. or MeOH abs./THF abs. 9:1, rt, 1 h.

to the product. After chromatographic purification the compounds were obtained in 70% to 90% yield, depending on the acyl chain length. After deprotection using the Zemplén procedure the lipids were finally obtained after recrystallization from methanol or after chromatographic purification (4:1, chloroform:methanol). Using this route, nine lipids with tetradecanoyl, hexadecanoyl, and oleoyl chains and lactose, maltose, and melibiose headgroups were synthesized in good yields and in gram scale.

Liquid Crystalline Phase Behavior

The thermotropic phase transitions were investigated using polarizing microscopy. The results are shown in Table 1. All compounds show liquid crystalline phase behavior upon heating. The six compounds with *N*-acyl chains (**22**, **23, 25, 26, 28, 29**) are crystalline at ambient temperature. The lactoside **24** and the melibioside **30** with the unsaturated oleoyl chain did not crystallize, but formed a glass. Also, a defined phase transition temperature of the transition from the glassy state to the liquid crystalline phase could not be determined. It was only observed that the compound transformed into the liquid crystalline state at temperatures above 50°C. The maltoside **27**, also carrying an oleoyl chain, was the only compound showing liquid crystalline phase



Scheme 2: Final synthesis of the lipids **22**–**30**. Reagents and conditions: ***i***) RCOCl, DMF abs., C_5H_5N abs., 0°C, 2 h; ***ii***) NaOMe, MeOH abs., rt, 4 h.

behavior already at ambient temperature. Interestingly, it was observed that all compounds formed only thermotropic smectic A (bilayer) liquid crystalline phases. This is surprising because their alkyl glycoside counterparts form other phases, such as cubic phases, besides the lamellar phase.[9] An explanation for this simplified phase behavior might be the interaction of the amide group. The formation of a hydrogen-bonding network in the hydrophobic part of the molecule disables the formation of complex phases like cubic phases. Another deviation from the liquid crystalline phase behavior of the corresponding alkyl glycosides can be seen in the transition temperatures. The compounds **24**–**30** show similar melting points as the n-alkyl glycosides; however, for the two lactosides **22** and **23** it was found that the melting points are 15°C to 20°C lower. Deviation between the alkyl glycosides and the investigated compounds is found for the clearing temperatures. The clearing temperatures are lowered for all compounds by 50°C to 75°C compared to

Table 1: Thermotropic phase transitions of the pure compounds.[a]

Lactosides					
22	Cr	147	SmA	208	d
23	Cr	148	SmA	212	d
24	g	?	SmA	180	I
Maltosides					
25	Cr	102	SmA	164	I
26	Cr	103	SmA	191	d
27	Cr	<20	SmA	123	I
Melibiosides					
28	Cr	151	SmA	205	I
29	Cr	152	SmA	210	I
30	g	?	SmA	195	I

[a]In °C. Cr, crystalline; g, glass; SmA, Smectic A phase; I, isotropic; d, decomposition.

their n-alkyl counterparts. Three compounds showed signs of decomposition near the clearing point. Again, this might be attributed to the interaction of the amide group in the hydrophobic part that disturbs the order of the acyl chains, which then leads to a reduced stability of the liquid crystalline phase.

The lyotropic phase sequences of the investigated compounds are shown in Table 2. The influence of the amino spacer on the lyotropic phase behavior in water is obvious at first glance. Compounds **22**, **23**, **25**, **26**, **28,** and **29** bearing n-alkyl chains only form lamellar phases upon addition of water. Due to the low water solubility of these compounds, myelin figures are

Table 2: Lyotropic phase sequence in the contact preparation with water.

22	Cr	L_α[a]		H_1
23	Cr	L_α[a]		
24	g	L_α[a]		
25	Cr	L_α[a]		
26	Cr	L_α[a]		
27	SmA	L_α[a]	V_1	H_1
28	Cr	L_α[a]		
29	Cr	L_α[a]		
30	g	L_α[a]		H_1
Pure compound				100% water

[a]Myelin figures were formed beyond the lamellar phase toward the water region. Cr, crystalline; g, glass; L_α, lamellar phase; H_1, hexagonal phase; V_1, bicontinuous cubic phase.

formed beyond the lamellar phase. The three compounds with the oleoyl chain (**24**, **27**, and **30**) show lyotropic polymorphism. Beyond the lamellar phase hexagonal phases of type I can be found. In the case of compound **27** with its maltose headgroup, a cubic phase is formed between the lamellar and the hexagonal phase. Above the cmc the maltoside **27** forms long and stiff cylindrical micelles, compared to oleyl maltoside, which forms polymer-like and flexible micelles.[13]

Since mixing of glycolipids with different phase behavior can induce new phases,[14] the simplified phase behavior of the *N*-acyl aminoethyl glycosides can be useful to control the phase behavior of lipid mixtures, where it might induce and/or stabilize phases that are of biological interest.

EXPERIMENTAL

General

Thin-layer chromatography was performed on silica gel (Merck GF_{254}), and detection was effected by spraying with a solution of ethanol/sulphuric acid (9:1), followed by heating. Column chromatography was performed using silica gel 60 (Merck, 0.063–0.200 mm, 230–400 mesh). NMR spectra were recorded on a Bruker AMX 400 or a Bruker DRX 5001 spectrometer (m_c = centred multiplet; d = doublet; t = triplet; dd = double doublet; dt = double triplet). Spectral assignments were made by the double-resonance technique COSY. Purity checks (combustion analysis or high-resolution FAB-MS) are provided only for the final compounds. An Olympus BH optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to identify thermal transitions and to characterize anisotropic textures. For the contact preparation a small amount of sample was placed on a microscope slide and covered with a cover glass before heating. Afterwards a small amount of solvent was placed on the slide at the edge of the cover glass. As soon as the solvent had moved under the cover glass and completely surrounded the sample with the solvent, the slide was placed again for a few seconds on the hot stage at a temperature of 100°C to 120°C and the phase behavior was investigated immediately afterwards by polarizing microscopy.

Synthesis

(2-Aminoethyl) 4-O-(2, 3, 4, 6-tetra-O-acetyl-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (10)

4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranoside (**1**; 13.6 g, 20 mmol) and anhydrous 2-bromoethanol

(1.85 mL, 3.2 g, 26 mmol) were dissolved in anhydrous dichloromethane (50 mL) under an atmosphere of dry nitrogen. Boron trifluoride etherate (6.5 mL, 7.4 g, 52 mmol) was added dropwise at 0°C under nitrogen. Stirring was continued for 2 h at 0°C and an additional 18 h at rt. The solution was poured on ice water (100 mL) and extracted twice with dichloromethane (50 mL). The combined organic phases were washed twice with saturated sodium hydrogen carbonate solution (50 mL) and twice with water (30 mL) and dried over magnesium sulfate, and the solvent removed in vacuo. The residue was purified by column chromatography [light petroleum (b.p. 50–70°C): ethyl acetate, 1:1). Yield: 8.2 g (62%) **4**. Compound **4** (7.4 g; 10 mmol) was dissolved in anhydrous *N*,*N*-dimethylformamide (100 mL). Sodium azide (6.5 g, 100 mmol) was added, and the reaction mixture was stirred overnight at ambient temperature. The reaction mixture was filtered and the filtrate was poured onto water (100 mL) and extracted three times with dichloromethane (100 mL). The combined organic phases were washed with brine (100 mL) and twice with water (100 mL) and dried over magnesium sulphate. Solvent was evaporated in vacuo to give compound **7** in quantitative yield as slight yellow syrup, which was used without further purification. Compound **7** (7.1 g, 10 mmol) was dissolved in a mixture of anhydrous methanol and tetrahydrofurane (100 mL, 9:1). Palladium on charcoal (10%, 30 mg) was added and the reaction mixture was stirred under an atmosphere of hydrogen for 2 h until TLC revealed the reaction to be complete [light petroleum (b.p. 50–70°C): ethyl acetate, 1:2]. The catalyst was filtered off and solvent was evaporated under reduced pressure. The residue was subjected to column chromatography [light petroleum (b.p. 50–70°C): ethyl acetate, 1:3].

