Synthesis and Cytotoxic Activity of Methyl Glycyrrhetinate Esterified with Amino Acids

René Csuk, Stefan Schwarz, Bianka Siewert, Ralph Kluge, and Dieter Ströhl

Martin-Luther-Universität Halle-Wittenberg, Bereich Organische Chemie, Kurt-Mothes-Str. 2, D-06120 Halle (Saale), Germany

Reprint requests to Prof. Dr. René Csuk. Fax: 0049 345 5527030.
E-mail: rene.csuk@chemie.uni-halle.de

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Methyl glycyrrhetinate was esterified at position C3 of ring A using different amino acids. A short, unbranched chain of four carbon atoms with two amino groups in positions 2 and 4 was shown to be the most active compound of this series (IC_{50} = 0.8 M on liposarcoma Lipo cells). These compounds trigger apoptosis as shown by an acridine orange/ethidium bromide assay, trypan blue tests and DNA-laddering experiments.

Key words: Glycyrrhetinic Acid, Antitumor Activity, Apoptosis

Introduction

The roots of the licorice plant contain several pharmacologically active substances, such as flavonoids [1 – 10] and terpenes [11 – 13] with glycyrrhizinic acid being most abundant and occurring in amounts of up to 24 % [14]. Glycyrrhetinic acid (GA) is the aglycon of glycyrrhizinic acid and possesses many pharmacological effects. Besides its anti-inflammatory [15, 16] and antiviral [17, 18] activity, its anti-carcinogenic potential is of pronounced scientific interest. Glycyrrhetinic acid derivatives show cytotoxic effects against various tumor cell lines [19 – 23], but also trigger apoptosis in cancer cells [24 – 26].

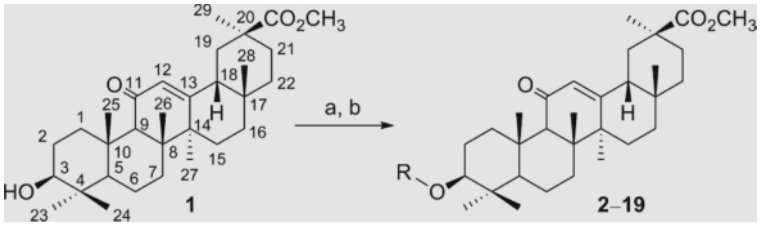
Herein, we targeted compounds of increased cytotoxicity (as compared to parent glycyrrhetinic acid) while maintaining the ability to induce apoptosis. Various amino acids of different lengths and structures were attached to carbon C3 while carbon C30 was esterified – based on the results of previous studies [27]. The influence of the substituents on cytotoxicity resulting from the different polarity pattern and lipophilicity along the molecule was studied in sulforhodamine B (SRB) assays. The apoptotic behavior for some of these compounds was evaluated using an acridine orange/ethidium bromide (AO/EB) test, a trypan blue assay as well as DNA-laddering experiments.

Results and Discussion

The compounds (Scheme 1, Table 1) were obtained by DCC mediated esterification from the corresponding *N*-Boc protected amino acids and the methyl ester of glycyrrhetinic acid (**1**). Deprotection was performed either with TFA in dry DCM or by treating the compounds with dry HCl gas in DCM (to obtain the hydrochlorides).

In a first series the influence of the side chain was investigated using SRB tests (Table 2). The highest increase of cytotoxicity was achieved by introducing amino acids possessing short sidechains like the alanyloxy or sarcosyloxy derivatives. For instance, the sarcosyloxy compound **6** showed IC_{50} values between 1.83 and 3.42 μM; compounds having a prolyloxy (**7**), phenylalanyloxy (**8**) or methionyloxy (**9**) substituent showed moderate cytotoxic effectsin the SRB assay with IC_{50} values between 5 and 25 μM. Compounds having a valyloxy (**10**), an isoleucyloxy (**11**) or a leucyloxy (**12**) group showed decreased of cytotoxicity (>30 μM) as compared to the parent methyl ester **1**.

The influence of the distance between the linking ester group and the terminal amino group was investigated using a panel of different ω-amino acid derived compounds. The data showed an optimal length of two carbon atoms as represented for a β-alanyloxy sub-



Scheme 1. Amino ester derivatives of GA methyl ester (**1**): a. Boc-amino acids, DCM, DMAP, DCC, 25 °C, 12 h (leading to *tert*-butoxycarbonylated **20**–**33**); b. TFA in DCM, 25 °C, 12 h or HCl_g in DCM, 25 °C, 12 h.

Compound	R	Compound	R	Compound	R
2	glycyl	**8**	L-phenylalanyl	**14**	5-aminopentanoyl
3	L-alanyl	**9**	L-methionyl	**15**	6-aminohexanoyl
4	D-alanyl	**10**	L-valyl	**16**	8-aminooctanoyl
5	β-alanyl	**11**	L-isoleucyl	**17**	L-2,4-diaminobutanoyl
6	sarcosyl	**12**	L-leucyl	**18**	L-ornithyl
7	L-prolyl	**13**	4-aminobutanoyl	**19**	L-lysyl

Table 1. Amino ester derivatives of GA methyl ester at carbon C3.

Cell line	8505C	A253	A2780	A549	DLD-1	Lipo	MCF-7
2[a]	7.45	6.26	5.99	6.42	8.59	7.54	7.10
3[a]	4.31	3.61	2.98	2.77	4.49	4.30	3.54
4[a]	2.92	2.26	2.24	2.26	3.35	3.56	2.25
5[a]	2.55	2.50	1.72	2.40	2.51	2.52	2.50
6	2.50	2.46	1.83	2.13	3.42	2.50	2.49
7	9.62	5.56	4.58	6.91	11.64	7.96	5.49
8	16.93	6.41	5.50	9.94	8.70	16.15	4.60
9	11.47	7.48	12.56	14.84	12.45	22.32	6.06
10	> 30	> 30	6.89	> 30	> 30	> 30	> 30
11	> 30	> 30	> 30	> 30	> 30	> 30	> 30
12	> 30	> 30	> 30	> 30	> 30	> 30	> 30

[a] Data from previous studies [27].

Table 2. Biological activity (IC_{50} values in μM from SRB assays), 7 tumor cell lines; error: ±10%.

Cell line	8505C	A253	A2780	A549	DLD-1	Lipo	MCF-7	NiH3T3
2[a]	7.45	6.26	5.99	6.42	8.59	7.54	7.10	5.73
5[a]	2.55	2.50	1.72	2.40	2.51	2.52	2.50	3.45
13	3.47	3.41	2.13	3.39	3.41	3.54	2.73	3.14
14	3.52	3.52	2.48	3.38	4.49	4.54	3.40	3.58
15	5.48	4.05	4.94	5.43	6.27	5.95	4.03	6.06
16	4.02	3.76	4.06	3.88	4.38	4.02	2.46	6.05

[a] Data from previous studies [27].

Table 3. Biological activity (IC_{50} values in μM) including seven tumor cell lines and mouse embryonic fibroblasts (NiH3T3); error: ±10%.

stituent (**5**). The lowest IC_{50} value for this compound was determined as 1.72 μM for A2780 ovarian carcinoma cells.

With the exception of compound **2**, all of the derivatives showed a slight selectivity towards the tumor cell lines. The selectivity was determined in a comparative test using mouse embryonic fibroblasts (NiH3T3). Compound **16** was most selective comparing NiH3T3 and MCF-7 cells (Table 3).

Finally, three different 2,ω-diamino acid derived substituents were used, and their influence on the cytotoxicity was investigated. All of these compounds possessed IC_{50} values <3 μM for all tumor cell lines. In particular, compound **17** showed an increased cytotoxicity for liposarcoma Lipo cells. Compound **19** having a lysyloxy substituent, showed the highest selectivity in this study (Table 4).

Evaluation of a trypan blue test gave an indication for an apoptotic behavior; a rate of apoptosis between 80 and 90% was determined for these compounds (Table 5). This rate is slightly higher than that of parent glycyrrhetinic acid (73.73% [28]).

Cell line	8505C	A253	A2780	A549	DLD-1	Lipo	MCF-7	NiH3T3
17	2.89	4.04	2.59	2.35	1.48	0.80	3.01	3.05
18	2.49	2.21	1.98	2.53	3.01	2.70	1.55	6.24
19	2.40	2.43	1.58	2.43	2.27	2.51	1.75	9.98

Table 4. Biological activity (IC_{50} values in μM) using seven tumor cell lines and mouse fibroblasts (NiH3T3); error: ±10 %.

Table 5. Apoptotic effect on A549 cells in % (± standard error, six experiments). Cells were treated with **2** (8 μM), **5** (5 μM), **13** (4 μM), **14** (4 μM), **15** (7 μM), **16** (6 μM), **17** (10 μM), **18** (4 μM) and **19** (4 μM).

Substance	**2**	**5**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Apoptosis	92.21 ± 1.01	81.64 ± 0.79	84.87 ± 0.96	89.52 ± 2.33	91.74 ± 0.42	84.72 ± 1.87	80.53 ± 3.16	78.82 ± 3.58	89.41 ± 1.04

In additional experiments the derivatives were tested in an acridine orange/ethidium bromide (AO/EB) assay. In each experiment most (80 % – 90 %) of the collected dead cells (800–1000) showed a green fluorescence. This fluorescence as well as the results of the trypan blue test indicated that the compounds trigger apoptosis in A549 cells. Compound **17** was additionally tested in a DNA laddering assay (A549 cells; 10 μM). The gel showed the typical fragmentation pattern of the DNA indicating apoptosis.

Conclusion

In this study we investigated the influence of an additional amino acid substituent at carbon C3 of methyl glcyrrhetinate onto cytotoxicity. These substituents differed in structure and length of the carbon chain as well as in the number of amino groups.

The cytotoxicity of each compound was determined in an SRB-assay. The IC_{50} values obtained from these experiments indicated that the structure of the amino acid's side chain affects the cytotoxicity most. A more lipophilic side chain leads to a decreased cytotoxicity while short side chains increase cytotoxicity. Compounds **8** and **9**, however, do not strictly obey this rule of thumb; this might result from stereoelectronic effects of the phenyl or the thiomethyl moiety.

The optimal linker length between a terminal amino group and the linking carboxyl function is two carbons. The implementation of a second amino group did not raise the cytotoxicity for the the compound with the butyryl chain (**17**), but for the compounds **18** and **19**. The tumor-to-control selectivity was altered: it was raised by the presence of a second amino group and by an increasing number of carbons. Compound **19** was determined to be the most selective substance of this study. The cytotoxicity of these compounds is comparable to that of well-known anti-tumor substances like CDODO-Me-11 (1.48 μM on HL-60 cells) or CDODO-Me-12 (0.36 μM on HL-60 cells) [29].

The compounds were subjected to AO/EB, trypan blue and DNA-laddering-tests. All of the active compounds triggered apoptosis in A549 cells, therefore making them interesting compounds for future *in vivo* investigations.

Experimental Section

Cell lines and culture conditions

The cell lines 8505C, A253, A2780, A549, DLD-1, LIPO, MCF-7, and NiH3T3 were included in this study. Cultures were maintained as monolayes in RPMI 1640 (PAA Laboratories, Pasching/Germany) supplemented with 10 % heat inactivated fetal bovine serum (Biochrom AG, Berlin/Germany) and penicillin/streptomycin (PAA Laboratories) at 37 °C in a humidified atmosphere of 5 % CO_2/95 % air.

Cytotoxicity assay [30]

The cytotoxicity of the test compounds was evaluated using the sulforhodamine-B (SRB) (Sigma Aldrich) microculture colorimetric assay. In short, exponentially growing cells were seeded into 96-well plates on day 0 at the appropriate cell densities to prevent confluence of the cells during the experiment. After 24 h, the cells were treated with serial dilutions of the test compounds (0 – 100 M) for 96 h. The final concentration of DMSO or DMF solvent never exceeded 0.5 %, which was non-toxic to the cells. The percentages of surviving cells relative to untreated controls were determined 96 h after the beginning of drug exposure. After a 96 h treatment, the supernatant medium from the 96 well plates was discarded, and the cells were fixed with 10 % trichloroacetic acid. For a thorough fixation, the plates were allowed to rest at 4 °C. After fixation, the cells were washed in a strip washer. The washing was done five times with water using alternate dispensing and aspiration procedures. Afterwards the plates were dyed with 100 μL of 0.4 % SRB (sulforhodamine B) for about 20 min. The plates were washed with 1 % acetic acid to remove the excess of the dye and allowed to air dry

overnight. 100 μL of 10 mM Tris base solution were added to each well and absorbance was measured at 570 nm (using a 96 well plate reader, Tecan Spectra, Crailsheim/Germany). The IC_{50} was estimated by linear regression between the value before and after the 50 % line is crossed in a dose-response curve.

