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# Synthesis and cytotoxicity of 3-amino-glycyrrhetinic acid derivatives

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**Abstract**: The aim of this study was to prepare 3-hydroximino- and 3-amino derivatives of glycyrrhetinic acid and derivatives to evaluate their in vitro cytotoxicity for a panel of human tumor cell lines. Thus, commercially available glycyrrhetinic acid (1) was acetylated or oxidized at position C-3 and transformed into a variety of different esters and amides followed by their conversion to 3-oximes and amines. While the parent compound was not cytotoxic at all, the 3-amino esters are highly cytotoxic. Interestingly, 3-amino amides were significantly less cytotoxic than 3-amino esters. The (3β, 18β, 20β) Benzyl 3-amino-11-oxoolean-12-en-30-oate was the most cytotoxic compound of this series showing an $EC_{50}$ = 1.3 μM for 518A2 melanoma cells.

**Keywords**: Glycyrrhetinic acid; Licorice; Cytotoxicity.

## Introduction

The roots of licorice, especially of *Glycyrrhiza uralensis* Fisch and *G. glabra*, have been used as herbal medicines for many centuries and in many cultures. Its use has been reported for the Traditional Chinese and Persian Medicine but extracts from this plant were also known to ancient Greek starting with Theophrastus in the 4th century BC followed by their applications by ancient Romans as reported by Plinius in the 1st century BC. In that time extracts of the root were applied as remedies for a broad variety of diseases. Nowadays, licorice is considered as a valuable natural product not only due to its use as a sweetening and flavoring agent but to its interesting biological activities, especially its cytotoxic activity and that of several of its derivatives.[1-5]

## Results and Discussion

Extending our previous work concerning analogs of glycyrrhetinic acid (**1**, Scheme 1) [1,6-9] we became interested in the synthesis and cytotoxicity of glycyrrhetinic acid derived amides inasmuch as several amides of other triterpenoic acids were shown to be good to excellent antitumor active compounds [10-15].

Acetylation of glycyrrhetinic acid (**1**, Scheme 1)[16] with acetic anhydride in pyridine gave acetate **2**.

Treatment of **2** with oxalyl chloride in DCM followed by the addition of ammonia yielded amide **3** [17] in good yield. Analogous reactions of **2** with oxalyl chloride and allylamine, benzylamine, methylamine or dimethylamine gave amides **4**-**7**. Treatment of amides **3**-**7** with methanolic potassium hydroxide in MeOH/DMF followed by chromatographic work-up furnished 3-*O*-deacetylated amides **8**-**12**. Jones oxidation [18] of the 3-hydroxyamides **8**-**12** at 25 °C for 2 hours yielded 3-keto-amides **13**-**17**. These compounds are characterized in their $^{13}C$ NMR spectra by the presence of a C = O carbon whose chemical shift was detected between δ = 217.2-217.0 ppm, respectively.

These amides **13**-**17** were allowed to react with hydroxylammonium chloride in dry pyridine at 60 °C for 3 hours [7] followed by a precipitation of the crude product by adding 1 M aqueous hydrochloric acid. Re-crystallization from methanol or chromatography yielded oximes **18**-**22**, respectively. Based on 2D-NOESY-NMR data, the absolute configuration of these oximes was assigned as (*E*). This is in agreement with previous findings reported in literature for oleanolic and ursolic acid, respectively [19-25].

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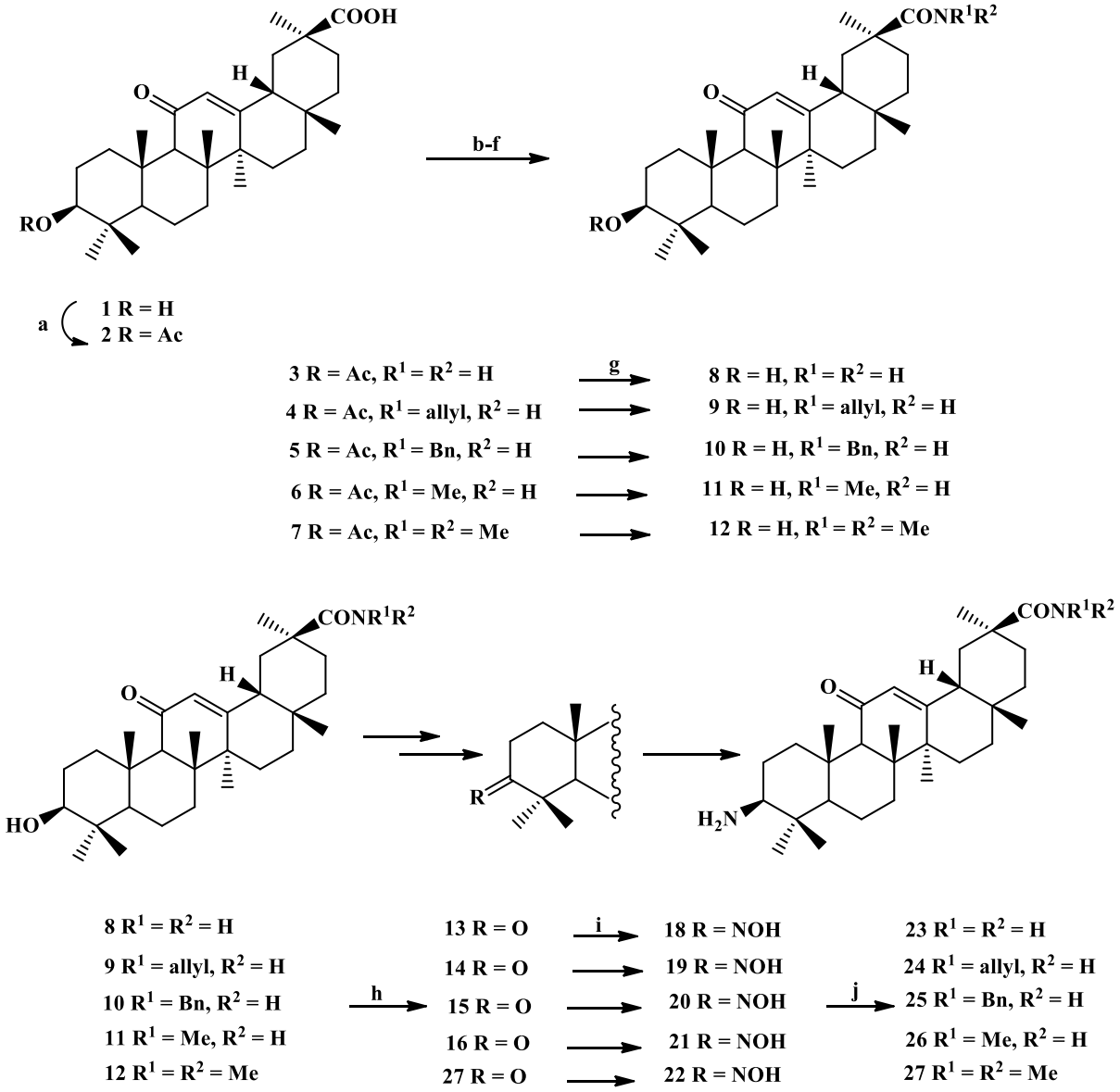
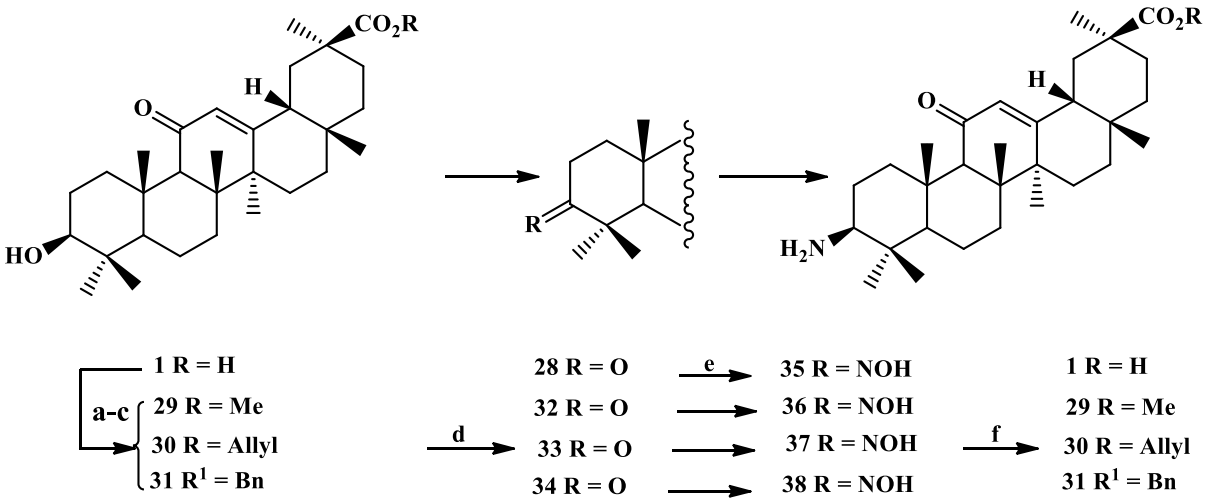



**Scheme 1.** a. $Ac_2O$, pyridine, DCM, 24 h, 25 °C, 93%; b. $(COCl)_2$, DCM, 25 °C then $NH_4OH$, 24 h, 25 °C, 82%; c. $(COCl)_2$, DCM, 25 °C then $NH_4OH$, 24 h, 25 °C, 77%; d. $(COCl)_2$, DCM, 25 °C then $NH_4OH$, 24 h, 25 °C, 71%; e. $(COCl)_2$, DCM, 25 °C then $NH_4OH$, 24 h, 25 °C, 71%; f. $(COCl)_2$, DCM, 25 °C then $NH_4OH$, 24 h, 25 °C, 48%; g. KOH/MeOH/DMF, 24 h, 25 °C: **8** (83%), **9** (77%), 10 (99%), **11** (78%), **12** (60%); h. Jones oxidation; **13** (87%), **14** (79%), **15** (84%), **16** (79%), **17** (85%); i. $NH_4OH.HCl$, pyridine, 3 h reflux: **18** (78%), **19** (76%), **20** (82%), **21** (83%), **22** (76%); j. $NH_4OAc$, $NaBH_3CN$, $TiCl_3$, 24 h, 25 °C: **23** (65%), **24** (80%), **25** (64%), **26** (65%); **27** (60%).

Reduction of the oximes **18**-**22** with sodium cyanoborohydride and ammonium acetate in the presence of $TiCl_3$ [16] for one day at room temperature gave amines **23**-**27**, respectively. Their absolute configuration at C-3 was deduced from their $^1H$ NMR spectra [coupling constant H-C (2)-H-C (3) and 2D-NOESY-NMR] as well as previous data reported in literature [26-29]. This reduction was not completely stereo-selective, but the epimers of opposite configuration at C-3 were only formed in minor amounts and could not be isolated [30-34]. Their formation was confirmed by HPTLC-MS experiments.

Jones oxidation of **1** gave 3-keto-glycyrrhetinic acid (**28**, Scheme 2). Esterification of **1** gave esters **29**-**31**; their Jones oxidation furnished 3-keto-compounds **32**-**34**. These keto compounds were transformed *via* their oximes **35**-**38** into amines **39**-**42**.




**Scheme 2.** a. MeI, $K_2CO_3$, DMF, 24 h, 24 °C, 90%; b. allyl bromide, $K_2CO_3$, DMF, 24 h, 24 °C, 68%; c; benzyl bromide, $K_2CO_3$, DMF, 24 h, 24 °C, 87%; d. Jones oxidation: **28** (87%), **32** (89%), **33** (85%), **34** (88%); e. $NH_4OH.HCl$, pyridine, 3 h reflux: **35** (93%), **36** (85%), **37** (84%), **38** (84%); f. $NH_4OAc$, $NaBH_3CN$, $TiCl_3$, 24 h, 25 °C: **39** (43%), **40** (74%), **41** (42%), **42** (76%).

For biological evaluation, all of the compounds were subjected to sulforhodamine B assays (SRB) employing several human tumor cell lines and non-malignant mouse fibroblasts (NIH 3T3). The results of these experiments are compiled in Table 1.