Yield: 6.7 g (98%). $[\alpha]_D^{20} = -6$ (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.54$ (dd, 1H, $^3J_{1',2'}$ 8.1, $^3J_{2',3'}$ 10.4, H-2′), 5.47 (dd, 1H, $^3J_{3',4'}$ 3.6, $^3J_{4',5'}$ 1.0, H-4′), 5.41 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.2, H-3), 5.26 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 5.10 (dd, 1H, H-3′), 4.52 (dd, 1H, $^3J_{5,6a}$ 2.0, $^2J_{6a,6b}$ 12.2, H-6a), 4.31 (d, 1H, H-1′), 4.22 (d, 1H, H-1), 4.14 (dd, 1H, $^3J_{5,6b}$ 6.1, H-6b), 4.05–4.12 (m, 2H, H-6a′, H-6b′), 3.80–3.85 (m, 1H, OCH_2CH_2N), 3.70–3.74 (m, 1H, OCH_2CH_2N) 3.63 (dd, 1H, $^3J_{4,5}$ 9.2, H-4), 3.44–3.50 (m, 3H, H-5′, OCH_2CH_2N), 3.20 (ddd, 1H, H-5), 1.97, 1.93, 1.84, 1.73, 1.70, 1.64, 1.54 (each s, 3H, OAc).

*(2-Aminoethyl) 4-O-(2,3,4,6-tetra-O-acetyl-α-*D*-glucopyranosyl)-2,3,6-tri-O-acetyl-β-*D*-glucopyranoside (11)*

4-*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranoside (13.6 g, 20 mmol) and anhydrous 2-bromoethanol (1.85 mL, 3.2 g, 26 mmol) were reacted as described for compound **4**. Yield: 9.8 g (74%) of compound **5**. Compound **5** (7.4 g, 10 mmol) was reacted as described for compound **7**. The product **8** was obtained in quantitative yield and used

without further purification. Compound **8** (7.1 g, 10 mmol) in anhydrous methanol (100 mL) was reacted as described for compound **10**.

Yield: 6.7 g (98%). $[\alpha]_D^{20} = +20$ (c = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 6.03$ (bs, 2H, NH), 5.35 (d, 1H, $^3J_{1',2'}$ 4.1, H-1′), 5.29 (dd, 1H, $^3J_{2',3'}$ 10.1, $^3J_{3',4'}$ 9.7, H-3′), 5.20 (dd, 1H, $^3J_{2,3}$ 9.2, $^3J_{3,4}$ 9.2, H-3), 4.99 (dd, 1H, $^3J_{4',5'}$ 9.9, H-4′), 4.80 (dd, 1H, H-2′), 4.77 (dd, 1H, $^3J_{1,2}$ 7.9, H-2), 4.53 (d, 1H, H-1), 4.43 (dd, 1H, $^3J_{5,6a}$ 2.8, $^2J_{6a,b}$ 12.2, H-6a), 4.19 (d, 1H, $^3J_{5',6a'}$ 2.3, $^2J_{6a',b'}$ 11.2, H-6a′), 4.16 (dd, 1H, $^3J_{5,6b}$ 4.3, H-6b), 3.98 (dd, 1H, $^3J_{5',6b'}$ 3.6, H-6b′), 3.95 (dd, 1H, $^3J_{4,5}$ 9.2, H-4), 3.84–3.93 (m, 2H, H-5′, OCH_2CH$_2$N), 3.70–3.75 (m, 1H, OCH_2CH$_2$N), 3.63 (ddd, 1H, H-5), 3.49 (m_c, 2H, OCH$_2$CH_2N), 2.08, 2.04 (each s, 3H, OAc), 1.98 (s, 6H, OAc), 1.96, 1.94, 1.93 (each s, 3H, OAc).

(2-Aminoethyl) 6-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-2,3,4-tri-O-acetyl-β-D-glucopyranoside (12)

6-*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranoside (13.6 g, 20 mmol) and anhydrous 2-bromoethanol (1.85 mL, 3.2 g, 26 mmol) were reacted as described for compound **4**. Yield: 8.6 g (65%) of compound **6**. Compound **6** (7.4 g, 10 mmol) was reacted as described for compound **7**. The product **9** was obtained in quantitative yield and used without further purification. Compound **9** (7.1 g, 10 mmol) in anhydrous methanol (100 mL) was reacted as described for compound **10**.

Yield: 6.5 g (96%). $[\alpha]_D^{20} = +40$ (c = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 5.45$ (dd, 1H, $^3J_{3',4'}$ 3.1, $^3J_{4',5'}$ 1.0, H-4′), 5.35 (dd, 1H, $^3J_{2',3'}$ 10.7, H-3′), 5.21 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.7, H-3), 5.16 (d, 1H, $^3J_{1',2'}$ 3.6, H-1′), 5.11 (dd, 1H, H-2′), 5.07 (dd, 1H, $^3J_{4,5}$ 9.7, H-4), 4.93 (d, 1H, $^3J_{1,2}$ 8.1, H-2), 4.48 (d, 1H, H-1), 4.25 (ddd, 1H, $^3J_{5',6a'}$ 5.6, $^3J_{5',6b'}$ 6.6, H-5′), 4.11 (dd, 1H, $^2J_{6a',6b'}$ 11.2, H-6a′), 4.06 (dd, 1H, H-6b′), 3.90–3.98 (m, 1H, OCH_2CH$_2$N), 3.66–3.78 (m, 2H, H-6a, OCH_2CH$_2$N), 3.65 (ddd, 1H, $^3J_{5,6a}$ 5.1, $^3J_{5,6b}$ 2.5, H-5), 3.58 (dd, 1H, $^2J_{6a,6b}$ 11.2, H-6b), 3.47–3.51 (m, 2H, OCH$_2$CH_2N), 2.13, 2.12, 2.05, 2.04, 2.03, 2.00, 1.98 (each s, 3H, OAc).

(N-Tetradecanoyl-2-aminoethyl) 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β- D-glucopyranoside (13)

Compound **10** (3.4 g, 5 mmol) and anhydrous pyridine (0.4 mL, 396 mg, 5 mmol) were dissolved in anhydrous *N*,*N*-dimethylformamide (80 mL). Freshly distilled tetradecanoyl chloride (1.4 mL, 1.2 g, 5 mmol) in anhydrous *N*,*N*-dimethylformamide (10 mL) was added dropwise at 0°C. Stirring was continued for 1 h at 0°C and for 14 h at rt. The solution was poured on ice water (60 mL) and extracted three times with dichloromethane (80 mL). The combined organic phases were washed two times with saturated sodium hydrogen carbonate solution (80 mL) and with water (50 mL) and dried over

magnesium sulfate, and solvent was removed in vacuo. The residue was purified by column chromatography [light petroleum (b.p. 50–70°C): ethyl acetate, 1:1].