Apoptosis test – acridine orange/ethidium bromide (AO/EB) [31, 32]

Apoptotic cell death was analyzed by acridine orange/ethidium bromide dye using fluorescence microscopy on A549 cells. Therefore around 500 000 cells were seeded in cell culture flasks and were allowed to grow for 24 hours. The medium was removed afterwards and the substance loaded medium was added. After another 24 – 48 hours the supernatant medium was collected and centrifuged. The pellet was suspended in phosphate-buffer saline (PBS) and centrifuged again. The liquid was removed, and the pellet was suspended in PBS. After mixing the suspension with a solution of AO/EB, it was analyzed under a fluorescence microscope. While a green fluorescence shows apoptosis, a red colored nucleus indicates necrotic cells.

Apoptosis test – trypan blue cell counting

Approximately 500 000 cells (A549) were seeded in cell culture flasks and were allowed to grow for 1 day. After removing the medium, the substance loaded medium was introduced and the flasks were incubated for about 24 – 48 hours. The supernatant medium was collected and centrifuged; the cell pellet was suspended in PBS and centrifuged again. Equal amounts of a trypan blue solution (0.4 % in phosphate-buffer saline, pH = 7.2), and the suspension of the pellet in PBS were mixed and put on chamber slides (invitrogen^{TM}). An automatic cell counter (invitrogen^{TM} countess® automated cell counter) was used for counting the cells, differing between cells with an intact cell membrane and cells without.

Synthesis and analysis

Reagents were bought from commercial suppliers without any further purification. Melting points were measured with a Leica hot stage microscope and were not corrected. NMR spectra were recorded on Varian Gemini 200, Gemini 2000 or Unity 500 spectrometers at 27 °C with tretramethylsilane as an internal standard; chemical shifts δ are given in ppm, coupling constants J in Hz. The assignment of the signals was performed using gHSQC, gHMBC, H,H-COSY, H,C-COSY, HET2DJ and NOESY NMR experiments. Mass spectra were taken on a Finnigan MAT TSQ 7000 (electrospray, voltage 4.5 kV, sheath gas nitrogen) instrument. Elemental analyses were measured on a Foss-Heraeus Vario EL unit. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer Spectrum 1000, optical rotations on a Perkin-Elmer 341 polarimeter (1 cm micro cell, 25 °C) and UV/Vis spectra on a Perkin-Elmer unit, Lambda 14. TLC was performed on silica gel (Merck 5554, detection by UV absorption). Solvents were dried according to usual procedures.

General procedure for the protection of the amino acids [33]

The amino acid (1 equiv.) was dissolved in a 1 : 1 mixture (50 mL) of a potassium hydroxide solution (2 M in water) and 1,4-dioxane. Di-*tert*-butyl dicarbonate (1.2 equiv.) was added, and the mixture was allowed to stir at 25 °C for 12 h. The solvent was removed under reduced pressure, and ethyl acetate (100 mL) was added. After washing with sodium hydrogensulfate (10 % in water, 10 mL), the mixture was extracted 3 times with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (10 mL), dried over sodium sulphate and filtered, and the solvent was evaporated. The crude product was used without any further purification; an analytic sample was obtained by chromatography.

General procedure for esterification at carbon C3 (method A)

The starting material (1 equiv.) was dissolved in dry DCM (50 mL), and DMAP (20 mg, 0.16 mmol) and the protected amino acid (1.2 equiv.) were added. After addition of DCC (1.2 equiv.), the mixture was stirred at 25 °C for 12 h and filtered, and the filtrate was washed with water and brine (10 mL each), dried over sodium sulphate and filtered, and the solvent was evaporated. Purification was performed by flash chromatography (silica gel, hexane-ethyl acetate, 8 : 2).

General procedure for the deprotection (method B)

To a solution of the Boc-protected compound in dry DCM, trifluoroacetic acid (1 mL per 10 mL DCM) was added. The mixture was stirred at 25 °C for 12 h. After completion of the reaction (as monitored by TLC), the reaction mixture was washed with an aq. solution of sodium hydrogen carbonate (satd., 25 mL), the aqueous layer was extracted with DCM (5 × 20 mL), the combined organic extracts were washed with brine (10 mL), dried over sodium sulphate and filtered, and the solvents were evaporated.

General procedure for the deprotection (method C)

The Boc-protected compound was dissolved in dry DCM. After saturation with dry hydrogen chloride gas for 15 min at 5 °C, stirring at 25 °C was continued for additional 12 h. After completion of the reaction (as monitored by TLC), the solvent was removed under reduced pressure. The residue was washed with ethyl acetate until no parent substance could be detected; analytic samples were obtained by recrystallization.

*Methyl (3β)-3-[(sarcosyl)oxy]-11-oxo-olean-12-en-30-oate (**6**)*

Obtained from **20** by method B as a colorless powder. Yield: 200 mg, 66 %. – M. p. 247 – 249 °C (decomp.). – R_f = 0.56 (dichloromethane-methanol, 9:1). – $[\alpha]_D$ = 114.07 (c = 0.58, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 249 nm (4.05). – IR (KBr): ν = 3443br, 2951s, 2876m, 1732s, 1654s, 1619w, 1464m, 1388m, 1362m, 1324w, 1280m, 1215s, 1162s, 1086m, 1049w, 1021w, 989m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.61 (dd, 1 H, J = 11.7, 4.8 Hz, 3-H), 3.69 (s, 3 H, OMe), 3.40 (s, 2 H, Sar-CH_2), 2.82 (ddd, 1 H, J = 13.7, 3.5, 3.5 Hz, 1-H), 2.49 (br, 1 H, NH), 2.47 (s, 3 H, NCH_3), 2.36 (s, 1 H, 9-H), 2.08 (dd, 1 H, J = 14.0, 3.1 Hz, 18-H), 2.03 (ddd, 1 H, J = 13.7, 13.7, 4.5 Hz, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, J = 13.6, 4.0, 2.6 Hz, 19-H), 1.80 (ddd, 1 H, J = 13.8, 13.8, 4.3 Hz, 16-H), 1.71 (m, 1 H, 2-H), 1.64 (m, 1 H, 7-H), 1.62 (m, 1 H, 2′-H), 1.59 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.55 (m, 1 H, 6-H), 1.45 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.37 (m, 1 H, 22-H), 1.34 (s, 3 H, 27-H), 1.29 (m, 2 H, 22′-H and 21′-H), 1.16 (m, 1 H, 16′-H), 1.14 (s, 3 H, 25-H), 1.12 (s, 3 H, 29-H), 1.10 (s, 3 H, 26-H), 1.04 (ddd, 1 H, J = 13.6, 13.6, 3.7 Hz, 1′-H), 0.99 (m, 1 H, 15′-H), 0.86 (s, 3 H, 24-H), 0.86 (s, 3 H, 23-H), 0.79 (m, 1 H, 5-H), 0.78 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 171.6 (Sar-COO), 169.2 (C-13), 128.5 (C-12), 81.4 (C-3), 61.7 (C-9), 55.0 (C-5), 52.5 (Sar-CH_2), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 35.8 (NCH_3), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 556.3 (100) $[M+H]^+$, 578.3 (2) $[M+Na]^+$, 833.9 (6) $[3M+2H]^{2+}$. – $C_{34}H_{53}NO_5$ (555.79): calcd. C 73.47, H 9.61, N, 2.52; found C 73.32, H 9.82, N 2.43.

*Methyl (3β)-3-[(L)-prolyloxy]-11-oxo-olean-12-en-30-oate (**7**)*

Obtained from **21** by method B as a colorless powder. Yield: 130 mg, 92 %. – M. p. 249 – 252 °C (decomp.). – R_f = 0.52 (dichloromethane-methanol, 9 : 1). – $[\alpha]_D$ = 105.45 (c = 0.34, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 267 nm (4.11). – IR (KBr): ν = 3439br, 2958s, 2873m, 1729s, 1656s, 1618w, 1464m, 1388m, 1355m, 1326m, 1278w, 1218s, 1160m, 1087m, 1049w, 1021w, 988m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.58 (dd, 1 H, J = 11.8, 4.7 Hz, 3-H), 3.85 (dd, 1 H, J = 8.2, 5.9 Hz, Pro-α-CH), 3.69 (s, 3 H, OMe), 3.18 (br, 2 H, Pro-NH_2), 3.13 (dt, 1 H, J = 10.4, 6.8 Hz, Pro-δ-CHH′), 2.99 (dt, 1 H, J = 10.4, 6.7 Hz, Pro-δ-CHH′), 2.82 (ddd, 1 H, J = 13.7, 3.4, 3.4 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.20 (m, 1 H, Pro-β-CHH′), 2.08 (m, 1 H, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (m, 1 H, 19-H), 1.90 (m, 1 H, Pro-β-CHH′), 1.84 (m, 1 H, 16-H), 1.83 (m, 2 H, Pro-γ-CH_2), 1.73 (m, 1 H, 2-H), 1.67 (m, 1 H, 7-H), 1.65 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.60 (m, 1 H, 6-H), 1.43 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.05 (ddd, 1 H, J = 13.7, 13.7, 3.5 Hz, 1-H′), 1.01 (m, 1 H, 15-H′), 0.89 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.81 (m, 1 H, 5-H), 0.80 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.9 (C-30), 174.3 (Pro-COO), 169.2 (C-13), 128.5 (C-12), 81.5 (C-3), 61.6 (C-9), 60.0 (Pro-α-CH), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 46.7 (Pro-δ-CH_2), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 30.2 (Pro-β-CH_2), 28.5 (C-29), 28.3 (C-28), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 25.2 (Pro-γ-CH_2), 23.5 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 582.4 (100) $[M+H]^+$. – $C_{36}H_{55}NO_5$ (581.83): C 74.32, H 9.53, N 2.41; found C 74.11, H 9.75, N 2.28.

*Methyl (3β)-3-[(L)-phenylalanyloxy]-11-oxo-olean-12-en-30-oate (**8**)*

Obtained from **22** by method B as a colorless powder. Yield: 460 mg, 98 %. M. p.: 155 – 158 °C: R_f = 0.88 (dichloromethane-methanol, 9 : 1). – $[\alpha]_D$ = 103.37 (c = 0.56, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 249 nm (3.96). – IR (KBr): ν = 3389br, 2952s, 2873m, 1731s, 1655s, 1618w, 1497w, 1455m, 1388m, 1368w, 1324w, 1286m, 1216s, 1180m, 1086w, 1022w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.18 (br, 5 H, Phe-Ar), 5.67 (s, 1 H, 12-H), 4.56 (dd, 1 H, J = 11.5, 4.9 Hz, 3-H), 3.82 (dd, 1 H, J = 7.8, 5.7 Hz, Phe-α-CH), 3.69 (s, 3 H, OMe), 3.19 (dd, 1 H, J = 13.7, 5.4 Hz, Phe-β-CHH′), 2.91 (dd, 1 H, J = 13.7, 8.0 Hz, Phe-β-CHH′), 2.81 (ddd, 1 H, J = 13.8, 3.7, 3.7 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.18 (br, 2 H, Phe-NH_2), 2.09 (dd, 1 H, J = 13.1, 3.5 Hz, 18-H), 2.03 (m, 1 H, 15-H), 2.00 (m, 1 H, 21-H), 1.93 (m, 1 H, 19-H), 1.83 (ddd, 1 H, J = 13.4, 13.4, 4.7 Hz, 16-H), 1.70 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.57 (m, 1 H, 6-H), 1.44 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.05 (m, 1 H, 1-H′), 1.02 (m, 1 H, 15-H′), 0.85 (s, 3 H, 24-H), 0.81 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.79 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.9 (C-30), 173.8 (Phe-COO), 169.2 (C-13), 136.8 (Phe-γ-C), 129.4 (Phe-Ar), 128.7 (C-12), 128.5 (Phe-Ar), 126.9 (Phe-Ar), 81.9 (C-3), 61.7 (C-9), 55.9 (Phe-α-CH), 55.0 (C-5), 51.7 (OMe), 48.4

(C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 40.4 (Phe-β-CH_2), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 632.3 (100) $[M+H]^+$, 948.3 (6) $[3M+2H]^{2+}$. – $C_{40}H_{57}NO_5$ (631.88): C 76.03, H 9.09, N 2.22; found C 75.83, H 9.24, N 2.10.

