

Synthesis of amide-spacered dimers of ursolic and oleanolic acid

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Abstract: Transdermal therapeutic systems can release drug substances slowly and in a controlled manner from a drug depot. To provide a slow-release form of ursolic and oleanolic acid amide-spacered dimers were synthesized from the parent acids and diamines of variable chain lengths. These dimers were assayed in sulforhodamine B (SRB) assays for their cytotoxicity since as a pre-requisite for their use in slow-release forms these substances must not exert any unfavorable side-effects such as cytotoxicity. As a result of long term incubation up to 96 hours, none of these compounds showed any significant cytotoxicity in sulforhodamine B assays.

Keywords: ursolic acid; oleanolic acid; triterpenes; dimers.

1. Introduction

In recent years, the search for biologically active compounds has increasingly turned to secondary natural substances. A newly awakened interest consists in the isolation, synthesis and biological investigation of dimeric compounds. Such dimers consist of two identical monomeric basic structures, which are connected to each other by a suitable linker. Some dimers seem to hold increased biological activity as compared to the corresponding monomers ¹⁻⁵. The formation of dimers, trimers, etc... is a common phenomenon in nature to regulate, for example, the activity of proteins ⁶, especially of enzymes. The synthesis and biological investigation, however, of dimeric structures derived from triterpenes have been fairly studied ⁷⁻¹⁰. The chemistry of triterpenoid dimers started with Dolby's and Debono's dimerization ¹¹ of citronellal. Since then several dimers have been described ⁷. Of special interest are 3-amino-oleanolic acid derived dimers holding an adipinic acid-derived spacer ¹² showing some activity for the HIV-1 protease; oleanolic acid derivatives ^{13, 14} were inhibitors of the glycogen phosphorylase.

The number of dimers obtained with an incorporation of the C-28 carboxyl group remains limited probably due to its steric hindrance ¹⁵ also found for lupane derived dimers ¹⁶. Only a few dimers holding an amide spacer ^{13, 14, 16} have been described so far. These compounds were tested as enzyme inhibitors or antivirals but – by and large – no cytotoxic data have been provided for these compounds.

To surpass some problems usually associated with low solubility and to develop an application providing a slow-release of the drug, trans-dermal applications have been suggested and used quite successfully for different kinds of drugs¹⁷. Thereby, the transdermal application involves the application of ointments, creams or gels to the skin, and the active ingredients of which are absorbed by the skin. This allows them to enter the bloodstream and from there to their actual site of action. Transdermal patches, also known as "transdermal therapeutic systems" (TTS), are a frequently used method of transdermal application. They can release drug substances slowly and in a controlled manner from a drug depot. As a pre-requisite for their use, these substances must not exert any unfavorable side-effects, such as cytotoxicity.

2. Results and Discussion

Oleanolic acid (OA) and ursolic acid (UA) exert weak cytotoxicity; previous studies showed an increase in cytotoxicity upon their acetylation ¹⁸⁻²⁰. Also, OA and UA derived amides holding an additional amino group attached distally to an alkyl group (or a cyclic amine) were shown to be higher cytotoxic than their parent compounds ¹⁸⁻²³.

We became interested in the syntheses of dimeric OA and UA amides linked together by an alkyl chain of variable length. OA and UA were acetylated and 3-O-acetylated **1** ²⁴⁻²⁶ and **2** ^{27, 28} were obtained (Scheme 1). The reaction of **1** with oxalyl chloride followed by the addition of 0.5 equivalents of ethylene-diamine gave dimeric **3**.

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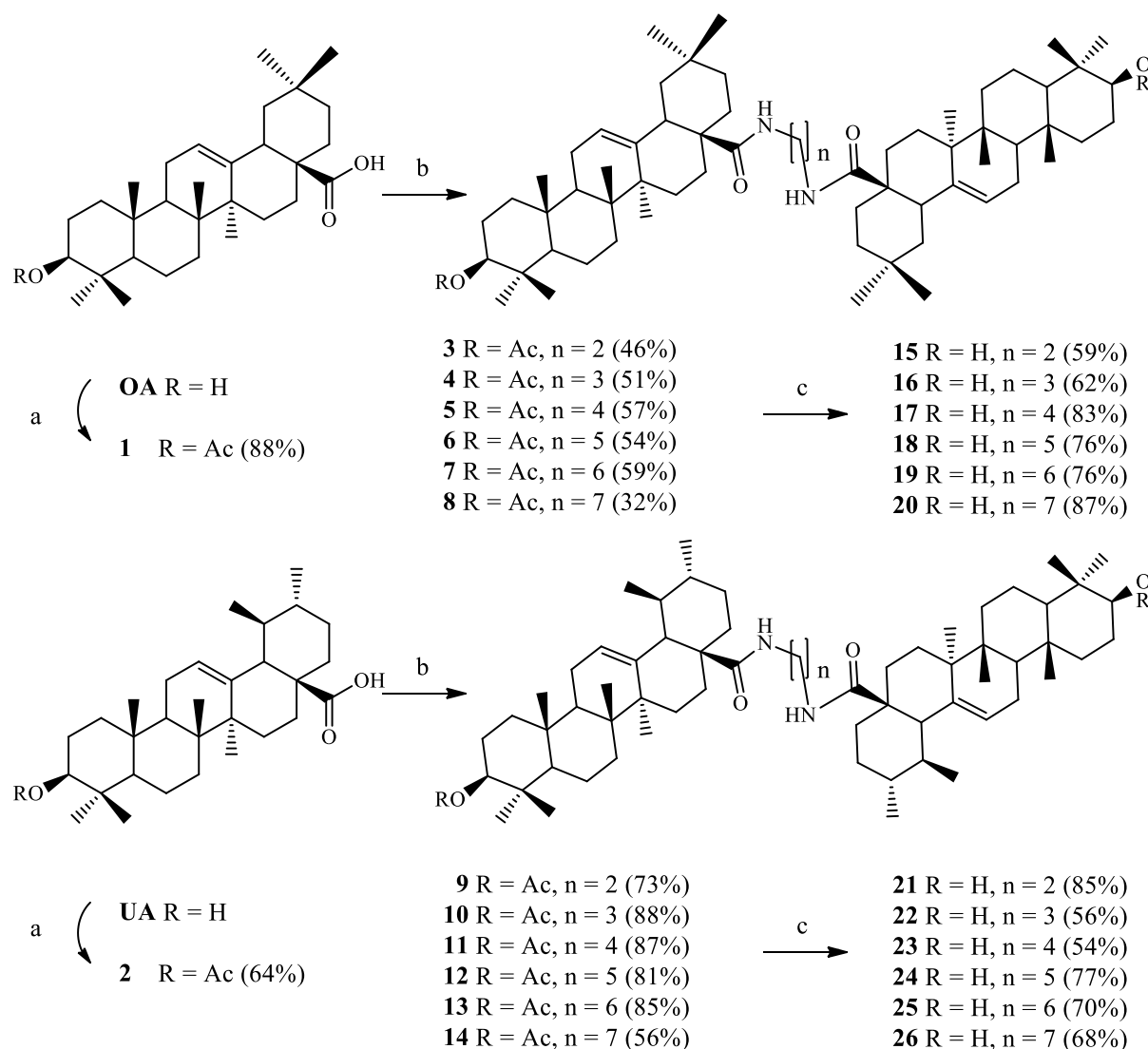
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The reaction of **1** with various diamines of variable spacer length furnished **OA** derived dimers **3-8**. Similarly, from **2**, **UA** derived dimers **9-14** were obtained in 56-88% isolated yield. Deacetylation of

3-14 gave dimers **15-26**, each holding an unprotected hydroxyl moiety at positions C-3 and C-3', respectively.



Scheme 1. a) Acetic anhydride, pyridine, cat. DMAP, stirring at 25 °C, 1 day; b) i. oxalyl chloride, triethylamine, dichloromethane, cat. DMF, stirring at 25 °C, 2 h, ii. DCM, 1,n-diamine, stirring at 25 °C, 2 h; c) KOH, MeOH, microwaves, $\lambda = 365$ nm, 100 °C, 5 min.

All of the dimers were screened for their cytotoxic activity in sulforhodamine assays (SRB), but none of these compounds showed any significant cytotoxicity ($EC_{50} > 30 \mu\text{M}$ cut-off) when tested with several human tumor cell lines (A375, HT29, SW1736, MCF7, A2780, FaDu, A549) as well with non-malignant mouse fibroblasts (NIH 3T3). No cytotoxic effect was observed even upon applying a prolonged incubation time of 96 hours. Presently, the skin penetration and the stability of these dimers as well as they're *in vivo* degradation is studied in more detail in our laboratories.

3. Conclusion

A slow-release form of ursolic and oleanolic acid, amide-spacered dimers were synthesized from the parent acids and diamines of variable chain lengths. These dimers were assayed in SRB assays; even upon long term incubation up to 96 hours, none of these compounds showed any significant cytotoxicity in sulforhodamine B assays.

4. Experimental

NMR spectra were recorded using the Varian spectrometers Gemini 2000 or Unity 500 (δ given in ppm, J in Hz; typical experiments: H-H-COSY, HMBC, HSQC, NOESY; Fig. 1 shows the numbering scheme as well as key HMBC correlations), MS

spectra were taken on a Finnigan MAT LCQ 7000 (electrospray, voltage 4.1 kV, sheath gas nitrogen) instrument. The optical rotations were measured on a Perkin-Elmer polarimeter at 20 °C; TLC was performed on silica gel (Merck 5554, detection with cerium molybdate reagent); melting points are uncorrected (*Leica* hot stage microscope or *BÜCHI* Melting Point M-565), and elemental analyses were performed on a Foss-Heraeus Vario EL (CHNS) unit.

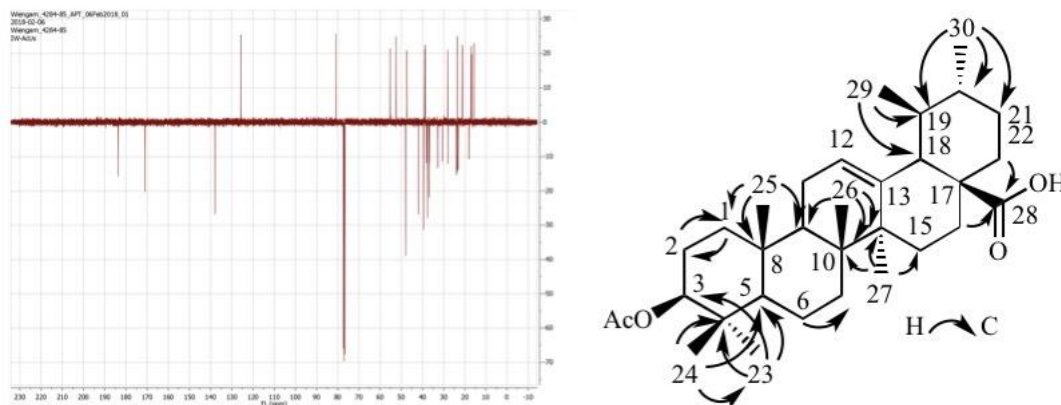


Figure 1. A typical ^{13}C APT-NMR spectrum of **2**, numbering scheme and key HMBC correlations.

(3 β) 3-Acetyloxy-olean-12-en-28-oic acid (**1**)

Acetylation of **OA** (5.0 g, 0.01 mol) with acetic anhydride (3.11 mL, 0.03 mol) in dry pyridine (50 mL) in the presence of a catal. amount of DMAP for 1 day at 25 °C followed by usual aqueous work-up and column chromatography (silica gel, *n*-hexane/ethyl acetate, 8:2) gave **1** (4.4 g, 88; R_F = 0.7 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); m.p.: 263–265 °C (lit.:²⁹ 260–261 °C); $[\alpha]_D = +117.7^\circ$ (*c* 0.37, CHCl_3), (lit.:³⁰ +119° (*c* 0.1, CHCl_3); MS (ESI, MeOH): m/z = 497.5 (75 %, $[\text{M}-\text{H}]^-$), 995.2 (100 %, $[\text{2M}-\text{H}]^-$), 1017.7 (29 %, $[\text{2M}-\text{2H}+\text{Na}]^-$).