**Table 1**: Cytotoxicity of glycyrrhetinic acid (**1**) and derivatives (**2-42**); $EC_{50}$ values in μM from SRB assay after 96 h of treatment; the values are averaged from three independent experiments performed each in triplicate; confidence interval CI = 95%; cut off: 30 μM. Human cancer cell lines: 518A2 (melanoma), A2780 (ovarian carcinoma), HT29 (colorectal carcinoma), MCF7 (breast carcinoma), A549 (lung adenocarcinoma), and nonmalignant mouse fibroblasts (NIH 3T3).

| Compound/ Cell line | 518A2 | A2780 | HT29 | MCF7 | A549 | NIH 3T3 |
|---|---|---|---|---|---|---|
| **1** | > 30 | > 30 | > 30 | > 30 | > 30 | > 30 |
| **2** | > 30 | > 30 | > 30 | > 30 | > 30 | > 30 |
| **3-12** | > 30 | > 30 | > 30 | > 30 | > 30 | > 30 |
| **13-17** | > 30 | > 30 | > 30 | > 30 | > 30 | > 30 |
| **18-22** | > 30 | > 30 | > 30 | > 30 | > 30 | > 30 |
| **23** | 6.8 ± 0.5 | 5.1 ± 0.4 | 9.3 ± 1.1 | 11.2 ± 0.9 | 9.5 ± 1.0 | 14.4 ± 1.2 |
| **24** | 5.4 ± 0.9 | 4.9 ± 0.7 | 7.0 ± 1.2 | 7.4 ± 0.7 | 12.3 ± 1.1 | 6.1 ± 0.5 |
| **25** | 7.1 ± 0.2 | 6.2 ± 0.1 | 9.5 ± 0.7 | 7.5 ± 0.4 | 14.1 ± 0.9 | 8.4 ± 1.3 |
| **26** | 5.1 ± 0.8 | 7.1 ± 0.8 | 8.2 ± 1.3 | 10.1 ± 0.9 | 10.0 ± 0.8 | 7.1 ± 1.1 |
| **27** | 6.2 ± 0.6 | 5.3 ± 1.0 | 9.1 ± 0.6 | 11.0 ± 1.3 | 9.1 ± 0.7 | 5.3 ± 1.4 |
| **28** | > 30 | > 30 | > 30 | > 30 | > 30 | > 30 |
| **29** | 27.5 ± 2.0 | 25.5 ± 2.0 | 27.5 ± 1.7 | 22.1 ± 1.6 | 23.1 ± 1.7 | 22.8 ± 2.5 |
| **30** | 15.3 ± 2.1 | 17.4 ± 1.6 | 23.7 ± 2.4 | 24.9 ± 1.9 | 20.3 ± 3.0 | 19.8 ± 2.5 |
| **31** | 18.2 ± 2.4 | 20.3 ± 3.1 | 11.5 ± 2.6 | 13.5 ± 0.8 | 6.1 ± 0.5 | 21.2 ± 2.8 |
| **32-34** | > 30 | > 30 | > 30 | > 30 | > 30 | > 30 |
| **35** | 17.2 ± 1.8 | 19.4 ± 1.9 | 21.9 ± 1.9 | 16.4 ± 1.7 | 18.1 ± 2.0 | 24.0 ± 2.7 |
| **36** | 19.4 ± 1.6 | 17.1 ± 1.4 | 15.3 ± 1.1 | 14.6 ± 1.6 | 17.0 ± 1.1 | 21.4 ± 2.3 |
| **37** | 18.2 ± 2.4 | 14.7 ± 1.1 | 16.4 ± 0.9 | 12.0 ± 1.3 | 11.7 ± 0.8 | 24.1 ± 3.6 |
| **38** | 16.0 ± 1.7 | 18.1 ± 1.5 | 11.4 ± 1.4 | > 30 | 23.6 ± 3.2 | > 30 |
| **39** | 3.1 ± 0.6 | 6.2 ± 1.1 | 5.3 ± 0.7 | 6.0 ± 1.1 | 5.4 ± 0.8 | 5.8 ± 1.2 |
| **40** | 1.8 ± 0.3 | 5.3 ± 1.0 | 2.6 ± 0.9 | 4.5 ± 1.2 | 4.0 ± 0.2 | 3.5 ± 0.7 |
| **41** | 2.1 ± 0.8 | 5.7 ± 0.6 | 3.0 ± 1.0 | 4.1 ± 0.6 | 3.9 ± 0.8 | 4.5 ± 0.5 |
| **42** | 1.3 ± 0.2 | 4.0 ± 0.7 | 2.9 ± 1.3 | 4.4 ± 0.9 | 3.3 ± 0.6 | 1.6 ± 0.6 |

As a result, parent compounds **1** and **2** and 3-keto **28** are of not of significant cytotoxicity at all. In general, compounds holding $EC_{50}$ values >30 are regarded as not cytotoxic. The same is true for C-30 amides **3-12** and amides **13-17** and their oximes **18-22**. Moderate cytotoxicity, however, was observed

for amines **23**-**27**. While ketones **32**-**34** showed none, oximes **35**-**38** again showed moderate cytotoxicity, amines **39**-**42**, however, were highly cytotoxic showing $EC_{50}$ values between 1.3-6.2 μM with compound **42** being most cytotoxic for the human melanoma cell line 518A2. Interestingly, 3-amino amides **23**-**27** were significantly less cytotoxic than 3-amino acid **39** and 3-amino esters **40**-**42**. It might be assumed that the esters are cleaved within the cell by esterases while the amides are stable under these conditions.

## Conclusion

Facile conversion of glycyrrhetinic acid allows access to highly cytotoxic 3-amino derivatives **23**-**27** and **39**-**42**. While the parent compound was not cytotoxic at all, the 3-amino esters **40**-**42** are highly cytotoxic for a variety of human tumor cell lines. Interestingly, 3-amino amides **23**-**27** were significantly less cytotoxic than 3-amino esters **40**-**42**. Compound **42** was the most cytotoxic compound of this series showing an $EC_{50}$ = 1.3 μM for 518A2 melanoma cells.

## 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), 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), and elemental analyses were performed on a Foss-Heraeus Vario EL (C-HNS) unit. IR spectra were recorded on a Perkin Elmer FT-IR spectrometer Spectrum 1000. The solvents were dried according to usual procedures. The purity of the compounds was determined by HPLC and found to be >96%. The SRB assays were performed as previously reported.[10, 13]

### (18β) Glycyrrhetinic acid (1)

The starting material for all syntheses was commercially obtained as a bulk chemical from Orgentis GmbH (Gatersleben) and used as received.

### (3β, 18β) 3-Acetoxy-11-oxoolean-12-en-30-oic acid (2)

Acetylation of **1** (5.0 g, 10.6 mmol) in dry DCM (150 mL) with acetic anhydride (10.7 mL, 0.11 mol) in the presence of dry pyridine (1.0 mL, 12.4 mmol) for 24 h at 25 °C followed by usual aqueous work-up and re-crystallization of the crude material from MeOH gave **2** (5.08 g, 93%) as a white solid; m.p. 273-275 °C (lit.: 310-313 °C [16]); $R_f$ = 0.48 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 132.4° (*c* = 0.38, $CHCl_3$) (lit.: + 143.7 (*c* = 0.44, $CHCl_3$ [35]); MS (ESI, MeOH): *m*/*z* = 513.3 (100%, $[M+H]^+$).

### (3β, 18β, 20β) 3-Acetoxy-11-oxoolean-12-en-30-amide (3)

Reaction of **2** (10.0 g, 19.53 mmol) with oxalyl chloride (5 mL) in dry DCM (200 mL) at 25 °C as previously described followed by the addition of an aq. solution of ammonium hydroxide (25%, 75 mL) and chromatographic work-up (silica gel, $CHCl_3$/MeOH, 9:1) gave **3** (8.17 g, 82%) as a white solid; m.p. 282-284 °C (lit.: 270-274 °C [17]); $R_f$ = 0.54 (MeOH/$CHCl_3$, 9:1); $[\alpha]_D$ = + 117.2 (*c* = 0.32, $CHCl_3$) (lit.: + 119.1 (*c* = 0.5, $CHCl_3$ [17]); MS (ESI, MeOH): *m*/*z* = 512.4 (100 %, $[M+H]^+$).

### (3β, 18β, 20β) 3-Acetoxy-*N*-allyl-11-oxoolean-12-en-30-amide (4)

Following the procedure given for the synthesis of **3** from **2** (2.5 g, 4.88 mmol), oxalyl chloride (1.35 mL) and allyl amine (1.0 mL, 13.3 mmol) followed by chromatographic work-up (silica gel, hexane/ethyl acetate, 7:3) **4** (2.08g, 77%) was obtained as a white solid; m.p. 212-214 °C (lit.: 230-231 °C [16]); $R_f$ = 0.36 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 124.3 (*c* = 0.3, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 244 nm (3.86); MS (ESI, MeOH): *m*/*z* = 552.5 (100 %, $[M+H]^+$), 574.4 (52 %, $[M+Na]^+$), 1103.5 (70 %, $[2M+H]^+$), 1125.5 (48 %, $[M+Na]^+$).

### (3β, 18β, 20β) 3-Acetoxy-*N*-benzyl-11-oxoolean-12-en-30-amide (5)

As described above, from **2** (2.5 g, 4.88 mmol) and benzylamine (2.0 mL, 18.35 mmol) followed by chromatographic workup (silica gel, hexane/ethyl acetate, 7:3) **5** (2.08 g, 71%) was obtained as a white solid; m.p. 150-152 °C (lit.: 150-152 °C [36]); $R_f$ = 0.37 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = 84.9 (*c* = 0.29, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 248 nm (4.02); MS (ESl, MeOH): *m*/*z* = 602.4 (100 %, $[M+H]^+$), 1203.6 (94 %, $[2M+H]^+$).

### (3β, 18β, 20β) 3-Acetoxy-*N*-methyl-11-oxoolean-12-en-30-amide (6)

As described above, from **2** (4.0 g, 7.81 mmol) and methylamine (12 mL, 2 M in dry MeOH) followed by chromatographic workup (silica gel, $CHCl_3$/MeOH, 99:1) **6** (2.90 g, 71%) was obtained as a white solid; m.p. 316-318 °C; $R_f$ = 0.23 (hexane/ethyl acetate, 1:1), $[\alpha]_D$ = + 126.5 (*c* = 0.35, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 248 nm (4.15); IR (KBr): ν = 3350*m*, 2968*s*, 2873*s*, 1743*s*, 1651*s*, 1543*s*, 1450*m*, 1391*s*, 1322*m*, 1143*m*, 1092*w*, 1028*s*, 984*s;*
$^1$H NMR (400 MHz, $CDCl_3$): δ = 5.68 (*d*, 1H, NH), 5.66 (*s*, 1H, 12-H), 4.50 (*dd*, *J* = 11.6, 4.8 Hz, 1H, 3-H), 2.82 (*d*, *J* = 4.7 Hz, 3H, 33-H), 2.78 (*m*, 1H, Hz, 1-H), 2.34 (*s*, 1H, 9-H), 2.14 (*dd*, *J* = 11.9, 5.34 Hz, 1H, 18-H), 2.04 (*s*, 3H, 32-H), 2.03 (*m*, 1H, 15-H), 1.92 (*m*, 1H, 21-H*)*, 1.82 (*m*, 1H, 16-H),

1.72 (*m*, 2H, 19-H), 1.66 (*m*, 1H, 2-H), 1.62 (*m*, 1H, 7-H), 1.59 (*m*, 1H, 2-H), 1.54 (*m*, 1H, 6-H), 1.46 (*m*, 1H, 6-H), 1.42 (*m*, 1H, 7-H), 1.37 (*m*, 3H, 22-H + 21-H), 1.36 (*s*, 3H, 27-H), 1.18 (*m*, 1H, 16-H), 1.15 (*s*, 3H, 25-H), 1.11 (*s*, 6H, 29-H + 26-H), 1.04 (*m*, 2H, 15-H + 1-H), 0.87 (*s*, 6H, 24-H + 23-H), 0.80 (*s*, 3H, 28-H), 0.79 (*m*, 1H, 5-H) ppm;

$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 200.0 (C-11), 176.4 (C-30), 171.0 (C-31), 169.3 (C-13), 128.4 (C-12), 80.6 (C-3), 61.7 (C-9), 55.0 (C-5), 48.2 (C-18), 45.4 (C-8), 43.6 (C-20), 43.2 (C-14), 41.9 (C-19), 38.8 (C-1), 38.0 (C-4), 37.5 (C-22), 36.9 (C-10), 32.7 (C-7), 31.9 (C-17), 31.4 (C-21), 29.6 (C-29), 28.4 (C-23), 28.0 (C-28), 26.5 (C-33), 26.4 (C-16), 26.4 (C-15), 23.5 (C-2), 23.3 (C-27), 21.3 (C-32), 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25) ppm;

MS (ESI, MeOH): *m*/*z* = 526.3 (100 %, $[M+H]^+$, 548.3 (54 %, $[M+Na]^+$);

Analysis calcd for $C_{33}H_{51}NO_4$ (525.77): C 75.39, H 9.78, N 2.66; found: C 75.17, H 9.93, N 2.46.