*Methyl (3β)-3-[(L)-methionyloxy]-11-oxo-olean-12-en-30-oate (**9**)*

Obtained from **23** by method B as a colorless powder. Yield: 210 mg, 90 %. M. p.: 239 – 242 °C. – R_f = 0.77 (dichloromethane-methanol, 9 : 1). – $[\alpha]_D$ = 110.17 (c = 0.23, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 268 nm (4.09). – IR (KBr): ν = 3374br, 2958s, 2928m, 2872m, 1727s, 1651s, 1466w, 1389w, 1363w, 1324w, 1279w, 1248w, 1217m, 1182m, 1154m, 1086w, 1050w, 1022w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.67 (s, 1 H, 12-H), 4.58 (dd, 1 H, 3-H, J = 11.7, 4.8 Hz), 3.69 (m, 1 H, Met-α-CH), 3.69 (s, 3 H, OMe), 2.83 (ddd, 1 H, J = 13.7, 3.5, 3.5 Hz, 1-H), 2.67 (dd, 2 H, J = 7.4, 7.4 Hz, Met-β-CH_2), 2.36 (s, 1 H, 9-H), 2.13 (m, 1 H, Met-γ-C*H*H′), 2.12 (s, 3 H, Met-CH_3), 2.09 (m, 1 H, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, J = 13.7, 4.0, 2.3 Hz, 19-H), 1.86 (m, 1 H, Met-γ-CH*H*′), 1.83 (m, 1 H, 16-H), 1.74 (m, 1 H, 2-H), 1.67 (m, 1 H, 7-H), 1.64 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.57 (m, 1 H, 6-H), 1.47 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.19 (m, 1 H, 16′-H), 1.17 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.06 (ddd, 1 H, J = 13.8, 13.8, 3.6 Hz, 1-H′), 1.02 (m, 1 H, 15-H′), 0.90 (s, 3 H, 24-H), 0.89 (s, 3 H, 23-H), 0.82 (m, 1 H, 5-H), 0.81 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.9 (C-30), 174.4 (Met-COO), 169.2 (C-13), 128.5 (C-12), 81.9 (C-3), 61.7 (C-9), 55.0 (C-5), 53.5 (Met-α-CH), 51.8 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 33.3 (Met-γ-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 30.4 (Met-β-CH_2), 28.5 (C-28), 28.3 (C-29), 28.2 (C-23), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.4 (C-27), 18.7 (C-26), 17.4 (C-6), 16.8 (C-24), 16.4 (C-25), 15.3 (Met-CH_3). – MS (ESI): m/z (%) = 616.3 (100) $[M+H]^+$, 638.4 (4) $[M+Na]^+$. – $C_{36}H_{57}NO_5S$ (615.91): C 70.20, H 9.33, N 2.27; found C 69.98, H 9.53, N 2.17.

*Methyl (3β)-3-[(L)-valyloxy]-11-oxo-olean-12-en-30-oate (**10**)*

Obtained from **24** by method B as a colorless powder. Yield: 240 mg, 94 %. M. p.: 248 – 250 °C. – R_f = 0.68 (dichloromethane-methanol, 9 : 1). – $[\alpha]_D$ = 130.46 (c = 0.10, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 267 nm (3.92). – IR (KBr): ν = 3390br, 2960s, 2873m, 1729s, 1653s, 1466m, 1389m, 1318w, 1277m, 1246m, 1218m, 1154m, 1087w, 1022w, 987m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.57 (dd, 1 H, J = 11.4, 5.0 Hz, 3-H), 3.33 (d, 1 H, J = 4.4 Hz, Val-α-CH), 3.69 (s, 3 H, OMe), 2.81 (ddd, 1 H, J = 13.7, 3.5, 3.5 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.12 (m, 1 H, Val-β-CH), 2.08 (m, 1 H, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, J = 13.6, 3.6, 2.7 Hz, 19-H), 1.84 (m, 1 H, 16-H), 1.72 (m, 1 H, 2-H), 1.67 (m, 1 H, 7-H), 1.64 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.47 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.17 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.06 (m, 1 H, 1-H′), 1.02 (m, 1 H, 15-H′), 1.02 (d, 3 H, J = 6.7 Hz, Val-CH_3), 0.90 (m, 3 H, Val-CH_3), 0.90 (s, 3 H, 24-H), 0.90 (s, 3 H, 23-H), 0.82 (m, 1 H, 5-H), 0.80 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 174.8 (Val-COO), 169.2 (C-13), 128.5 (C-12), 81.4 (C-3), 61.7 (C-9), 60.2 (Val-α-CH), 55.1 (C-5), 51.8 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.7 (Val-β-CH), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 28.2 (C-23), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 19.6 (Val-CH_3), 18.7 (C-26), 17.4 (C-6), 16.9 (Val-CH_3), 16.8 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 584.3 (100) $[M+H]^+$. – $C_{36}H_{57}NO_5$ (583.84): C 74.06, H 9.84, N 2.40; found C 73.87, H 9.94, N 2.23.

*Methyl (3β)-3-[(L)-isoleucyloxy]-11-oxo-olean-12-en-30-oate (**11**)*

Obtained from **25** by method B as a colorless powder. Yield: 30 mg, 32 %. M. p.: 244 – 247 °C. – R_f = 0.65 (dichloromethane-methanol, 9 : 1). – $[\alpha]_D$ = 124.45 (c = 0.36, MeOH). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 267 nm (4.04). – IR (KBr): ν = 3392br, 2962s, 2875s, 1729s, 1653s, 1616m, 1465m, 1389m, 1362m, 1318m, 1278m, 1260m, 1235m, 1218s, 1154m, 1087m, 1051w, 1022w, 986m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.56 (dd, 1 H, J = 11.3, 5.1 Hz, 3-H), 3.68 (s, 3 H, OMe), 3.36 (d, 1 H, J = 4.5 Hz, Ile-α-CH), 2.81 (ddd, 1 H, J = 13.7, 3.5, 3.5 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.08 (dd, 1 H, J = 14.1, 3.4 Hz, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.92 (ddd, 1 H, J = 13.3, 3.9, 2.7 Hz, 19-H), 1.83 (m, 1 H, Ile-β-CH), 1.81 (m, 1 H, 16-H), 1.71 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.64 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.47 (m, 1 H, 6′-H), 1.42 (m, 2 H, Ile-γ-CH_2), 1.41 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.17 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.06 (m, 1 H, 1-H′), 1.01 (m, 1 H, 15-H′), 0.99 (d,

3 H, $J = 6.8$ Hz, Ile-β-CH_3), 0.91 (t, 3 H, $J = 7.4$ Hz, Ile-γ-CH_3), 0.90 (s, 3 H, 24-H), 0.89 (s, 3 H, 23-H), 0.82 (m, 1 H, 5-H), 0.80 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.0$ (C-11), 176.9 (C-30), 175.1 (Ile-COO), 169.2 (C-13), 128.5 (C-12), 81.3 (C-3), 61.7 (C-9), 59.8 (Ile-α-CH), 55.1 (C-5), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (Ile-β-CH), 38.7 (C-1), 38.0 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 24.3 (Ile-γ-CH_2), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.9 (C-24), 16.3 (C-25), 15.9 (Ile-β-CH_3), 11.7 (Ile-γ-CH_3). – MS (ESI): m/z (%) = 598.2 (100) $[M+H]^+$. – $C_{37}H_{59}NO_5$ (597.87): C 74.33, H 9.95, N 2.34; found C 74.13, H 10.03, N 2.27.

*Methyl (3β)-3-[(L)-leucyloxy]-11-oxo-olean-12-en-30-oate (**12**)*

Obtained from **26** by method B as a colorless powder. Yield: 290 mg, 98 %. M. p.: 234 – 236 °C. – $R_f = 0.69$ (dichloromethane-methanol, 9 : 1). – $[\alpha]_D = 127.03$ ($c = 0.28$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 267$ nm (4.01). – IR (KBr): $\nu = 3406$br, 2957s, 2873m, 2361w, 1728s, 1652s, 1464m, 1388m, 1324w, 1261m, 1212m, 1190m, 1168m, 1086w, 1021w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.66$ (s, 1 H, 12-H), 4.56 (dd, 1 H, $J = 11.6$, 4.8 Hz, 3-H), 3.69 (s, 3 H, OMe), 3.49 (dd, 1 H, $J = 8.6$, 5.4 Hz, Leu-α-CH), 2.82 (ddd, 1 H, $J = 13.7$, 3.5, 3.5 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.15 (br, 2 H, Leu-NH_2), 2.08 (m, 1 H, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, $J = 13.6$, 3.4, 2.6 Hz, 19-H), 1.84 (m, 1 H, 16-H), 1.81 (m, 1 H, Leu-γ-CH), 1.72 (m, 1 H, 2-H), 1.65 (m, 1 H, 7-H), 1.61 (dd, 1 H, $J = 13.3$, 13.3 Hz, 19′-H), 1.60 (m, 1 H, 2′-H), 1.59 (m, 1 H, Leu-β-C*H*H′), 1.57 (m, 1 H, 6-H), 1.48 (m, 1 H, Leu-β-CH*H*′), 1.44 (m, 1 H, 6′-H), 1.41 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.19 (m, 1 H, 16′-H), 1.17 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.06 (ddd, 1 H, $J = 13.6$, 13.6, 3.7 Hz, 1-H′), 1.02 (m, 1 H, 15-H′), 0.96 (d, 3 H, $J = 6.4$ Hz, Leu-γ-CH_3), 0.94 (d, 3 H, $J = 6.4$ Hz, Leu-γ-CH_3), 0.90 (s, 3 H, 24-H), 0.89 (s, 3 H, 23-H), 0.82 (m, 1 H, 5-H), 0.80 (s, 3 H, 29-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.0$ (C-11), 176.9 (C-30), 175.9 (Leu-COO), 169.2 (C-13), 128.5 (C-12), 81.2 (C-3), 61.7 (C-9), 55.0 (C-5), 53.2 (Leu-α-CH), 51.8 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.9 (Leu-β-CH_2), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 28.2 (C-23), 26.5 (C-16), 26.4 (C-15), 24.8 (Leu-γ-CH), 23.6 (C-2), 23.3 (C-27), 23.0 (Leu-γ-CH_3), 21.8 (Leu-γ-CH_3), 18.7 (C-26), 17.4 (C-6), 16.8 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 598.3 (100) $[M+H]^+$. – $C_{37}H_{59}NO_5$ (597.87): C 74.33, H 9.95, N 2.34; found C 74.24, H 10.15, N 2.08.

*Methyl (3β)-3-[(4-aminobutanoyl)oxy]-11-oxoolean-12-en-30-oate (**13**)*

Obtained from **27** by method B as a colorless powder. Yield: 320 mg, 93 %. M. p.: 255 – 259 °C. – $R_f = 0.12$ (dichloromethane-methanol, 9 : 1). – $[\alpha]_D = 109.54$ ($c = 0.43$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 250$ nm (4.07). – IR (KBr): $\nu = 3438$br, 2951s, 1729s, 1654s, 1465s, 1388s, 1324m, 1280m, 1256m, 1213s, 1166s, 1086m, 1022m, 987m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.66$ (s, 1 H, 12-H), 4.53 (dd, 1 H, $J = 11.6$, 4.8 Hz, 3-H), 3.69 (s, 3 H, OMe), 3.18 (br, 1 H, chain-NH_2), 2.87 (t, 2 H, $J = 7.1$ Hz, chain-γ-CH_2), 2.80 (ddd, 1 H, $J = 13.6$, 3.4, 3.4 Hz, 1-H), 2.42 (t, 2 H, $J = 7.4$ Hz, chain-α-CH_2), 2.36 (s, 1 H, 9-H), 2.08 (dd, 1 H, $J = 13.8$, 3.4 Hz, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (m, 1 H, 19-H), 1.88 (m, 2 H, chain-β-CH_2), 1.82 (m, 1 H, 16-H), 1.71 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.5$, 13.5 Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.48 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.05 (m, 1 H, 1-H′), 1.02 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.8$ (C-11), 176.7 (C-30), 172.8 (chain-COO), 169.0 (C-13), 128.3 (C-12), 80.7 (C-3), 61.5 (C-9), 54.8 (C-5), 51.6 (OMe), 48.2 (C-18), 45.2 (C-8), 43.8 (C-20), 43.0 (C-14), 40.9 (C-19), 40.6 (chain-γ-CH_2), 38.6 (C-1), 37.9 (C-4), 37.5 (C-22), 36.7 (C-10), 32.5 (C-7), 31.8 (chain-α-CH_2), 31.6 (C-17), 30.9 (C-21), 28.3 (C-28), 28.1 (C-29), 27.9 (C-23), 26.7 (chain-β-CH_2), 26.3 (C-16), 26.2 (C-15), 23.4 (C-2), 23.2 (C-27), 18.5 (C-26), 17.2 (C-6), 16.6 (C-24), 16.2 (C-25). – MS (ESI): m/z (%) = 570.4 (100) $[M+H]^+$, 592.3 (2) $[M+Na]^+$, 855.4 (10) $[3M+2H]^{2+}$, 903.3 (16) $[3M+2H+3MeOH]^{2+}$, 1139.2 (6) $[2M+H]^+$. – $C_{35}H_{55}NO_5$ (569.81): C 73.77, H 9.73, N 2.46; found C 73.62, H 9.91, N 2.33.