(3 β) 3-Acetyloxy-urs-12-en-28-oic acid (**2**)

Following the procedure given for the synthesis of **1**, from **UA** compound **2** (3.5 g, 64%) was obtained; R_F = 0.7 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); m.p.: 242–244 °C (lit.:³¹ 242.7–244.1 °C); $[\alpha]_D = +69.89^\circ$ (*c* 0.86, CHCl_3), (lit.:³¹ +71.2° (*c* 1.0, CHCl_3); MS (ESI, MeOH): m/z = 497.5 (64 %, $[\text{M}-\text{H}]^-$), 542.9 (30 %, $[\text{M}+\text{HCO}_2]^-$), 995.1 (68 %, $[\text{2M}-\text{H}]^-$), 1017.5 (100 %, $[\text{2M}-\text{2H}+\text{Na}]^-$).

General procedure for the synthesis of the dimers

To a solution of **1** or **2** (0.37 mmol) in dry DCM (abs., 30 mL) at 0 °C oxalyl chloride (1.2 mmol), triethylamine (1.2 mmol) and DMF (2 drops) were slowly added, and the mixture was allowed to react at 25 °C for 2 h. The volatiles were removed under reduced pressure, the residue was dissolved in dry DCM (5 mL), and the amine (0.18 mmol) and catalyst amounts of DMAP were added. After stirring at 25 °C

IR spectra were recorded on a Perkin Elmer FT-IR spectrometer Spectrum 1000 or a Perkin-Elmer Spectrum Two (UATR Two Unit). The solvents were dried according to usual procedures. The purity of the compounds was determined by HPLC and found to be >96%. Ursolic (**UA**), oleanolic (**OA**) acid were obtained from different commercial suppliers in bulk quantities. All compounds were obtained as colorless solids.

for 1 h, usual aqueous workup followed by column chromatography gave dimeric **3–14**.

General procedure for deacetylation

To a solution of compound **3–14**, (1 equiv) in dry MeOH (5 mL) powdered KOH (20 equiv) was added, and the mixture was stirred at 100 °C (microwave irradiation, \square = 365 nm) for 5 min. Usual aqueous workup followed by column chromatography furnished products **15–26**; respectively.

N¹, **N**²-Bis-[(3 β)-3-acetyloxy-olean-12-en-28-oyl]-1,2-diaminoethane (**3**)

Compound **3** (0.17 g, 46%) showed: m.p. 240–242 °C; R_F = 0.7 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +49.56^\circ$ (*c* 0.32, CHCl_3);

IR (KBr): ν = 3424 br , 2948 m , 2878 m , 1736 s , 1638 m , 1524 m , 1466 m , 1368 m , 1246 m , 1212 w , 1186 w , 1148 w , 1096 w , 1028 m , 1008 m , 986 m cm^{-1} ;

^1H NMR (500 MHz, CDCl_3): δ = 6.47 (*s*, 2H, 2 x NH), 5.39 (*t*, J = 3.5 Hz, 2H, 2 x 12-H), 4.52–4.46 (*m*, 2H, 2 x 3-H), 3.50–3.40 (*m*, 2H, 2 x 33-H), 3.11 (*td*, 2H, 2 x 33-H), 2.54 (*dd*, J = 13.1, 4.0 Hz, 2H, 2 x 18-H), 2.04 (*s*, 6H, 2 x 32-H), 2.00 (*dd*, J = 13.8 Hz, 4.0 Hz, 2H, 2 x 16-H), 1.96–1.89 (*m*, 2H, 2 x 11-H), 1.72–1.55 (*m*, 18H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H), 1.53–1.49 (*m*, 2H, 2 x 15-H), 1.47–1.40 (*m*, 2H, 2 x 22-H), 1.40–1.26 (*dd*, J = 12.5, 3.3 Hz, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.25 (*dd*, J = 10.1, 2.2 Hz, 2H, 2 x 22-H), 1.19 (*d*, J = 3.9 Hz, 4H, 2 x 19-H + 2 x 21-H), 1.15 (*s*, 6H, 2 x 27-H) 1.02 (*dd*, J = 10.6, 3.3 Hz, 4H, 2 x 1-H + 2 x 15-H), 0.93 (*s*, 6H, 2 x 25-H), 0.90 (*s*, 6H, 2 x 29-H), 0.89 (*s*, 6H, 2 x 30-H), 0.86 (*s*, 6H,

2 x 23-H), 0.85 (s, 6H, 2 x 26-H), 0.82 (s, 2H, 2 x 5-H), 0.74 (s, 6H, 2 x 24-H);

^{13}C NMR (125 MHz, CDCl_3): δ = 179.3 (2 x C-28), 170.9 (2 x C-28), 144.5 (2 x C-13), 122.9 (2 x C-12), 80.8 (2 x C-3), 55.19 (2 x C-5), 47.5 (2 x C-9), 46.6 (2 x C-17), 46.2 (2 x C-19), 41.9 (2 x C-18), 41.9 (2 x C-14), 39.9 (2 x C-33), 39.4 (2 x C-8), 38.1 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.8 (2 x C-7), 32.2 (2 x C-22), 30.6 (2 x C-20), 28.0 (2 x C-23), 27.3 (2 x C-15), 25.7 (2 x C-27), 23.6 (2 x C-11), 23.5 (2 x C-30), 23.5 (2 x C-2), 23.5 (2 x C-16), 21.2 (2 x C-32), 18.1 (2 x C-6), 16.8 (2 x C-24), 16.6 (2 x C-26), 15.4 (2 x C-25) ppm;

MS (ESI, MeOH): m/z = 1021.7 (50 %, $[\text{M}+\text{H}]^+$), 1043.8 (100 %, $[\text{M}+\text{Na}]^+$);

analysis calcd for $\text{C}_{66}\text{H}_{104}\text{N}_2\text{O}_6$ (1021.54): C 77.60, H 10.26, N 2.74; found: C 77.41, H 10.45, N 2.49.

N^1 , N^3 -Bis-[(β)-3-acetyloxy-olean-12-en-28-oyl]-1,3-diaminopropane (4)

Compound **4** (0.18g, 51%) showed: m.p. 204–206°C; R_F = 0.5 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D$ = +52.27° (c 0.32, CHCl_3);

IR (KBr): ν = 3337br, 2945m, 2863w, 1736m, 1635m, 1526m, 1433m, 1365m, 1244s, 1026m cm^{-1} ;

^1H NMR (500 MHz, CDCl_3): δ = 6.42 (t, J = 5.9 Hz, 2H, 2 x NH), 5.40 (t, J = 3.3 Hz, 2H, 2 x 12-H), 4.48 (dd, J = 10.0, 5.9 Hz, 2H, 2 x 3-H), 3.25 (dq, J = 12.9, 6.5 Hz, 2H, 2 x 33-H), 3.11 (dq, J = 12.3, 6.0 Hz, 2H, 2 x 33-H), 2.64 (dd, J = 13.0, 3.1 Hz, 2H, 2 x 18-H), 2.04 (s, 6H, 2 x 32-H), 1.97 (td, J = 13.6, 3.5 Hz, 2H, 2 x 16-H), 1.92–1.87 (m, 2H, 2 x 11-H), 1.78–1.55 (m, 20H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H + 2 x 34-H), 1.52–1.49 (m, 2H, 2 x 15-H), 1.44 (dd, J = 12.6, 3.5 Hz, 2H, 2 x 22-H), 1.35 (qd, J = 14.0, 13.0, 3.5 Hz, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.26 (d, J = 13.1 Hz, 2H, 2 x 22-H), 1.21–1.15 (m, 4H, 2 x 19-H + 2 x 21-H), 1.14 (s, 6H, 2 x 27-H), 1.06–1.00 (m, 4H, 2 x 1-H + 2 x 15-H), 0.92 (s, 6H, 2 x 25-H), 0.91 (s, 6H, 2 x 29-H), 0.90 (s, 6H, 2 x 30-H), 0.86 (s, 6H, 2 x 23-H), 0.84 (s, 6H, 2 x 26-H), 0.82 (s, 2H, 2 x 5-H), 0.74 (s, 6H, 2 x 24-H) ppm;

^{13}C NMR (125 MHz, CDCl_3): δ = 178.5 (2 x C-28), 170.9 (2 x C-28), 144.6 (2 x C-13), 122.6 (2 x C-12), 80.8 (2 x C-3), 55.1 (2 x C-5), 47.4 (2 x C-9), 46.6 (2 x C-17), 46.2 (2 x C-19), 41.95 (2 x C-18), 41.8 (2 x C-14), 39.3 (2 x C-8), 38.1 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 36.0 (2 x C-33), 34.2 (2 x C-21), 33.0 (2 x C-29), 32.9 (2 x C-7), 32.3 (2 x C-22), 30.7 (2 x C-20), 29.7 (C-34), 28.0 (2 x C-23), 27.3 (2 x C-15), 25.7 (2 x C-27), 23.6 (2 x C-11), 23.6 (2 x C-30), 23.5 (2 x C-2), 23.4 (2 x C-16), 21.2 (2 x C-32), 18.1 (2 x C-6), 16.9 (2 x C-24), 16.6 (2 x C-26), 15.4 (2 x C-25) ppm;

MS (ESI, MeOH): m/z = 1035.7 (86 %, $[\text{M}+\text{H}]^+$), 1057.8 (100 % $[\text{M}+\text{Na}]^+$);

analysis calcd for $\text{C}_{67}\text{H}_{106}\text{N}_2\text{O}_6$ (1035.57): C 77.71, H 10.32, N 2.71; found: C 77.50, H 10.46, N 2.42.

N^1 , N^4 -Bis-[(β)-3-acetyloxy-olean-12-en-28-oyl]-1,4-diaminobutane (5)

Compound **5** (0.21g, 57%) showed: m.p. 180–186°C; R_F = 0.5 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D$ = +46.94° (c 0.37, CHCl_3);

IR (KBr): ν = 3398br, 2950m, 2874m, 1736s, 1644m, 1522m, 1466m, 1366w, 1246s, 1212w, 1148w, 1048w, 1098m, 1006w cm^{-1} ;

^1H NMR (500 MHz, CDCl_3): δ = 6.04 (s, 2H, 2 x NH), 5.38 (t, J = 3.6 Hz, 2H, 2 x 12-H), 4.52–4.47 (m, 2H, 2 x 3-H), 3.36 (dq, J = 13.0, 6.6 Hz, 2H, 2 x 33-H), 3.04 (dq, J = 11.3, 6.3 Hz, 2H, 2 x 33-H), 2.54 (dd, J = 13.0, 4.0 Hz, 2H, 2 x 18-H), 2.06 (s, 6H, 2 x 32-H), 1.97 (d, J = 3.6 Hz, 2H 2 x 16-H), 1.92 (dd, J = 8.8, 3.2 Hz, 2H, 2 x 11-H), 1.81–1.51 (m, 22H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H + 2 x 34-H), 1.48 (dt, J = 6.5, 3.4 Hz, 2H, 2 x 15-H), 1.43 (s, 2H, 2 x 22-H), 1.41–1.35 (m, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.30–1.25 (m, 2H 2 x 22-H), 1.23–1.19 (m, 4H, 2 x 19-H + 2 x 21-H), 1.16 (s, 6H 2 x 27-H), 1.06 (s, 4H, 2 x 1-H + 2 x 15-H), 0.97 (d, J = 6.6 Hz, 6H, 2 x 25-H), 0.95 (s, 6H 2 x 29-H), 0.91 (s, 6H 2 x 30-H), 0.88 (s, 6H, 2 x 23-H), 0.87 (s, 6H 2 x 26-H), 0.86–0.82 (m, 2H, 2 x 5-H), 0.76 (s, 6H 2 x 24-H) ppm;

^{13}C NMR (125 MHz, CDCl_3): δ = 178.2 (2 x C-28), 170.9 (2 x C-28), 145.0 (2 x C-13), 122.6 (2 x C-12), 80.8 (2 x C-3), 55.1 (2 x C-5), 47.4 (2 x C-9), 46.7 (2 x C-17), 46.2 (2 x C-19), 42.2 (2 x C-18), 42.0 (2 x C-14), 39.3 (2 x C-8), 38.9 (2 x C-33), 38.1 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.6 (2 x C-7), 32.3 (2 x C-22), 30.7 (2 x C-20), 28.0 (2 x C-23), 27.2 (2 x C-15), 26.9 (2 x C-34), 25.6 (2 x C-27), 23.7 (2 x C-11), 23.6 (2 x C-30), 23.5 (2 x C-2), 23.4 (2 x C-16), 21.2 (2 x C-32), 18.1 (2 x C-6), 16.9 (2 x C-24), 16.6 (2 x C-26), 15.4 (2 x C-25) ppm;

MS (ESI, MeOH): m/z = 1049.7 (78 %, $[\text{M}+\text{H}]^+$), 1071.7 (100 %, $[\text{M}+\text{Na}]^+$);

analysis calcd for $\text{C}_{68}\text{H}_{108}\text{N}_2\text{O}_6$ (1049.60): C 77.81, H 10.37, N 2.67; found: C 77.62, H 10.53, N 2.55.