**(3β, 18β, 20β) 3-Acetoxy-N, -*N*-dimethyl-11-oxoolean-12-en-30-amide (7)**

As described above, from **2** (4.0 g, 7.81 mmol) and dimethylamine (3.95 mL, 40%, aq.) followed by chromatographic workup (silica gel, $CHCl_3$/MeOH, 99:1) **7** (2.01 g, 48%) was obtained as a white solid; m.p. 261-263 °C; $R_f$ = 0.20 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 128.7° (*c* = 0.29, $CHCl_3$), UV-Vis: $\lambda_{max}$ (log ε) = 246 nm (3.94); IR (KBr): ν = 3436*w*, 2951*s*, 2861*m*, 1727*s*, 1652*s*, 1624*s*, 1459*w*, 1390*w*, 1367*m*, 1326*w*, 1253*s*, 1210*m*, 1137*m*, 1082*w*, 1030*m* $cm^{-1}$;

$^1$H NMR (500 MHz, $CDC1_3$): δ = 5.67 (*s*, 12-H), 4.51 (*dd*, *J* = 11.7, 4.8 Hz, 1H, 3-H), 3.03 (*s*, 6H, 33-H + 34-H), 2.78 (*ddd*, *J* = 13.4, 3.3, 3.3 Hz, 1H, 1-H), 2.35 (*s*, 1H, 9-H), 2.17 (*m*, 2H, 21-H) + 18-H), 2.08 (*m*, 2H, 19-H + 15-H), 2.04 (*s*, 3H, 32-H), 1.82 (*ddd*, *J* = 13.6, 13.6, 4.1 Hz, 1H, 16-H), 1.71 (*m*, 1H, 2-H), 1.65 (*m*, 1H, 19-H), 1.62 (*m*, 1 H, 7-H), 1.57 (*m*, 1H, 2-H), 1.48 (*m*, 1H, 6-H), 1.42 (*m*, 1H, 22-H), 1.36 (*m*, 3H, 22-H + 7-H + 6-H), 1.35 (*s*, 3H, 27-H), 1.27 (*m*, 1H, 21-H), 1.20 (*s*, 3H, 29-H) 1.15 (*m*, 1H, 16-H), 1.15 (*s*, 3H, 25-H), 1.11 (*s*, 3H, 26-H), 1.04 (*m*, 2H, 15-H + 1-H), 0.87 (*s*, 6H, 24-H + 23-H), 0.80 (*s*, 3H, 28-H), 0.79 (*m*, 1H, 5-H) ppm;

$^{13}$C NMR (125 MHz, $CDC1_3$): δ = 200.0 (C-11), 175.0 (C-30), 171.0 (C-31), 169.8 (C-13), 128.4 (C-12), 80.6 (C-3), 61.7 (C-9), 55.0 (C-5), 48.5 (C-18), 45.3 (C-8), 44.2 (C-20), 43.4 (C-19), 43.3 (C-14), 38.8 (C-1), 38.6 (C-33), 38.6 (C-34), 38.0 (C-4), 37.7 (C-22), 37.0 (C-10), 33.6 (C-21), 32.8 (C-7), 31.9 (C-17), 28.4 (C-28), 28.0 (C-23), 26.8 (C-16), 26.6 (C-29), 26.5 (C-15), 23.5 (C-2), 23.0 (C-27), 21.3 (C-32) 18.7 (C-26), 17.4 (C-6), 16.7 (C-24), 16.4 (C-25) ppm;

MS (ESI, MeOH) *m*/*z* = 540.9 (76 %, $[M+H]^+$), 562.8 (42 %, $[M+Na]^+$) 1079.8 (100 %, $[2M+H]^+$), 1101.7 (60 %, $[2M + Na]^+$);

Analysis calcd for $C_{34}H_{53}NO_4$ (539.80): C 75.65, H 9.90, N 2.59; found: C 75.51, H 10.03, N 2.70.

**(3β, 18β, 20β) 3-Hydroxy-11-oxoolean-12-en-30-amide (8)**

To a solution of **3** (8.0 g, 15.65 mmol) in THF (150 mL) a solution of KOH (1.75 g, 31.3 mmol) in MeOH (50 mL) and DMF (20 mL) was added, and stirring at 25 °C was continued for one day. The volatiles were removed under diminished pressure, and the remaining oil was poured into ice/water. The crude product was filtered off and purified by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) to yield **8** (6.1 g, 83%) as a white solid; m.p. 323 °C; $R_f$ = 0.40 (MeOH/$CHCl_3$) ; $[\alpha]_D$ = + 123.3 (*c* = 0.09, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 246 nm (3.94); IR (KBr): ν = 3410*s*, 2927*m*, 1642*s*, 1384*s*, 1182*w*, 1040*w* $cm^{-1}$;

$^1$H NMR (400MHz, DMSO-$d_6$): δ = 7.10 (*s*, 1H, NH), 6.72 (*s*, 1H, NH), 5.45 (*s*, 1H, 12-H), 4.27 (*d*, *J* = 4.7 Hz, 1H, OH*)*, 3.00 (*m*, 1H, 3-H), 2.57 (*ddd*, *J* = 13.3, 3.2, 3.2 Hz, 1H, 1-H), 2.29 (*s*, 1H, 9-H), 2.05 (*ddd*, *J* = 13.6, 13.3, 3.8 Hz, 1H, 15-H), 2.04 (*ddd*, 1H, 18-H), 1.85 (*m*, 21-H), 1.74 (*m*, 2H, 19-H + 16-H), 1.63 (*m*, 1H, 7-H), 1.56 (*m*, 1H, 19-H), 1.49 (*m*, 2H, 6-H) + 2-H), 1.40 (*m*, 1H, 2-H), 1.34 (*m*, 2H, 7-H + 6-H), 1.32 (*s*, 3H, 27-H), 1.27 (*m*, 3H, 22-H + 21-H), 1.12 (*m*, 1H, 16-H), 1.01 (*s*, 9H, 29-H + 26-H + 25-H ), 0.93 (*m*, 2H, 15-H + 1-H), 0.89 (*s*, 3H, 23-H), 0.72 (*s*, 3H, 28-H), 0.68 (*m*, 1H, 5-H), 0.67 (*s*, 3H, 24-H) ppm;

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 199.5 (C-11), 178.0 (C-30), 170.2 (C-13), 127.9 (C-12), 77.0 (C-3), 61.0 (C-9), 54.6 (C-5), 48.2 (C-18), 45.3 (C-8), 43.3 (C-20), 43.3 (C-14$_t$), 41.3 (C-19), 39.4 (C-1), 39.0 (C-4), 37.8 (C-22), 37.1 (C-10), 32.6 (C-7), 31.8 (C-21), 31.0 (C-17), 29.1 (C-29), 28.9 (C-23), 28.6 (C-28), 27.5 (C-2) 26.5 (C-16), 26.4 (C-15), 23.5 (C-27), 18.8 (C-26), 17.6 (C-6), 16.6 (C-25), 16.4 (C-24) ppm;

MS (ESI, MeOH) *m*/*z* = 456.4 (100 %, $[M+H]^+$);

Analysis calcd for $C_{29}H_{45}NO_x$ (455.68): C 76.44, H 9.95, N 3.07; found: C 76.23, H 10.17, N 2.86.

**(3β, 18β, 20β) *N*-Allyl-3-hydroxy-11-oxoolean-12-en-30-amide (9)**

As described above from **4** (2.0 g, 3.62 mmol) followed by re-crystallization from methanol, compound **9** (1.42 g, 77%) was obtained as a white solid; m.p. 279-282 °C (lit.: > 260 °C LL33); $R_f$ = 0.23 (hexane/ethyl acetate, 1:1); $[\alpha]_D$ = + 142.6 (*c* = 0.31, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 237 nm (3.43); IR (KBr): ν = 3464*m*, 2933*m*, 2868*m*, 1655*s*, 1637*s*, 1530*m*, 1464w, 1386*m*, 1263*w*, 1207*w*, 1182*m*, 994*m* $cm^{-1}$;

$^1$H NMR (400 MHz, $CDCl_3$): δ = 5.83 (*m*, 1H, 32-H), 5.67 (*dd*, *J* = 5.44, 5.44 Hz, 1H, NH), 5.64 (*s*, 1H, 12-H), 5.17 (*m*, 2H, 33-H), 3.89 (*m*, 2H, 31-H), 3.22 (*dd*, *J* = 10.7, 5.6 Hz, 1H, 3-H), 2.78 (*ddd*, *J* = 13.4, 3.4, 3.4 Hz, 1H, 1-H), 2.33 (*s*, 1H, 9-H), 2.17 (*dd*, *J* = 1 1.7, 5.9 Hz, 1H, 18-H),

2.04 (*ddd*, *J* = 13.6, 13.5, 4.3 Hz, 1H, 15-H), 1.94 (*m*, 1H, 21-H), 1.83 (*ddd*, *J* = 13.7. 13.6, 4.4 Hz, 1 H, 16-H), 1.75 (*m*, 2H, 19-H), 1.70 - 1.60 (*m*, 3H, 7-H + 2-H), 1.58 (*m*, 1H, 6-H), 1.50 (*m*, 2H, 22-H + 6-H), 1.43 (*m*, 1H, 22-H), 1.39 (*m*, 2H, 7-H + 21-H), 1.37(*s*, 3H, 27-H), 1.19 (*m*, 1H, 16-H), 1.14 (*s*, 3H, 29-H), 1.13 (*s*, 3H, 25-H), 1.12 (*s*, 3H, 26-H), 1.02 (*m*, 1H, 15-H), 1.00 (*s*, 3H, 23-H), 0.95 (*m*, 1H, 1-H), 0.82 (*s*, 3H, 28-H), 0.80 (*s*, 3H, 24-H), 0.69 (*m*, 1H, 5-H) ppm;

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 200.1 (C-11), 175.5 (C-30), 169.1 (C-13), 134.4 (C-32), 128.5 (C-12), 116.5 (C-33), 78.8 (C-3), 61.8 (C-9), 55.0 (C-5), 48.1 (C-18), 45.4 (C-8), 43.6 (C-20), 43.2 (C-14), 41.9 (C-31) 41.9 (C-19), 39.1 (C-1), 39.1 (C-4), 37.4 (C-22), 37.1 (C-10), 32.8 (C-7), 31.9 (C-17), 31.5 (C-21), 29.7 (C-29), 28.5 (C-23), 28.1 (C-28), 27.3 (C-2), 26.5 (C-16), 26.4 (C-15), 23.4 (C-27), 18.7 (C-26), 17.5 (C-6), 16.3 (C-25), 15.5 (C-24) ppm;

MS (ESI, MeOH): *m*/*z* = 510.4 (78 %, $[M+H]^+$), 1019.7 (100 %, $[2M+H]^+$), 1041.6 (60 %, $[2M+Na]^+$);

Analysis calcd for $C_{33}H_{51}NO_3$ (509.78): C 77.75, H 10.08, N 2.75; found: C 77.59, H 10.26, N 2.62.

**(3β, 18β, 20β) *N*-Benzyl-3-hydroxy-11-oxoolean-12-en-30-amide (10)**

Deacetylation of **5** (2.0 g, 3.32 mmol) as described above followed by re-crystallization from methanol gave **10** (1.85 g, 99%); m.p. 208-209 °C; $R_f$ = 0.27 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = 130.6 (*c* = 0.36, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 248 nm (4.05); IR (KBr): ν = 3420*s*, 2931*m*, 1655*s*, 1528*w*, 1453*m*, 1387*m*, 1258*w*, 1206*w*, 1038*w* $cm^{-1}$;

$^1$H NMR (400 MHz, $CDC1_3$): δ = 7.35 - 7.25 (*m*, 5H, aryl), 5.99 (*dd*, *J* = 5.3, 5.3 Hz, 1H, NH), 5.55 (*s*, 1H, 12-H*)*, 4.45 (*m*, 2H, 31-H), 3.19 (*dd*, *J* = 10.0, 5.0 Hz, 1H, 3-H), 2.76 (*ddd*, *J* = 10.2, 3.3, 3.3 Hz, 1H 1-H), 2.30 (*s*, 1H, 9-H), 2.15 (*dd*, *J* = 12.6, 4.2 Hz, 1H, 18-H), 2.03 (*ddd*, *J* = 13.6, 13.5, 1H, 4.3 Hz, 15-H), 1.94 (*m*, 1H, 21-H), 1.84 (*m*, 1H, (*m*, 1H, 16-H) 1.80 - 1.70 (*m*, 2H, 19-H), 1.65 - 1.55 (*m*, 5H, 22-H + 7-H + 6-H + 2-H), 1.47 - 1.38 (*m*, 4H, 22-H + 21-H + 7-H + 6-H), 1.34 (*s*, 3H, 27-H*)*, 1.21 (*m*, 1H, 16-H), 1.15 (*s*, 3H, 29-H), 1.11 (*s*, 3H, 26-H), 1.11 (*s*, 3H, 25-H), 1.02 (*m*, lH, 15-H), 0.99 (*s*, 3H, 23-H), 0.94 (*m*, 1H, 1-H), 0.80 (*s*, 3H, 28-H), 0.80 (*s*, 3H, 24-H), 0.67 (*m*, 1H, 5-H) ppm;

$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 200.0 (C-11), 175.6 (C-30), 169.0 (C-13), 138.6 (aryl), 128.8 (aryl), 128.8 (aryl), 128.4 (C-12), 127.8 (aryl), 127.7 (aryl), 127.6 (aryl), 78.7 (C-3), 61.8 (C-9), 55.0 (C-5), 48.1 (C-18), 45.3 (C-8), 43.8 (C-20), 43.6 (C-31), 43.2 (C-14), 41.9 (C-19), 39.2 (C-1), 39.1 (C-4), 37.4 (C-22), 37.0 (C-10), 32.8 (C-7), 31.9 (C-17), 31.5 (C-21), 29.5 (C-29), 28.4 (C-23), 28.1 (C-28), 27.3 (C-2), 26.5 (C-16), 26.4 (C-15), 23.3 (C-27), 18.7 (C-26), 17.5 (C-6), 16.2 (C-25), 15.5 (C-24) ppm;

MS (ESI, MeOH): *m*/*z* = 559.7 (100 %, $[M+H]^+$), 1119.7 (78 %, $[2M+H]^+$), 1141.7 (56 %, $[2M+Na]^+$);

Analysis calcd for $C_{37}H_{53}NO_3$ (559.84): C 79.38, H 9.54, N 2.50; found: C 79.17, H 9.70, N 2.31.