Yield: 3.2 g (72%). $[\alpha]_D^{20} = -15$ (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 6.04$ (s, 1H, NH), 5.28 (dd, 1H, $^3J_{3',4'}$ 3.5, $^3J_{4',5'}$ 1.0, H-4′), 5.13 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.7, H-3), 5.04 (dd, 1H, $^3J_{1',2'}$ 8.1, $^3J_{2',3'}$ 10.1, H-2′), 4.88 (dd, 1H, H-3′), 4.83 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 4.50 (d, 1H, H-1), 4.42 (dd, 1H, $^3J_{5,6a}$ 2.0, $^3J_{6a,b}$ 12.2, H-6a), 4.41 (d, 1H, H-1′), 3.98–4.09 (m, 3H, H-6b, H-6a′, H-6b′), 3.77–3.86 (m, 2H, H-5′, OC$H_2$$CH_2$N), 3.72 (dd, 1H, $^3J_{4,5}$ 9.7, H-4), 3.60–3.64 (m, 1H, OC$H_2$$CH_2$N), 3.53 (ddd, 1H, $^3J_{5,6b}$ 6.1, H-5), 3.48–3.51 (m, 2H, OCH_2CH_2N), 2.20 (m_c, 2H, alkyl-α-CH_2), 2.08, 2.05, 1.99 (each s, 3H, OAc), 1.98 (s, 6H, 2x OAc), 1.97, 1.90 (each s, 3H, OAc), 1.44–1.50 (m, 2H, alkyl ß-CH_2), 1.14–1.28 (m, 20H, alkyl-CH_2), 0.81 (t, 3H, alkyl-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$ + TMS): $\delta = 172.10$ (C═O, amide), 170.88, 170.67, 170.18, 170.01, 169.77 (C═O, OAC), 100.09 (C-1′), 99.67 (C-1), 71.84 (C-3), 71.63 (C-5), 70.70 (C-2), 70.62 (O$CH_2$$CH_2$N), 70.02 (C-3′), 69.70 (C-5′), 68.13 (C-2′), 65.63 (C-4′), 61.03 (C-6), 59.78 (C-6′), 47.56 ($OCH_2$$CH_2$N), 42.10 (alkyl-α-$CH_2$), 36.72 (alkyl-β-$CH_2$), 32.19, 30.14, 30.07, 30.04, 30.01, 29.92, 29.77, 26.50 (alkyl-CH_2), 21.28, 21.23, 21.11, 21.04, 20.98 (CH_3, OAc), 14.54 (alkyl-CH_3).

(N-Hexadecanoyl-2-aminoethyl) 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (14)[10]

Compound **10** (3.4 g, 5 mmol) and freshly distilled hexadecanoyl chloride (1.5 mL, 1.4 g, 5 mmol) were reacted as described for compound **13**.

Yield: 3.4 g (73%). $[\alpha]_D^{20} = -16$ (c = 1.1, $CHCl_3$). No optical rotation value was reported in the reference.

^{1}H NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 6.05$ (s, 1H, NH), 5.24 (dd, 1H, $^3J_{3',4'}$ 3.5, $^3J_{4',5'}$ 1.0, H-4′), 5.14 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.7, H-3), 5.05 (dd, 1H, $^3J_{1',2'}$ 8.1, $^3J_{2',3'}$ 10.1, H-2′), 4.89 (dd, 1H, H-3′), 4.82 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 4.51 (d, 1H, H-1), 4.43 (dd, 1H, $^3J_{5,6a}$ 2.0, $^3J_{6a,b}$ 12.2, H-6a), 4.42 (d, 1H, H-1′), 3.97–4.09 (m, 3H, H-6b, H-6a′, H-6b′), 3.76–3.87 (m, 2H, H-5′, OC$H_2$$CH_2$N), 3.72 (dd, 1H, $^3J_{4,5}$ 9.7, H-4), 3.61–3.66 (m, 1H, OC$H_2$$CH_2$N), 3.54 (ddd, 1H, $^3J_{5,6b}$ 6.1, H-5), 3.48–3.52 (m, 2H, OCH_2CH_2N), 2.23 (m_c, 2H, alkyl-α-CH_2), 2.09, 2.04, 2.00 (each s, 3H, OAc), 1.98 (s, 6H, 2x OAc), 1.97, 1.92 (each s, 3H, OAc), 1.44–1.53 (m, 2H, alkyl ß-CH_2), 1.14–1.29 (m, 24H, alkyl-CH_2), 0.82 (t, 3H, alkyl-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$ + TMS): $\delta = 172.12$ (C═O, amide), 170.89, 170.68, 170.19, 170.09, 169.87 (C═O, OAC), 100.07 (C-1′), 99.68 (C-1), 71.85 (C-3), 71.64 (C-5), 70.72 (C-2), 70.63 (O$CH_2$$CH_2$N), 70.08 (C-3′), 69.68 (C-5′), 68.12 (C-2′), 65.62 (C-4′), 61.05 (C-6), 59.80 (C-6′), 47.59 ($OCH_2$$CH_2$N), 42.08 (alkyl-α-$CH_2$), 36.70 (alkyl-β-$CH_2$), 32.18, 30.12, 30.05, 30.01, 29.92, 29.75, 29.67, 26.48 (alkyl-CH_2), 21.26, 21.21, 21.11, 21.05, 20.99 (CH_3, OAc), 14.52 (alkyl-CH_3).

(N-9-Z-Octadecenoyl-2-aminoethyl) 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (15)

Compound **10** (3.4 g, 5 mmol) and freshly distilled oleoyl chloride (1.6 mL, 1.5 g, 5 mmol) were reacted using as described for compound **13**.

Yield: 3.1 g (65%). $[\alpha]_D^{20} = -18$ (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 6.04$ (s, 1H, NH), 5.32–5.39 (m, 2H, H-olefinic), 5.24 (dd, 1H, $^3J_{3',4'}$ 3.5, $^3J_{4',5'}$ 1.0, H-4′), 5.14 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.7, H-3), 5.05 (dd, 1H, $^3J_{1',2'}$ 8.1, $^3J_{2',3'}$ 10.1, H-2′), 4.89 (dd, 1H, H-3′), 4.82 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 4.51 (d, 1H, H-1), 4.43 (dd, 1H, $^3J_{5,6a}$ 2.0, $^3J_{6a,b}$ 12.2, H-6a), 4.42 (d, 1H, H-1′), 3.97–4.09 (m, 3H, H-6b, H-6a′, H-6b′), 3.76–3.87 (m, 2H, H-5′, OCH_2CH_2N), 3.72 (dd, 1H, $^3J_{4,5}$ 9.7, H-4), 3.61–3.66 (m, 1H, OCH_2CH_2N), 3.54 (ddd, 1H, $^3J_{5,6b}$ 6.1, H-5), 3.48–3.52 (m, 2H, OCH_2CH_2N), 2.23 (m_c, 2H, alkyl-α-CH_2), 2.09, 2.04, 2.00 (each s, 3H, OAc), 1.98 (s, 6H, 2x OAc), 1.97, 1.92 (each s, 3H, OAc), 1.90–1.97 (m, 4H, allyl-CH_2), 1.44–1.53 (m, 2H, alkyl ß-CH_2), 1.14–1.29 (m, 20H, alkyl-CH_2), 0.82 (t, 3H, alkyl-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$ + TMS): $\delta = 172.12$ (C═O, amide), 170.89, 170.68, 170.19, 170.09, 169.87 (C═O, OAC), 131.54, 131.48 (C-olefin.), 100.07 (C-1′), 99.68 (C-1), 71.85 (C-3), 71.64 (C-5), 70.72 (C-2), 70.63 (OCH_2N), 70.08 (C-3′), 69.68 (C-5′), 68.12 (C-2′), 65.62 (C-4′), 61.05 (C-6), 59.80 (C-6′), 47.59 (OCH_2CH_2CH_2N), 41.39 (alkyl-α-CH_2), 32.18, 30.12, 30.05, 30.01, 29.92, 29.75, 29.67, 26.48 (alkyl-CH_2), 21.26, 21.21, 21.11, 21.05, 20.99 (CH_3, OAc), 14.52 (alkyl-CH_3).