N^1 , N^5 -Bis-[(β)-3-acetyloxy-olean-12-en-28-oyl]-1,5-diaminopentane (6)

Compound **6** (0.21g, 54%) showed: m.p. 175°C; R_F = 0.5 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D$ = +47.07° (c 0.333, CHCl_3);

IR (KBr): ν = 3426br, 2946s, 2876m, 1735s, 1641m, 1522m, 14465m, 1366m, 1245s, 1212w, 1148w, 1096w, 1027m, 1006m, 986m, 970w cm^{-1} ;

^1H NMR (500 MHz, CDCl_3): δ = 5.91 (s, 2H, 2 x NH), 5.37 (t, J = 3.6 Hz, 2H, 2 x 12-H), 4.49 (dd, J = 10.3, 5.7 Hz, 2H, 2 x 3-H), 3.34 (dq, J = 13.8, 7.1 Hz, 2H, 2 x 33-H), 3.03–2.93 (m, 2H, 2 x 33-H), 2.50 (dd, J = 13.2, 4.0 Hz, 2H, 2 x 18-H), 2.05 (s, 6H, 2 x 32-H), 1.98 (d, J = 3.8 Hz, 2H, 2 x 16-H), 1.92 (dt, J = 8.8, 4.8 Hz, 2H, 2 x 11-H), 1.81–1.51 (m, 26H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H +

2 x 16-H + 2 x 19-H + 2 x 34-H + 2 x 35-H), 1.48 (*q*, $J = 7.0, 6.1$ Hz, 2H, 2 x 15-H), 1.45–1.40 (*m*, 2H, 2 x 22-H), 1.36 (*ddd*, $J = 17.6, 8.2, 4.3$ Hz, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.33–1.24 (*m*, 2H, 2 x 22-H), 1.22–1.17 (*m*, 4H, 2 x 19-H + 2 x 21-H), 1.16 (*s*, 6H, 2 x 27-H), 1.12–1.00 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.94 (*s*, 6H, 2 x 25-H), 0.90 (*s*, 6H, 2 x 29-H), 0.90 (*s*, 6H, 2 x 30-H), 0.87 (*s*, 6H, 2 x 23-H), 0.86 (*s*, 6H, 2 x 26-H), 0.83 (*m*, 2H, 2 x 5-H), 0.76 (*s*, 6H, 2 x 24-H) ppm;

^{13}C NMR (125 MHz, CDCl_3): $\delta = 178.2$ (2 x C-28), 170.9 (2 x C-28), 145.1 (2 x C-13), 122.6 (2 x C-12), 80.7 (2 x C-3), 55.1 (2 x C-5), 47.4 (2 x C-9), 46.7 (2 x C-17), 46.2 (2 x C-19), 42.3 (2 x C-18), 42.0 (2 x C-14), 39.3 (2 x C-8), 39.3 (2 x C-33), 38.1 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.5 (2 x C-7), 32.3 (2 x C-22), 30.7 (2 x C-20), 29.1 (2 x C-34), 28.0 (2 x C-23), 27.2 (2 x C-27), 25.6 (2 x C-15), 24.6 (C-35), 23.7 (2 x C-11), 23.6 (2 x C-30), 23.5 (2 x C-2), 23.5 (2 x C-16), 21.2 (2 x C-32), 18.1 (2 x C-6), 16.9 (2 x C-24), 16.6 (2 x C-26), 15.4 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 1063.7$ (100 %, $[\text{M}+\text{H}]^+$), 1085.7 (80 %, $[\text{M}+\text{Na}]^+$);

analysis calcd for $\text{C}_{69}\text{H}_{110}\text{N}_2\text{O}_6$ (1063.62): C 77.92, H 10.42, N 2.63; found: C 77.67, H 10.69, N 2.47.

N^1, N^6 -Bis-[(3 β)-3-acetyloxy-olean-12-en-28-oyl]-1,6-diaminohexane (7)

Compound **7** (0.23g, 54%) showed: m.p. 188–190°C (lit.: ^{13, 14} 191–192 °C); $R_F = 0.4$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +47.07^\circ$ (*c* 0.333, CHCl_3);

IR (KBr): $\nu = 3427br, 2946s, 2876m, 1736s, 1654m, 1522m, 1466m, 1368m, 1246s, 1212w, 1148w, 1096w, 1028m, 1008m, 986m$ cm^{-1} ;

^1H NMR (500 MHz, CDCl_3): $\delta = 6.41$ (*t*, $J = 6.0$ Hz, 2H, 2 x NH), 5.40 (*t*, $J = 3.3$ Hz, 2H, 2 x 12-H), 4.49 (*dd*, $J = 9.7, 6.2$ Hz, 2H, 2 x 3-H), 3.26 (*dq*, $J = 12.9, 6.4$ Hz, 2H, 2 x 33-H), 3.12 (*dq*, $J = 12.4, 6.0$ Hz, 2H, 2 x 33-H), 2.64 (*dd*, $J = 13.3, 4.6$ Hz, 2H, 2 x 18-H), 2.04 (*s*, 6H, 2 x 32-H), 1.98 (*td*, $J = 13.7, 3.7$ Hz, 2H, 2 x 16-H), 1.93–1.87 (*m*, 2H, 2 x 11-H), 1.79–1.48 (*m*, 30H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H + 2 x 34-H + 2 x 35-H), 1.46 (*d*, $J = 2.7$ Hz, 2H, 2 x 15-H), 1.43 (*d*, $J = 3.0$ Hz, 2H, 2 x 22-H), 1.42–1.33 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.29 (*dd*, $J = 18.6, 7.7$ Hz, 2H, 2 x 22-H), 1.20 (*d*, $J = 2.4$ Hz, 4H, 2 x 19-H + 2 x 21-H), 1.16 (*s*, 6H, 2 x 27-H), 1.10–0.99 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.92 (*s*, 6H, 2 x 25-H), 0.91 (*s*, 6H, 2 x 29-H), 0.90 (*s*, 6H, 2 x 30-H), 0.86 (*s*, 6H, 2 x 23-H), 0.85 (*s*, 6H, 2 x 26-H), 0.82 (*s*, 2H, 2 x 5-H), 0.74 (*s*, 6H, 2 x 24-H) ppm;

^{13}C NMR (125 MHz, CDCl_3): $\delta = 178.1$ (2 x C-28), 170.9 (2 x C-28), 145.1 (2 x C-13), 122.5 (2 x C-12), 80.7 (2 x C-3), 55.1 (2 x C-5), 47.4 (2 x C-9), 46.7 (2 x C-17), 46.2 (2 x C-19), 42.3 (2 x C-18), 42.0 (2 x C-14), 39.3 (2 x C-8), 39.2 (2 x C-33), 38.1 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.5 (2 x C-7), 32.3 (2 x C-22), 30.7 (2 x

C-20), 29.2 (2 x C-34), 28.0 (2 x C-23), 27.2 (2 x C-27), 26.6 (2 x C-15), 25.6 (2 x C-35), 23.7 (2 x C-11), 23.6 (2 x C-30), 23.5 (2 x C-2), 23.4 (2 x C-16), 21.2 (2 x C-32), 18.1 (2 x C-6), 16.9 (2 x C-24), 16.6 (2 x C-26), 15.4 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 558.6$ (5 %, $[\text{M}+\text{Ca}]^{2+}$), 1077.7 (100 %, $[\text{M}+\text{H}]^+$), 1099.9 (65 %, $[\text{M}+\text{Na}]^+$); analysis calcd for $\text{C}_{70}\text{H}_{112}\text{N}_2\text{O}_6$ (1077.65): C 78.02, H 10.48, N 2.60; found: C 77.76, H 10.61, N 2.44.

N^1, N^7 -Bis-[(3 β)-3-acetyloxy-olean-12-en-28-oyl]-1,7-diaminoheptane (8)

Compound **8** (0.12g, 32%) showed: m.p. 166°C; $R_F = 0.4$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +47.82^\circ$ (*c* 0.31, CHCl_3);

IR (KBr): $\nu = 3426br, 2944s, 2876m, 1734s, 1640m, 1524m, 1466m, 1370m, 1248s, 1212w, 1148w, 1096w, 1028m, 1008m, 986m$ cm^{-1} ;

^1H NMR (400 MHz, CDCl_3): $\delta = 5.90$ (*t*, $J = 5.3$ Hz, 2H, 2 x NH), 5.36 (*t*, $J = 3.4$ Hz, 2H, 2 x 12-H), 4.49 (*dd*, $J = 9.6, 6.3$ Hz, 2H, 2 x 3-H), 3.34 (*dq*, $J = 13.6, 7.1$ Hz, 2H, 2 x 33-H), 3.03–2.93 (*m*, 2H, 2 x 33-H), 2.49 (*dd*, $J = 12.8, 3.5$ Hz, 2H, 2 x 18-H), 2.04 (*s*, 6H, 2 x 32-H), 1.97 (*dd*, $J = 13.7, 3.6$ Hz, 2H, 2 x 16-H), 1.91 (*dd*, $J = 8.6, 3.3$ Hz, 2H, 2 x 11-H), 1.81–1.50 (*m*, 32H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H + 2 x 34-H + 2 x 35-H + 36-H), 1.45 (*dd*, $J = 12.8, 5.9$ Hz, 2H, 2 x 15-H), 1.39 (*m*, 2H, 2 x 22-H), 1.35 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.28 (*dd*, $J = 12.9, 8.0$ Hz, 2H, 2 x 22-H), 1.19 (*d*, $J = 6.3$ Hz, 4H, 2 x 19-H + 2 x 21-H), 1.15 (*s*, 6H, 2 x 27-H), 1.04 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.94 (*s*, 6H, 2 x 25-H), 0.90 (*s*, 6H, 2 x 29-H), 0.90 (*s*, 6H, 2 x 30-H), 0.87 (*s*, 6H, 2 x 23-H), 0.85 (*s*, 6H, 2 x 26-H), 0.82 (*s*, 2H, 2 x 5-H), 0.76 (*s*, 6H, 2 x 24-H) ppm;

^{13}C NMR (125 MHz, CDCl_3): $\delta = 178.0$ (2 x C-28), 170.9 (2 x C-28), 145.1 (2 x C-13), 122.5 (2 x C-12), 80.8 (2 x C-3), 55.1 (2 x C-5), 47.4 (2 x C-9), 46.7 (2 x C-17), 46.2 (2 x C-19), 42.3 (2 x C-18), 42.1 (2 x C-14), 39.3 (2 x C-8), 39.2 (2 x C-33), 38.1 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.5 (2 x C-7), 32.3 (2 x C-22), 30.7 (2 x C-20), 29.3 (2 x C-34), 28.9 (C-36), 28.0 (2 x C-23), 27.2 (2 x C-27), 27.0 (2 x C-15), 25.6 (2 x C-35), 23.7 (2 x C-11), 23.5 (2 x C-30), 23.5 (2 x C-2), 23.4 (2 x C-16), 21.2 (2 x C-32), 18.1 (2 x C-6), 16.9 (2 x C-24), 16.6 (2 x C-26), 15.4 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 1092.9$ (20 %, $[\text{M}+\text{H}]^+$), 1114.8 (100 %, $[\text{M}+\text{Na}]^+$);

analysis calcd for $\text{C}_{71}\text{H}_{114}\text{N}_2\text{O}_6$ (1091.68): C 78.11, H 10.53, N 2.57; found: C 77.94, H 10.61, N 2.36.