**(3β, 18β, 20β) 3-Hydroxy-*N*-methyl-11-oxoolean-12-en-30-amide (11)**

Deacetylation of **6** (2.9 g, 5.52 mmol) as described above followed by chromatography (silica gel, chloroform/methanol, 10:1) gave **11** (2.09 g, 78%) as a white solid; m.p. 342-345 °C; $R_f$ = 0.61 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 150.2 (*c* = 0.27, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.03); IR (KBr): ν = 3503*s*, 3379*s*, 2919*s*, 2860*s*, 1660*s*, 1631*s*, 1529*s*, 1464*s*, 1387*s*, 1365*m*, 1299*m*, 1088*m* $cm^{-1}$;

$^1$H NMR (500 MHz, $CDC1_3$): δ = 5.73 (*d*, *J* = 8.1 Hz, 1H, NH), 5.65 (*s*, 1H, 12-H), 3.21 (*dd*, J = 10.8, 5.3 Hz, 1H, 3-H*)*, 2.81 (*d*, *J* = 3 Hz, 3H, 31-H), 2.77 (*ddd*, *J* = 13.6, 3.3, 3.3 Hz, 1H 1-H), 2.32 (*s*, 1H, 9-H), 2.14 (*dd*, *J* = 12.7, 3.9 Hz, 1H, 18-H), 2.03 (*ddd*, *J* = 13.7, 4.2, 4.2 Hz, 1H, 5-H), 1.92 (*m*, 1H, 21-H), 1.82 (*ddd*, *J* = 13.8, 13.6, 3.8 Hz, 1H, 16-H), 1.73 (*m*, 2H, 19-H), 1.66 (*m*, 1H, 7-H), 1.62 (*m*, 2H, 2-H), 1.57 (*m*, 1H, 6-H, 1.45 (*m*, 1H, 6-H), 1.41 (*m*, 1H, 7-H), 1.37 (*m*, 2H, 22-H), 1.36 (*s*, 3H, 27-H), 1.35 (*m*, 1H, 21-H) 1.18 (*m*, 1H, 1H, 16-H), 1.11 (*s*, 3H, 29-H), 1.11 (*s*, 6H, 26-H + 25-H), 1.01 (*m*, 1H, 15-H), 0.99 (*s*, 3H, 23-H), 0.94 (*m*, 1 H, 1-H), 0.80 (*s*, 3H, 28-H), 0.79 (*s*, 3H, 24-H), 0.68 (*m*, 1H, 5-H) ppm;

$^{13}$C-NMR (125 MHz, CDCI3): δ = 200.1 (C-11), 176.4 (C-30), 169.3 (C-13), 128.5 (C-12), 78.7 (C-3), 61.8 (C-9), 55.0 (C-5), 48.1 (C-18), 45.4 (C-8), 43.6 (C-20), 43.2 (C-14), 41.9 (C-19), 39.2 (C-1), 39.1 (C-4), 37.5 (C-22), 37.0 (C-10), 32.8 (C-7), 31.9 (C-17), 31.5 (C-21), 29.6 (C-29), 28.4 (C-23), 28.0 (C-28), 27.3 (C-2), 26.5 (C-31), 26.5 (C-16), 26.4 (C-15), 23.4 (C-27), 18.7 (C-26), 17.5 (C-6), 16.3 (C-24), 15.5 (C-24) ppm;

MS (ESI, MeOH): *m*/*z* = 484.4 (44 %, $[M+H]^+$), 967.5 (100 %, $[2M+H]^+$), 989.5 (68 %, $[2M+Na]^+$);

Analysis calcd for $C_{31}H_{49}NO_2$ (483.74): C 76.97, H 10.21, N 2.90; found: C 76.77, H 10.56, N 2.68.

**(3β, 18β, 20β) 3-Hydroxy-*N*, *N*-dimethyl-11-oxoolean-12-en-30-amide (12)**

Deacetylation of **7** (1.9 g, 3.5 mmol) as described above followed by chromatography (silica gel, hexane/ethyl acetate, 1:1) gave **12** (1.04 g, 60%) as a white solid; m.p. 327-330 °C; $R_f$ = 0.27 (hexane/ethyl acetate, 1:1); $[\alpha]_D$ = + 130.6 (*c* = 0.36, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.10); IR (KBr): ν = 3466*s*, 2960*s*, 1652*s*, 1607*s*, 1454*m*, 1385*s*, 1296*m*, 1128*m*, 1078*m*, 1044*m*, 996*m*, 983*m*, 879*m* $cm^{-1}$;

$^1$H NMR (400 MHz, $CDCl_3$): δ = 5.67 (*s*, 1H, 12-H), 4.68 (*br*, 1H, OH*)*, 3.22 (*dd*, *J* = 10.9, 5.3 Hz, 1H, 3-H), 3.03 (*s*, 6H, 33-H + 34-H), 2.78 (*ddd*, *J* = 12.6, 2.9, 2.9 Hz, 1H, 1-H, 2.33 (*s*, 1H, 9-H), 2.18 (*m*, 2H, 2-H + 18-H), 2.08 (*m*, 2H, 19-H + 15-H), 1.84 (*ddd*, *J* = 13.7, 13.7, 4.4 Hz, 1H, 16-H),

1.80 - 1.70 (*m*, 2H, 2-H + 19-H), 1.69 - 1.62 (*m*, 2H, 7-H + 2-H), 1.58 (*m*, lH, 6-H), 1.50 (*m*, 1H, 22-H), 1.44 (*m*, 1H, 6-H), 1.40 (*m*, 1 H, 7-H), 1.35 (*s*, 3H, 27-H), 1.30 (*m*, 1H, 21-H), 1.20 (*s*, 3H, 29-H) 1.15 (*m*, 1H, 16-H), 1.13 (*s*, 3H, 26-H), 1.11 (*s*, 3H, 25-H), 0.99 (*s*, 3H, 23-H, 0.98 (*m*, 2H, 15-H + 1-H), 0.80 (*s*, 6H, 28-H + 24-H), 0.69 (*m*, 1H, 5-H) ppm;
$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 200.2 (C-11), 175.1 (C-30), 169.8 (C-13), 128.4 (C-12), 78.7 (C-3), 61.8 (C-9), 55.0 (C-5), 48.5 (C-18), 45.3 (C-8), 44.2 (C-20), 43.5 (C-19), 43.3 (C-14), 39.1 (C-1), 39.1 (C-4), 38.6 (C-31), 38.6 (C-32), 37.8 (C-22), 37.1 (C-10), 33.5 (C-21), 32.8 (C-7), 31.9 (C-17), 28.4 (C-28), 28.1 (C-23), 27.3 (C-2), 26.8 (C-16), 26.6 (C-29), 26.5 (C-15), 23.0 (C-27), 18.7 (C-26), 17.5 (C-6), 16.4 (C-25), 15.6 (C-24) ppm;
MS (ESI, MeOH): *m*/*z* = 498.4 (100 %, $[M+H]^+$, 995.5 (94 %, $[2M+H]^+$), 1017.5 (68 %, $[2M+Na]^+$);
Analysis calcd for $C_{32}H_{51}NO_3$ (497.76): C 77.22, H 10.33, N 2.81; found: C 77.01, H 10.57, N 2.65.

**(18β, 20β) 3, 11-Dioxoolean-12-en-30-amide (13)**
Jones oxidation of **8** (4.5 g, 9.5 mmol) followed by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) gave **13** (3.85 g, 87%) as a white solid; m.p. 364-366 °C; $R_f$ = 0.46 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = 160.0 (*c* = 0.35, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.10); IR (KBr): ν = 3495*s*, 3381*s*, 2963*s*, 2870*m*, 1669*s*, 1643*s*, 1594*m*, 1458*m*, 1386*s*, 1207*m*, 1040*w* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDC1_3$): δ = 5.75 (*br*, 1H, NH), 5.67 (*br*, 1H, NH), 5.67 (*s*, 1H, 12-H, 2.88 (*ddd*, *J* = 13.4, 7.0, 4.0 Hz, 1H, 1-H), 2.56 (*ddd*, *J* = 15.9, 11.1, 7.1 Hz, 1H, 2-H), 2.36 (*s*, 1H, 9-H), 2.29 (*ddd*, *J* = 15.8, 6.4, 4.0 Hz, 1H, 2-H), 2.18 (*dd*, *J* = 13.0, 3.4 Hz, 1H, 18-H), 1.98 (*ddd*, *J* = 13.6, 13.6, 4.3 Hz, 1H, 15-H), 1.81 (*m*, 2H, 21-H + 16-H), 1.72 (*m*, 1H, 19-H), 1.64 (*m*, 2H, 19-H + 7-H), 1.49 (*m*, 2H, 6-H), 1.42 - 1.33 (*m*, 5H, 22-H + 21-H + 7-H + 1-H), 1.31 (*s*, 3H, 27-H), 1.23 (*dd*, *J* = 10.5, 3.6 Hz, 1H, 5-H), 1.20 (*s*, 3H, 25-H), 1.16 (*m*, 1H, 16-H), 1.12 (*s*, 3H, 29-H), 1.10 (*s*, 3H, 24-H), 1.04 (*s*, 3H, 23-H), 1.00 (*s*, 3H, 26-H), 0.98 (*m*, 1H, 15-H), 0.78 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 217.1 (C-3), 199.4 (C-11), 178.6 (C-30), 169.6 (C-13), 128.4 (C-12), 61.1 (C-9), 55.4 (C-5), 48.1 (C-18), 47.8 (C-4), 45.2 (C-8), 43.7 (C-20), 43.3 (C-14), 42.0 (C-19), 39.8 (C-1), 37.4 (C-22), 36.7 (C-10), 34.2 (C-2), 32.1 (C-7), 31.9 (C-21), 31.5 (C-17), 29.5 (C-29), 28.4 (C-28), 26.5 (C-23), 26.4 (C-16), 26.4 (C-15), 23.3 (C-27), 21.4 (C-26), 18.7 (C-6), 18.5 (C-24), 15.6 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 468.4 (30 %, $[M+H]^+$), 936.7 (100 %, $[2M+H]^+$);
Analysis calcd for $C_{30}H_{45}NO_3$ (467.69): C 77.04, H 9.70, N 2.99; found: C 76.81, H 9.94, N 2.58.

**(18β, 20β) -*N*-Allyl-3, 11-dioxoolean-12-en-30-amide (14)**
Jones oxidation of **9** (1.0 g, 1.96 mmol) followed by chromatography (silica gel, hexane/ethyl acetate, 7:3) gave **14** (0.79 g, 79%) as a white solid; m.p. 222-223 °C; $R_f$ = 0.17 (hexane/ethyl acetate, 7:3), $[\alpha]_D$ = + 151.6 (*c* = 0.27, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 239 nm (3.60); IR (KBr): ν = 3579*w*, 3443*m*, 3330*m*, 2957*m*, 2820*m*, 1701*s*, 1651*s*, 1552*m*, 1456*w*, 1388*m*, 1259*w*, 1206*w* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDC1_3$) δ = 5.83 (*m*, 1H, 32-H), 5.71 (*m*, 1H, NH), 5.69 (*s*, 1H, 12-H), 5.16 (*m*, 2H, 33-H), 3.90 (*m*, 2H, 31-H), 2.94 (*ddd*, *J* = 13.4, 7.0, 4.0 Hz, 1H, 1-H), 2.62 (*ddd*, *J* = 16.0, 11.1, 7.1 Hz, 1H, 2-H), 2.42 (*s*, 1H, 9-H), 2.35 (*ddd*, *J* = 15.7, 6.3, 4.0 Hz, 1H, 2-H), 2.20 (*dd*, *J* = 12.9, 3.5 Hz, 1H, 18-H), 2.05 (*ddd*, *J* = 13.6, 13.5, 4.2 Hz, 1H, 15-H), 1.92 (*m*, 1H, 21-H), 1.86 (*dd*, *J* = 13.6, 4.2 Hz, 1H, 16-H), 1.80 (*m*, 2H, 19-H), 1.69 (*m*, 1H, 7-H), 1.54 (*m*, 2H, 6-H), 1.45 (*m*, 1H, 7-H), 1.41 (*m*, 3H, 22-H + 21-H), 1.37 (*s*, 3H, 27-H), 1.26 (*m*, 1H, 5-H), 1.25 (*s*, 3H, 25-H), 1.21 (*m*, 1H, 6-H), 1.16 (*s*, 3H, 24-H), 1.14 (*s*, 3H, 29-H), 1.09 (*s*, 3H, 23-H), 1.05 (*s*, 3H, 26-H), 1.02 (*m*, 1H, 15-H), 0.83 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 217.2 (C-3), 199.4 (C-11), 175.5 (C-30), 169.7 (C-13), 134.4 (C-32), 128.4 (C-12), 116.4 (HC = $CH_2$), 61.1 (C-9), 55.4 (C-5), 48.1 (C-18), 47.8 (C-4), 45.2 (C-8), 43.6 (C-20), 43.3 (C-14), 41.8 (C-31), 41.8 (C-19), 39.8 (C-1), 37.4 (C-22), 36.7 (C-10), 34.2 (C-2), 32.1 (C-7), 32.0 (C-21), 31.5 (C-17), 29.6 (C-29), 28.5 (C-28), 26.5 (C-23), 26.4 (C-16), 26.4 (C-15), 23.3 (C-27), 21.4 (C-26), 18.8 (C-6), 18.5 (C-24), 15.6 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 508.4 (100 %, $[M+H]^+$), 1015.6 (50 %, $[2M+H]^+$);
Analysis calcd for $C_{33}H_{49}NO_3$ (507.76): C 78.06, H 9.73, N 2.76; found: C 77.85, H 9.97, N 2.51.