*Methyl (3β)-3-[(5-aminopentanoyl)oxy]-11-oxoolean-12-en-30-oate (**14**)*

Obtained from **28** by method B as a colorless powder. Yield: 300 mg, 95 %. M. p.: 231 – 235 °C. – $R_f = 0.17$ (dichloromethane-methanol, 9 : 1). – $[\alpha]_D = 106.11$ ($c = 0.53$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 248$ nm (4.06). – IR (KBr): $\nu = 3438$br, 2951s, 1730s, 1662s, 1535w, 1464m, 1432w, 1387m, 1323w, 1258m, 1206s, 1139s, 1087w, 1023w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.22$ (br, 2 H, chain-NH_2), 5.66 (s, 1 H, 12-H), 4.50 (dd, 1 H, $J = 11.7$, 4.7 Hz, 3-H), 3.69 (s, 3 H, OMe), 2.94 (t, 2 H, $J = 6.0$ Hz, chain-δ-CH_2), 2.80 (ddd, 1 H, $J = 13.6$, 3.6, 3.6 Hz, 1-H), 2.37 (s, 1 H, 9-H), 2.35 (t, 2 H, $J = 6.4$ Hz, chain-α-CH_2), 2.09 (dd, 1 H, $J = 13.8$, 4.0 Hz, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, $J = 13.7$,

3.4, 2.2 Hz, 19-H), 1.82 (ddd, 1 H, $J = 13.3, 13.3, 4.0$ Hz, 16-H), 1.72 (m, 1 H, 2-H), 1.70 (m, 2 H, chain-β-CH_2), 1.70 (m, 2 H, chain-γ-CH_2), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.6, 13.6$ Hz, 19′-H), 1.59 (m, 1 H, 6-H), 1.46 (m, 1 H, 6′-H), 1.40 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.19 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.12 (s, 3 H, 26-H), 1.07 (m, 1 H, 1-H′), 1.02 (m, 1 H, 15-H′), 0.87 (s, 3 H, 24-H), 0.86 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.79 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.1$ (C-11), 176.9 (C-30), 173.2 (chain-COO), 169.4 (C-13), 128.5 (C-12), 81.1 (C-3), 61.7 (C-9), 55.0 (C-5), 51.8 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 39.5 (chain-δ-CH_2), 38.7 (C-1), 38.0 (C-4), 37.8 (C-22), 36.9 (C-10), 33.8 (chain-α-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 28.0 (C-23), 27.3 (chain-γ-CH_2), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 21.8 (chain-β-CH_2), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 584.4 (100) $[M+H]^+$, 606.4 (2) $[M+Na]^+$, 876.0 (1) $[2M+2H]^{2+}$, 1167.2 (2) $[2M+H]^+$. – $C_{36}H_{57}NO_5$ (583.84): C 74.06, H 9.84, N 2.40; found C 73.95, H 2.69, N 2.25.

*Methyl (3β)-3-[(6-aminohexanoyl)oxy]-11-oxoolean-12-en-30-oate (**15**)*

Obtained from **29** by method B as a colorless powder. Yield: 90 mg, 58 %. M. p.: 254 – 257 °C. – $R_f = 0.16$ (dichloromethane-methanol, 9 : 1). – $[\alpha]_D = 100.55$ ($c = 0.25$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 250$ nm (4.06). – IR (KBr): $\nu = 3433$br, 2950s, 1730s, 1655s, 1465m, 1388w, 1323w, 1258w, 1212m, 1087w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.66$ (s, 1 H, 12-H), 4.51 (dd, 1 H, $J = 11.7, 4.4$ Hz, 3-H), 3.69 (s, 3 H, OMe), 3.21 (br, 2 H, chain-NH_2), 2.79 (m, 2 H, chain-ε-CH_2), 2.78 (m, 1 H, 1-H), 2.36 (s, 1 H, 9-H), 2.31 (m, 2 H, chain-α-CH_2), 2.08 (dd, 1 H, $J = 13.9, 3.7$ Hz, 18-H), 2.02 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.92 (m 1 H, 19-H), 1.82 (ddd, 1 H, $J = 13.7, 13.7, 4.3$ Hz, 16-H), 1.69 (m, 1 H, 2-H), 1.68 (m, 1 H, 7-H), 1.64 (m, 2 H, chain-β-CH_2), 1.62 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.6, 13.6$ Hz, 19′-H), 1.58 (m, 2 H, chain-δ-CH_2), 1.55 (m, 1 H, 6-H), 1.44 (m, 1 H, 6′-H), 1.41 (m, 1 H, 7′-H), 1.40 (m, 1 H, 22-H), 1.38 (m, 2 H, chain-β-CH_2), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.12 (s, 3 H, 26-H), 1.05 (ddd, 1 H, $J = 13.6, 13.6, 3.7$ Hz, 1-H′), 1.01 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.80 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.0$ (C-11), 176.9 (C-30), 173.4 (chain-COO), 169.2 (C-13), 128.5 (C-12), 80.5 (C-3), 61.7 (C-9), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 40.8 (chain-ε-CH_2), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 34.5 (chain-α-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 30.4 (chain-δ-CH_2), 28.5 (C-28), 28.3 (C-29), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 26.1 (chain-β-CH_2), 24.6 (chain-γ-CH_2), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 598.4 (100) $[M+H]^+$, 944.9 (4) $[3M+2H+3MeOH]^{2+}$. – $C_{37}H_{59}NO_5$ (597.87): C 74.33, H 9.95, N 2.34; found C 74.26, H 10.12, N 2.15.

*Methyl (3β)-3-[(6-aminooctanoyl)oxy]-11-oxoolean-12-en-30-oate (**16**)*

Obtained from **30** by method B as a colorless powder. Yield: 310 mg, 97 %. M. p.: 190 – 193 °C (decomp.). – $R_f = 0.25$ (dichloromethane-methanol, 9 : 1). – $[\alpha]_D = 102.65$ ($c = 0.56$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 249$ nm (4.07). – IR (KBr): $\nu = 3437$br, 2933s, 2875s, 1730s, 1660s, 1465s, 1388m, 1364m, 1323m, 1280m, 1250m, 1217s, 1154s, 1086m, 1049w, 1023w, 987m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.66$ (s, 1 H, 12-H), 4.52 (dd, 1 H, $J = 11.7, 4.7$ Hz, 3-H), 3.69 (s, 3 H, OMe), 2.80 (m, 1 H, 1-H), 2.78 (m, 2 H, chain-η-CH_2), 2.44 (br, 1 H, chain-NH_2), 2.36 (s, 1 H, 9-H), 2.29 (t, 2 H, $J = 7.4$ Hz, chain-α-CH_2), 2.08 (dd, 1 H, $J = 14.0, 4.1$ Hz, 18-H), 2.03 (ddd, 1 H, $J = 13.5, 13.5, 4.4$ Hz, 15-H), 1.99 (m, 1 H, 21-H), 1.92 (ddd, 1 H, $J = 13.6, 3.9, 2.7$ Hz, 19-H), 1.82 (ddd, 1 H, $J = 13.6, 13.6, 4.4$ Hz, 16-H), 1.69 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.62 (m, 2 H, chain-β-CH_2), 1.61 (dd, 1 H, $J = 13.5, 13.5$ Hz, 19′-H), 1.56 (m, 1 H, 6-H), 1.47 (m, 1 H, 6′-H), 1.43 (m, 2 H, chain-ζ-CH_2), 1.41 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.33 (m, 6 H, chain-δ-CH_2 and chain-γ-CH_2, chain-ε-CH_2), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.12 (s, 3 H, 26-H), 1.05 (ddd, 1 H, $J = 13.6, 13.6, 3.8$ Hz, 1-H′), 1.01 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.80 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.8$ (C-11), 176.9 (C-30), 173.6 (chain-COO), 169.2 (C-13), 128.5 (C-12), 80.3 (C-3), 61.7 (C-9), 55.0 (C-5), 51.8 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.3 (chain-η-CH_2), 41.1 (C-19), 38.8 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 34.7 (chain-α-CH_2), 32.7 (C-7), 31.8 (C-17), 31.4 (chain-ζ-CH_2), 31.1 (C-21), 29.0 (chain-δ-CH_2), 28.9 (chain-γ-CH_2), 28.5 (C-28), 28.3 (C-29), 28.1 (C-23), 26.5 (chain-ε-CH_2), 26.5 (C-16), 26.4 (C-15), 25.0 (chain-β-CH_2), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.8 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 626.5 (100) $[M+H]^+$. – $C_{39}H_{63}NO_5$ (625.92): C 74.84, H 10.15, N 2.24; found C 74.75, H 10.23, N 2.02.

*Methyl (3β)-3-[(2,4-diaminobutanoyl)oxy]-11-oxoolean-12-en-30-oate dihydrochloride (**17**)*

Obtained from **31** by method C as a colorless powder. Yield: 160 mg, 52 %. M. p.: > 300 °C (decomp.). – $R_f =$

0.02 (methanol-triethylamine, 95 : 5). – $[\alpha]_D = 117.45$ ($c = 0.47$, MeOH). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon) = 249$ nm (3.99). – IR (KBr): $\nu = 3438$br, 2950s, 1729s, 1659s, 1466m, 1387m, 1323m, 1218s, 1153s, 1085m, 989m, 948m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.44$ (s, 1 H, 12-H), 4.60 (dd, 1 H, $J = 12.1$, 5.1 Hz, 3-H), 4.24 (dd, 1 H, $J = 7.8$, 5.5 Hz, Dab-α-CH), 3.63 (s, 3 H, OMe), 3.02 (m, 2 H, Dab-γ-CH_2), 2.67 (ddd, 1 H, $J = 13.3$, 3.5, 3.5 Hz, 1-H), 2.43 (s, 1 H, 9-H), 2.25 (m, 1 H, Dab-β-C*H*H′), 2.18 (m, 1 H, 18-H), 2.10 (m, 1 H, Dab-β-CH*H*′), 2.08 (m, 1 H, 15-H), 2.01 (m, 1 H, 21-H), 1.83 (m, 1 H, 19-H), 1.86 – 1.61 (m, 5 H, 16-H, H-7, H-6, H-6′, 7′-H), 1.54 (m, 1 H, 2-H), 1.53 (m, 1 H, 2′-H), 1.40 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.36 (m, 2 H, 22′-H and 21′-H), 1.15 (m, 1 H, 16′-H), 1.08 (s, 3 H, 25-H), 1.12 (m, 1 H, 1-H′), 1.11 (s, 3 H, 23-H), 1.06 (s, 3 H, 26-H), 0.94 (m, 1 H, 15-H′, 0.92 (m, 1 H, 5-H), 0.89 (s, 3 H, 24-H), 0.88 (s, 3 H, 28-H), 0.75 (s, 3 H, 29-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.4$ (C-11), 176.7 (C-30), 170.1 (Dab-COO), 169.1 (C-13), 127.7 (C-12), 83.1 (C-3), 61.2 (C-9), 53.9 (C-5), 52.1 (Dab-α-CH), 50.3 (OMe), 48.4 (C-18), 45.3 (C-8), 44.0 (C-20), 43.4 (C-14), 40.6 (C-19), 39.4 (C-1), 38.2 (C-4), 37.8 (C-22), 36.9 (C-10), 35.8 (Dab-β-CH_2), 32.3 (C-7), 32.0 (C-17), 30.8 (C-21), 28.7 (C-29), 28.4 (Dab-γ-CH_2), 28.2 (C-28), 28.1 (C-23), 26.5 (C-16), 26.2 (C-15), 23.6 (C-2), 23.4 (C-27), 18.6 (C-26), 17.3 (C-6), 17.1 (C-24), 16.6 (C-25). – MS (ESI): m/z (%) = 585.5 (100) $[M+H]^+$. – $C_{35}H_{58}Cl_2N_2O_5$ (657.75): C 63.91, H 8.89, N 4.26; found C 63.78, H 9.02, N 4.13.