N^1, N^2 -Bis-[(3 β)-3-acetyloxy-urs-12-en-28-oyl]-1,2-diaminoethane (9)

Compound **9** (0.28g, 73%) showed: m.p. 218°C; $R_F = 0.5$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +43.5^\circ$ (*c* 0.34, CHCl_3);

IR (KBr): $\nu = 3420br, 2948s, 2872m, 1736s, 1646m, 1522m, 1466m, 1456m, 1390m, 1370m, 1246s, 1146w, 1092w, 1028m, 1006w \text{ cm}^{-1}$;

^1H NMR (400 MHz, CDCl_3): $\delta = 6.50$ (*m*, 2H, 2 x NH), 5.36 (*t*, $J = 3.4$ Hz, 2H, 2 x 12-H), 4.49 (*dd*, $J = 9.7, 6.1$ Hz, 2H, 2 x 3-H), 3.46 (*d*, $J = 9.0$ Hz, 2H, 2 x 33-H), 3.08 (*d*, $J = 8.7$ Hz, 2H, 2 x 33-H), 2.04 (*s*, 6H, 2 x 32-H), 1.99 (*d*, $J = 4.1$ Hz, 2H, 2 x 16-H), 1.95 (*dd*, $J = 7.6, 3.4$ Hz, 2H, 2 x 11-H), 1.90 (*m*, 2H, 2 x 18-H), 1.89–1.82 (*m*, 2H, 2 x 22-H), 1.75–1.60 (*m*, 12H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H), 1.52 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.47–1.40 (*m*, 6H, 2 x 21-H + 2 x 22-H + (2 x 19-H)), 1.41–1.24 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.08 (*s*, 6H, 2 x 27-H), 1.07–1.01 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.95 (*s*, 6H, 2 x 30-H), 0.94 (*s*, 6H, 2 x 25-H), 0.88 (*s*, 6H, 2 x 24-H), 0.86 (*s*, 6H, 2 x 23-H), 0.85 (*s*, 6H, 2 x 26-H), 0.82 (*m*, 2H, 2 x 5-H), 0.75 (*s*, 6H, 2 x 29-H) ppm;

^{13}C NMR (100 MHz, CDCl_3): $\delta = 179.3$ (2 x C-28), 170.9 (2 x C-28), 139.3 (2 x C-13), 125.8 (2 x C-12), 80.8 (2 x C-3), 55.2 (2 x C-5), 53.4 (2 x C-18), 47.6 (2 x C-17), 47.4 (2 x C-9), 42.3 (2 x C-14), 39.8 (C-33), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.0 (2 x C-20), 38.2 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 36.7 (2 x C-22), 32.5 (2 x C-7), 30.8 (2 x C-21), 28.0 (2 x C-23), 27.8 (2 x C-15), 24.7 (2 x C-16), 23.5 (2 x C-27), 23.3 (2 x C-2), 21.2 (2 x C-32), 21.1 (2 x C-30), 18.1 (2 x C-6), 17.2 (2 x C-24), 16.8 (2 x C-29), 16.7 (2 x C-26), 15.5 (2 x C-25) ppm;
MS (ESI, MeOH): $m/z = 530.5$ (10 %, $[\text{M}+\text{Ca}]^{2+}$), 1021.7 (100 %, $[\text{M}+\text{H}]^+$), 1043.8 (80 %, $[\text{M}+\text{Na}]^+$); analysis calcd for $\text{C}_{66}\text{H}_{104}\text{N}_2\text{O}_6$ (1021.54): C 77.60, H 10.26, N 2.74; found: C 77.45, H 10.41, N 2.51.

N^1, N^3 -Bis-[(3 β)-3-acetyloxy-urs-12-en-28-oyl]-1,3-diaminopropane (10)

Compound **10** (0.33g, 88%) showed: m.p. 206°C; $R_F = 0.5$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +30.34^\circ$ (*c* 0.31, CHCl_3);

IR (KBr): $\nu = 3393br, 2939m, 2860m, 1735s, 1645m, 1517m, 1454m, 1369m, 1246s, 1146w, 1092w, 1028m, 1006w \text{ cm}^{-1}$;

^1H NMR (500 MHz, CDCl_3): $\delta = 6.36$ (*t*, $J = 5.4$ Hz, 2H, 2 x NH), 5.35 (*t*, $J = 3.5$ Hz, 2H, 2 x 12-H), 4.49 (*dd*, $J = 10.5, 5.3$ Hz, 2H, 2 x 3-H), 3.24 (*dq*, $J = 13.1, 6.6$ Hz, 2H, 2 x 33-H), 3.09 (*dq*, $J = 11.8, 5.8$ Hz, 2H, 2 x 33-H), 2.04 (*s*, 6H, 2 x 32-H), 1.99 (*d*, $J = 3.9$ Hz, 2H, 2 x 16-H), 1.94 (*ddd*, $J = 17.8, 10.4, 2.7$ Hz, 2H, 2 x 11-H), 1.88 (*m*, 2H, 2 x 18-H), 1.87–1.82 (*m*, 2H, 2 x 22-H), 1.76–1.52 (*m*, 14H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H), 1.49 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.48–1.40 (*m*, 6H, 2 x 21-H + 2 x 22-H + (2 x 19-H)), 1.37–1.26 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.05 (*s*, 6H, 2 x 27-H), 1.07–1.01 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.95 (*s*, 6H, 2 x 30-H), 0.93 (*s*, 6H, 2 x 25-H), 0.88 (*s*, 6H, 2 x 24-H), 0.87 (*s*, 6H, 2 x 23-H), 0.86 (*s*, 6H, 2 x 26-H), 0.82 (*s*, 2H, 2 x 5-H), 0.76 (*s*, 6H, 2 x 29-H) ppm;

^{13}C NMR (125 MHz, CDCl_3): $\delta = 178.5$ (2 x C-28), 170.9 (2 x C-28), 139.4 (2 x C-13), 125.6 (2 x C-12), 80.8 (2 x C-3), 55.2, (2 x C-5), 53.5 (2 x C-18), 47.7 (2 x C-17), 47.4 (2 x C-9), 42.3 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 38.9 (2 x C-20), 38.3 (2 x C-1), 37.6 (2 x C-4), 37.4 (2 x C-10), 36.8 (2 x C-22), 36.3 (C-33), 32.7 (2 x C-7), 30.9 (2 x C-21), 29.6 (C-34), 28.0 (2 x C-23), 27.8 (2 x C-15), 24.8 (2 x C-16), 23.4 (2 x C-2), 23.2 (2 x C-27), 21.2 (2 x C-32), 21.1 (2 x C-30), 18.1 (2 x C-6), 17.2 (2 x C-24), 17.0 (2 x C-29), 16.8 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 1035.7$ (100 %, $[\text{M}+\text{H}]^+$), 1057.8 (70 %, $[\text{M}+\text{Na}]^+$);

analysis calcd for $\text{C}_{67}\text{H}_{106}\text{N}_2\text{O}_6$ (1035.57): C 77.71, H 10.32, N 2.71; found: C 77.58, H 10.46, N 2.53.

N^1, N^4 -Bis-[(3 β)-3-acetyloxy-urs-12-en-28-oyl]-1,4-diaminobutane (11)

Compound **11** (0.33g, 87%) showed: m.p. 206°C; $R_F = 0.4$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +30.2^\circ$ (*c* 0.32, CHCl_3);

IR (KBr): $\nu = 3445br, 2942m, 2859m, 1735s, 1637m, 1421m, 1325m, 1245s, 1147w, 1045w, 1028m, 1005w \text{ cm}^{-1}$;

^1H NMR (500 MHz, CDCl_3): $\delta = 5.99$ (*t*, $J = 5.1$ Hz, 2H, 2 x NH), 5.31 (*t*, $J = 3.9$ Hz, 2H, 2 x 12-H), 4.49 (*dd*, $J = 10.5, 5.4$ Hz, 2H, 2 x 3-H), 3.36 (*dd*, $J = 13.4, 6.5$ Hz, 2H, 2 x 33-H), 2.99 (*dq*, $J = 11.0, 6.1$ Hz, 2H, 2 x 33-H), 2.05 (*s*, 6H, 2 x 32-H), 2.00–1.98 (*m*, 2H, 2 x 16-H), 1.95 (*ddd*, $J = 13.5, 7.0, 3.5$ Hz, 2H, 2 x 11-H), 1.90–1.87 (*m*, 2H, 2 x 18-H), 1.86 (*m*, 2H, 2 x 22-H), 1.76–1.55 (*m*, 16H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H), 1.54–1.49 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.45 (*m*, 6H, 2 x 21-H + 2 x 22-H + (2 x 19-H)), 1.41–1.26 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.09 (*s*, 6H, 2 x 27-H), 1.07–1.02 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.95 (*s*, 6H, 2 x 30-H), 0.88 (*s*, 6H, 2 x 24-H), 0.86 (*s*, 6H, 2 x 23-H), 0.85 (*s*, 6H, 2 x 26-H), 0.76 (*s*, 6H, 2 x 29-H) ppm;

^{13}C NMR (125 MHz, CDCl_3): $\delta = 178.0$ (2 x C-28), 170.9 (2 x C-28), 140.0 (2 x C-13), 125.4 (2 x C-12), 80.8 (2 x C-3), 55.2 (2 x C-5), 53.8 (2 x C-18), 47.7 (2 x C-17), 47.4 (2 x C-9), 42.4 (2 x C-14), 39.7 (2 x C-33), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.0 (2 x C-20), 38.9 (2 x C-1), 37.6 (2 x C-4), 36.8 (2 x C-10), 36.7 (2 x C-22), 32.6 (2 x C-7), 30.8 (2 x C-21), 28.0 (2 x C-23), 27.8 (2 x C-15), 27.0 (2 x C-34), (2 x C-16), 23.5 (2 x C-27), 23.1 (2 x C-2), 21.2 (2 x C-32), 21.1 (2 x C-30), 17.7 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 16.7 (2 x C-26), 15.5 (2 x C-25) ppm;
MS (ESI, MeOH): $m/z = 1049.7$ (100 %, $[\text{M}+\text{H}]^+$), 545.0 (20 %, $[\text{M}+\text{Ca}]^{2+}$), 1069.3 (54 %, $[\text{2M}+\text{Ca}]^{2+}$), 1071.8 (40 %, $[\text{M}+\text{Na}]^+$);

analysis calcd for $\text{C}_{68}\text{H}_{108}\text{N}_2\text{O}_6$ (1049.60): C 77.81, H 10.37, N 2.67; found: C 77.69, H 10.57, N 2.41.