**(18β, 20β) *N*-Benzyl-3, 11-dioxoolean-12-en-30-amide (15)**
Jones oxidation of **10** (1.75 g, 3.13 mmol) followed by chromatography (hexane/ethyl acetate, 7:3) gave **15** (1.46 g, 84%) as a white solid; m.p. 194-196 °C; $R_f$ = 0.25 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 191.2 (*c* = 0.27, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 243 nm (3.88); IR (KBr): ν = 3364*s*, 2969*m*, 2820*m*, 1962*m*, 1659*s*, 1528*m*, 1454*m*, 1386*m* $cm^{-1}$;
$^1$H (NMR (500 MHz, $CDC1_3$): δ = 7.27 (*m*, 2H, aryl), 7.21 (*m*, 3H, aryl), 5.87 (*br*, NH), 5.54 (*s*, 1H, 12-H), 4.40 (*m*, 2H, 31-H), 2.87 (*ddd*, *J* = 13.4. 6.9, 3.9 Hz, 1H, 1-H), 2.55 (*ddd*, *J* = 15.8, 11.2, 7.2 Hz, 1H, 2-H), 2.34 (*s*, 1H, 9-H), 2.28 (*ddd*, *J* = 15.7, 6.3, 4.0 Hz, 1H, 2-H), 2.13 (*dd*, *J* = 13.2, 3.6 Hz, 1H, 18-H), 1.98 (*ddd*, *J* = 13.6, 13.5, 4.4 Hz, 1H, 15-H), 1.86 (*m*, 1 H, *21-H)*, 1.79 (*dd*, *J* = 13.7. 4.4 Hz, 1H, 16-H), 1.74 (*m*, 1H, 19-H), 1.66 (*m*, 1H, 19-H), 1.61 (*m*, 1H, 7-H), 1.49 (*m*, 2H, 6-H), 1.39 (*m*, 2H, 21-H + 7-H), 1.33 (*m*, 3H, 22-H + 1-H), 1.29 (*s*, 3H, 27-H), 1.22 (*m*, 1H, 5-H), 1.19 (*s*, 3H, 25-H),

1.14 (*m*, 1H, 16-H), 1.09 (*s*, 6H, 29-H + 24-H), 1.03 (*s*, 3H, 23-H), 0.99 (*s*, 3H, 26-H), 0.97 (*m*, 1H, 15-H), 0.75 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 217.1 (C-3), 199.3 (C-11), 175.5 (C-30), 169.5 (C-13), 138.6 (aryl), 128.8 (aryl), 128.4 (C-12), 127.9 (aryl) 127.9 (aryl), 127.7 (aryl), 127.6 (aryl), 61.0 (C-9), 55.4 (C-5), 48.1 (C-18), 47.8 (C-4), 45.2 (C-8), 43.8 (C-20), 43.6 (C-31), 43.3 (C-14), 42.0 (C-19), 39.8 (C-1), 37.4 (C-22), 36.7 (C-10), 34.2 (C-2), 32.1 (C-1*)*, 32.0 (C-21), 31.5 (C-17), 29.5 (C-29), 28.5 (C-28), 26.5 (C-23), 26.4 (C-16), 26.4 (C-15), 23.3 (C-27), 21.4 (C-26), 18.8 (C-6), 18.5 (C-24), 15.6 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 558.7 (100 %, $[M+H]^+$), 1115.7 (100 %, $[2M+H]^+$);
Analysis calcd for $C_{37}H_{51}NO_3$ (557.82): C 79.67, H 9.22, N 2.51; found: C 79.46, H 9.47, N 2.30.

**(18β, 20β) *N*-Methyl-3, 11-dioxoolean-12-en-30-amide (16)**
Jones oxidation of **11** (1.5 g, 3.1 mmol) followed by chromatography (silica gel, $CHCl_3$/MeOH, 10:1) gave **16** (1.18 g, 79%) as a white solid; m.p. 309-313 °C; $R_f$ = 0.17 (hexane/ethyl acetate, 1:1); $[\alpha]_D$ = 177.2 (*c* = 0.52, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.14); IR (KBr): ν = 3448*s*, 2952*s*, 2874*m*, 1701*s*, 1651*s*, 1520*s*, 1446*m*, 1285*m*, 1205*m*, 997*m* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDC1_3$): δ = 5.70 (*s*, 1H, 12-H*)*, 5.63 (*br*, 1H, NH), 2.95 (*ddd*, *J* = 13.2, 7.0, 4.0 Hz, 1H 1-H), 2.82 (*d*, *J* = 4.6 Hz, 3H, 31-H), 2.56 (*ddd*, *J* = 16.0, 11.2, 7.1 Hz, 1H, 2-H), 2.42 (*s*, 1H, 9-H), 2.35 (*ddd*, *J* = 15.8, 6.4, 4.1 Hz, 1H, 2-H), 2.18 (*dd*, *J* = 13.0, 3.6 Hz, 1H, 18-H), 2.04 (*ddd*. *J* = 13.6, 13.6, 4.2 Hz, 1H, 15-H), 1.90 (*m*, 1H, 21-H), 1.81 (*m*, 1H, 16-H), 1.77 (*m*, 1H, 19-H), 1.71 (*m*, 1H, 19-H), 1.66 (*m*, 1H, 7-H), 1.54 (*m*, 2H, 6-H), 1.46 (*m*, 1H, 7-H), 1.43 (*m*, 1H, 1-H), 1.41 (*m*, 1H, 21-H), 1.39 (*m*, 2H, 22-H), 1.37 (*s*, 3H, 27-H), 1.28 (*m*, 1H, 5-H), 1.26 (*s*, 3H, 25-H), 1.21 (*m*, 1H, 16-H), 1.16 (*s*, 3H, 24-H), 1.12 (*s*, 3H, 29-H), 1.09 (*s*, 3H, 23-H), 1.06 (*s*, 3H, 26-H), 1.02 (*m*, 1H, 15-H), 0.82 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 217.1 (C-3), 199.3 (C-11), 176.3 (C-30). 169.7 (C-13), 128.4 (C-12), 61.1 (C-9), 55.5 (C-5), 48.1 (C-18), 47.8 (C-4), 45.2 (C-8), 43.6 (C-20), 43.3 (C-14), 41.9 (C-19), 39.8 (C-1), 37.4 (C-22), 36.7 (C-10), 34.2 (C-2), 32.1 (C-7), 31.9 (C-17), 31.6 (C-21), 29.6 (C-29), 28.5 (C-28), 26.5 (C3I, $CH_3$), 26.5 (C-16), 26.4 (C-15), 26.4 (C-23), 23.3 (C-27), 21.4 (C-26), 18.8 (C-6), 18.5 (C-24), 15.6 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 482.3 (100 %, $[M+H]^+$), 963.5 (100 %, $2M+H^+$);
Analysis calcd for $C_{31}H_{47}NO_3$ (481.72): C 77.29, H 9.83, N 2.91; found: C 76.99, H 10.03, N 2.85.

**(18β, 20β) *N, N*-Dimethyl-3, 11-dioxoolean-12-en-30-amide (17)**
Jones oxidation of **12** (1.0 g, 2.01 mmol) followed by chromatography (silica gel, $CHCl_3$/MeOH, 99:1) gave **17** (0.85 g, 85%) as a white solid; m.p. 199-201 °C; $R_f$ = 0.33 (hexane/ethyl acetate); $[\alpha]_D$ = 236.2 (*c* = 0.30, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 247 nm (4.54); IR (KBr): ν = 3447*s*, 2942*s*, 1742*s*, 1648*s*, 1627*s*, 1464*m*, 1386*s*, 1124*m*, 1071*w* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDC1_3$): δ = 5.72 (*s*, 1H, 12-H), 3.03 (*s*, 6H, 33-H + 34-H), 2.95 (*ddd*, *J* = 13.3, 7.0, 4.0 Hz, 1H 1-H), 2.56 (*ddd*, *J* = 16.2, 11.1, 7.1 Hz, 1H, 2-H), 2.42 (*s*, 1 H, 9-H), 2.34 (*ddd*, *J* = 15.7, 6.2, 4.0 Hz, 1H, 2-H), 2.24 (18-H), 2.14 (*m*, 1H, 21-H), 2.06 (*m*, 2H, 19-H + 15-H), 1.85 (*ddd*, *J* = 13.6, 13.6, 4.3 Hz, 1H, 16-H), 1.66 (*m*, 1H, 7-H), 1.59 (*m*, 1H, 19-H), 1.52 (*m*, 2H, 6-H, 1.46 (*m*, 1H, 22-H), 1.44 (*m*, 1H, 7-H), 1.40 (*m*, 1H, 1-H), 1.36 (*m*, 1H, 22-H), 1.35 (*s*, 3H, 27-H), 1.28 (*m*, 2H, 21-H + 5-H), 1.26 (*s*, 3H, 25-H), 1.20 (*m*, 1H, 15-H), 1.19 (*s*, 3H, 29-H), 1.15 (*s*, 3H, 24-H), 1.08 (*s*, 3H, 23-H), 1.05 (*s*, 3H, 26-H), 1.04 (*m*, 1H, 16-H), 0.98 (*m*, 1H, 15-H), 0.81 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 199.4 (C-11), 175.0 (C-30), 170.2 (C-13), 128.4 (C-12), 61.0 (C-9), 55.5 (C-5), 48.4 (C-18), 47.8 (C-4), 45.1 (C-8), 44.2 (C-20), 43.7 (C-19), 43.4 (C-14), 39.8 (C-1), 38.6 (C-31), 38.6 (C-32), 37.7 (C-22), 36.7 (C-10), 34.2 (C-2), 33.3 (C-21), 32.2 (C-7), 31.9 (C-17), 28.5 (C-28), 26.8 (C-16), 26.6 (C-29), 26.5 (C-15), 26.3 (C-23), 23.0 (C-27), 21.4 (C-26), 18.8 (C-6), 18.5 (C-24), 15.6 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 496.5 (86 %, $[M+H]^+$), 991.7 [96 %, $[2M+H]^+$), 1013.5 (100 % $[2M+Na]^+$);
Analysis calcd for $C_{32}H_{49}NO_3$ (495.75): C 77.53, H 9.96, N 2.83; found: C 77.41, H 10.17, N 2.58.

**(3E, 18β, 20β) 3-Hydroxyimino-11-oxoolean-12-en-30-amide (18)**
To a suspension of **13** (2.4 g, 5.13 mmol) in pyridine (70 mL) hydroxylammonium hydrochloride (0.9 g, 10 mmol) were added, and the mixture was heated under reflux for 3 hours. After cooling to 25 °C, the product was precipitated by the slow addition of aq. 1 N hydrochloric acid, filtered off and purified by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) to yield **18** (1.94 g, 78%) as a white solid; m.p. 296-297 °C; $R_f$ = 0.52 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 107.9 (*c* = 0.33, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 254 nm (4.03); IR (KBr): ν = 3476*s*, 3370*s*, 2074*s*, 2863*s*, 2918*s*, 2825*m*, 1663*s*, 1588*s*, 1455*s*, 1364*s*, 1289*s*, 1245*w*, 1204*s*, 1191*s*, 1137w, 1024*w*, 980*m*, 921*s*, 883*m*, 737*m*, 680*m* $cm^{-1}$;
$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 10.24 (*s*, 1H, NOH), 7.11 (*s*, 1H, NH), 6.73 (*s*, 1H, NH), 5.49 (*s*, 1H, 12-H), 2.82 (*m*, 1 H, 2-H), 2.61 (*m*, 1H, 1-H), 2.37 (*s*, 1 H, 9-H), 2.09 (*m*, 3H, 18-H + 15-H + 2-H), 1.83 (*m*, 1H, 21-H), 1.76 (*m*, 2H, 19-H + 16-H), 1.65 (*m*, 1H, 19-H), 1.56 (*m*, 2H, 7-H + 6-H), 1.44 (*m*, 1H, 6-H), 1.40 - 1.30 (*m*, 3H, 23-H),

1.09 (*s*, 3H, 29-H), 1.05 (*s*, 3H, 26-H), 1.02 (*s*, 3H, 24-H), 0.97 (*m*, 3H, 15-H + 5-H + 1-H), 0.73 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 199.3 (C-11), 178.0 (C-30), 170.4 (C-13), 163.7 (C-3), 127.8 (C-12), 61.1 (C-9), 55.0 (C-5), 48.2 (C-18), 45.2 (C-8), 43.5 (C-20), 43.3 (C-14), 41.3 (C-19), 40.5 (C-4), 38.7 (C-1), 37.8 (C-22), 37.0 (C-10), 32.2 (C-7), 31.9 (C-17), 30.9 (C-21), 29.0 (C-29), 28.9 (C-28), 27.9 (C-23), 26.5 (C-15), 26.4 (C-16), 23.8 (C-27), 23.2 (C-24), 18.7 (C-26), 18.2 (C-6), 17.0 (C-2), 15.8 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 483.5 (42 %, $[M+H]^+$), 965.5 $[2M+H]^+$);
Analysis calcd for $C_{30}H_{46}N_2O_3$ (482.71): C 74.65, H 9.61, N 5.80; found: C 74.47, H 9.84, N 5.65.