*Methyl (3β)-3-[(L)-ornithyloxy)]-11-oxoolean-12-en-30-oate (**18**)*

Obtained from **32** by method B as a colorless powder. Yield: 90 mg, 31 %. M. p.: 219 – 223 °C. – $R_f = 0.08$ (dichloromethane-methanol, 9 : 1). – $[\alpha]_D = 103.91$ ($c = 0.58$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon) = 249$ nm (4.03). – IR (KBr): $\nu = 3438$br, 2951s, 2872m, 1729s, 1655s, 1465m, 1388m, 1323w, 1217m, 1153m, 1086w, 1022w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.67$ (s, 1 H, 12-H), 4.56 (dd, 1 H, $J = 11.4$, 4.3 Hz, 3-H), 3.69 (s, 3 H, OMe), 3.45 (m, 1 H, Orn-α-CH), 2.82 (ddd, 1 H, $J = 13.5$, 3.5, 3.5 Hz, 1-H), 2.75 (m, 2 H, Orn-δ-CH_2), 2.37 (s, 1 H, 9-H), 2.09 (m, 1 H, 18-H), 2.03 (m, 1 H, 15-H), 2.00 (m, 1 H, 21-H), 1.93 (m, 1 H, 19-H), 1.87 (m, 1 H, Orn-β-C*H*H′), 1.83 (m, 1 H, 16-H), 1.72 (m, 1 H, 2-H), 1.68 (m, 1 H, 7-H), 1.67 (m, 1 H, Orn-β-CH*H*′), 1.64 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.5$, 13.5 Hz, 19′-H), 1.60 (m, 1 H, 6-H), 1.58 (m, 2 H, Orn-γ-CH_2), 1.46 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.41 (m, 1 H, 22-H), 1.38 (s, 3 H, 27-H), 1.32 (m, 2 H, 22′-H and 21′-H), 1.19 (m, 1 H, 16′-H), 1.15 (s, 3 H, 25-H), 1.13 (s, 3 H, 29-H), 1.11 (s, 3 H, 26-H), 1.07 (m, 1 H, 1-H′), 1.02 (m, 1 H, 15-H′), 0.90 (s, 3 H, 24-H), 0.89 (s, 3 H, 23-H), 0.82 (m, 1 H, 5-H), 0.81 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.2$ (C-11), 176.9 (C-30), 174.9 (Orn-COO), 169.1 (C-13), 128.5 (C-12), 78.7 (C-3), 61.8 (C-9), 54.9 (C-5), 53.7 (Orn-α-CH), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.7 (Orn-δ-CH_2), 41.1 (C-19), 39.1 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 29.8 (Orn-β-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-28), 28.1 (C-23), 27.3 (Orn-γ-CH_2), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.4 (C-27), 18.7 (C-26), 17.5 (C-6), 16.8 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 599.5 (1100) $[M+H]^+$. – $C_{36}H_{58}N_2O_5$ (598.86): C 72.20, H 9.76, N 4.68; found C 72.01, H 9.90, N 4.55.

*Methyl (3β)-3-[(L)-lysyloxy]-11-oxoolean-12-en-30-oate (**19**)*

Obtained from **33** by method B as a colorless powder. Yield: 240 mg, 87 %. M. p.: 255 – 257 °C (decomp.). – $R_f = 0.02$ (dichloromethane-methanol, 9 : 1). – $[\alpha]_D = 112.21$ ($c = 0.41$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon) = 267$ nm (4.09). – IR (KBr): $\nu = 3432$br, 2929s, 2858m, 1729s, 1653s, 1464m, 1388m, 1323w, 1260w, 1216m, 1188m, 1154m, 1087w, 1022w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.64$ (s, 1 H, 12-H), 4.53 (dd, 1 H, $J = 11.8$, 4.7 Hz, 3-H), 3.66 (s, 3 H, OMe), 3.41 (m, 1 H, Lys-α-CH), 2.79 (ddd, 1 H, $J = 13.7$, 3.5, 3.5 Hz, 1-H), 3.69 (m, 2 H, Lys-ε-CH_2), 2.34 (s, 1 H, 9-H), 2.05 (m, 1 H, 18-H), 1.99 (m, 1 H, 15-H), 1.98 (m, 1 H, 21-H), 1.91 (m, 1 H, 19-H), 1.81 (m, 1 H, 16-H), 1.78 (m, 1 H, Lys-β-C*H*H′), 1.72 (m, 1 H, 2-H), 1.63 (m, 1 H, 7-H), 1.61 (m, 1 H, 2′-H), 1.60 (dd, 1 H, $J = 13.6$, 13.6 Hz, 19′-H), 1.59 (m, 1 H, 6-H), 1.58 (m, 1 H, Lys-β-CH*H*′), 1.45 (m, 2 H, Lys-δ-CH_2), 1.42 (m, 1 H, 6′-H), 1.41 (m, 2 H, Lys-γ-CH_2), 1.39 (m, 1 H, 7′-H), 1.36 (m, 1 H, 22-H), 1.35 (s, 3 H, 27-H), 1.32 (m, 2 H, 22′-H and 21′-H), 1.17 (m, 1 H, 16′-H), 1.15 (s, 3 H, 25-H), 1.13 (s, 3 H, 29-H), 1.11 (s, 3 H, 26-H), 1.04 (m, 1 H, 1-H′), 1.00 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.86 (s, 3 H, 23-H), 0.80 (m, 1 H, 5-H), 0.79 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.0$ (C-11), 176.9 (C-30), 175.8 (Lys-COO), 169.2 (C-13), 128.5 (C-12), 80.7 (C-3), 61.7 (C-9), 55.0 (C-5), 54.7 (Lys-α-CH), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.9 (Lys-ε-CH_2), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 34.5 (Lys-β-CH_2), 33.2 (Lys-δ-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-29), 28.3 (C-28), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 22.9 (Lys-γ-CH_2), 18.6 (C-26), 17.3 (C-6), 16.8 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 613.4 (100) $[M+H]^+$, 671.3 (38) $[M+2NH_4+MeOH]^+$. – $C_{37}H_{60}N_2O_5$ (612.88): C 72.51, H 9.87, N 4.57; found C 72.37, H 9.99, N 4.51.

*Methyl (3β)-3-{N-[(tert-butoxycarbonyl)-sarcosyl]oxy}-11-oxo-olean-12-en-30-oate (**20**)*

Obtained from **1** by method A as a colorless powder. Yield: 420 mg, 94 %. M. p.: 202 – 204 °C (decomp.). – R_f = 0.52 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 102.81$ ($c = 0.48$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon) = 250$ nm (4.08). – IR (KBr): ν = 3435br, 2972s, 1726s, 1701s, 1655s, 1618m, 1485m, 1457s, 1423m, 1392s, 1367s, 1320m, 1302m, 1264s, 1238s, 1219s, 1154s, 1088w, 1011w, 982m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.57 (dd, 1 H, J = 11.3, 4.9 Hz, 3-H), 3.90 (s, 2 H, Sar-CH_2), 3.68 (s, 3 H, OMe), 2.93 (s, 3 H, NCH_3), 2.81 (m, 1 H, 1-H), 2.36 (s, 1 H, 9-H), 2.08 (m, 1 H, 18-H), 2.02 (ddd, 1 H, J = 13.9, 13.9, 4.4 Hz, 15-H), 1.99 (m, 1 H, 21-H), 1.92 (ddd, 1 H, J = 13.4, 3.6, 2.4 Hz, 19-H), 1.82 (ddd, 1 H, J = 13.7, 13.7, 4.0 Hz, 16-H), 1.70 (m, 1 H, 2-H), 1.65 (m, 1 H, 2′-H), 1.63 (m, 1 H, 7-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.57 (m, 1 H, 6-H), 1.43 (s, 9 H, Boc-CH_3), 1.41 (m, 1 H, 6′-H), 1.40 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 29-H), 1.14 (s, 3 H, 25-H), 1.12 (s, 3 H, 26-H), 1.06 (m, 1 H, 1-H′), 1.01 (m, 1 H, 15-H′), 0.89 (s, 3 H, 24-H), 0.88 (s, 3 H, 23-H), 0.81 (m, 1 H, 5-H), 0.80 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 169.7 (Sar-COO), 169.3 (C-13), 155.4 (Boc-COO), 128.5 (C-12), 81.6 (C-3), 80.1 (Boc-*quart.*-C), 61.7 (C-9), 55.0 (C-5), 51.7 (OMe), 51.3 (Sar-CH_2), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 35.6 (NCH_3), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (Boc-CH_3), 28.2 (C-29), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 656.0 (7) $[M+H]^+$, 678.4 (100) $[M+Na]^+$, 1006.3 (10) $[3M+Na]^{2+}$. – $C_{39}H_{61}NO_7$ (655.90): C 71.42, H 9.37, N 2.14; found C 71.31, H 9.52, N 2.09.

*Methyl (3β)-3-{N-[(tert-butoxycarbonyl)-(L)-prolyl]oxy}-11-oxo-olean-12-en-30-oate (**21**)*

Obtained from **1** by method A as a colorless powder. Yield: 260 mg, 62 %. M. p.: 155 – 158 °C (decomp.). – R_f = 0.42 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 68.01$ (c = 0.26, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon) = 249$ nm (4.04). – IR (KBr): ν = 3442br, 2972s, 2876m, 2361w, 1731s, 1694s, 1657s, 1619w, 1455m, 1401s, 1365m, 1324m, 1281m, 1262m, 1215s, 1160s, 1126m, 1084m, 1021w, 988m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.64 (s, 1 H, 12-H), 4.51 (m, 1 H, 3-H), 4.21 (m, 1 H, Pro-α-CH), 3.67 (s, 3 H, OMe), 3.50 (m, 1 H, Pro-δ-C*H*H′), 3.40 (m, 1 H, Pro-δ-CH*H*′), 2.79 (ddd, 1 H, J = 13.7, 3.3, 3.3 Hz, 1-H), 2.33 (s, 1 H, 9-H), 2.20 (m, 1 H, Pro-β-C*H*H′), 2.06 (m, 1 H, 18-H), 1.98 (m, 1 H, 15-H), 1.96 (m, 1 H, 21-H), 1.94 (m, 1 H, Pro-β-CH*H*′), 1.90 (m, 1 H, 19-H), 1.86 (m, 1 H, 2-H), 1.85 (m, 2 H, Pro-γ-CH_2), 1.79 (m, 1 H, 16-H), 1.63 (m, 1 H, 7-H), 1.62 (m, 1 H, 2′-H), 1.60 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.42 (m, 1 H, 6′-H), 1.40 (m, 1 H, 7′-H), 1.40 (s, 9 H, Boc-CH_3), 1.38 (m, 1 H, 22-H), 1.34 (s, 3 H, 27-H), 1.29 (m, 2 H, 22′-H and 21′-H), 1.17 (m, 1 H, 16′-H), 1.14 (s, 3 H, 25-H), 1.12 (s, 3 H, 29-H), 1.09 (s, 3 H, 26-H), 1.04 (m, 1 H, 1-H′), 1.00 (m, 1 H, 15-H′), 0.86 (s, 3 H, 24-H), 0.85 (s, 3 H, 23-H), 0.80m, 1 H, 5-H), 0.78 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 172.8 (Pro-COO), 169.3 (C-13), 155.9 (Boc-COO), 128.5 (C-12), 81.4 (C-3), 79.9 (Boc-*quart.*-C), 61.1 (C-9), 59.4 (Pro-α-CH), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 46.3 (Pro-δ-CH_2), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 30.2 (Pro-β-CH_2), 28.5 (C-29), 28.4 (Boc-CH_3), 28.3 (C-28), 28.2 (C-23), 26.5 (C-16), 26.4 (C-15), 24.3 (Pro-γ-CH_2), 23.5 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 682.2 (10) $[M+H]^+$, 704.4 (100) $[M+Na]^+$, 1045.3 (8) $[3M+2Na]^{2+}$, 1385.2 (14) $[2M+Na]^+$. – $C_{41}H_{63}NO_7$ (681.94): C 72.21, H 9.31, N 2.05; found C 72.00, H 9.55, N 1.88.

*Methyl (3β)-3-{N-[(tert-butoxycarbonyl)-(L)-phenylalanyl]oxy}-11-oxo-olean-12-en-30-oate (**22**)*

Obtained from **1** by method A as a colorless powder. Yield: 630 mg, 80 %. M. p.: 128 – 131 °C (decomp.). – R_f = 0.58 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 92.60$ (c = 0.51, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon) = 249$ nm (4.07). – IR (KBr): ν = 3328br, 2973s, 2866s, 1731s, 1645s, 1531s, 1496s, 1455s, 1390s, 1366s, 1318s, 1280s, 1247s, 1167s, 1085m, 1050s, 1027m, 983s, 915w, 881w, 864m, 832w, 780w, 768w, 746m, 699s cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.16 (br, 5 H, Phe-Ar), 5.67 (s, 1 H, 12-H), 4.89 (d, 1 H, J = 8.8 Hz, Phe-NH), 4.57 (m, 1 H, Phe-α-CH), 4.53 (dd, 1 H, J = 9.8, 5.3 Hz, 3-H), 3.69 (s, 3 H, OMe), 3.13 (dd, 1 H, J = 13.6, 5.9 Hz, Phe-β-C*H*H′), 3.04 (dd, 1 H, J = 14.2, 6.4 Hz, Phe-β-CH*H*′), 2.80 (m, 1 H, 1-H), 2.35 (s, 1 H, 9-H), 2.08 (m, 1 H, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, J = 13.3, 3.5, 1.9 Hz, 19-H), 1.82 (ddd, 1 H, J = 13.6, 13.6, 4.5 Hz, 16-H), 1.68 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.55 (m, 1 H, 6-H), 1.45 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.41 (m, 1 H, 22-H), 1.40 (s, 9 H, Boc-CH_3), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.15 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.12 (s, 3 H, 26-H), 1.07 (m, 1 H, 1-H′), 1.02 (m, 1 H, 15-H′), 0.82 (s, 3 H, 24-H), 0.81 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.78 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 171.8 (Phe-COO), 169.2 (C-13), 157.3 (Boc-COO), 136.1 (Phe-γ-C), 129.4 (Phe-Ar), 128.5 (C-12), 128.5 (Phe-Ar), 82.1 (C-3), 79.8 (Boc-*quart.*-

C), 61.7 (C-9), 55.0 (C-5), 54.7 (Phe-α-CH), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.4 (Phe-β-CH_2), 38.0 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (Boc-CH_3), 28.3 (C-29), 28.0 (C-23), 26.5 (C-16), 26.4 (C-15), 23.4 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 732.1 (18) $[M+H]^+$, 749.3 (10) $[M+NH_4]^+$, 754.4 (100) $[M+Na]^+$, 1119.8 (8) $[3M+2Na]^{2+}$, 1464.0 (6) $[2M+2H]^+$, 1486.2 (14) $[2M+Na]^+$. – $C_{45}H_{65}NO_7$ (732.00): C 73.84, H 8.95, N 1.91; found C 73.68, H 9.02, N 1.76.