N^1, N^5 -Bis-[(3 β)-3-acetyloxy-urs-12-en-28-oyl]-1,5-diaminopentane (12)

Compound **12** (0.31g, 81%) showed: m.p. 188°C; $R_F = 0.4$ (silica gel, toluene/ethyl acetate/formic

acid/heptane, 80:26:5:1); $[\alpha]_D = +36.32^\circ$ (*c* 0.31, CHCl₃);

IR (KBr): $\nu = 3403br, 2926m, 2871m, 1734s, 1638m, 1514m, 1454m, 1369m, 1243s, 1147w, 1093w, 1027m, 1006w$ cm⁻¹;

¹H NMR (500 MHz, CDCl₃): $\delta = 5.99$ (*t*, *J* = 5.1 Hz, 2H, 2 x NH), 5.31 (*t*, *J* = 3.9 Hz, 2H, 2 x 12-H), 4.49 (*dd*, *J* = 10.5, 5.4 Hz, 2H, 2 x 3-H), 3.36 (*dd*, *J* = 13.4, 6.5 Hz, 2H, 2 x 33-H), 2.99 (*dq*, *J* = 11.0, 6.1 Hz, 2H, 2 x 33-H), 2.05 (*s*, 6H, 2 x 32-H), 2.00–1.98 (*m*, 2H, 2 x 16-H), 1.95 (*ddd*, *J* = 13.5, 7.0, 3.5 Hz, 2H, 2 x 11-H), 1.90–1.87 (*m*, 2H, 2 x 18-H), 1.86 (*m*, 2H, 2 x 22-H), 1.76–1.55 (*m*, 18H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H + 35-H), 1.54–1.49 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.45 (*m*, 6H, 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.41–1.26 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.09 (*s*, 6H, 2 x 27-H), 1.07–1.02 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.95 (*s*, 6H, 2 x 30-H), 0.88 (*s*, 6H, 2 x 24-H), 0.86 (*s*, 6H, 2 x 23-H), 0.85 (*s*, 6H, 2 x 26-H), 0.76 (*s*, 6H, 2 x 29-H) ppm;

¹³C NMR (125 MHz, CDCl₃): $\delta = 178.2$ (2 x C-28), 170.9 (2 x C-28), 140.0 (2 x C-13), 125.4 (2 x C-12), 80.7 (2 x C-3), 55.2 (2 x C-5), 53.9 (2 x C-18), 47.6 (2 x C-17), 47.4 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.3 (2 x C-33), 39.1 (2 x C-20), 38.3 (2 x C-1), 37.6 (2 x C-4), 37.2 (2 x C-10), 36.8 (2 x C-22), 32.6 (2 x C-7), 30.8 (2 x C-21), 29.0 (2 x C-34), 28.0 (2 x C-23), 27.8 (2 x C-15), 24.8 (2 x C-16), 24.5 (C-35), 23.4 (2 x C-2), 23.1 (2 x C-27), 21.2 (2 x C-32), 21.1 (2 x C-30), 18.1 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 16.7 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): *m/z* = 1063.7 (100 %, [M+H]⁺), 1085.8 (90 %, [M+Na]⁺), 551.5 (10 %, [M+Ca]²⁺); analysis calcd for C₆₉H₁₁₀N₂O₆ (1063.62): C 77.92, H 10.42, N 2.63; found: C 77.63, H 10.69, N 2.50.

N¹, N⁶-Bis-[(3β)-3-acetyloxy-urs-12-en-28-oyl]-1,6-diaminohexane (13)

Compound **13** (0.33g, 85%) showed: m.p. 162°C; *R_F* = 0.6 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +38.90^\circ$ (*c* 0.32, CHCl₃);

IR (KBr): $\nu = 3428br, 2946m, 2872m, 1736s, 1646m, 1522m, 1456m, 1370m, 1246s, 1148w, 1092w, 1028m, 1006w$ cm⁻¹;

¹H NMR (500 MHz, CDCl₃): $\delta = 5.94$ (*t*, *J* = 5.5 Hz, 2H, 2 x NH), 5.31–5.29 (*m*, 2H, 2 x 12-H), 4.49 (*dd*, *J* = 10.5, 5.3 Hz, 2H, 2 x 3-H), 3.30 (*dq*, *J* = 13.6, 6.9 Hz, 2H, 2 x 33-H), 3.03–2.95 (*m*, 2H, 2 x 33-H), 2.05 (*s*, 6H, 2 x 32-H), 2.02–1.98 (*m*, 2H, 2 x 16-H), 1.95 (*ddd*, *J* = 14.9, 6.2, 3.3 Hz, 2H, 2 x 11-H), 1.90–1.87 (*m*, 4H, 2 x 18-H + 2 x 22-H), 1.77–1.55 (*m*, 20H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H + (2 x 35-H)), 1.50 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.48–1.39 (*m*, 6H, 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.39–1.27 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.09 (*s*, 6H, 2 x 27-H), 1.07–1.01 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.95 (*s*, 6H, 2 x 30-H), 0.88 (*s*, 6H,

2 x 24-H), 0.87 (*s*, 6H, 2 x 23-H), 0.86 (*s*, 6H, 2 x 26-H), 0.82 (*m*, 2H, 2 x 5-H), 0.77 (*s*, 6H, 2 x 29-H) ppm;

¹³C NMR (125 MHz, CDCl₃): $\delta = 178.2$ (2 x C-28), 170.9 (2 x C-28), 140.0 (2 x C-13), 125.4 (2 x C-12), 80.8 (2 x C-3), 55.2 (2 x C-5), 53.9 (2 x C-18), 47.7 (2 x C-17), 47.4 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.2 (2 x C-33), 39.1 (2 x C-20), 38.3 (2 x C-1), 37.6 (2 x C-4), 37.2 (2 x C-10), 36.7 (2 x C-22), 32.6 (2 x C-7), 30.8 (2 x C-21), 29.2 (2 x C-34), 28.0 (2 x C-23), 27.8 (2 x C-15), 24.8 (2 x C-16), 24.5 (2 x C-35), 23.4 (2 x C-2), 23.2 (2 x C-27), 21.2 (2 x C-32), 21.1 (2 x C-30), 18.1 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 16.7 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): *m/z* = 1077.7 (100 %, [M+H]⁺), 1099.8 (72 %, [M+Na]⁺), 558.5 (5 %, [M+Ca]²⁺); analysis calcd for C₇₀H₁₁₂N₂O₆ (1077.65): C 78.02, H 10.48, N 2.60; found: C 77.88, H 10.69, N 2.41.

N¹, N⁷-Bis-[(3β)-3-acetyloxy-urs-12-en-28-oyl]-1,7-diaminoheptane (14)

Compound **14** (0.23g, 56%) showed: m.p. 176°C; *R_F* = 0.4 (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +36.18^\circ$ (*c* 0.33, CHCl₃);

IR (KBr): $\nu = 3418br, 2925m, 2855m, 1735s, 1655m, 1516m, 1454m, 1369m, 1243s, 1147w, 1092w, 1027m, 1005w$ cm⁻¹;

¹H NMR (400 MHz, CDCl₃): $\delta = 5.91$ (*t*, *J* = 5.4 Hz, 2H, 2 x NH), 5.30 (*m*, 2H, 2 x 12-H), 4.52–4.47 (*m*, 2H, 2 x 3-H), 3.31 (*dq*, *J* = 13.5, 7.0 Hz, 2H, 2 x 33-H), 3.04–2.95 (*m*, 2H, 2 x 33-H), 2.04 (*s*, 6H, 2 x 32-H), 2.00 (*d*, *J* = 4.2 Hz, 2H, 2 x 16-H), 1.99–1.91 (*m*, 2H, 2 x 11-H), 1.89–1.80 (*m*, 4H, 2 x 18-H + 2 x 22-H), 1.77–1.53 (*m*, 22H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H + 2 x 35-H + 36-H), 1.50 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.49–1.41 (*m*, 6H, 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.40–1.25 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.09 (*s*, 6H, 2 x 27-H), 1.05 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.95 (*s*, 6H, 2 x 30-H), 0.88 (*s*, 6H, 2 x 24-H), 0.87 (*s*, 6H, 2 x 23-H), 0.86 (*s*, 6H, 2 x 26-H), 0.81 (*m*, 2H, 2 x 5-H), 0.78 (*s*, 6H, 2 x 29-H) ppm;

¹³C NMR (100 MHz, CDCl₃): $\delta = 178.1$ (2 x C-28), 170.9 (2 x C-28), 140.1 (2 x C-13), 125.4 (2 x C-12), 80.8 (2 x C-3), 55.2 (2 x C-5), 54.0 (2 x C-18), 47.6 (2 x C-17), 47.4 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.4 (2 x C-33), 39.1 (2 x C-20), 38.3 (2 x C-1), 37.6 (2 x C-4), 37.1 (2 x C-10), 36.8 (2 x C-22), 32.6 (2 x C-7), 30.8 (2 x C-21), 29.2 (2 x C-34), 28.9 (C-36), 28.0 (2 x C-23), 27.8 (2 x C-15), 27.0 (2 x C-35), 24.8 (2 x C-16), 23.4 (2 x C-2), 23.1 (2 x C-27), 21.2 (2 x C-32), 21.1 (2 x C-30), 18.1 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 16.7 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): *m/z* = 1091.7 (100 %, [M+H]⁺), 1113.0 (92 %, [M+Na]⁺), 565.9 (5 %, [M+Ca]²⁺); analysis calcd for C₇₁H₁₁₄N₂O₆ (1091.68): C 78.11, H 10.53, N 2.57; found: C 78.01, H 10.64, N 2.38.

N¹,N²-Bis-[(3β)-3-hydroxy-olean-12-en-28-oyl]-1,2-diaminoethane (15)

Compound **15** (0.22 g, 59%) showed: m.p. 239°C; $R_F = 0.5$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +51.41^\circ$ (*c* 0.35, CHCl₃);

IR (KBr): $\nu = 3393m, 2927m, 2865w, 1640m, 1518m, 1463m, 1386w, 1364w, 1262w, 1094w, 1029m, 996m$ cm⁻¹; ¹H NMR (400 MHz, CDCl₃): $\delta = 6.55$ (*s*, 2H, 2 x NH), 5.40 (*t*, $J = 3.3$ Hz, 2H, 2 x 12-H), 3.46 (*d*, $J = 9.3$ Hz, 2H, (2 x 31-H)), 3.21 (*dd*, $J = 11.1, 4.6$ Hz, 2H, 2 x 3-H), 3.12 (*d*, $J = 8.7$ Hz, 2H, (2 x 31-H)), 2.54 (*dd*, $J = 13.1, 3.4$ Hz, 2H, 2 x 18-H), 2.00 (*dd*, $J = 13.7, 3.9$ Hz, 2H, 2 x 16-H), 1.93 (*dd*, $J = 11.0, 7.3$ Hz, 2H, 2 x 11-H), 1.79–1.53 (*m*, 18H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H), 1.52–1.50 (*m*, 2H, 2 x 15-H), 1.49–1.39 (*m*, 2H, 2 x 22-H), 1.39–1.29 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.29–1.22 (*m*, 2H, 2 x 22-H), 1.21–1.17 (*m*, 4H, 2 x 19-H + 2 x 21-H), 1.15 (*s*, 6H, 2 x 27-H), 1.02 (*dd*, $J = 14.2, 3.7$ Hz, 4H, 2 x 1-H + 2 x 15-H), 0.98 (*s*, 6H, 2 x 23-H), 0.90 (*s*, 6H, 2 x 25-H), 0.89 (*s*, 6H, (2 x 30-H)), 0.89 (*s*, 6H, 2 x 29-H), 0.77 (*s*, 6H, 2 x 24-H), 0.73 (*s*, 6H, 2 x 26-H), 0.71 (*s*, 2H, 2 x 5-H) ppm;

¹³C NMR (100 MHz, CDCl₃): $\delta = 179.3$ (2 x C-28), 144.4 (2 x C-13), 123.1 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 47.5 (2 x C-9), 46.6 (2 x C-17), 46.1 (2 x C-19), 41.9 (2 x C-18), 41.9 (2 x C-14), 40.1 (2 x C-31), 39.3 (2 x C-8), 38.7 (2 x C-1), 38.4 (2 x C-4), 36.9 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.7 (2 x C-7), 32.3 (2 x C-22), 30.6 (2 x C-20), 28.0 (2 x C-23), 27.3 (2 x C-15), 27.1 (2 x C-2), 25.8 (2 x C-27), 23.6 (2 x C-11), 23.5 (2 x C-30), 23.5 (2 x C-16), 18.2 (2 x C-6), 16.8 (2 x C-26), 15.5 (2 x C-24), 15.3 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 938.1$ (42 %, [M+H]⁺), 960.2 (100 %, [M+Na]⁺);

analysis calcd for C₆₂H₁₀₀N₂O₄ (937.47): C 79.43, H 10.75, N 2.99; found: C 79.17, H 10.91, N 2.76.