**(3 E, 18β, 20β) *N*-Allyl-3-hydroxyimino-11-oxoolean-12-en-30-amide (19)**
As described above, from **14** (1.0 g, 1.97 mmol) and hydroxylammonium chloride (0.3 g, 4.3 mmol) followed by re-crystallization from methanol compound **19** (0.77 g, 76%) was obtained as a white solid; m.p. 276-278 °C; $R_f$ = 0.43 (hexane/ethyl acetate, 1:1); $[\alpha]_D$ = + 112.0 (*c* = 0.39, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 254 nm (3.96); IR (KBr): ν = 3456*m*, 3324*s*, 2970*s*, 2925*s*, 2864*m*, 1655*s*, 1520*s*, 1456*m*, 1386*m*, 1323*w*, 1260*m*, 1179*w*, 980*w*, 944*m*, 929*m* $cm^{-1}$;
$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 10.23 (*s*, 1H, NOH), 7.72 (*dd*, *J* = 5.6, 5.6 Hz, 1H, NH), 5.78 (*ddt*, *J* = 16.9, 10.1, 5.0 Hz, 1H, 32-H), 5.49 (*s*, 1H, 12-H, 5.06 (*dd*, *J* = 17.2, 1.7 Hz, 1H, 33-H), 5.02 (*dd*, *J* = 10.3, 6.5 Hz, 1H, 33-H), 3.74 (*m*, 1H, 31-H), 3.64 (*m*, 1H, 31-H), 2.82 (*ddd*, *J* = 15.0, 4.2, 4.2 Hz, 1H, 2-H), 2.61 (*m*, 1H, 1-H), 2.37 (*s*, 1H, 9-H), 2.11 (*m*, 2H, 18-H + 2-H), 1.91 (*m*, 1H, 5-H), 1.83 (*m*, 1H, 21-H), 1.76 (*m*, 1H, 16-H), 1.75 (*m*, 1H, 19-H), 1.66 (*m*, 1H, 19-H), 1.61 (*m*, 1H, 7-H), 1.54 (*m*, 1H, 6-H), 1.41 (*m*, 1H, 6-H), 1.37 (*m*, 1H, 7-H), 1.33 (*s*, 3H, 27-H), 1.27 (*m*, 3H, 22-H + 21-H), 1.24 (*s*, 3H, 25-H) 1.16 (*m*, 1H, 16-H), 1.12 (*s*, 3H, 23-H), 1.09 (*s*, 3H, 29-H), 1.04 (*s*, 3H, 26-H), 1.01 (*s*, 3H, 24-H), 1.02 (*m*, 3H, 15-H + 5-H + 1-H), 0.71 (*s*, 3H, 28-H) ppm; $^{13}$C NMR (100 MHz, $CDC1_3$): δ = 199.2 (C-11), 175.4 (C-30), 170.4 (C-13), 163.7 (C-3), 136.5 (C-32), 127.9 (C-12), 114.8 (HC = $CH_2$), 61.0 (C-9), 55.0 (C-5), 48.2 (C-18), 45.2 (C-8), 43.5 (C-20), 43.4 (C-14), 41.4 (C-31), 41.3 (C-19), 40.4 (C-4), 38.7 (C-1), 37.7 (C-22), 37.0 (C-10), 32.1 (C-7), 31.9 (C-17), 30.9 (C-21), 29.1 (C-29), 28.9 (C-28), 27.9 (C-23), 26.5 (C-15), 26.4 (C-16), 23.8 (C-27), 23.4 (C-24), 18.7 (C-26), 18.2 (C-6), 17.0 (C-2), 15.8 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 523.5 (48 %, $[M+H]^+$), 1045.5 (100 % $[2M+H]^+$), 1067.5 (100 % $[2M+Na]^+$);
Analysis calcd for $C_{33}H_{50}N_2O_3$ (522.77): C 75.82, H 9.64, N 5.36; found: C 75.69, H 9.81, N 5.17.

**(3 E, 18β, 20β) *N*-Benzyl-3-hydroxyimino-11-oxoolean-12-en-30-amide (20)**
As described above from **15** (0.5 g, 0.89 mmol) and hydroxylammonium chloride (0.15 g, 2.15 mmol) followed by re-crystallization from methanol compound **20** (0.42 g, 82%) was obtained as a white solid; m.p. 244-246 °C; $R_f$ = 0.67 (hexane/ethyl acetate, 1:1); $[\alpha]_D$ = 105.9 (*c* = 0.28, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.12); IR (KBr): ν = 3547*m*, 3341*s*, 2974*s*, 2930*s*, 2863*s*, 1659*s*, 1613*m*, 1520*s*, 1455*m*, 1384*m*, 1253*w*, 1205*m*, 1179*m*, 1115*w*, 1081*w*, 929*m*, 696*m* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDC1_3$): δ = 7.33 (*m*, 2H, aryl), 7.27 (*m*, 3H, aryl), 5.90 (*dd*, *J* = 5.65, 5.65 Hz, 1H, NH), 5.67 (*s*, 1H, 12-H), 4.50 (*dd*, *J* = 14.6, 5.7 Hz, 1H, *31-H*, 4.43 (*dd*, *J* = 14.6, 5.5 Hz, 1H, *31-H*, 3.03 (*dd*, *J* = 15.6, 4.9, 3.9 Hz, 1H, 2-H), 2.85 (*ddd*, *J* = 13.4, 5.6, 3.8 Hz, 1H, 1-H), 2.34 (*s*, 1H, 9-H), 2.25 (*ddd*, *J* = 15.6, 12.8, 5.8 Hz, 1H, 2-H), 2.17 (*dd*, *J* = 13.0, 4.2 Hz, 1H, 18-H), 2.03 (*m*, 1H, 15-H), 1.94 (*m*, 1H, 21-H), 1.84 (*ddd*, *J* = 13.5, 13.5, 4.3 Hz, 1H, 16-H), 1.79 (*m*, 1H, 19-H), 1.74 (*m*, 1H, 19-H), 1.67 (*m*, 1H, 7-H), 1.61 (*m*, 1H, 6-H), 1.51 (*m*, 1H, 6-H), 1.45 (*m*, 1H, 7-H), 1.42 (*m*, 1H, 22-H), 1.39 (*m*, 1H, 22-H), 1.37 (*m*, 1H, 21-H), 1.30 (*s*, 3H, 27-H), 1.24 (*s*, 3H, 25-H) 1.19 (*m*, 1H, 16-H), 1.16 (*s*, 3H, 23-H), 1.15 (*s*, 3H, 29-H), 1.14 (*s*, 3H, 26-H), 1.07 (*s*, 3H, 24-H), 1.04 (*m*, 3H, 15-H + 5-H + 1-H), 0.81 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 199.6 (C-11), 175.5 (C-30), 169.2 (C-13), 167.0 (C-3), 138.6 (aryl), 128.8 (aryl), 128.8 (aryl), 128.4 (C-12), 128.4 (aryl), 127.7 (aryl), 127.6 (aryl), 61.3 (C-9). 55.6 (C-5), 48.2 (C-18), 45.3 (C-8), 43.7 (C-20), 43.6 (C-14), 43.3 (C-31), 41.4 (C-19), 40.4 (C-4), 39.0 (C-1), 37.5 (C-22), 37.0 (C-10), 32.4 (C-7), 31.9 (C-17), 31.5 (C-21), 29.5 (C-29), 28.4 (C-28), 27.1 (C-23), 26.5 (C-15), 26.4 (C-16), 23.2 (C-27), 23.2 (C-24). 18.6 (C-26), 18.2 (C-6), 17.1 (C-2), 15.7 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 574.3 (100 %, $[M+H]^+$);
Analysis calcd for $C_{37}H_{52}N_2O_3$ (572.83): C 77.58, H 9.15, N 4.89; found: C 77.42, H 9.37, N 4.56.

**(3 E, 18β, 20β) *N*-Methyl-3-hydroxyimino-11-oxoolean-12-en-30-amide (21)**
As described above from **16** (1.0 g, 2.07 mmol) and hydroxylammonium chloride (0.3 g, 4.2 mmol) followed by chromatography (silica gel, hexane/ethyl acetate, 1:1) **21** (0.86 g, 83%) was obtained as a white solid; m.p.153-156 °C; $R_f$ = 0.29 (hexane/ethyl acetate, 1:1); $[\alpha]_D$ = + 90.9 (*c* = 0.37, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (5.05); IR (KBr): ν = 3385*s*, 1954*s*, 1869*s*, 1652*s*, 1541*m*, 1455*s*, 1411*w*, 1384*s*, 1328*w*, 1205*m*, 1091*w*, 1025*w*, 754*s*, 664*m* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDC1_3$): δ = 5.68 (*s*, 1H, 12-H, 5.60 (*m*, 1H, NH), 3.04 (*m*, 1H, 2-H), 2.87 (*m*, 1H 1-H), 2.82 (*d*, *J* = 4.7 Hz, 3H, 31-H), 2.37 (*s*, 1H, 9-H), 2.27 (*ddd*, *J* = 15.6, 12.8, 5.8 Hz, 1H, 2-H), 2.16 (*dd*, *J* = 12.5, 4.4 Hz, 1H, 18-H),

2.04 (*m*, 1H, 15-H), 1.91 (*m*, 1H, 21-H), 1.83 (*m*, 1H, 16-H), 1.75 (*m*, 2H, 19-H), 1.68 (*m*, 1H, 7-H), 1.62 (*m*, 1H, 6-H), 1.51 (*m*, 1 H, 6-H), 1.44 (*m*, 1H, 7-H), 1.38 (*m*, 2H, 22-H), 1.36 (*m*, 1H, 21-H), 1.35 *s*, 3H, 27-H), 1.25 (*s*, 3H, 25-H) 1.21 (*m*, 1H, 16-H), 1.17 (*s*, 3H, 23-H), 1.15 (*s*, 3H, 29-H), 1.11 (*s*, 3H, 26-H), 1.08 (*s*, 3H, 24-H), 1.03 (*m*, 3H, 15-H + 5-H + 1-H), 0.82 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 199.6 (C-11), 176.3 (C-30), 169.4 (C-13), 167.2 (C-3), 128.4 (C-12), 61.4 (C-9), 55.6 (C-5), 48.1 (C-18), 45.3 (C-8), 43.6 (C-20), 43.2 (C-14), 41.9 (C-19). 40.4 (C-4), 39.1 (C-1), 37.4 (C-22), 37.1 (C-10), 32.4 (C-7), 31.9 (C-17), 31.5 (C-21), 29.6 (C-29), 28.4 (C-28), 27.1 (C-23), 26.5 (C-31), 26.5 (C-15), 26.4 (C-16), 23.3 (C-27), 23.2 (C-24), 18.7 (C-26), 18.2 (C-6), 17.12 (C-2), 15.7 (C-25) ppm;

MS (ESI, MeOH): *m*/*z* = 497.5 (76 %, $[M+H]^+$), 993.5 (100 %, $[M+H]^+$);

Analysis calcd for $C_{31}H_{48}N_2O_3$ (496.74): C 74.96, H 9.74, N 5.64; found: C 74.77, H 9.96, N 5.48.