*Methyl (3β)-3-{N-[(tert-butoxycarbonyl)-(L)-methionyl]oxy}-11-oxo-olean-12-en-30-oate (**23**)*

Obtained from **1** by method A as a colorless powder. Yield: 410 mg, 96 %. M. p.: 220 – 223 °C (decomp.). – R_f = 0.56 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D$ = 69.15 (c = 0.25, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 249 nm (4.01). – IR (KBr): ν = 3386br, 2972s, 2873m, 1724s, 1655s, 1513m, 1455m, 1390m, 1367m, 1249m, 1217s, 1166s, 1086m, 1049w, 1024w, 984m, 916m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 5.10 (d, 1 H, J = 7.5, Met-NH), 4.56 (dd, 1 H, J = 11.7, 4.7 Hz, 3-H), 4.39 (m, 1 H, Met-α-CH), 3.68 (s, 3 H, OMe), 2.82 (ddd, 1 H, J = 13.7, 3.6, 3.6 Hz, 1-H), 2.55 (m, 2 H, Met-β-CH_2), 2.35 (s, 1 H, 9-H), 2.15 (m, 1 H, Met-γ-C*H*H′), 2.10 (s, 3 H, Met-CH_3), 2.08 (m, 1 H, 18-H), 2.02 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (m, 1 H, 19-H), 1.84 (m, 1 H, 16-H), 1.75 (m, 1 H, Met-γ-CH*H*′), 1.72 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.6, 13.6 Hz, 19′-H), 1.57 (m, 1 H, 6-H), 1.48 (m, 1 H, 6′-H), 1.44 (s, 9 H, Boc-CH_3), 1.42 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.05 (ddd, 1 H, J = 13.6, 13.6, 3.6 Hz, 1-H′), 1.01 (m, 1 H, 15-H′), 0.90 (s, 3 H, 24-H), 0.88 (s, 3 H, 23-H), 0.80 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.9 (C-30), 171.9 (Met-COO), 169.2 (C-13), 155.3 (Boc-COO), 128.5 (C-12), 82.2 (C-3), 79.9 (Boc-*quart.*-C), 61.6 (C-9), 55.0 (C-5), 53.2 (Met-α-CH), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.6 (C-7), 32.5 (Met-γ-CH_2), 31.8 (C-17), 31.1 (C-21), 30.0 (Met-β-CH_2), 28.5 (C-28), 28.3 (Boc-CH_3), 28.3 (C-29), 28.2 (C-23), 26.4 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.8 (C-24), 16.3 (C-25), 15.4 (Met-CH_3). – MS (ESI): m/z (%) = 733.1 (10) $[M+NH_4]^+$, 738.3 (100) $[M+Na]^+$, 1096.1 (6) $[3M+2Na+H]^{2+}$, 1453.6 (7) $[2M+Na]^+$. – $C_{41}H_{65}NO_7S$ (716.02): C 68.77, H 9.15, N 1.96. – S, 4.48; found C 68.72, H 9.32, N 1.85. – S, 4.32.

*Methyl (3β)-3-{N-[(tert-butoxycarbonyl)-(L)-valyl]oxy}-11-oxo-olean-12-en-30-oate (**24**)*

Obtained from **1** by method A as a colorless powder. Yield: 420 mg, 96 %. M. p.: 209 – 213 °C (decomp.). – R_f = 0.66 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D$ = 78.84 (c = 0.33, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 249 nm (3.95). – IR (KBr): ν = 3401br, 2968s, 2874m, 2120w, 1727s, 1659s, 1511m, 1465m, 1391m, 1367m, 1305m, 1258m, 1216m, 1161s, 1087m, 1020w m^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.99 (d, 1 H, J = 8.8 Hz, Val-NH), 4.55 (dd, 1 H, J = 11.4, 4.9 Hz, 3-H), 4.22 (dd, 1 H, J = 8.8, 4.0 Hz, Val-α-CH), 3.68 (s, 3 H, OMe), 2.81 (ddd, 1 H, J = 13.7, 3.4, 3.4 Hz, 1-H), 2.35 (s, 1 H, 9-H), 2.17 (m, 1 H, Val-β-CH), 2.08 (dd, 1 H, J = 14.1, 3.4 Hz, 18-H), 2.02 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.92 (ddd, 1 H, J = 13.9, 4.0, 2.3 Hz, 19-H), 1.82 (m, 1 H, 16-H), 1.72 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.5, 13.5 Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.46 (m, 1 H, 6′-H), 1.44 (s, 9 H, Boc-CH_3), 1.43 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.14 (s, 3 H, 29-H), 1.12 (s, 3 H, 26-H), 1.08 (m, 1 H, 1-H′), 1.03 (m, 1 H, 15-H′), 0.99 (d, 3 H, Val-CH_3, J = 6.8 Hz), 0.88 (m, 3 H, Val-CH_3), 0.89 (s, 3 H, 24-H), 0.88 (s, 3 H, 23-H), 0.80 (s, 3 H, 28-H), 0.79 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.9 (C-30), 172.0 (Val-COO), 169.2 (C-13), 155.7 (Boc-COO), 128.5 (C-12), 81.9 (C-3), 79.6 (Boc-*quart.*-C), 61.7 (C-9), 58.9 (Val-α-CH), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 45.3 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.0 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.2 (Val-β-CH), 31.1 (C-21), 28.5 (C-28), 28.3 (Boc-CH_3), 28.3 (C-29), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 19.3 (Val-CH_3), 18.7 (C-26), 17.3 (C-6), 17.2 (Val-CH_3), 16.8 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 684.1 (10) $[M+H]^+$, 701.3 (15) $[M+NH_4]^+$, 706.3 (100) $[M+Na]^+$, 1048.3 (10) $[3M+2Na+H]^{2+}$, 1367.0 (8) $[2M+H]^+$, 1390.1 (20) $[2M+Na]^+$. – $C_{41}H_{65}NO_7$ (683.96): C 72.00, H 9.58, N 2.05; found C 71.92, H 9.77, N 1.90.

*Methyl (3β)-3-{N-[(tert-butoxycarbonyl)-(L)-isoleucyl]oxy}-11-oxo-olean-12-en-30-oate (**25**)*

Obtained from **1** by method A as a colorless powder. Yield: 220 mg, 49 %. M. p.: 183 – 186 °C (decomp.). – R_f = 0.69 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D$ = 87.63 (c = 0.54, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 249 nm (3.91). – IR (KBr): ν = 3387br, 2968s, 2876m, 1728s, 1652s, 1510m, 1464m, 1390m, 1365m, 1335m, 1290m, 1248m, 1215s, 1159s, 1085m, 1049m, 1023m, 984m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.99 (d, 1 H, J = 9.0 Hz, Ile-NH), 4.56 (dd, 1 H, J = 11.4, 4.9 Hz, 3-H), 4.26 (dd, 1 H, J = 9.0, 3.8 Hz, Ile-α-CH), 3.69 (s, 3

H, OMe), 2.81 (ddd, 1 H, $J = 13.7, 3.5, 3.5$ Hz, 1-H), 2.35 (s, 1 H, 9-H), 2.08 (dd, 1 H, $J = 14.0, 3.4$ Hz, 18-H), 2.02 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.90 (m, 1 H, 19-H), 1.82 (m, 1 H, Ile-β-CH), 1.82 (m, 1 H, 16-H), 1.70 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.6, 13.6$ Hz, 19′-H), 1.56 (m, 1 H, 6-H), 1.45 (m, 1 H, 6′-H), 1.44 (s, 9 H, Boc-CH_3), 1.41 (m, 1 H, 7′-H), 1.40 (m, 2 H, Ile-γ-CH_2), 1.38 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.08 (m, 1 H, 1-H′), 1.01 (m, 1 H, 15-H′), 0.96 (d, 3 H, $J = 6.8$ Hz, Ile-β-CH_3), 0.91 (t, 3 H, $J = 7.3$ Hz, Ile-γ-CH_3), 0.90 (s, 3 H, 24-H), 0.88 (s, 3 H, 23-H), 0.80 (s, 3 H, 28-H), 0.79 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.9$ (C-11), 176.9 (C-30), 171.9 (Ile-COO), 169.2 (C-13), 155.6 (Boc-COO), 128.5 (C-12), 81.9 (C-3), 79.6 (Boc-*quart.*-C), 61.7 (C-9), 58.5 (Ile-α-CH), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.0 (C-4), 37.9 (Ile-β-CH), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (Boc-CH_3), 28.3 (C-29), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 24.7 (Ile-γ-CH_2), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.8 (C-24), 16.3 (C-25), 15.7 (Ile-β-CH_3), 11.6 (Ile-γ-CH_3). – MS (ESI): m/z (%) = 698.2 (16) $[M+H]^+$, 709.7 (8) $[2M+Na+H]^{2+}$, 715.2 (15) $[M+NH_4]^+$, 720.4 (100) $[M+Na]^+$, 1058.2 (4) $[3M+Na+2H]^{2+}$, 1066.7 (7) $[3M+K+2H]^{2+}$, 1069.3 (12) $[3M+2Na]^{2+}$, 1418.1 (22) $[2M+Na]^+$. – $C_{42}H_{67}NO_7$ (697.98): C 72.27, H 9.68, N 2.01; found C 72.07, H 9,81, N 1.89.

*Methyl (3β)-3-{N-[(tert-butoxycarbonyl)-(L)-leucyl]oxy}-11-oxo-olean-12-en-30-oate (**26**)*

Obtained from **1** by method A as a colorless powder. Yield: 460 mg, 98 %. M. p.: 215 – 219 °C (decomp.). – $R_f = 0.65$ (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 73.31$ ($c = 0.30$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 249$ nm (4.04). – IR (KBr): $\nu = 3387$br, 2955s, 2871m, 1731s, 1661s, 1506m, 1455m, 1390m, 1367m, 1250m, 1216s, 1166s, 1087w, 1048w, 1021w, 985m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.66$ (s, 1 H, 12-H), 4.87 (m, 1 H, Leu-NH), 4.54 (dd, 1 H, $J = 11.7, 4.7$ Hz, 3-H), 4.29 (m, 1 H, Leu-α-CH), 3.68 (s, 3 H, OMe), 2.81 (ddd, 1 H, $J = 13.6, 3.5, 3.5$ Hz, 1-H), 2.35 (s, 1 H, 9-H), 2.08 (dd, 1 H, $J = 13.9, 3.6$ Hz, 18-H), 2.02 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.92 (ddd, 1 H, $J = 13.5, 3.4, 2.7$ Hz, 19-H), 1.82 (ddd, 1 H, $J = 13.5, 13.5, 4.1$ Hz, 16-H), 1.76 (m, 1 H, Leu-γ-CH), 1.72 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.5, 13.5$ Hz, 19′-H), 1.59 (m, 1 H, Leu-β-C*H*H′), 1.58 (m, 1 H, 6-H), 1.48 (m, 1 H, Leu-β-CH*H*′), 1.44 (s, 9 H, Boc-CH_3), 1.44 (m, 1 H, 6′-H), 1.42 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.12 (s, 3 H, 26-H), 1.04 (m, 1 H, 1-H′), 1.01 (m, 1 H, 15-H′), 0.96 (d, 3 H, $J = 6.4$ Hz, Leu-γ-CH_3), 0.95 (d, 3 H, $J = 6.4$ Hz, Leu-γ-CH_3), 0.89 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.80 (s, 3 H, 29-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.9$ (C-11), 176.9 (C-30), 173.1 (Leu-COO), 169.2 (C-13), 155.3 (Boc-COO), 128.5 (C-12), 81.6 (C-3), 79.6 (Boc-*quart.*-C), 61.7 (C-9), 55.0 (C-5), 52.5 (Leu-α-CH), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 42.0 (Leu-β-CH_2), 41.1 (C-19), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (Boc-CH_3), 28.3 (C-29), 28.2 (C-23), 26.4 (C-16), 26.4 (C-15), 24.8 (Leu-γ-CH), 23.5 (C-2), 23.3 (C-27), 22.9 (Leu-γ-CH_3), 21.9 (Leu-γ-CH_3), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 697.9 (10) $[2M+H]^{2+}$, 720.3 (100) $[M+Na]^+$, 1069.3 (4) $[3M+2Na]^{2+}$, 1418.1 (12) $[2M+Na]^+$. – $C_{42}H_{67}NO_7$ (697.98): C 72.27, H 9.68, N 2.01; found C 72.17, H 9.83, N 1.88.