(N-Tetradecanoyl-2-aminoethyl) 4-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (16)

Compound **11** (3.4 g, 5 mmol) and freshly distilled tetradecanoyl chloride (1.4 mL, 1.2 g, 5 mmol) were reacted as described for compound **13**.

Yield: 3.5 g (79%). $[\alpha]_D^{20} = +30$ (c = 1.4, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$ + TMS): $\delta = 6.51$ (s, 1H, NH), 5.41 (d, 1H, $^3J_{1',2'}$ 4.1, H-1′), 5.35 (dd, 1H, $^3J_{2',3'}$ 10.2, $^3J_{3',4'}$ 10.2, H-3′), 5.24 (dd, 1H, $^3J_{2,3}$ 9.2, $^3J_{3,4}$ 9.2, H-3), 5.04 (dd, 1H, $^3J_{4',5'}$ 10.2, H-4′), 4.85 (dd, 1H, H-2′), 4.80 (dd, 1H, $^3J_{1,2}$ 7.6, H-2), 4.50 (d, 1H, H-1), 4.46 (dd, 1H, $^3J_{5,6a}$ 2.5, $^2J_{6a,b}$ 12.2, H-6a), 4.25 (dd, 1H, $^3J_{5',6a'}$ 4.1, $^3J_{6a',b'}$ 12.2, H-6a′), 4.22 (dd, 1H, $^3J_{5,6b}$ 4.6, H-6b), 4.03 (dd, 1H, $^3J_{5',6b'}$ 2.0, H-6b′), 3.99 (dd, 1H, $^3J_{4,5}$ 9.2, H-4), 3.95 (ddd, 1H, H-5′), 3.82–3.88 (m, 1H, OCH_2CH_2N), 3.66 (ddd, 1H, H-5), 3.45 (m_c, 1H, OCH_2CH_2N), 3.38–3.42 (m, 2H, OCH_2CH_2N), 2.17–2.21 (m, 2H, alkyl-α-CH_2), 2.13, 2.09, 2.04, 2.02, 2.00 (each s, 3H, OAc), 1.99 (s, 6H, OAc), 1.49–1.59 (m, 2H, alkyl-ß-CH_2), 1.19–1.31 (m, 20H, alkyl-CH_2), 0.86 (t, 2H, alkyl-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$ + TMS): $\delta = 172.9$ (C═O, amide), 170.54, 170.50, 170.27, 170.01, 169.62, 169.43 (C═O, OAc), 100.31 (C-1), 95.38 (C-1′), 75.51

(C-3), 72.84 (C-4), 72.26, 72.11 (C-2, C-5), 70.18 (O*CH*$_2$CH$_2$N), 69.99 (C-2′), 69.40 (C-3′), 68.58 (C-5′), 68.07 (C-4′), 62.95 (C-6), 61.56 (C-6′), 46.25 (OCH$_2$*CH*$_2$N), 42.08 (alkyl-α-CH$_2$), 36.80 (alkyl-β-CH$_2$), 32.16, 29.45, 29.30, 25.95, 24.83, 24.69, 24.17, 23.18, 22.70 (alkyl-CH$_2$), 20.94, 20.85, 20.69, 20.62, 20.59 (-CH$_3$, OAc), 14.16 (alkyl-CH$_3$).

(N-Hexadecanoyl-2-aminoethyl) 4-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (17)

Compound **11** (3.4 g, 5 mmol) and freshly distilled tetradecanoyl chloride (1.5 mL, 1.4 g, 5 mmol) were reacted as described for compound **13**.

Yield: 3.7 g (80%). $[\alpha]_D^{20} = +30$ (c = 1.2, CHCl$_3$).

^{1}H NMR (500 MHz, CDCl$_3$ + TMS): $\delta = 6.02$ (s, 1H, NH), 5.37 (d, 1H, $^3J_{1',2'}$ 3.8, H-1′), 5.34 (dd, 1H, $^3J_{2',3'}$ 9.8, $^3J_{3',4'}$ 9.8, H-3′), 5.20 (dd, 1H, $^3J_{2,3}$ 9.5, $^3J_{3,4}$ 9.1, H-3), 5.08 (dd, 1H, $^3J_{4',5'}$ 9.8, H-4′), 4.84 (dd, 1H, H-2′), 4.77 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 4.48 (d, 1H, H-1), 4.46 (dd, 1H, $^3J_{5,6a}$ 2.8, $^2J_{6a,b}$ 12.0, H-6a), 4.23 (dd, 1H, $^3J_{5',6a'}$ 4.1, $^2J_{6a',b'}$ 12.3, H-6a′), 4.20 (dd, 1H, $^3J_{5,6b}$ 4.4, H-6b), 4.05 (dd, 1H, $^3J_{5',6b'}$ 2.2, H-6b′), 3.96 (dd, 1H, $^3J_{4,5}$ 9.1, H-4), 3.92 (m$_c$, 1H, H-5′), 3.80–3.85 (m, 1H, OC*H*$_2$CH$_2$N), 3.64 (ddd, 1H, H-5), 3.55–3.63 (m, 1H, OC*H*$_2$CH$_2$N), 3.44–3.49 (m, 2H, OCH$_2$C*H*$_2$N), 2.20 (t, 2H, alkyl-α-CH$_2$), 2.11, 2.08, 2.01, 1.98, 1.97 (je s, 3H, OAc), 1.95 (s, 6H, OAc), 1.54–1.60 (m, 2H, alkyl-ß-CH$_2$), 1.17–1.44 (m, 24H, alkyl-CH$_2$), 0.86 (t, 3H, alkyl-CH$_3$).

^{13}C NMR (125 MHz, CDCl$_3$ + TMS): $\delta = 171.02$ (C═O, amide), 170.09, 170.08, 170.07, 169.78, 169.45, 169.30 (C═O, OAc), 100.12 (C-1), 95.30 (C-1′), 75.45 (C-3), 71.84 (C-4), 71.24, 71.20 (C-2, C-5), 70.09 (O*CH*$_2$N), 69.98 (C-2′), 69.30 (C-3′), 68.42 (C-5′), 68.01 (C-4′), 62.89 (C-6), 61.47 (C-6′), 46.18 (OCH$_2$*CH*$_2$N), 42.43 (alkyl-α-CH$_2$), 36.70 (alkyl-β-CH$_2$), 32.15, 29.98, 29.45, 29.35, 29.30, 25.74, 23.01, 22.92, 21.75, 21.06 (alkyl-CH$_2$), 20.90, 29.85, 20.62, 20.59, 20.55, 20.51 (CH$_3$, OAc), 14.16 (alkyl-CH$_3$).