**(3 E, 18β, 20β) *N, N*-Dimethyl-3-hydroxyimino-11-oxoolean-12-en-30-amide (22)**

As described above from **17** (0.7 g, 1.4 mmol) and hydroxylammonium chloride (0.2 g, 2.8 mmol) followed by chromatography (silica gel, $CHCl_3$/MeOH, 99:1) compound **22** (0.54 g, 76%) was obtained as a white solid; m.p. 262-264 °C; $R_f$ = 0.33 (hexane/ethyl acetate, 1:1), $[\alpha]_D$ = + 117.7 (*c* = 0.35, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 253 nm (4.00); IR (KBr): ν = 3340*s*, 2971*s*, 2872*m*, 1656*s*, 1609*s*, 1465*w*, 1388*s*, 1260*w*, 1130*w*, 1053*w*, 953*m* $cm^{-1}$;

$^1$H NMR (400 MHz, $CDC1_3$): δ = 5.70 (*s*, 1H, 12-H), 3.03 (*s*, 6H, 31-H + 32-H), 3.03 (*m*, 1H, 2-H), 2.85 (*ddd*, *J* = 13.4, 5.2, 3.8 Hz, 1H, 1-H), 2.37 (*s*, 1H, 9-H), 2.25 (*m*, 1H, 2-H)**,** 2.16 (*m*, 2H, 21-H + 18-H), 2.04 (*m*, 2H, 15-H + 19-H), 1.83 (*ddd*, *J* = 13.5, 13.5, 4.3 Hz, 1H, 16-H), 1.67 (*m*, 1H, 7-H), 1.61 (*m*, 1H, 6-H), 1.58 (*m*, 1H, 19-H), 1.50 (*m*, 1 H, 6-H), 1.46 (*m*, 1H, 7-H), 1.42 (*m*, 1H, 22-H), 1.39 (*m*, 1H, 21-H), 1.33 (*s*, 3H, 27-H), 1.31 (*m*, 1H, 22-H), 1.24 (*s*, 3H, 25-H) 1.24 (*m*, 1H, 16-H), 1.19 (*s*, 3H, 23-H), 1.16 (*s*, 3H, 29-H), 1.14 (*s*, 3H, 26-H), 1.07 (*s*, 3H, 24-H), 1.05 (*m*, 3H, 15-H + 5-H + 1-H), 0.81 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 199.8 (C-11). 175.0 (C-30), 170.0 (C-13), 167.0 (C-3), 128.4 (C-12), 61.3 (C-9), 55.6 (C-5), 48.5 (C-18), 45.2 (C-8), 44.2 (C-20), 43.5 (C-14), 43.4 (C-19), 40.4 (C-4), 39.0 (C-1), 38.6 (C-31), 38.6 (C-32), 37.8 (C-22), 37.0 (C-10), 33.5 (C-21), 32.5 (C-7), 31.9 (C-17), 28.5 (C-28), 27.2 (C-23), 26.8 (C-15), 26.6 (C-29), 26.5 (C-16), 23.3 (C-27), 23.0 (C-24), 18.6 (C-26), 18.2 (C-6), 17.2 (C-2), 15.7 (C-25) ppm;

MS (ESI, MeOH): *m*/*z* = 511.5 (100 %, $[M+H]^+$), 1021.6 (100 %, $[2M+H]^+$);

Analysis calcd for $C_{32}H_{50}N_2O_3$ (510.76): C 75.25, H 9.87, N 5.48; found: C 75.03, H 10.13, N 5.30.

**(3β, 18β, 20β) 3-Amino-11-oxoolean-12-en-30-amide (23)**

To a solution of **18** (100 mg, 0.21 mmol) in dry EtOH/dry THF (25 mL/7.5 mL) under argon at 0 °C ammonium acetate (0.16 g, 2.0 mmol) and sodium cyanoborohydride (69 mg, 1.05 mmol) were added. After stirring for 5 min a solution of $TiCl_3$ (0.12 mL, 12% in HCl) was slowly added, and stirring at 25 °C was continued for one day. The pH of the solution was adjusted to 10 by adding aq. sodium hydroxide (10 M). Extraction with $CHCl_3$, evaporation of the volatiles under reduced pressure followed by chromatography (silica gel, MeOH/$CHCl_3$, 9:1) yielded **23** (63 mg, 65%) as a white solid; m.p. 277-280 °C; $R_f$ = 0.19 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 32.1 (*c* = 0.31, DMSO), UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 255 nm (3.33); IR (KBr): ν = 3441*s*, 2963*w*, 1639*s*, 1384*s*, 1216*w*, 1047*w*, 554*m* $cm^{-1}$;

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.67 (*br*, 2H, $NH_2$), 7.11 (*s*, 1H, NH), 6.72 (*s*, 1H, NH 5.46 (*s*, 1H, 12-H), 2.80 (*dd*, *J* = 12.4, 3.9 Hz, 1H, 3-H), 2.63 (*m*, 1H, 1-H), 2.34 (*s*, 1H, 9-H), 2.05 (*m*, 2H, 18-H + 15-H), 1.84 (*m*, 1H, 21-H), 1.74 (*m*, 2H, 19-H + 16-H), 1.63 (*m*, 3H, 19-H + 7-H + 2-H), 1.53 (*m*, 2H, 6-H + 2-H), 1.35 (*m*, 2H, 7-H + 6-H), 1.31 (*s*, 3H, 27-H), 1.26 (*m*, 3H, 21-H + 22-H), 1.13 (*m*, 1H, 6-H), 1.04 (*m*, 1H, 1-H), 1.01 (*s*, 9H, 29-H + 26-H + 25-H ), 0.98 (*s*, 3H, 23-H), 0.94 (*m*, 1H, 15-H), 0.86 (*m*, 1H, 5-H), 0.76 (*s*, 3H, 24-H), 0.71 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 199.4 (C-11), 178.2 (C-30), 170.5 (C-13), 127.8 (C-12), 61.1 (C-9), 59.3 (C-3), 54.0 (C-5), 48.2 (C-18), 45.3 (C-14), 43.4 (C-20), 43.2 (C-8), 41.3 (C-19), 38.1 (C-4), 37.8 (C-1), 36.9 (C-10), 36.8 (C-22), 32.3 (C-7), 31.8 (C-17), 30.9 (C-21), 29.1 (C-29), 28.7 (C-28), 27.9 (C-23), 26.5 (C-16), 26.3 (C-15), 23.7 (C-27), 23.4 (C-2), 18.7 (C-26), 17.4 (C-6), 16.4 (C-25), 16.2 (C-24) ppm;

MS (ESI, MeOH): *m*/*z* = 469.3 (100 %, $[M+H]^+$);

Analysis calcd for $C_{30}H_{48}N_2O_2$ (468.73): C 76.87, H 10.32, N 5.98; found: C 76.58, H 10.51, N 5.77.

**(3β, 18β, 20β) *N*-Allyl 3-amino-11-oxoolean-12-en-30-amide (24)**

As described above from **19** (500 mg, 0.09 mmol) followed by chromatography (silica gel, MeOH/$CHCl_3$, 9:1) compound **24** (402 mg, 80%) was obtained as a white solid; m.p. 224-225 °C; $R_f$ = 0.25 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 108.6 (*c* = 0.45, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 250 nm (3.69); IR (KBr): ν = 3425*s*, 2956*m*, 1633*s*, 1384*s*, 1045w, 539*m* $cm^{-1}$;

$^1$H-NMR (500 MHz, DMSO-$d_6$): δ = 7.74 (*dd*, *J* = *5.7, 5.7* Hz, 1H, HN), 7.68 (*br*, 2H, $NH_2$), 5.77 (*ddt*, *J* = 16.0, 10.5, 5.3 Hz, 1H, 32-H), 5.47 (*s*, 1H, 12-H), 5.06 (*m*, 1H, 33-H), 5.25 (*m*, 1H, 33-H), 3.73 (*m*, 1H, 31-H), 3.64 (*m*, 1H, 31-H), 2.80 (*m*, 1H, 3-H), 2.63 (*m*, 1H, 1-H), 2.36 (*s*, 1H, 9-H), 2.06 (*m*, 2H, 18-H + 15-H), 1.90 (*m*, 1H, 21-H), 1.80 (*m*, 1H, 19-H), 1.73 (*m*, 1H, 16-H), 1.64 (*m*, 2H, 7-H + 2-H), 1.58 (*m*, 1H, 19-H), 1.54 (*m*, 2H, 6-H + 2-H),

1.37 (*m*, 1H, 6-H), 1.33 (*s*, 3H, 27-H), 1.33 (*m*, lH, 21-H + 7-H), 1.27 (*m*, 2H, 22-H), 1.13 (*m*, 1H, 16-H), 1.04 (*m*, 1H, 1-H), 1.02 (*s*, 9H, 29-H + 26-H + 25-H ), 0.98 (*s*, 3H, 23-H), 0.94 (*m*, 1H, 15-H), 0.86 (*m*, 1H, 5-H), 0.76 (*s*, 3H, 24-H), 0.70 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 199.3 (C-11), 175.4 (C-30), 170.5 (C-13), 136.5 (C-32), 127.8 (C-12), 114.8 (C-33), 61.1 (C-9), 59.2 (C-3), 54.0 (C-5), 48.2 (C-18), 45.2 (C-14), 43.4 (C-20), 43.4 (C-8), 41.3 (C-19), 41.2 (C-31), 38.7 (C-4), 37.7 (C-1), 36.9 (C-10), 36.8 (C-22), 32.3 (C-7), 31.8 (C-17), 31.0 (C-21), 29.1 (C-29), 29.0 (C-28), 27.9 (C-23), 26.3 (C-16), 26.3 (C-15), 23.5 (C-27), 23.4 (C-2). 18.7 (C-26), 17.4 (C-6), 16.3 (C25. $CH_3$). 16.1 (C-24) ppm;

MS (ESI, MeOH): *m*/*z* = 509.4 (100 %, $[M+H]^+$);

Analysis calcd for $C_{33}H_{52}N_2O_2$ (508.79): C 77.90, H 10.30, N 5.51; found: C 77.74, H 10.55, N 5.39.

**(3β, 18β, 20β) *N*-Benzyl 3-amino-11-oxoolean-12-en-30-amide (25)**

As described above from **20** (250 mg) followed by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) **25** (156 mg, 64%) was obtained as a white solid; m.p. 199-201 °C; $R_f$ = 0.17 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 100.4 (*c* = 0.32, DMSO), UV-Vis ( $CHCl_3$): $\lambda_{max}$ (log ε) = 255 nm (3.83); IR (KBr): ν = 3424*s*, 2953*m*, 1654*s*, 1527*w*, 1384*s*, 1106*w* $cm^{-1}$;

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 8.12 (*dd*, *J* = 6.0, 6.0 Hz, 1H, NH), 7.64 (d, *J* = 4.3 Hz, 2H, $NH_2$), 7.28 (*m*, 2H, aryl), 7.20 (*m*, 3H, aryl), 5.44 (*s*, 1H, 12-H), 4.32 (*dd*, *J* = 15.1, 6.1 Hz, 1H, *31-H*), 4.23 (*dd*, *J* = 15.2, 5.9 Hz, 1H, 31-H), 2.80 (*ddd*, *J* = 11.8, 5.0, 5.0 Hz, 1H, 3-H), 2.64 (*m*, 1 H, 1-H), 2.35 (*s*,1H, 9-H), 2.09 (*m*, 1H, 15-H), 2.04 (*m*, 1H, 18-H) 1.93 (*m*, 1H, 21-H), 1.83 (*m*, 1H, 19-H), 1.73 (*m*, 1H, 16-H), 1.64 (*m*, 3H, 19-H + 7-H + 2-H), 1.55 (*m*, 2H, 6-H + + 2-H), 1.46 (*m*, 1 H, 6-H), 1.36 (*m*, 1H, 7-H), 1.33 (*s*, 3H, 27-H), 1.26 (*m*, 3H, 22-H + 21-H), 1.14 (*m*, 1H, 16-H), 1.05 (*s*, 3H, 29-H), 1.02 (*s*, 6H, 26-H + 25-H), 1.02 (*m*, 1H, 1-H), 0.98 (*s*, 3H, 23-H), 0.94 (*m*, 1H, 15-H), 0.86 (*m*, 1H, 5-H), 0.76 (*s*, 3H, 24-H), 0.69 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 199.3 (C-11), 175.6 (C-30), 170.4 (C-13), 140.8 (C-32), 140.8 (aryl), 128.6 (aryl), 128.6 (aryl), 127.8 (C-12), 127.4 (aryl), 127.4 (aryl), 127.0 (aryl), 61.1 (C-9), 59.3 (C-3), 54.1 (C-5), 48.1 (C-18), 45.2 (C-14), 43.4 (C-31), 43.3 (C-20), 43.3 (C-8), 41.3 (C-19), 38.0 (C-4), 37.7 (C-1), 36.9 (C-10), 36.8 (C-22), 32.3 (C-7), 31.8 (C-17), 30.9 (C-21), 29.1 (C-29), 28.8 (C-28), 28.0 (C-23), 26.5 (C-16), 26.5 (C-15), 23.4 (C-27), 23.4 (C-2), 18.8 (C-26), 17.4 (C-6), 16.4 (C-25), 16.2 (C-24) ppm;

MS (ESI, MeOH): *m*/*z* = 559.3 (100 %, $[M+H]^+$);

Analysis calcd for $C_{37}H_{54}N_2O_2$ (558.85): C 79.52, H 9.74, N 5.01; found: C 79.46, H 9.90, N 4.86.