N¹,N³-Bis-[(3β)-3-hydroxy-olean-12-en-28-oyl]-1,3-diaminopropane (16)

Compound **16** (0.22 g, 59%) showed: m.p. 218°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +50.78^\circ$ (*c* 0.30, CHCl₃);

IR (KBr): $\nu = 3374br, 2928m, 2864w, 1632s, 1527s, 1465m, 1432m, 1380w, 1363w, 1262w, 1094w, 1045m, 1030m, 998w, 773w$ cm⁻¹;

¹H NMR (500 MHz, CDCl₃): $\delta = 6.47$ (*t*, $J = 5.1$ Hz, 2H, 2 x NH), 5.41 (*t*, $J = 3.5$ Hz, 2H, 2 x 12-H), 3.27 (*dq*, $J = 13.4, 6.8$ Hz, 2H, 2 x 31-H), 3.21 (*dd*, $J = 11.4, 4.3$ Hz, 2H, 2 x 3-H), 3.13 (*dq*, $J = 12.0, 5.9$ Hz, 2H, 2 x 31-H), 2.65 (*dd*, $J = 13.0, 4.0$ Hz, 2H, 2 x 18-H), 2.02–1.93 (*m*, 2H, 2 x 16-H), 1.93–1.87 (*m*, 2H, 2 x 11-H), 1.79–1.50 (*m*, 20H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 15-H + 2 x 16-H + 2 x 19-H + 32-H), 1.44 (*dd*, $J = 12.2, 3.1$ Hz, 2H, 2 x 22-H), 1.41–1.30 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.30–1.24 (*m*, 2H, 2 x 22-

H), 1.22–1.17 (*m*, 4H, 2 x 19-H + 2 x 21-H), 1.16 (*s*, 6H, 2 x 27-H), 1.04 (*dt*, $J = 13.5, 2.9$ Hz, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.92 (*s*, 6H, 2 x 25-H), 0.90 (*s*, 6H, (2 x 30-H)), 0.90 (*s*, 6H, 2 x 29-H), 0.78 (*s*, 6H, 2 x 24-H), 0.74 (*s*, 6H, 2 x 26-H), 0.72 (*s*, 2H, 2 x 5-H) ppm;

¹³C NMR (125 MHz, CDCl₃): $\delta = 178.5$ (2 x C-28), 144.5 (2 x C-13), 122.8 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 47.5 (2 x C-9), 46.7 (2 x C-17), 46.3 (2 x C-19), 41.9 (2 x C-18), 41.84 (2 x C-14), 39.3 (2 x C-8), 38.7 (2 x C-1), 38.4 (2 x C-4), 36.9 (2 x C-10), 36.1 (2 x C-31), 34.2 (2 x C-21), 33.01 (2 x C-29), 32.9 (2 x C-7), 32.4 (2 x C-22), 30.7 (2 x C-20), 29.6 (CH₂, C32), 28.0 (2 x C-23), 27.3 (2 x C-15), 27.15 (2 x C-2), 25.7 (2 x C-27), 23.6 (2 x C-11), 23.6 (2 x C-30), 23.5 (2 x C-16), 18.2 (2 x C-6), 16.9 (2 x C-26), 15.5 (2 x C-24), 15.3 (2 x C-25) ppm; MS (ESI, MeOH): $m/z = 952.1$ (100 %, [M+H]⁺), 974.0 (22 %, [M+Na]⁺);

analysis calcd for C₆₃H₁₀₂N₂O₄ (951.50): C 79.52, H 10.81, N 2.94; found: C 79.35, H 11.03, N 2.77.

N¹,N⁴-Bis-[(3β)-3-hydroxy-olean-12-en-28-oyl]-1,4-diaminobutane (17)

Compound **17** (0.13 g, 83%) showed: m.p. 186°C; $R_F = 0.4$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +47.00^\circ$ (*c* 0.31, CHCl₃);

IR (KBr): $\nu = 3390br, 2926m, 2864w, 1640m, 1520m, 1463m, 1386w, 1260s, 1092s, 1026s$ cm⁻¹;

¹H NMR (400 MHz, CDCl₃): $\delta = 6.06$ (*t*, $J = 5.6$ Hz, 2H, 2 x NH), 5.37 (*t*, $J = 3.5$ Hz, 2H, 2 x 12-H), 3.35 (*dq*, $J = 12.9, 6.4$ Hz, 2H, 2 x 31-H), 3.21 (*dd*, $J = 11.1, 4.6$ Hz, 2H, 2 x 3-H), 3.04 (*dq*, $J = 11.6, 6.5$ Hz, 2H, (2 x 31-H)), 2.53 (*dd*, $J = 12.9, 4.1$ Hz, 2H, 2 x 18-H), 2.01–1.92 (*m*, 2H, 2 x 16-H), 1.95–1.87 (*m*, 2H, 2 x 11-H), 1.81–1.56 (*m*, 22H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H + 2 x 32-H), 1.54 (*dt*, $J = 13.9, 3.4$ Hz, 2H, 2 x 15-H), 1.50–1.39 (*m*, 2H, 2 x 22-H), 1.39–1.27 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.27–1.22 (*m*, 2H, 2 x 22-H), 1.22–1.17 (*m*, 4H, 2 x 19-H + 2 x 21-H), 1.18–1.14 (*s*, 6H, 2 x 27-H), 1.07–0.99 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.91 (*s*, 6H, 2 x 25-H), 0.91 (*s*, 6H, (2 x 30-H)), 0.90 (*s*, 6H, 2 x 29-H), 0.78 (*s*, 6H, 2 x 24-H), 0.75 (*s*, 6H, 2 x 26-H), 0.71 (*s*, 2H, 2 x 5-H) ppm;

¹³C NMR (100 MHz, CDCl₃): $\delta = 178.2$ (2 x C-28), 145.0 (2 x C-13), 122.7 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 47.5 (2 x C-9), 46.7 (2 x C-17), 46.2 (2 x C-19), 42.1 (2 x C-18), 42.0 (2 x C-14), 39.3 (2 x C-8), 39.0 (2 x C-31), 38.7 (2 x C-1), 38.4 (2 x C-4), 36.9 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.5 (2 x C-7), 32.3 (2 x C-22), 30.7 (2 x C-20), 28.0 (2 x C-23), 27.3 (2 x C-32), 27.1 (2 x C-2), 26.9 (2 x C-15), 25.7 (2 x C-27), 23.7 (2 x C-11), 23.6 (2 x C-30), 23.5 (2 x C-16), 18.2 (2 x C-6), 16.9 (2 x C-6), 15.5 (2 x C-24), 15.3 (2 x C-25) ppm; MS (ESI, MeOH): $m/z = 965.3$ (92 %, [M-H]⁻);

analysis calcd for C₆₄H₁₀₄N₂O₄ (965.52): C 79.61, H 10.86, N 2.90; found: C 79.40, H 10.99, N 2.73.

N¹,N⁵-Bis-[(3β)-3-hydroxy-olean-12-en-28-oyl]-1,5-diaminopentane (18)

Compound **18** (0.04 g, 76%) showed: m.p. 182°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +35.37^\circ$ (*c* 0.36, CHCl₃);

IR (KBr): $\nu = 3387br, 2924m, 2854w, 1638m, 1518m, 1455m, 1363m, 1037m, 996m$ cm⁻¹;

¹H NMR (500 MHz, CDCl₃): $\delta = 6.00$ (*t*, *J* = 5.5 Hz, 2H, 2 x NH), 5.31 (*t*, *J* = 3.5 Hz, 2H, 2 x 12-H), 3.31 (*dq*, *J* = 13.4, 6.8 Hz, 2H, 2 x 31-H), 3.25–3.18 (*dd*, *J* = 11.2, 4.6 Hz, 2H, 2 x 3-H), 3.01 (*dq*, *J* = 12.8, 6.5 Hz, 2H, (2 x 31-H)), 2.02–1.98 (*m*, 2H 2 x 16-H), 1.98–1.94 (*m*, 2H, 2 x 11-H), 1.93 (*d*, *J* = 3.3 Hz, 2H, 2 x 18-H), 1.87 (*dt*, *J* = 11.0, 2.9 Hz, 2H, 2 x 22-H), 1.78–1.50 (*m*, 20H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H + 2 x 35-H), 1.44 (*m*, 12H, 2 x 15-H + 2 x 7-H + 2 x 6-H + 2 x 21-H + 2 x 22-H + (2 x 19-H)), 1.40–1.25 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.10 (*s*, 6H, 2 x 27-H), 1.08–1.00 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, (2 x 23-H)), 0.95 (*s*, 6H, 2 x 30-H), 0.92 (*s*, 6H, 2 x 25-H), 0.87 (*s*, 6H, 2 x 26-H), 0.78 (*s*, 6H, 2 x 24-H), 0.78 (*s*, 6H, 2 x 29-H), 0.71 (*m*, 2H, 2 x 5-H) ppm;

¹³C NMR (125 MHz, CDCl₃): $\delta = 178.1$ (2 x C-28), 140.0 (2 x C-13), 125.5 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 53.9 (2 x C-18), 47.7 (2 x C-17), 47.5 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.2 (2 x C-31), 39.1 (2 x C-20), 38.7 (2 x C-1), 38.6 (2 x C-4), 37.2 (2 x C-22), 36.9 (2 x C-10), 32.7 (2 x C-7), 30.8 (2 x C-21), 28.1 (2 x C-23), 27.8 (2 x C-15), 27.1 (2 x C-32), 26.4 (2 x C-33), 24.8 (2 x C-2), 24.5 (2 x C-16), 23. (2 x C-27), 23.2 (2 x C-2), 21.2 (2 x C-30), 18.2 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 15.6 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 994.7$ (100 %, [M+H]⁺), 1017.6 (90 %, [M+Na]⁺);

analysis calcd for C₆₅H₁₀₆N₂O₄ (979.55): C 79.70, H 10.91, N 2.86; found: C 79.51, H 11.13, N 2.64.

N¹,N⁶-Bis-[(3β)-3-hydroxy-urs-12-en-28-oyl]-1,6-diaminohexane (19)

Compound **19** (0.18 g, 76%) showed: m.p. 183°C (lit.: 191–193 °C); $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +50.40^\circ$ (*c* 0.33, CHCl₃);

IR (KBr): $\nu = 3404br, 2927s, 2863m, 1639s, 1521s, 1463s, 1386s, 1242m, 1030s, 996s$ cm⁻¹;

¹H NMR (400 MHz, CDCl₃): $\delta = 5.98$ –5.93 (*m*, 2H, 2 x NH), 5.37 (*t*, *J* = 3.5 Hz, 2H, 2 x 12-H), 3.35 (*dq*, *J* = 13.7, 7.0 Hz, 2H, 2 x 31-H), 3.22 (*dd*, *J* = 11.2, 4.5 Hz, 2H, 2 x 3-H), 3.03–2.93 (*m*, 2H, 2 x 31-H), 2.50 (*dd*, *J* = 12.8, 3.8 Hz, 2H, 2 x 18-H), 1.97 (*dd*, *J* = 13.6, 3.8 Hz, 2H, 2 x 16-H), 1.91 (*m*, 2H, 2 x 11-H), 1.81–1.57 (*m*, 28H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H + 2 x 32-H + 2 x 33-H), 1.57–1.51 (*m*, 2H, 2 x 15-H), 1.50–1.40 (*m*, 2H, 2 x 22-H), 1.40–1.27 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.25 (*m*, 2H 2 x 22-H), 1.19 (*d*, *J* = 11.3 Hz, 4H, 2 x 19-H + 2 x 21-H), 1.16 (*s*, 6H, 2 x 27-H), 1.07–1.00 (*m*, 4H, 2 x 1-H + 2 x 15-H),

0.99 (*s*, 6H, 2 x 23-H), 0.91 (*s*, 6H, 2 x 25-H), 0.91 (*s*, 6H, (2 x 30-H)), 0.90 (*s*, 6H, 2 x 29-H), 0.78 (*s*, 6H, 2 x 24-H), 0.76 (*s*, 6H, 2 x 26-H), 0.72 (*s*, 2H, 2 x 5-H) ppm;

¹³C NMR (100 MHz, CDCl₃): $\delta = 178.1$ (2 x C-28), 145.1 (2 x C-13), 122.6 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 47.5 (2 x C-9), 46.7 (2 x C-17), 46.2 (2 x C-19), 42.3 (2 x C-18), 42.1 (2 x C-14), 39.3 (2 x C-8), 39.2 (2 x C-31), 38.7 (2 x C-1), 38.4 (2 x C-4), 36.9 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.4 (2 x C-7), 32.4 (2 x C-22), 30.7 (2 x C-20), 29.3 (2 x C-32), 28.0 (2 x C-23), 27.2 (2 x C-2), 27.1 (2 x C-15), 26.6 (2 x C-33), 25.7 (2 x C-27), 23.7 (2 x C-11), 23.6 (2 x C-30), 23.5 (2 x C-16), 18.2 (2 x C-6), 16.9 (2 x C-6), 15.5 (2 x C-24), 15.3 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 994.6$ (90 %, [M+H]⁺), 1016.6 (100 %, [M+Na]⁺);

analysis calcd for C₆₆H₁₀₈N₂O₄ (993.58): C 79.78, H 10.96, N 2.82; found: C 79.62, H 11.07, N 2.69.