(N-9-Z-Octadecenoyl-2-aminoethyl) 4-O-(2, 3, 4, 6-tetra-O-acetyl-α-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (18)

Compound **11** (3.4 g, 5 mmol) and freshly distilled oleoyl chloride (1.6 mL, 1.5 g, 5 mmol) were reacted as described for compound **13**.

Yield: 3.3 g (70%). $[\alpha]_D^{20} = +30$ (c = 0.9, CHCl$_3$).

^{1}H NMR (500 MHz, CDCl$_3$ + TMS): $\delta = 6.02$ (s, 1H, NH), 5.34–5.41 (m, 2H, H-olefin.), 5.37 (d, 1H, $^3J_{1',2'}$ 3.8, H-1′), 5.33 (dd, 1H, $^3J_{2',3'}$ 9.8, $^3J_{3',4'}$ 9.8, H-3′), 5.21 (dd, 1H, $^3J_{2,3}$ 9.5, $^3J_{3,4}$ 9.1, H-3), 5.01 (dd, 1H, $^3J_{4',5'}$ 9.8, H-4′), 4.82 (dd, 1H, H-2′), 4.77 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 4.47 (d, 1H, H-1), 4.44 (dd, 1H, $^3J_{5,6a}$ 2.8, $^2J_{6a,b}$ 12.0, H-6a), 4.22 (dd, 1H, $^3J_{5',6a'}$ 4.1, $^2J_{6a',b'}$ 12.3, H-6a′), 4.20 (dd, 1H, $^3J_{5,6b}$ 4.4, H-6b), 4.01 (dd, 1H, $^3J_{5',6b'}$ 2.2, H-6b′), 3.97 (dd, 1H, $^3J_{4,5}$ 9.1, H-4), 3.93 (m$_c$, 1H, H-5′), 3.82 (m$_c$, 1H, OC*H*$_2$CH$_2$N), 3.64 (ddd, 1H,

H-5), 3.58–3.65 (m, 1H, OCH_2CH$_2$N), 3.45–3.51 (m, 2H, OCH$_2$CH_2N), 2.23 (m, 2H, alkyl-α-CH$_2$), 2.11, 2.07, 2.01, 1.99, 1.98 (je s, 3H, OAc), 1.97 (s, 6H, OAc), 1.89–1.95 (m, 4H, allyl-CH$_2$), 1.49–1.55 (m, 2H, alkyl-ß-CH$_2$), 1.18–1.32 (m, 20H, alkyl-CH$_2$), 0.85 (t, 3H, alkyl-CH$_3$).

^{13}C NMR (125 MHz, CDCl$_3$ + TMS): δ = 173.09 (C═O, Amid), 170.14, 170.10, 170.08, 169.87, 169.51, 169.34 (C═O, OAc), 131.50, 131.45 (C-olefin) 100.22 (C-1), 95.44 (C-1′), 75.41 (C-3), 71.74 (C-4), 71.17, 71.99 (C-2, C-5), 70.15 (OCH_2CH$_2$N), 69.93 (C-2′), 69.30 (C-3′), 68.41 (C-5′), 67.98 (C-4′), 62.85 (C-6), 61.45 (C-6′), 46.25 (OCH$_2$$CH_2$N), 41.37 (alkyl-$\alpha$-CH$_2$), 31.84, 29.61, 29.57, 29.53, 29.31, 29.27, 29.24 (alkyl-CH$_2$), 20.84, 29.75, 20.59, 20.54, 20.52, 20.49 (CH$_3$, OAc), 14.03 (alkyl-CH$_3$).

(N-Tetradecanoyl-2-aminoethyl) 6-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-2,3,4-tri-O-acetyl-β-D-glucopyranoside (19)

Compound **12** (3.4 g, 5 mmol) and freshly distilled tetradecanoyl chloride (1.4 mL, 1.2 g, 5 mmol) were reacted as described for compound **13**.

Yield: 3.6 g (80%). $[\alpha]_D^{20} = +48$ (c = 1.1, CHCl$_3$).

^{1}H NMR (400 MHz, CDCl$_3$ + TMS): δ = 6.07 (s, 1H, NH), 5.37 (dd, 1H, H-4′), 5.26 (dd, 1H, $^3J_{2',3'}$ 11.0, $^3J_{3',4'}$ 3.5, H-3′), 5.14 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.7, H-3), 5.08 (d, 1H, $^3J_{1',2'}$ 3.6, H-1′), 5.02 (dd, 1H, H-2′), 5.00 (dd, 1H, $^3J_{4,5}$ 9.7, H-4), 4.86 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 4.52 (d, 1H, H-1), 4.17 (ddd, 1H, $^3J_{4',5'}$ 1.3, $^3J_{5',6a'}$ 5.6, $^3J_{5',6b'}$ 6.6, H-5′), 4.05 (dd, 1H, $^3J_{6a',b'}$ 11.2, H-6a′), 4.02 (dd, 1H, H-6b′), 3.84 (m$_c$, 1H, OCH_2CH$_2$N), 3.68 (dd, 1H, $^3J_{5,6a}$ 5.0, $^3J_{6a,b}$ 11.1, H-6a), 3.55–3.66 (m, 4H, H-5, OCH_2CH_2N), 3.51 (dd, 1H, $^3J_{5,6b}$ 2.0, H-6b), 2.18 (m$_c$, alkyl-α-CH$_2$), 2.07, 2.06, 1.98, 1.97, 1.95, 1.94, 1.92 (je s, 3H, OAc), 1.42–1.50 (m, 2H, alkyl-ß-CH$_2$), 1.16–1.28 (m, 24H, alkyl-CH$_2$), 0.85 (t, 3H, alkyl-CH$_3$).

^{13}C NMR (100 MHz, CDCl$_3$ + TMS): δ = 172.89 (C═O, amide), 170.56, 170.35, 170.21, 169.87, 169.36, 169.31 (C═O, OAc), 100.56 (C-1), 96.47 (C-1′), 72.93 (C-3), 72.66 (C-5), 71.58 (C-2), 70.02 (OCH_2CH$_2$N), 69.08 (C-4), 68.09, 68.02 (C-4′, C-2′), 67.47 (C-3′), 66.48 (C-5′), 66.45 (C-6), 61.67 (C-6′), 47.05 (OCH$_2$$CH_2$N), 42.03 (alkyl-$\alpha$-CH$_2$), 36.81 (alkyl-$\beta$-CH$_2$), 31.94, 29.72, 29.66, 29.44, 29.40, 29.37, 25.90, 22.70 (alkyl-CH$_2$), 20.80, 20.71, 20.67, 20.65 (CH$_3$, OAc), 14.13 (alkyl-CH$_3$).

(N-Hexadecanoyl-2-aminoethyl) 6-O-(2, 3, 4, 6-tetra-O-acetyl-α-D-galactopyranosyl)-2,3,4-tri-O-acetyl-β-D-glucopyranoside (20)

Compound **12** (3.4 g, 5 mmol) and freshly distilled hexadecanoyl chloride (1.5 mL, 1.4 g, 5 mmol) were reacted as described for compound **13**.