*Methyl (3β)-3-({4-[(tert-butoxycarbonyl)amino]butanoyl}-oxy)-11-oxoolean-12-en-30-oate (**27**)*

Obtained from **1** by method A as a colorless powder. Yield: 440 mg, 52 %. M. p.: 195 – 198 °C (decomp.). – $R_f = 0.38$ (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 108.46$ ($c = 0.43$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 249$ nm (4.08). – IR (KBr): $\nu = 3329$br, 2965s, 2873m, 1733s, 1706s, 1682s, 1653s, 1616w, 1537m, 1454m, 1390m, 1365m, 1324m, 1252m, 1210m, 1171s, 1087w, 1044w, 1026w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.66$ (s, 1 H, 12-H), 4.62 (br, 1 H, chain-NH), 4.56 (dd, 1 H, $J = 11.5, 4.7$ Hz, 3-H), 3.69 (s, 3 H, OMe), 3.17 (dt, 2 H, $J = 6.4, 6.4$ Hz, chain-γ-CH_2), 2.81 (ddd, 1 H, $J = 13.7, 3.4, 3.4$ Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.35 (t, 2 H, $J = 7.4$ Hz, chain-α-CH_2), 2.08 (dd, 1 H, $J = 14.1, 3.8$ Hz, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, $J = 13.5, 3.8, 2.5$ Hz, 19-H,), 1.82 (m, 1 H, 16-H), 1.81 (m, 2 H, chain-β-CH_2), 1.70 (m, 1 H, 2-H), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.5, 13.5$ Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.45 (m, 1 H, 6′-H), 1.44 (s, 9 H, Boc-CH_3), 1.41 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.05 (ddd, 1 H, $J = 13.6, 13.6, 4.0$ Hz, 1-H′), 1.02 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.7$ (C-11), 176.7 (C-30), 172.8 (chain-COO), 168.9 (C-13), 155.8 (Boc-COO), 128.4 (C-12), 80.7 (C-3), 79.6 (Boc-*quart.*-C), 61.8 (C-9), 55.1 (C-5), 51.8 (OMe), 48.5 (C-18), 45.5 (C-8), 44.1 (C-20), 43.3 (C-14), 41.2 (C-19), 40.2 (chain-γ-CH_2), 38.9 (C-1), 38.2 (C-4), 37.8 (C-22), 37.1 (C-10), 32.8 (C-7), 32.1 (chain-α-CH_2), 31.9 (C-17), 31.3 (C-21), 28.6 (C-28),

28.5 (Boc-CH_3), 28.4 (C-29), 28.2 (C-23), 26.6 (C-16), 26.6 (C-15), 25.5 (chain-β-CH_2), 23.7 (C-2), 23.4 (C-27), 18.8 (C-26), 17.5 (C-6), 16.9 (C-24), 16.5 (C-25). – MS (ESI): m/z (%) = 670.4 (4) $[M+H]^+$, 689.6 (1) $[2M+K+H]^{2+}$, 692.5 (100) $[M+Na]^+$, 1024.8 (6) $[3M+K+2H]^{2+}$, 1027.4 (30) $[3M+2Na]^{2+}$, 1361.3 (26) $[2M+Na]^+$. – $C_{40}H_{63}NO_7$ (669.93): C 71.71, H 9.48, N 2.09; found C 71.58, H 9.54, N 2.00.

*Methyl (3β)-3-({5-[(tert-butoxycarbonyl)amino]-pentanoyl}oxy)-11-oxoolean-12-en-30-oate (**28**)*

Obtained from **1** by method A as a colorless powder. Yield: 470 mg, 47 %. M. p.: 185 – 188 °C. – R_f = 0.35 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D$ = 110.18 (c = 0.47, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 248 nm (4.18). – IR (KBr): ν = 3401br, 2970s, 2872m, 1732s, 1714s, 1660s, 1619w, 1520m, 1458m, 1386m, 1364m, 1345w, 1318w, 1279m, 1249s, 1212m, 1170s, 1141m, 1105m, 1088w, 1020w, 982m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.67 (s, 1 H, 12-H), 4.54 (br, 1 H, chain-NH), 4.52 (dd, 1 H, J = 11.6, 4.8 Hz, 3-H), 3.69 (s, 3 H, OMe), 3.13 (dt, 2 H, J = 6.2, 6.2 Hz, chain-δ-CH_2), 2.80 (ddd, 1 H, J = 13.6, 3.4, 3.4 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.33 (t, 2 H, J = 7.4 Hz, chain-α-CH_2), 2.08 (dd, 1 H, J = 14.0, 4.2 Hz, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, J = 13.7, 3.5, 2.7 Hz, 19-H), 1.83 (ddd, 1 H, J = 13.6, 13.6, 4.7 Hz, 16-H), 1.70 (m, 1 H, 2-H), 1.66 (m, 2 H, chain-β-CH_2), 1.66 (m, 1 H, 7-H), 1.63 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.3, 13.3 Hz, 19′-H), 1.57 (m, 1 H, 6-H), 1.52 (m, 2 H, chain-γ-CH_2), 1.46 (m, 1 H, 6′-H), 1.44 (s, 9 H, Boc-CH_3), 1.42 (m, 1 H, 7′-H), 1.39 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.32 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.17 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.06 (ddd, 1 H, J = 13.4, 13.4, 3.9 Hz, 1-H′), 1.01 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.8 (C-30), 172.2 (chain-COO), 169.1 (C-13), 155.8 (Boc-COO), 128.5 (C-12), 80.5 (C-3), 78.3 (Boc-*quart.*-C), 61.7 (C-9), 54.9 (C-5), 51.7 (OMe), 48.3 (C-18), 45.3 (C-8), 43.9 (C-20), 43.1 (C-14), 41.0 (C-19), 40.0 (chain-δ-CH_2), 38.7 (C-1), 38.0 (C-4), 37.6 (C-22), 36.9 (C-10), 34.2 (chain-α-CH_2), 32.6 (C-7), 31.7 (C-17), 31.0 (C-21), 29.5 (chain-γ-CH_2), 28.4 (C-28), 28.3 (Boc-CH_3), 28.2 (C-29), 28.0 (C-23), 26.4 (C-16), 26.3 (C-15), 23.5 (C-2), 23.2 (C-27), 22.1 (chain-β-CH_2), 18.6 (C-26), 17.3 (C-6), 16.7 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 684.3 (15) $[M+H]^+$, 695.7 (2) $[2M+Na+H]^{2+}$, 706.5 (100) $[M+Na]^+$, 1045.3 (4) $[3M+K+2H]^{2+}$, 1048.3 (19) $[3M+2Na]^{2+}$, 1389.2 (26) $[3M+2Na]^{2+}$, 1405.1 (3) $[2M+K]^+$. – $C_{41}H_{65}NO_7$ (683.96): C 72.00, H 9.58, N 2.05; found C 71.87, H 9.75, N 1.93.

*Methyl (3β)-3-({6-[(tert-butoxycarbonyl)amino]hexanoyl}-oxy)-11-oxoolean-12-en-30-oate (**29**)*

Obtained from **1** by method A as a colorless powder. Yield: 290 mg, 64 %. M. p.: 140 – 143 °C. – R_f = 0.44 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D$ = 77.46 (c = 0.51, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 249 nm (4.02). – IR (KBr): ν = 3406br, 2934s, 1732s, 1652s, 1515m, 1456m, 1390m, 1366m, 1251m, 1212m, 1169s, 1087w cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.52 (dd, 1 H, J = 11.5, 4.7 Hz, 3-H), 4.51 (br, 1 H, chain-NH), 3.69 (s, 3 H, OMe), 3.11 (dt, 2 H, J = 5.8, 5.8 Hz, chain-ε-CH_2), 2.80 (ddd, 1 H, J = 13.7, 3.4, 3.4 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.31 (dt, 2 H, J = 7.4, 2.1 Hz, chain-α-CH_2), 2.08 (dd, 1 H, J = 13.8, 3.9 Hz, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.92 (ddd, 1 H, J = 13.5, 3.5, 2.7 Hz, 19-H), 1.82 (ddd, 1 H, J = 13.6, 13.6, 4.6 Hz, 16-H), 1.70 (m, 1 H, 2-H), 1.67 (m, 1 H, 7-H), 1.64 (m, 2 H, chain-β-CH_2), 1.62 (m, 1 H, 2′-H), 1.61 (dd, 1 H, J = 13.7, 13.7 Hz, 19′-H,), 1.57 (m, 1 H, 6-H), 1.49 (m, 2 H, chain-δ-CH_2), 1.46 (m, 1 H, 6′-H), 1.43 (s, 9 H, Boc-CH_3), 1.41 (m, 1 H, 7′-H), 1.37 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.35 (m, 2 H, chain-β-CH_2), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.16 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.05 (ddd, 1 H, J = 13.6, 13.6, 3.8 Hz, 1-H′), 1.01 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.80 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.0 (C-11), 176.9 (C-30), 173.3 (chain-COO), 169.2 (C-13), 155.9 (Boc-COO), 128.5 (C-12), 80.4 (C-3), 78.4 (Boc-*quart.*-C), 61.7 (C-9), 55.0 (C-5), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 40.4 (chain-ε-CH_2), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 34.6 (chain-α-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 29.7 (chain-δ-CH_2), 28.5 (C-28), 28.4 (Boc-CH_3), 28.3 (C-29), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 26.3 (chain-β-CH_2), 24.7 (chain-γ-CH_2), 23.6 (C-2), 23.3 (C-27), 18.6 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 698.3 (66) $[M+H]^+$, 720.5 (100) $[M+Na]^+$, 1417.4 (24) $[2M+Na]^+$. – $C_{42}H_{67}NO_7$ (697.98): C 72.27, H 9.68, N 2.01; found C 72.18, H 9.83, N 1.91.

*Methyl (3β)-3-({6-[(tert-butoxycarbonyl)amino]octanoyl}-oxy)-11-oxoolean-12-en-30-oate (**30**)*

Obtained from **1** by method A as a colorless powder. Yield: 490 mg, 70 %. M. p.: 150 – 152 °C. – R_f = 0.52 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D$ = 98.61 (c = 0.58, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log\varepsilon)$ = 249 nm (4.08). – IR (KBr): ν = 3384br, 2929s, 2859s, 1715s, 1656s, 1620m, 1531s, 1456s, 1392s, 1365s, 1348m, 1322m, 1252s, 1211s, 1171s, 1090m, 1014m, 986m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 1 H, 12-H), 4.52 (dd, 1 H, J = 11.6, 4.8 Hz, 3-H), 4.51 (br, 1 H, chain-NH), 3.69 (s, 3 H, OMe), 3.09 (m, 2 H, chain-η-CH_2), 2.80 (ddd, 1 H, J = 13.7, 3.5,

3.5 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.29 (t, 2 H, $J = 7.4$ Hz, chain-α-CH_2), 2.08 (dd, 1 H, $J = 13.8$, 4.1 Hz, 18-H), 2.03 (m, 1 H, 15-H), 1.99 (m, 1 H, 21-H), 1.93 (ddd, 1 H, $J = 13.4$, 4.3, 2.9 Hz, 19-H), 1.83 (ddd, 1 H, $J = 13.5$, 13.5, 4.4 Hz, 16-H), 1.70 (m, 1 H, 2-H), 1.65 (m, 1 H, 7-H), 1.63 (m, 2 H, chain-β-CH_2), 1.62 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.6$, 13.6 Hz, 19′-H), 1.59 (m, 1 H, 6-H), 1.48 (m, 1 H, 6′-H), 1.46 (m, 2 H, chain-ζ-CH_2), 1.44 (s, 9 H, Boc-CH_3), 1.43 (m, 1 H, 7′-H), 1.41 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.32 (m, 4 H, chain-δ-CH_2 and chain-γ-CH_2), 1.31 (m, 2 H, 22′-H and 21′-H), 1.30 (m, 2 H, chain-ε-CH_2), 1.18 (m, 1 H, 16′-H), 1.17 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.06 (m, 1 H, 1′-H), 1.01 (m, 1 H, 15′-H), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 200.1$ (C-11), 176.9 (C-30), 173.6 (chain-COO), 169.2 (C-13), 156.0 (Boc-COO), 128.5 (C-12), 80.3 (C-3), 78.6 (Boc-*quart.*-C), 61.7 (C-9), 55.0 (C-5), 51.8 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.0 (C-19), 40.6 (chain-η-CH_2), 38.8 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 34.8 (chain-α-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 30.0 (chain-ζ-CH_2), 29.1 (chain-δ-CH_2), 28.9 (chain-γ-CH_2), 28.5 (C-28), 28.4 (Boc-CH_3), 28.3 (C-29), 28.1 (C-23), 26.6 (chain-ε-CH_2), 26.4 (C-16), 26.4 (C-15), 25.0 (chain-β-CH_2), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.4 (C-6), 16.8 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 726.4 (84) $[M+H]^+$, 784.5 (100) $[M+Na]^+$, 1473.5 (37) $[2M+Na]^+$. – $C_{44}H_{71}NO_7$ (726.04): C 72.79, H 9.86, N 1.93; found C 72.58, H 91, N 1.86.