N¹,N⁷-Bis-[(3β)-3-hydroxy-olean-12-en-28-oyl]-1,7-diaminoheptane (20)

Compound **20** (0.12 g, 87%) showed: m.p. 183°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +45.85^\circ$ (*c* 0.36, CHCl₃);

IR (KBr): $\nu = 3407br, 2927s, 2861m, 1641s, 1519m, 1462s, 1386m, 1363m, 1212m, 1030m, 996m$ cm⁻¹;

¹H NMR (400 MHz, CDCl₃): $\delta = 5.93$ –5.88 (*m*, 2H, 2 x NH), 5.37 (*t*, *J* = 3.5 Hz, 2H, 2 x 12-H), 3.34 (*dq*, *J* = 13.7, 7.1 Hz, 2H, (2 x 31-H)), 3.21 (*dd*, *J* = 11.2, 4.5 Hz, 2H, 2 x 3-H), 3.03–2.93 (*m*, 2H, (2 x 31-H)), 2.49 (*dd*, *J* = 12.8, 3.6 Hz, 2H, 2 x 18-H), 1.97 (*dd*, *J* = 13.7, 3.7 Hz, 2H, 2 x 16-H), 1.91 (*dd*, *J* = 8.9, 3.3 Hz, 2H, 2 x 11-H), 1.81–1.56 (*m*, 30H, 2 x 1-H + 2 x 2-H + 2 x 6-H + 2 x 7-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 19-H + 2 x 32-H + 2 x 33-H + 2 x 34-H), 1.54 (*dd*, *J* = 9.7, 4.3 Hz, 2H, 2 x 15-H), 1.50–1.40 (*m*, 2H, 2 x 22-H), 1.40–1.27 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.25 (*m*, 2H 2 x 22-H), 1.19 (*d*, *J* = 11.3 Hz, 4H, 2 x 19-H + 2 x 21-H), 1.16 (*s*, 6H, 2 x 27-H), 1.03 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.91 (*s*, 6H, 2 x 25-H), 0.91 (*s*, 6H, (2 x 30-H)), 0.90 (*s*, 6H, 2 x 29-H), 0.78 (*s*, 6H, 2 x 24-H), 0.76 (*s*, 6H, 2 x 26-H), 0.72 (*s*, 2H, 2 x 5-H) ppm;

¹³C NMR (100 MHz, CDCl₃): $\delta = 178.1$ (2 x C-28), 145.1 (2 x C-13), 122.6 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 47.5 (2 x C-9), 46.8 (2 x C-17), 46.2 (2 x C-19), 42.3 (2 x C-18), 42.0 (2 x C-14), 39.4 (2 x C-8), 39.3 (2 x C-31), 38.7 (2 x C-1), 38.4 (2 x C-4), 36.9 (2 x C-10), 34.1 (2 x C-21), 32.9 (2 x C-29), 32.5 (2 x C-7), 32.3 (2 x C-22), 30.7 (2 x C-20), 29.3 (2 x C-32), 28.9 (C-34), 28.0 (2 x C-23), 27.2 (2 x C-2), 27.1 (2 x C-15), 27.0 (2 x C-33), 25.7 (2 x C-27), 23.8 (2 x C-11), 23.5 (2 x C-30), 23.5 (2 x C-16), 18.2 (2 x C-6), 16.9 (2 x C-6), 15.5 (2 x C-24), 15.3 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 1008.8$ (14 %, [M+H]⁺), 1031.7 (43 %, [M+Na]⁺);

analysis calcd for $C_{67}H_{110}N_2O_4$ (xx): C 79.86, H 11.00, N 2.78; found: C 79.68, H 11.18, N 2.69.

N^1, N^2 -Bis-[(β)-3-hydroxy-urs-12-en-28-oyl]-1,2-diaminoethane (21)

Compound **21** (0.18 g, 85%) showed: m.p. 228°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +44.32^\circ$ (*c* 0.31, $CHCl_3$);

IR (KBr): $\nu = 3383br, 2927s, 2870m, 1632s, 1533m, 1455m, 1378w, 1280w, 1089w, 1030m, 995m$ cm^{-1} ;

1H NMR (400 MHz, $CDCl_3$): $\delta = 6.53$ (*m*, 2H, 2 x NH), 5.36 (*t*, $J = 3.4$ Hz, 2H, 2 x 12-H), 3.48 (*d*, $J = 9.4$ Hz, 2H, 2 x 31-H), 3.21 (*dd*, $J = 11.2, 4.6$ Hz, 2H, 2 x 3-H), 3.09 (*d*, $J = 9.0$ Hz, 2H, (2 x 31-H)), 2.02 (*d*, $J = 4.1$ Hz, 2H 2 x 16-H), 2.00–1.94 (*m*, 2H, 2 x 11-H), 1.91 (*m*, 2H, 2 x 18-H), 1.89–1.84 (*m*, 2H, 2 x 22-H), 1.76–1.51 (*m*, 12H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H), 1.50–1.48 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.47 (*m*, 6H, 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.40–1.25 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.09 (*s*, 6H, 2 x 27-H), 1.08–1.02 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.95 (*s*, 6H, 2 x 30-H), 0.92 (*s*, 6H, 2 x 25-H), 0.87 (*s*, 6H, 2 x 26-H), 0.78 (*s*, 6H, 2 x 24-H), 0.75 (*s*, 6H, 2 x 29-H), 0.72 (*m*, 2H, 2 x 5-H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 178.1$ (2 x C-28), 139.2 (2 x C-13), 125.9 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 53.3 (2 x C-18), 47.6 (2 x C-17), 47.5 (2 x C-9), 42.3 (2 x C-14), 39.7 (2 x C-8), 39.9 (2 x C-31), 39.5 (2 x C-19), 39.0 (2 x C-20), 38.7 (2 x C-1), 38.5 (2 x C-4), 37.4 (2 x C-22), 36.9 (2 x C-10), 32.6 (2 x C-7), 30.8 (2 x C-21), 28.1 (2 x C-23), 27.8 (2 x C-15), 27.1 (2 x C-2), 24.7 (2 x C-16), 23.5 (2 x C-27), 23.3 (2 x C-11), 21.2 (2 x C-30), 18.1 (2 x C-6), 17.2 (2 x C-24), 16.8 (2 x C-29), 16.7 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 938.5$ (60 %, $[M+H]^+$), 960.5 (100 %, $[M+Na]^+$);

analysis calcd for $C_{62}H_{100}N_2O_4$ (937.49): C 79.43, H 10.75, N 2.99; found: C 70.23, H 10.95, N 2.71.

N^1, N^3 -Bis-[(β)-3-hydroxy-urs-12-en-28-oyl]-1,3-diaminopropane (22)

Compound **22** (0.02 g, 56%) showed: m.p. 242°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +20.84^\circ$ (*c* 0.3, $CHCl_3$);

IR (KBr): $\nu = 3383br, 2927s, 2870m, 1632m, 1532m, 1454m, 1378m, 1259s, 1088m, 1029m, 996w$ cm^{-1} ;

1H NMR (500 MHz, $CDCl_3$): $\delta = 6.42$ (*m*, 2H, 2 x NH), 5.36 (*t*, $J = 3.5$ Hz, 2H, 2 x 12-H), 3.31–3.22 (*d*, $J = 9.4$ Hz, 2H, (2 x 31-H)), 3.20 (*m*, 2H, 2 x 3-H), 3.10 (*dd*, $J = 13.4, 5.9$ Hz, 2H, 2 x 31-H), 2.03 (*d*, $J = 4.2$ Hz, 2H 2 x 16-H), 2.01–1.94 (*m*, 2H, 2 x 11-H), 1.92 (*m*, 2H, 2 x 18-H), 1.90–1.82 (*m*, 2H, 2 x 22-H), 1.79–1.50 (*m*, 14H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H), 1.49 (*m*, 6H, 2 x 15-H + 2 x 7-H + 2 x 6-H), 1.48–1.44 (*m*, 6H, 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.43–1.24 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.10 (*s*, 6H, 2 x 27-H), 1.08–1.00

(*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.94 (*s*, 6H, 2 x 30-H), 0.91 (*s*, 6H, 2 x 25-H), 0.87 (*s*, 6H, 2 x 26-H), 0.78 (*s*, 6H, 2 x 24-H), 0.76 (*s*, 6H, 2 x 29-H), 0.71 (*m*, 2H, 2 x 5-H) ppm;

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 178.1$ (2 x C-28), 139.3 (2 x C-13), 125.7 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 53.5 (2 x C-18), 47.7 (2 x C-17), 47.5 (2 x C-9), 42.4 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.0 (2 x C-20), 38.7 (2 x C-1), 38.6 (2 x C-4), 37.4 (2 x C-22), 36.9 (2 x C-10), 36.4 (2 x C-31), 32.8 (2 x C-7), 30.9 (2 x C-21), 28.1 (2 x C-23), 27.8 (2 x C-15), 27.1 (2 x C-2), 27.2 (2 x C-32), 24.7 (2 x C-16), 23.4 (2 x C-27), 23.3 (2 x C-2), 21.2 (2 x C-30), 18.2 (2 x C-6), 17.2 (2 x C-24), 17.0 (2 x C-29), 15.5 (2 x C-26), 15.5 (2 x C-25) ppm; MS (ESI, MeOH): $m/z = 951.9$ (40 %, $[M+H]^+$), 973.8 (8 %, $[M+Na]^+$);

analysis calcd for $C_{63}H_{102}N_2O_4$ (951.49): C 79.52, H 10.81, N 2.94; found: C 79.32, H 11.03, N 2.76.