Yield: 3.6 g. (79%). $[\alpha]_D^{20} = +47$ (c = 0.7, CHCl$_3$).

^{1}H NMR (400 MHz, CDCl$_3$ + TMS): δ = 6.05 (s, 1H, NH), 5.38 (dd, 1H, $^3J_{3',4'}$ 3.5, $^3J_{4',5'}$ 1.3, H-4′), 5.27 (dd, 1H, H-3′), 5.14 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.7, H-3),

5.09 (d, 1H, $^3J_{1',2'}$ 3.8, H-1′), 5.03 (dd, 1H, $^3J_{2',3'}$ 11.0, H-2′), 5.00 (dd, 1H, $^3J_{4,5}$ 9.8, H-4), 4.87 (dd, 1H, $^3J_{1,2}$ 8.2, H-2), 4.53 (d, 1H, H-1), 4.17 (ddd, 1H, $^3J_{5',6a'}$ 5.6, $^3J_{5',6b'}$ 6.6, H-5′), 4.06 (dd, 1H, $^3J_{6a',b'}$ 11.2, H-6a′), 4.01 (dd, 1H, H-6b′), 3.82 (m_c, 1H, OCH_2CH_2N), 3.68 (dd, 1H, $^3J_{5,6a}$ 5.0, $^3J_{6a,b}$ 11.4, H-6a), 3.56–3.67 (m, 4H, H-5, OCH_2CH_2N), 3.52 (dd, 1H, $^3J_{5,6b}$ 2.0, H-6b), 2.20 (m_c, alkyl-α-CH_2), 2.07, 2.06, 1.98, 1.97, 1.96, 1.93, 1.92 (je s, 3H, OAc), 1.44–1.50 (m, 2H, alkyl-ß-CH_2), 1.15–1.26 (m, 24H, alkyl-CH_2), 0.81 (t, 3H, alkyl-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$ + TMS): $\delta = 172.88$ (C═O, amide), 170.52, 170.31, 170.17, 169.83, 169.32, 169.27 (C═O, OAc), 100.52 (C-1), 96.43 (C-1′), 72.93 (C-3), 72.62 (C-5), 71.99 (O*C*H_2CH_2N), 71.34 (C-2), 69.04 (C-4), 68.05, 68.04 (C-4′, C-2′), 67.43 (C-3′), 66.44 (C-5′), 66.41 (C-6), 61.63 (C-6′), 47.11 (OCH_2*C*H_2N), 42.02 (alkyl-α-CH_2), 36.71 (alkyl-β-CH_2), 32.35, 31.90, 29.68, 29.62, 29.40, 29.23, 25.86, 22.66 (alkyl-CH_2), 20.76, 20.67, 20.63, 20.61 (CH_3, OAc), 14.09 (alkyl-CH_3).

(N-9-Z-Octadecenoyl-2-aminoethyl) 6-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-2,3,4-tri-O-acetyl-β-D-glucopyranoside (21)

Compound **12** (3.4 g, 5 mmol) and freshly distilled oleoyl chloride (1.6 mL, 1.5 g, 5 mmol) were reacted as described for compound **13**.

Yield: 3.4 g (73%). $[\alpha]_D^{20} = +50$ (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 6.04$ (s, 1H, NH), 5.32–5.40 (m, 2H, H-olefin.), 5.40 (dd, 1H, $^3J_{3',4'}$ 3.5, $^3J_{4',5'}$ 1.3, H-4′), 5.25 (dd, 1H, $^3J_{2',3'}$ 11.0, H-3′), 5.15 (dd, 1H, $^3J_{2,3}$ 9.7, $^3J_{3,4}$ 9.7, H-3), 5.09 (d, 1H, $^3J_{1',2'}$ 3.6, H-1′), 5.03 (dd, 1H, H-2′), 5.01 (dd, 1H, $^3J_{4,5}$ 9.7, H-4), 4.87 (dd, 1H, $^3J_{1,2}$ 8.1, H-2), 4.51 (d, 1H, H-1), 4.18 (ddd, 1H, $^3J_{5',6a'}$ 5.6, $^3J_{5',6b'}$ 6.6, H-5′), 4.06 (dd, 1H, $^3J_{6a',b'}$ 11.2, H-6a′), 4.03 (dd, 1H, H-6b′), 3.85 (m_c, 1H, OCH_2CH_2N), 3.69 (dd, 1H, $^3J_{5,6a}$ 5.0, $^3J_{6a,b}$ 11.1, H-6a), 3.52–3.64 (m, 4H, H-5, OCH_2CH_2N), 3.52 (dd, 1H, $^3J_{5,6b}$ 2.0, H-6b), 2.17 (m_c, alkyl-α-CH_2), 2.06, 2.05, 2.00, 1.99, 1.96, 1.95, 1.92 (je s, 3H, OAc), 1.85–1.92 (m, 4H, allyl-CH_2), 1.43–1.50 (m, 2H, alkyl-ß-CH_2), 1.17–1.29 (m, 24H, alkyl-CH_2), 0.85 (t, 3H, alkyl-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$ + TMS): $\delta = 172.88$ (C═O, amide), 170.52, 170.31, 170.17, 169.83, 169.32, 169.27 (C═O, OAc), 131.45, 131.42 (C-olefin), 100.51 (C-1), 96.48 (C-1′), 72.91 (C-3), 72.64 (C-5), 71.97 (O*C*H_2CH_2N) 71.32 (C-2), 69.08 (C-4), 68.04, 68.01 (C-4′, C-2′), 67.42 (C-3′), 66.46 (C-5′), 66.42 (C-6), 61.63 (C-6′), 47.09 (OCH_2*C*H_2N), 41.58 (alkyl-α-CH_2), 32.35, 31.90, 29.66, 29.64, 29.41, 29.24, 25.85, 22.66 (alkyl-CH_2), 20.76, 20.64, 20.63, 20.60 (CH_3, OAc), 14.12 (alkyl-CH_3).

(N-Tetradecanoyl-2-aminoethyl) 4-O-(β-D-galactopyranosyl)-β-D-glucopyranoside (22)

Compound **13** (3.0 g, 3.4 mmol) was dissolved in anhydrous methanol (50 mL) and sodium methoxide was added (pH 8–9). The solution was stirred

at ambient temperature until TLC revealed the reaction to be complete. It was neutralized then using DOWEX 50WX ion-exchange resin (protonated form), filtrated, and evaporated in vacuo. The product was recrystallized from methanol.

Yield: 1.6 g (80%). $[\alpha]_D^{20} = -6$ (c = 0.5, DMSO).

^{1}H NMR (400 MHz, pyridine-d_5): $\delta = 5.46$ (d, 1H, $^3J_{1,2}$ 8.1, H-1′), 5.24 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.82–5.00 (m, 5H, H-6a, H-2′, H-3′, H-4′, H-5′), 4.59–4.70 (m, 2H, H-6a′, H-6b′), 4.51–4.58 (m, 2H, H-5, H-6b), 4.40 (dd, 1H, $^3J_{3,4}$ 9.5, $^3J_{4,5}$ 9.5, H-4), 4.21–4.34 (m, 3H, H-2, H-3, OCH_2CH$_2$N), 3.81 (m_c, 2H, OCH$_2$CH_2N), 3.55 (m_c, 2H, alkyl-α-CH$_2$), 1.91–1.99 (m, 2H, alkyl-ß-CH$_2$), 1.51–1.60 (m, 20H, alkyl-CH$_2$), 1.20 (t, 3H, alkyl-CH$_3$).