*Methyl (3β)-3-({2,4-bis[(tert-butoxycarbonyl)amino]-butanoyl}oxy)-11-oxo-olean-12-en-30-oate (**31**)*

Obtained from **1** by method A as a colorless powder. Yield: 670 mg, 54 %. M. p.: 117 – 120 °C. – $R_f = 0.35$ (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 70.24$ ($c = 0.57$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 249$ nm (4.06). – IR (KBr): $\nu = 3386$br, 2976s, 2873m, 1719s, 1660s, 1513m, 1456m, 1391m, 1367s, 1250s, 1218s, 1166s, 1087w, 1048w, 1022w, 987m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.64$ (s, 1 H, 12-H), 5.16 (m, 2 H, Dab-NH), 4.53 (dd, 1 H, $J = 11.8$, 5.0 Hz, 3-H), 4.34 (m, 1 H, Dab-α-CH), 3.69 (s, 3 H, OMe), 3.42 (m, 1 H, Dab-γ-C*H*H′), 3.00 (m, 1 H, Dab-γ-CH*H*′), 2.82 (ddd, 1 H, $J = 13.7$, 3.2, 3.2 Hz, 1-H), 2.35 (s, 1 H, 9-H), 2.08 (m, 1 H, 18-H), 2.05 (m, 1 H, 15-H), 2.01 (m, 1 H, 21-H), 1.92 (ddd, 1 H, $J = 13.3$, 3.9, 2.5 Hz, 19-H), 1.83 (ddd, 1 H, $J = 13.1$, 13.1, 4.2 Hz, 16-H), 1.73 (m, 1 H, 2-H), 1.65 (m, 1 H, 7-H), 1.64 (m, 1 H, 2′-H), 1.63 (m, 1 H, Dab-β-C*H*H′), 1.61 (dd, 1 H, , $J = 13.7$, 13.7 Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.59 (m, 1 H, Dab-β-CH*H*′), 1.46 (m, 1 H, 6′-H), 1.44 (s, 18 H, Boc-CH_3), 1.42 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.36 (s, 3 H, 27-H), 1.31 (m, 2 H, 22′-H and 21′-H), 1.18 (m, 1 H, 16′-H), 1.17 (s, 3 H, 25-H), 1.15 (s, 3 H, 29-H), 1.13 (s, 3 H, 26-H), 1.02 (m, 1 H, 1-H′), 1.04 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.87 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.79 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.9$ (C-11), 176.9 (C-30), 172.4 (Dab-COO), 169.2 (C-13), 155.9 (Boc-COO), 128.4 (C-12), 82.3 (C-3), 80.0 (Boc-*quart.*-C), 61.7 (C-9), 55.0 (C-5), 51.8 (OMe), 51.4 (Dab-α-CH), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 38.7 (C-1), 38.2 (C-4), 37.7 (C-22), 36.9 (C-10), 36.6 (Dab-γ-CH_2), 32.8 (Dab-β-CH_2), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 28.4 (C-29), 28.3 (C-28), 28.3 (Boc-CH_3), 28.2 (C-23), 26.5 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.7 (C-24), 16.4 (C-25). – MS (ESI): m/z (%) = 785.3 (26) $[M+H]^+$, 802.3 (24) $[M+NH_4]^+$, 807.5 (100) $[M+Na]^+$, 823.3 (4) $[M+K]^+$, 1199.9 (14) $[3M+2Na]^+$, 1591.3 (27) $[2M+Na]^+$. – $C_{45}H_{72}N_2O_9$ (785.06): C 68.85, H 9.24, N 3.57; found C 68.69, H 9.43, N 3.44.

*Methyl (3β)-3-{[N^2,N^5-bis(tert-butoxycarbonyl)-(L)-ornithyl]oxy}-11-oxoolean-12-en-30-oate (**32**)*

Obtained from **1** by method A as a colorless powder. Yield: 440 mg, 52 %. M. p.: 88 – 90 °C. – $R_f = 0.29$ (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 80.20$ ($c = 0.55$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 249$ nm (4.17). – IR (KBr): $\nu = 3385$br, 2975s, 2872m, 1718s, 1660s, 1514m, 1455m, 1390m, 1366s, 1324m, 1250s, 1217s, 1167s, 1087w, 1049w, 1020w, 985m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.67$ (s, 1 H, 12-H), 5.06 (m, 2 H, Orn-NH), 4.56 (dd, 1 H, $J = 11.8$, 4.8 Hz, 3-H), 4.28 (m, 1 H, Orn-α-CH), 3.69 (s, 3 H, OMe), 3.14 (m, 2 H, Orn-δ-CH_2), 2.82 (ddd, 1 H, $J = 13.8$, 3.4, 3.4 Hz, 1-H), 2.36 (s, 1 H, 9-H), 2.09 (m, 1 H, 18-H), 2.03 (m, 1 H, 15-H), 2.00 (m, 1 H, 21-H), 1.93 (ddd, 1 H, $J = 13.1$, 4.4, 2.5 Hz, 19-H), 1.87 (m, 1 H, Orn-β-C*H*H′), 1.83 (ddd, 1 H, $J = 13.0$, 13.0, 4.2 Hz, 16-H), 1.73 (m, 1 H, 2-H), 1.68 (m, 1 H, 7-H), 1.66 (m, 1 H, Orn-β-CH*H*′), 1.64 (m, 1 H, 2′-H), 1.61 (dd, 1 H, $J = 13.6$, 13.6 Hz, 19′-H), 1.59 (m, 1 H, 6-H), 1.57 (m, 2 H, Orn-γ-CH_2), 1.45 (m, 1 H, 6′-H), 1.44 (s, 18 H, Boc-CH_3), 1.42 (m, 1 H, 7′-H), 1.38 (m, 1 H, 22-H), 1.37 (s, 3 H, 27-H), 1.32 (m, 2 H, 22′-H and 21′-H), 1.17 (m, 1 H, 16′-H), 1.15 (s, 3 H, 25-H), 1.13 (s, 3 H, 29-H), 1.11 (s, 3 H, 26-H), 1.05 (m, 1 H, 1-H′), 1.02 (m, 1 H, 15-H′), 0.90 (s, 3 H, 24-H), 0.88 (s, 3 H, 23-H), 0.81 (s, 3 H, 28-H), 0.80 (m, 1 H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.9$ (C-11), 176.9 (C-30), 172.2 (Orn-COO), 169.2 (C-13), 155.9 (Boc-COO), 128.5 (C-12), 82.0 (C-3), 79.6 (Boc-*quart.*-C), 61.6 (C-9), 55.0 (C-5), 53.5 (Orn-α-CH), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 40.0 (Orn-δ-CH_2), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 31.8 (C-17), 31.1 (C-21), 30.2 (Orn-β-CH_2), 28.5 (C-29), 28.4 (Boc-CH_3), 28.3 (C-28), 28.1 (C-23), 26.5 (C-16), 26.4 (C-15), 26.1 (Orn-γ-CH_2), 23.6 (C-2), 23.3 (C-27), 18.7 (C-26), 17.3 (C-6), 16.8 (C-24), 16.3 (C-25). – MS (ESI): m/z (%)

= 799.3 (17) $[M+H]^+$, 816.3 (41) $[M+NH_4]^+$, 821.5 (100) $[M+Na]^+$, 837.3 (5) $[M+K]^+$, 1217.8 (6) $[3M+K+H]^{2+}$, 1619.3 (28) $[2M+Na]^+$. – $C_{46}H_{74}N_2O_9$ (799.09): C 69.14, H 9.33, N 3.51; found C 68.96, H 9.51, N 3.42.

*Methyl (3β)-3-{[N^2,N^6-bis(tert-butoxycarbonyl)-(L)-lysyl]oxy}-11-oxoolean-12-en-30-oate (**33**)*

Obtained from **1** by method A as a colorless powder. Yield: 740 mg, 90 %. M. p.: 145 – 148 °C (decomp.). – R_f = 0.56 (hexane-ethyl acetate, 7 : 3). – $[\alpha]_D = 69.88$ ($c = 0.37$, $CHCl_3$). – UV/Vis (methanol): $\lambda_{max}(\log \varepsilon) = 251$ nm (4.05). – IR (KBr): $\nu = 3385$br, 2976s, 2870m, 1717s, 1660s, 1518s, 1456m, 1391m, 1366s, 1323m, 1250s, 1217s, 1170s, 1087w, 1048w, 1020w, 987m cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.64$ (s, 1 H, 12-H), 5.06 (m, 2 H, Lys-NH), 4.54 (dd, 1 H, $J = 11.7$, 4.8 Hz, 3-H), 4.29 (m, 1 H, Lys-α-CH), 3.67 (s, 3 H, OMe), 3.09 (m, 2 H, Lys-ε-CH_2), 2.80 (ddd, 1 H, $J = 13.6$, 3.6, 3.6 Hz, 1-H), 2.33 (s, 1 H, 9-H), 2.07 (m, 1 H, 18-H), 2.01 (m, 1 H, 15-H), 1.98 (m, 1 H, 21-H), 1.91 (m, 1 H, 19-H), 1.82 (m, 1 H, Lys-β-C*H*H′), 1.80 (m, 1 H, 16-H), 1.72 (m, 1 H, 2-H), 1.64 (m, 1 H, Lys-β-CH*H*′), 1.63 (m, 1 H, 7-H), 1.61 (m, 1 H, 2′-H), 1.60 (dd, 1 H, $J = 13.6$, 13.6 Hz, 19′-H), 1.58 (m, 1 H, 6-H), 1.47 (m, 2 H, Lys-δ-CH_2), 1.43 (s, 18 H, Boc-CH_3), 1.43 (m, 1 H, 6′-H), 1.41 (m, 1 H, 7′-H), 1.40 (m, 1 H, 22-H), 1.35 (s, 3 H, 27-H), 1.35 (m, 2 H, Lys-γ-CH_2), 1.32 (m, 2 H, 22′-H and 21′-H), 1.17 (m, 1 H, 16′-H), 1.15 (s, 3 H, 25-H), 1.13 (s, 3 H, 29-H), 1.11 (s, 3 H, 26-H), 1.04 (m, 1 H, 1-H′), 1.00 (m, 1 H, 15-H′), 0.88 (s, 3 H, 24-H), 0.86 (s, 3 H, 23-H), 0.80 (m, 1 H, 5-H), 0.79 (s, 3 H, 28-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9 (C-11), 176.9 (C-30), 172.4 (Lys-COO), 169.2 (C-13), 156.0 (Boc-COO), 128.5 (C-12), 81.9 (C-3), 79.7 (Boc-*quart.*-C), 61.6 (C-9), 55.0 (C-5), 53.6 (Lys-α-CH), 51.7 (OMe), 48.4 (C-18), 45.4 (C-8), 44.0 (C-20), 43.2 (C-14), 41.1 (C-19), 40.1 (Lys-ε-CH_2), 38.7 (C-1), 38.1 (C-4), 37.7 (C-22), 36.9 (C-10), 32.7 (C-7), 32.5 (Lys-β-CH_2), 31.8 (C-17), 31.1 (C-21), 29.6 (Lys-δ-CH_2), 28.5 (C-29), 28.4 (Boc-CH_3), 28.3 (C-28), 28.1 (C-23), 26.4 (C-16), 26.4 (C-15), 23.6 (C-2), 23.3 (C-27), 22.4 (Lys-γ-CH_2), 18.7 (C-26), 17.3 (C-6), 16.8 (C-24), 16.3 (C-25). – MS (ESI): m/z (%) = 813.3 (16) $[M+H]^+$, 830.2 (18) $[M+NH_4]^+$, 835.5 (100) $[M+Na]^+$, 851.3 (4) $[M+K]^+$, 1241.7 (6) $[3M+2Na]^{2+}$, 1647.1 (10) $[2M+Na]^+$. – $C_{47}H_{76}N_2O_9$ (813.11): C 69.42, H 9.42, N 3.45; found C 69.32, H 9.57, N 3.25.

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