N^1, N^4 -Bis-[(β)-3-hydroxy-urs-12-en-28-oyl]-1,4-diaminobutane (23)

Compound **23** (0.03 g, 54%) showed: m.p. 245°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +33.23^\circ$ (*c* 0.16, $CHCl_3$);

IR (KBr): $\nu = 3422br, 2926s, 2870m, 1638s, 1517m, 1454s, 1378m, 1243w, 1045m, 1029m, 997m$ cm^{-1} ;

1H NMR (400 MHz, $CDCl_3$): $\delta = 5.97$ (*m*, 2H, 2 x NH), 5.31 (*t*, $J = 3.6$ Hz, 2H, 2 x 12-H), 3.40–3.29 (*m*, 2H, 2 x 31-H), 3.22 (*dt*, $J = 10.8, 5.3$ Hz, 2H, 2 x 3-H), 2.99 (*dd*, $J = 12.2, 5.8$ Hz, 2H, 2 x 31-H), 2.00 (*t*, $J = 2.3$ Hz, 2H 2 x 16-H), 1.95 (*m*, 2H, 2 x 11-H), 1.88 (*d*, $J = 3.2$ Hz, 2H, 2 x 18-H), 1.85 (*d*, $J = 3.1$ Hz, 2H, 2 x 22-H), 1.77–1.50 (*m*, 16H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H), 1.45 (*m*, 12H, 2 x 15-H + 2 x 7-H + 2 x 6-H + 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.41–1.24 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.10 (*s*, 6H, 2 x 27-H), 1.08–1.00 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.95 (*s*, 6H, 2 x 30-H), 0.92 (*s*, 6H, 2 x 25-H), 0.87 (*s*, 6H, 2 x 26-H), 0.78 (*s*, 6H, 2 x 24-H), 0.77 (*s*, 6H, 2 x 29-H), 0.72 (*m*, 2H, 2 x 5-H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 178.1$ (2 x C-28), 140.0 (2 x C-13), 125.5 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 53.8 (2 x C-18), 47.6 (2 x C-17), 47.5 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.1 (2 x C-20), 38.9 (2 x C-31), 38.7 (2 x C-1), 38.6 (2 x C-4), 37.2 (2 x C-22), 36.9 (2 x C-10), 32.7 (2 x C-7), 30.9 (2 x C-21), 28.1 (2 x C-23), 27.8 (2 x C-15), 27.1 (2 x C-32), 26.9 (2 x C-2), 24.7 (2 x C-16), 23.4 (2 x C-27), 23.2 (2 x C-2), 21.2 (2 x C-30), 18.2 (2 x C-6), 17.2 (2 x C-24), 17.0 (2 x C-29), 15.5 (2 x C-26), 15.5 (2 x C-25) ppm; MS (ESI, MeOH): $m/z = 967.5$ (60 %, $[M+H]^+$), 990.5 (100 %, $[M+Na]^+$);

analysis calcd for $C_{64}H_{104}N_2O_4$ (965.52): C 79.61, H 10.86, N 2.90; found: C 79.45, H 11.03, N 2.84.

N¹,N⁵-Bis-[(3β)-3-hydroxy-urs-12-en-28-oyl]-1,5-diaminopentane (24)

Compound **24** (0.1 g, 77%) showed: m.p. 158°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +42.57^\circ$ (*c* 0.31, CHCl₃);

IR (KBr): $\nu = 3396br, 2924m, 2869w, 1641m, 1520w, 1455w, 1386w, 1260m, 1091s, 1026s$ cm⁻¹;

¹H NMR (400 MHz, CDCl₃): $\delta = 5.92$ (*t*, *J* = 5.6 Hz, 2H, 2 x NH), 5.31 (*t*, *J* = 3.2 Hz, 2H, 2 x 12-H), 3.3 (*dq*, *J* = 13.5, 6.9 Hz, 2H, 2 x 31-H), 3.25–3.18 (*m*, 2H, 2 x 3-H), 3.03–2.92 (*m*, 2H, 2 x 31-H), 2.00 (*d*, *J* = 4.2 Hz, 2H 2 x 16-H), 1.98–1.94 (*m*, 2H, 2 x 11-H), 1.83 (*d*, *J* = 2.3 Hz, 2H, 2 x 18-H), 1.91–1.82 (*m*, 2H, 2 x 22-H), 1.78–1.50 (*m*, 18H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H + 35-H), 1.49–1.42 (*m*, 12H, 2 x 15-H + 2 x 7-H + 2 x 6-H + 2 x 21-H + 2 x 22-H + (2 x 19-H), 1.41–1.26 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.09 (*s*, 6H, 2 x 27-H), 1.08–1.00 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, (2 x 23-H), 0.95 (*s*, 6H, 2 x 30-H), 0.92 (*s*, 6H, 2 x 25-H), 0.87 (*s*, 6H, 2 x 26-H), 0.78 (*s*, 6H, 2 x 24-H), 0.77 (*s*, 6H, 2 x 29-H), 0.71 (*m*, 2H, 2 x 5-H) ppm;

¹³C NMR (100 MHz, CDCl₃): $\delta = 178.1$ (2 x C-28), 140.0 (2 x C-13), 125.5 (2 x C-12), 78.9 (2 x C-3), 55.2 (2 x C-5), 53.9 (2 x C-18), 47.6 (2 x C-17), 47.5 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.3 (2 x C-31), 39.1 (2 x C-20), 38.7 (2 x C-1), 38.6 (2 x C-4), 37.2 (2 x C-22), 36.9 (2 x C-10), 32.7 (2 x C-7), 30.8 (2 x C-21), 29.0 (C-33), 28.1 (2 x C-23), 27.8 (2 x C-15), 27.1 (2 x C-32), 24.8 (2 x C-2), 24.5 (2 x C-16), 23.4 (2 x C-27), 23.2 (2 x C-2), 21.2 (2 x C-30), 18.2 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 15.6 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 980.3$ (20 %, [M+H]⁺), 1002.3 (100 %, [M+Na]⁺);

analysis calcd for C₆₅H₁₀₆N₂O₄ (979.55): C 79.50, H 10.91, N 2.86; found: C 79.36, H 11.13, N 2.67.

N¹,N⁶-Bis-[(3β)-3-hydroxy-urs-12-en-28-oyl]-1,6-diaminohexane (25)

Compound **25** (0.11 g, 70%) showed: m.p. 182°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +35.37^\circ$ (*c* 0.36, CHCl₃);

IR (KBr): $\nu = 3387br, 2924m, 2854w, 1638m, 1518m, 1455m, 1363m, 1037m, 996m$ cm⁻¹;

¹H NMR (500 MHz, CDCl₃): $\delta = 6.00$ (*t*, *J* = 5.5 Hz, 2H, 2 x NH), 5.31 (*t*, *J* = 3.5 Hz, 2H, 2 x 12-H), 3.31 (*dq*, *J* = 13.4, 6.8 Hz, 2H, 2 x 31-H), 3.25–3.18 (*dd*, *J* = 11.2, 4.6 Hz, 2H, 2 x 3-H), 3.01 (*dq*, *J* = 12.8, 6.5 Hz, 2H, 2 x 31-H), 2.02–1.98 (*m*, 2H 2 x 16-H), 1.98–1.94 (*m*, 2H, 2 x 11-H), 1.93 (*d*, *J* = 3.3 Hz, 2H, 2 x 18-H), 1.87 (*dt*, *J* = 11.0, 2.9 Hz, 2H, 2 x 22-H), 1.78–1.50 (*m*, 20H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H + 2 x 35-H), 1.44 (*m*, 12H, 2 x 15-H + 2 x 7-H + 2 x 6-H + 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.40–1.25 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.10 (*s*, 6H, 2 x 27-H), 1.08–1.00 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.95 (*s*, 6H, 2 x 30-H), 0.92 (*s*, 6H, 2 x 25-H), 0.87 (*s*, 6H,

2 x 26-H), 0.78 (*s*, 6H, 2 x 24-H), 0.78 (*s*, 6H, 2 x 29-H), 0.71 (*m*, 2H, 2 x 5-H) ppm;

¹³C NMR (125 MHz, CDCl₃): $\delta = 178.1$ (2 x C-28), 140.0 (2 x C-13), 125.5 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 53.9 (2 x C-18), 47.7 (2 x C-17), 47.5 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.2 (2 x C-31), 39.1 (2 x C-20), 38.7 (2 x C-1), 38.6 (2 x C-4), 37.2 (2 x C-22), 36.9 (2 x C-10), 32.7 (2 x C-7), 30.8 (2 x C-21), 28.1 (2 x C-23), 27.8 (2 x C-15), 27.1 (2 x C-32), 26.4 (2 x C-33), 24.8 (2 x C-2), 24.5 (2 x C-16), 23. (2 x C-27), 23.2 (2 x C-2), 21.2 (2 x C-30), 18.2 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 15.6 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 994.7$ (100 %, [M+H]⁺), 1017.6 (90 %, [M+Na]⁺);

analysis calcd for C₆₆H₁₀₈N₂O₄ (993.58): C 79.78, H 10.96, N 2.82; found: C 79.51, H 11.15, N 2.69.

N¹,N⁷-Bis-[(3β)-3-hydroxy-urs-12-en-28-oyl]-1,7-diaminoheptane (26)

Compound **26** (0.05 g, 68%) showed: m.p. 188°C; $R_F = 0.3$ (silica gel, toluene/ethyl acetate/formic acid/heptane, 80:26:5:1); $[\alpha]_D = +30.29^\circ$ (*c* 0.30, CHCl₃);

IR (KBr): $\nu = 3406br, 2963m, 2925w, 1641m, 1519w, 1455w, 1377w, 1260w, 1260s, 1088s, 1016s, 865w$ cm⁻¹;

¹H NMR (500 MHz, CDCl₃): $\delta = 5.90$ (*t*, *J* = 5.4 Hz, 2H, 2 x NH), 5.30 (*t*, *J* = 3.6 Hz, 2H, 2 x 12-H), 3.31 (*dq*, *J* = 13.6, 7.0 Hz, 2H, 2 x 31-H), 3.22 (*dd*, *J* = 11.2, 4.7 Hz, 2H, 2 x 3-H), 2.99 (*dq*, *J* = 12.7, 7.0 Hz, 2H, 2 x 31-H), 1.99 (*d*, *J* = 3.5 Hz, 2H 2 x 16-H), 1.96 (*m*, 2H, 2 x 11-H), 1.92 (*td*, *J* = 16.7, 3.4 Hz, 2H, 2 x 18-H), 1.89–1.83 (*m*, 2H, 2 x 22-H), 1.78–1.50 (*m*, 20H, 2 x 1-H + 2 x 2-H + 2 x 9-H + 2 x 11-H + 2 x 16-H + 2 x 34-H + 2 x 35-H + 36-H), 1.49–1.41 (*m*, 12H, 2 x 15-H + 2 x 7-H + 2 x 6-H + 2 x 21-H + 2 x 22-H + 2 x 19-H), 1.40–1.25 (*m*, 6H, 2 x 6-H + 2 x 7-H + 2 x 21-H), 1.10 (*s*, 6H, 2 x 27-H), 1.08–1.00 (*m*, 4H, 2 x 1-H + 2 x 15-H), 0.99 (*s*, 6H, 2 x 23-H), 0.95 (*s*, 6H, 2 x 30-H), 0.93 (*s*, 6H, 2 x 25-H), 0.87 (*s*, 6H, 2 x 26-H), 0.78 (*s*, 6H, 2 x 24-H), 0.78 (*s*, 6H, 2 x 29-H), 0.71 (*m*, 2H, 2 x 5-H) ppm;

¹³C NMR (125 MHz, CDCl₃): $\delta = 178.1$ (2 x C-28), 140.0 (2 x C-13), 125.5 (2 x C-12), 78.9 (2 x C-3), 55.1 (2 x C-5), 54.0 (2 x C-18), 47.6 (2 x C-17), 47.5 (2 x C-9), 42.5 (2 x C-14), 39.7 (2 x C-8), 39.5 (2 x C-19), 39.4 (2 x C-31), 39.1 (2 x C-20), 38.7 (2 x C-1), 38.6 (2 x C-4), 37.1 (2 x C-22), 36.9 (2 x C-10), 32.7 (2 x C-7), 30.9 (2 x C-21), 29.2 (C-34), 28.9 (2 x C-33), 28.1 (2 x C-23), 27.8 (2 x C-15), 27.1 (2 x C-32), 24.8 (2 x C-2), 24.4 (2 x C-16), 23.4 (2 x C-27), 23.2 (2 x C-2), 21.2 (2 x C-30), 18.2 (2 x C-6), 17.2 (2 x C-24), 16.9 (2 x C-29), 15.6 (2 x C-26), 15.5 (2 x C-25) ppm;

MS (ESI, MeOH): $m/z = 1008.9$ (55 %, [M+H]⁺), 1030.9 (30 %, [M+Na]⁺);

analysis calcd for C₆₇H₁₁₀N₂O₄ (1007.60): C 79.86, H 11.00, N 2.78; found: C 79.66, H 11.18, N 2.67.

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