$C_{28}H_{53}O_{12}N$ (595.3568).

Anal. Calcd. for C, 56.45; H, 8.97; N, 2.35. Found: C, 56.25; H, 8.93; N, 2.34.

(N-Hexadecanoyl-2-aminoethyl) 4-O-(β-D-galactopyranosyl)-β-D-glucopyranoside (23)[10]

Compound **14** (3.2 g, 3.5 mmol) was reacted as described for compound **22**. The product was recrystallized from methanol.

Yield: 1.8 g (82%). $[\alpha]_D^{20} = -6$ (c = 0.4, DMSO). No optical rotation value was reported in the reference.

^{1}H NMR (400 MHz, pyridine-d_5): $\delta = 5.45$ (d, 1H, $^3J_{1,2}$ 8.1, H-1′), 5.22 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.82–5.02 (m, 5H, H-6a, H-2′, H-3′, H-4′, H-5′), 4.53–4.70 (m, 2H, H-6a′, H-6b′), 4.51–4.60 (m, 2H, H-5, H-6b), 4.42 (dd, 1H, $^3J_{3,4}$ 9.5, $^3J_{4,5}$ 9.5, H-4), 4.21–4.38 (m, 3H, H-2, H-3, OCH_2CH$_2$N), 3.84 (m_c, 2H, OCH$_2$CH_2N), 3.57 (m_c, 2H, alkyl-α-CH$_2$), 1.92–2.00 (m, 2H, alkyl-ß-CH$_2$), 1.50–1.62 (m, 24H, alkyl-CH$_2$), 1.21 (t, 3H, alkyl-CH$_3$).

$C_{30}H_{57}O_{12}N$ (623.3881).

Anal. Calcd. for C, 57.77; H, 9.21; N, 2.25. Found: C, 57.85; H, 9.24; N, 2.25.

(N-9-Z-Octadecenoyl-2-aminoethyl) 4-O-(β-D-galactopyranosyl)-β-D-glucopyranoside (24)

Compound **15** (2.9 g, 3.1 mmol) was reacted as described for compound **22**. The product was purified by column chromatography (chloroform: methanol, 9:1).

Yield: 1.9 g (95%). $[\alpha]_D^{20} = -7$ (c = 0.4, MeOH).

^{1}H NMR (400 MHz, pyridine-d_5): $\delta = 5.30$–5.44 (m, 3H, H-1′, H-olefin), 5.20 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.82–5.01 (m, 5H, H-6a, H-2′, H-3′, H-4′, H-5′), 4.53–4.69 (m, 2H, H-6a′, H-6b′), 4.51–4.61 (m, 2H, H-5, H-6b), 4.41 (dd, 1H, $^3J_{3,4}$ 9.5, $^3J_{4,5}$ 9.5, H-4), 4.21–4.39 (m, 3H, H-2, H-3, OCH_2CH$_2$N), 3.83 (m_c, 2H, OCH$_2$CH_2N), 3.56 (m_c, 2H, alkyl-α-CH$_2$), 2.20–2.26 (m, 4H, allyl-CH$_2$), 1.92–2.01 (m, 2H, alkyl-ß-CH$_2$), 1.50–1.62 (m, 20H, alkyl-CH$_2$), 1.21 (t, 3H, alkyl-CH$_3$).

$C_{32}H_{59}O_{12}N$ (649.4037).

HIRES-FAB-MS: Calc: m/z = 673.3935 $[M + Na]^+$ Found: m/z = 673.3945.

(N-Tetradecanoyl-2-aminoethyl) 4-O-(α-D-glucopyranosyl)-β-D-glucopyranoside (25)

Compound **16** (3.3 g, 3.7 mmol) was reacted as described for compound **22**. The product was recrystallized from methanol.

Yield: 1.8 g (81%). $[\alpha]_D^{20} = +28$ (c = 0.7, MeOH).

^{1}H NMR (400 MHz, d_4-Methanol): $\delta = 5.18$ (d, 1H, $^3J_{1',2'}$ 3.5, H-1′), 4.34 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.02 (dd, 1H, $^3J_{5,6a}$ 2.0, $^2J_{6a,b}$ 11.9, H-6a), 3.90 (dd, 1H, $^3J_{5,6b}$ 4.5, H-6b), 3.79–3.88 (m, 2H, H-4′, H-6a′), 3.47–3.76 (m, 9H, H-3, H-4, H-3′, H-5′, H-6b′, OC*H*$_2$CH$_2$N), 3.45 (dd, 1H, $^3J_{2',3'}$ 10.2, H-2′), 3.40 (ddd, 1H, $^3J_{4,5}$ 9.7, H-5), 3.15–3.34 (m, 5H, H-2, OCH$_2$C*H*$_2$N, alkyl-α-CH$_2$), 1.58 (m_c, 2H, alkyl-β-CH$_2$), 1.21–1.41 (m, 20H, alkyl-CH$_2$), 0.88 (t, 3H, alkyl-CH$_3$).

$C_{28}H_{53}O_{12}N$ (595.3568).

Anal. Calcd. for C, 56.45; H, 8.97; N, 2.35. Found: C, 56.65; H, 9.33; N, 2.23.

(N-Hexadecanoyl-2-aminoethyl) 4-O-(α-D-glucopyranosyl)-β-D-glucopyranoside (26)

Compound **17** (3.4 g, 3.7 mmol) was reacted as described for compound **22**. The product was recrystallized from methanol.

Yield: 1.8 g (79%). $[\alpha]_D^{20} = +28$ (c = 0.6, MeOH).

^{1}H NMR (400 MHz, d_4-Methanol): $\delta = 5.20$ (d, 1H, $^3J_{1',2'}$ 3.6, H-1′), 4.31 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.03 (dd, 1H, $^3J_{5,6a}$ 2.0, $^2J_{6a,b}$ 12.0, H-6a), 3.91 (dd, 1H, $^3J_{5,6b}$ 4.6, H-6b), 3.78–3.88 (m, 2H, H-4′, H-6a′), 3.48–3.76 (m, 9H, H-3, H-4, H-3′, H-5′, H-6b′, OC*H*$_2$CH$_2$N), 3.45 (dd, 1H, $^3J_{2',3'}$ 10.1, H-2′), 3.39 (ddd, 1H, $^3J_{4,5}$ 9.7, H-5), 3.15–3.30 (m, 5H, H-2, OCH$_2$C*H*$_2$N, alkyl-α-CH$_2$), 1.61–1.71 (m, 2H, alkyl-β-CH$_2$), 1.27–1.48 (m, 24H, alkyl-CH$_2$), 0.90 (t, 3H, alkyl-CH$_3$).

$C_{30}H_{57}O_{12}N$ (623.3881).

Anal. Calcd. for C, 57.77; H, 9.21; N, 2.25. Found: C, 57.80; H, 9.25; N, 2.23.

(N-9-Z-Octadecenoyl-2-aminoethyl) 4-O-(α-D-glucopyranosyl)-β-D-glucopyranoside (27)

Compound **18** (3.0 g, 3.2 mmol) was reacted as described for compound **22**. The product was purified by column chromatography (chloroform:methanol, 9:1).

Yield: 2.0 g (94%). $[\alpha]_D^{20} = +27$ (c = 0.3, MeOH).

^{1}H NMR (500 MHz, d_4-Methanol): $\delta = 5.27–5.38$ (m, 2H, H-olefin.), 5.14 (d, 1H, $^3J_{1',2'}$ 3.6, H-1′), 4.31 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 3.88 (dd, 1H, $^3J_{5,6a}$ 2.1, $^2J_{6a,b}$ 12.2, H-6a), 3.79–3.87 (m, 3H, H-4′, H-6b, H-6a′), 3.65–3.73 (m, 2H, H-5′, H-6b′), 3.61 (m, 2H, H-3, H-3′), 3.56–3.59 (m, 2H, H-4, OC*H*$_2$CH$_2$N), 3.43–3.50

(m, H, H-2′, OCH_2CH$_2$N), 3.38 (ddd, 1H, $^3J_{4,5}$ 9.3, $^3J_{5,6b}$ 5.6, H-5), 3.25–3.32 (m, 3H, H-2, OCH$_2$CH_2N), 3.16–3.21 (m, 2H, alkyl-α-CH$_2$), 1.92–2.05 (m, 4H, allyl-CH$_2$), 1.48–1.57 (m, 2H, alkyl-β-CH$_2$), 1.16–1.41 (m, 20H, alkyl-CH$_2$), 0.88 (t, 3H, alkyl-CH$_3$).

$C_{32}H_{59}O_{12}N$ (649.4037).

HIRES-FAB-MS: Calc: m/z = 673.3935 $[M + Na]^+$ Found: m/z = 673.3938.

(N-Tetradecanoyl-2-aminoethyl) 6-O-(α-D-galactopyranosyl)-β-D-glucopyranoside (28)

Compound **19** (3.4 g, 3.8 mmol) was reacted as described for compound **22**. The product was recrystallized from methanol.

Yield: 1.8 g (81%). $[\alpha]_D^{20} = +41$ (c = 1.0, MeOH).

^{1}H NMR (400 MHz, d$_4$-MeOH): d = 4.90 (d, 1H, $^3J_{1',2'}$ 3.6, H-1′), 4.32 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.02 (dd, 1H, $^3J_{5,6a}$ 4.1, $^2J_{6a,6b}$ 11.2, H-6a), 3.91–3.96 (m, 2H, H-4′, H-5′), 3.70–3.81 (m, 6H, H-2′, H-3′, H-6a′, H-6b′, H-6b, OCH_2CH$_2$N), 3.52–3.67 (m, 3H, OCH_2CH_2N), 3.51 (ddd, 1H, $^3J_{4,5}$ 9.2, $^3J_{5,6b}$ 2.0, H-5), 3.44 (dd,1H, $^3J_{3,4}$ 9.2, H-4), 3.39 (dd, 1H, $^3J_{2,3}$ 9.2, H-3), 3.22 (dd, 1H, H-2), 2.20 (m$_c$, 2H, alkyl-α-CH$_2$), 1.61–1.71 (m, 2H, alkyl-β-CH$_2$), 1.28–1.46 (m, 24H, alkyl-CH$_2$), 0.94 (t, 3H, alkyl-CH$_3$).

$C_{28}H_{53}O_{12}N$ (595.3568).

Anal. Calcd. for C, 56.45; H, 8.97; N, 2.35. Found: C, 56.28; H, 8.90; N, 2.24.

(N-Hexadecanoyl-2-aminoethyl) 6-O-(α-D-galactopyranosyl)-β-D-glucopyranoside (29)

Compound **20** (3.4 g, 3.7 mmol) was reacted as described for compound **22**. The product was recrystallized from methanol.

Yield: 2.0 g (85%). $[\alpha]_D^{20} = +43$ (c = 1.1, MeOH).

^{1}H NMR (400 MHz, d$_4$-MeOH): d = 4.90 (d, 1H, $^3J_{1',2'}$ 3.5, H-1′), 4.31 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.03 (dd, 1H, $^3J_{5,6a}$ 4.0, $^2J_{6a,6b}$ 11.2, H-6a), 3.90–3.96 (m, 2H, H-4′, H-5′), 3.71–3.81 (m, 6H, H-2′, H-3′, H-6a′, H-6b′, H-6b, OCH_2CH$_2$N), 3.51–3.65 (m, 3H, OCH_2CH_2N), 3.49 (ddd, 1H, $^3J_{4,5}$ 9.2, $^3J_{5,6b}$ 2.0, H-5), 3.44 (dd,1H, $^3J_{3,4}$ 9.2, H-4), 3.38 (dd, 1H, $^3J_{2,3}$ 9.2, H-3), 3.22 (dd, 1H, H-2), 2.19 (m$_c$, 2H, alkyl-α-CH$_2$), 1.61–1.70 (m, 2H, alkyl-β-CH$_2$), 1.28–1.48 (m, 28H, alkyl-CH$_2$), 0.94 (t, 3H, alkyl-CH$_3$).

$C_{30}H_{57}O_{12}N$ (623.3881).

Anal. Calcd. for C, 57.77; H, 9.21; N, 2.25. Found: C, 57.72; H, 9.19; N, 2.23.

(N-9-Z-Octadecenoyl-2-aminoethyl) 6-O-(α-D-galactopyranosyl)-β-D-glucopyranoside (30)

Compound **31** (3.1 g, 3.3 mmol) was reacted as described for compound **22**. The product was purified by column chromatography (chloroform:methanol, 9:1).

Yield: 2.0 g (93%). $[\alpha]_D^{20} = +40$ (c = 0.5, MeOH).

^{1}H NMR (400 MHz, d_4-MeOH): d = 5.26–5.35 (m, 2H, H-olefin), 4.91 (d, 1H, $^3J_{1',2'}$ 3.5, H-1′), 4.32 (d, 1H, $^3J_{1,2}$ 8.1, H-1), 4.03 (dd, 1H, $^3J_{5,6a}$ 4.0, $^2J_{6a,6b}$ 11.2, H-6a), 3.91–3.98 (m, 2H, H-4′, H-5′), 3.70–3.81 (m, 6H, H-2′, H-3′, H-6a′, H-6b′, H-6b, OCH_2CH_2N), 3.52–3.67 (m, 3H, OCH_2CH_2N), 3.51 (ddd, 1H, $^3J_{4,5}$ 9.2, $^3J_{5,6b}$ 2.0, H-5), 3.45 (dd, 1H, $^3J_{3,4}$ 9.2, H-4), 3.38 (dd, 1H, $^3J_{2,3}$ 9.2, H-3), 3.22 (dd, 1H, H-2), 2.15–2.20 (m, 2H, alkyl-α-CH_2), 1.93–2.04 (m, 4H, allyl-CH_2), 1.63–1.72 (m, 2H, alkyl-β-CH_2), 1.30–1.48 (m, 28H, alkyl-CH_2), 0.94 (t, 3H, alkyl-CH_3).

$C_{32}H_{59}O_{12}N$ (649.4037).

HIRES-FAB-MS: Calc: m/z = 672.3935 $[M + Na]^+$ Found: m/z = 672.3941.

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