**(3β, 18β, 20β) *N*-Methyl 3-amino-11-oxoolean-12-en-30-amide (26)**

As described above from **21** (390 mg, 0.78 mmol) followed by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) 26 (245 mg, 65%) was obtained as a white solid; m.p. 167-170 °C; $R_f$ = 0.12 ($CHCl_3$/MeOH, 9:1), $[\alpha]_D$ = +123.7 (*c* = 0.17, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 251 nm (3.87); IR (KBr): ν = 3430*s*, 2956*s*, 1660*s*, 1590*s*, 1455*m*, 1383*s*, 1325*s*, 1217*m*, 1130*w*, 1077*w*, 750*m* $cm^{-1}$;

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 7.71 (*br*, 1H, NH), 5.48 (*s*, 1H, 12-H), 2.95 (*s* 6H, 31-H + 32-H), 2.82 (*ddd*, *J* = 11.5, 5.0, 5.0 Hz, 1H, 3-H), 2.66 (*ddd*, *J* = 13.5, 3.3, 3.3 Hz, 1H, 1-H), 2.38 (*s*, 1 H, 9-H), 2.11 (*dd*, *J* = 12.8, 2.5 Hz, 1H, 18-H), 2.05 (*m*, 1 H, 15-H) 2.00 (*m*, 1 H, 19-H), 1.91 (*m*, 1H, 21-H), 1.74 (*m*, 1H, 16-H), 1.65 (*m*, 1H, 2-H), 1.60 (*m*, 2H 19-H + 7-H), 1.57 (*m*, 2H, 6-H + 2-H), 1.39 (*m*, 2H, 7-H + 6-H), 1.32 (*m*, 1H, 21-H), 1.31 (*s*, 3H, 27-H), 1.26 (*m*, 2H, 22-H), 1.10 (*s*, 3H, 29-H), 1.07 (*m*, 1H, 16-H), 1.01 (*s*, 6H, 26-H + 25-H), 1.00 (*m*, 1H, 1-H), 0.98 (*s*, 3H, 23-H), 0.94 (*m*, 1H, 15-H), 0.89 (*m*, 1H, 5-H), 0.78 (*s*, 3H, 24-H), 0.68 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 199.9 (C-11), 174.1 (C-30), 170.5 (C-13), 127.3 (C-12), 60.9 (C-9), 59.6 (C-3), 54.5 (C-5), 48.1 (C-18), 45.1 (C-14), 44.0 (C-20), 43.9 (C-8), 41.4 (C-19), 38.3 (C-4), 37.5 (C-1), 37.1 (C-10), 36.5 (C-22), 32.3 (C-21), 32.2 (C-7), 32.0 (C-17), 28.8 (C-28), 28.2 (C-23), 26.3 (C-16), 26.2 (C-15), 26.1 (C-29), 22.8 (C-2), 23.1 (C-27), 19.1 (C-26), 17.5 (C-6), 16.4 (C-25), 16.0 (C-24) ppm;

MS (ESI, MeOH): *m*/*z* = 483.4 (100 %, $[M+H]^+$);

Analysis calcd for $C_{31}H_{50}N_2O_2$ (482.75): C 77.13, H 10.44, N 5.80; found: C 77.01, H 10.67, N 5.71.

**(3β, 18β, 20β) *N*, *N*-Dimethyl-3-amino-11-oxoolean-12-en-30-amide (27)**

As described above from **22** (400 mg, 0.78 mmol) **27** (234 mg, 60%) was obtained as a white solid; m.p. 178-181 °C; $R_f$ = 0.25 ($CHCl_3$/MeOH, 9:1), $[\alpha]_D$ = + 112.2 (*c* = 0.28, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 252 nm (3.92); IR (KBr): ν = 3427*s*, 2958*s*, 1659*s*, 1591*s*, 1455*m*, 1384*s*, 1324*s*, 1215*m*, 1131*w*, 1078*w*, 751*m* $cm^{-1}$; $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 7.66 (d, *J* = 4.0 Hz, 2H, $NH_2$), 5.47 (*s*, 1H, 12-H), 2.93 (*s* 6H, 31-H + 32-H), 2.80 (*ddd*, *J* = 11.5, 5.0, 5.0 Hz, 1H, 3-H), 2.64 (*ddd*, *J* = 13.5, 3.3, 3.3 Hz, 1H, 1-H), 2.37 (*s*, 1 H, 9-H), 2.09 (*dd*, *J* = 12.8, 2.5 Hz, 1H, 18-H), 2.07 (*m*, 1 H, 15-H) 2.01 (*m*, 1 H, 19-H), 1.89 (*m*, 1H, 21-H), 1.74 (*m*, 1H, 16-H), 1.68 (*m*, 1H, 2-H), 1.62 (*m*, 2H 19-H + 7-H), 1.55 (*m*, 2H, 6-H + 2-H), 1.37 (*m*, 2H, 7-H + 6-H), 1.34 (*m*, 1H, 21-H), 1.33 (*s*, 3H, 27-H), 1.26 (*m*, 2H, 22-H), 1.11 (*s*, 3H, 29-H), 1.05 (*m*, 1H, 16-H), 1.02 (*s*, 6H, 26-H + 25-H), 1.02 (*m*, 1H, 1-H), 0.98 (*s*, 3H, 23-H), 0.95 (*m*, 1H, 15-H), 0.86 (*m*, 1H, 5-H), 0.76 (*s*, 3H, 24-H), 0.71 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 199.3 (C-11), 174.5 (C-30), 170.8 (C-13), 127.7 (C-12),

61.0 (C-9), 59.3 (C-3), 54.1 (C-5), 48.3 (C-18), 45.1 (C-14), 44.2 (C-20), 43.8 (C-8), 41.5 (C-19), 38.0 (C-4), 37.8 (C-1), 36.9 (C-10), 36.8 (C-22), 32.4 (C-21), 32.4 (C-7), 32.0 (C-17), 28.7 (C-28), 28.0 (C-23), 26.4 (C-16), 26.4 (C-15), 26.3 (C-29), 23.1 (C-2), 23.0 (C-27), 18.8 (C-26), 17.4 (C-6), 16.4 (C-25), 16.2 (C-24) ppm;
MS (ESI, MeOH): *m/z* = 497.5 (100 %, $[M+H]^+$);
Analysis calcd for $C_{32}H_{52}N_2O_2$ (496.78): C 77.37, H 10.55, N 5.64; found: C 77.21, H 10.73, N 5.51.

**(18β, 20β) 3, 11-Diooxoolean-12-en-30-oic acid (28)**
Jones oxidation of **1** (10.0 g, 21.2 mmol) followed by chromatography (silica gel, hexane/ethyl acetate, 1:1) gave **28** (8.66 g, 87%) as a white solid; m.p. 308-311 °C (lit.: 308-311 °C [35]); $R_f$ = 0.32 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 179.8 (*c* = 0.38, $CHCl_3$) (lit.: 172.8 (*c* = 0.49, $CHCl_3$) [35]);
MS (ESI, MeOH): *m/z* = 467.4 (100 %, $[M-H]^-$ ), 935.3 (88 %, $[2M-H]^-$).

**(3β, 18β, 20β) Methyl 3-hydroxy-11-oxoolean-12-en-30-oate (29)**
Esterification of **1** (10.0 g, 21.3 mmol) with methyl iodide (1.7 mL) as previously described followed by re-crystallization gave **29** (9.22 g, 90%) as a white solid; m.p. 253-254 °C (lit.: 250-251 °C [16]); $R_f$ = 0.37 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 148.7 (*c* = 0.39, $CHCl_3$) (lit.: + 141.8 (*c* = 0.44, $CHCl_3$ [16]);
MS (ESI, MeOH): *m/z* = 484.4 (48 %, $[M + H^+]$, 969.3 (62 %, $[2M+H]^+$), 991.4 (100 %, $[2M+Na]^+$).

**(3β, 18β, 20β) Allyl 3-hydroxy-11-oxoolean-12-en-30-oate (30)**
To a solution of **1** (3.0 g, 5.6 mmol) in dry DMF (50 mL), finely grounded potassium carbonate (1.33 g, 9.53 mmol) and allyl bromide (0.63 mL, 7.53 mmol) were added. After completion of the reaction (as indicated by tlc) followed by usual work-up and chromatography (silica gel, hexane/ethyl acetate, 7:3) **30** (1.95 g, 68%) was obtained as a white solid; m.p. 197-199 °C (lit.: 208-210 °C [16]); $R_f$ = 0.42 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 148.2 (*c* = 0.32, $CHCl_3$) (lit.: $[\alpha]_D$ = + 144.6 (*c* = 0.5, $CHCl_3$ [16]);
UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.09);
MS (ESI, MeOH): *m/z* = 511.4 (38 %, $[M+H]^+$), 1021.4 (100 %, $[2M+H]^+$).

**(3β, 18β, 20β) Benzyl 3-hydroxy-11-oxoolean-12-en-30-oate (31)**
As described above from **1** (15 g, 31.9 mmol), potassium carbonate (7.4 g, 53.7 mmol) and benzyl bromide (4.75 mL, 40.0 mmol) compound **31** (15.5 g, 87%) was obtained as a white solid; m.p. 133-135 °C (lit.: 129-130 [16]); $R_f$ = 0.41 (hexane, ethyl acetate, 7:3); $[\alpha]_D$ = + 140.9 (*c* = 0.33, $CHCl_3$) (lit.: 141.5 (*c* = 0.018, $CHCl_3$) [16]); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.07);
MS (ESI, MeOH): *m/z* = 561.3 (74 %, $[M+H]^+$), 1121.3 (90 %, $[2M+H]^+$), 1143.4 (100 %, $[2M+Na]^+$).

**(18β, 20β) Methyl 3, 11-dioxoolean-12-en-30-oate (32)**
Jones oxidation of **29** (5.0 g, 10.3 mmol) followed by chromatography (silica gel, hexane/ethyl acetate, 7:3) gave **32** (4.47 g, 89%) as a white solid; m.p. 246-247 °C (lit.: 244-246 °C [35]); $R_f$ = 0.62 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 168.8 (*c* = 0.36, $CHCl_3$) (lit.: 172.9 (*c* = 0.31, $CHCl_3$) [35]);
MS (ESI, MeOH): *m/z* = 483.5 (100 %, $[M+H]^+$), 965.4 (86 %, $[2M+H]^+$), 987.4 (92 %, $[2M+Na]^+$).

**(18β, 20β) Allyl 3, 11-dioxoolean-12-en-30-oate (33)**
Jones oxidation of **30** (1.5 g, 2.94 mmol) followed by chromatography (silica gel, hexane/ethyl acetate, 1:1) gave **33** (1.27 g, 85%) as a white solid; m.p. 148-149 °C; $R_f$ = 0.68 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 173.6 (*c* = 0.36, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.10); IR (KBr): ν = 3436*w*, 3089*w*, 2943*s*, 2875*s*, 1729*s*, 1701*s*, 1654*s*, 1613w, 1465*s*, 1386*s*, 1315*m*, 1278*s*, 1152*s*, 1072*s*, 1026*m*, 983*s*, 913*s*, 868*m*, 767*m*, 543*m* $cm^{-1}$;
$^1H$ NMR (400 MHz, $CDC1_3$): δ = 5.91 (*ddt*, *J* = 16.1, 10.5, 5.7 Hz, 1H, 32-H), 5.68 (*s*, 1H, 12-H), 5.33 (*dd*, *J* = 17.2, 1.4 Hz, 1H, 33-H), 5.25 (*dd*, *J* = 10.4, 1.1 Hz, 1H, 33-H), 4.59 (*m*, 2H, 31-H), 2.96 (*ddd*, *J* = 13.4, 6.9, 4.0 Hz, 1H, 1-H), 2.63 (*ddd*, *J* = 16.0, 11.1, 7.1 Hz, 1H, 2-H), 2.43 (*s*, 1H, 9-H), 2.36 (*ddd*, *J* = 15.8, 6.4, 4.0 Hz, 1H, 2-H), 2.14 (*dd*, *J* = 13.4, 3.1 Hz, 1H, 18-H), 2.03 (*m*, 2H, 21-H + 15-H), 1.94 (*m*, 1H, 19-H), 1.84 (*ddd*, *J* = 13.8, 13.7, 4.3 Hz, 1H, 16-H), 1.69 (*m*, 1H, 7-H), 1.60 (*m*, 1H, 19-H), 1.54 (*m*, 2H, 6-H), 1.46 (*m*, 1H, 7-H) 1.41 (*m*, 1 H, 1-H), 1.39 (*m*, 1H, 22-H), 1.37 (*s*, 3H, 27-H), 1.33 (*m*, 2H, 22-H) + 21-H), 1.28 (*m*, 1H, 5-H), 1.26 (*s*, 3H, 25-H), 1.20 (*m*, 1H, 16-H), 1.16 (*s*, 3H, 29-H), 1.16 (*s*, 3H, 26-H), 1.10 (*s*, 3H, 23-H), 1.06 (*s*, 3H, 24-H), 1.02 (*m*, 1H, 15-H), 0.82 (*s*, 3H, 28-H) ppm;
$^{13}C$ NMR (100 MHz, $CDC1_3$): δ = 217.1 (C-3), 199.4 (C-11), 176.0 (C-30), 169.6 (CH, C = CH), 132.2 (C-32), 128.4 (C-12), 118.4 (C-33), 65.0 (C-31), 61.0 (C-9), 55.4 (C-5), 48.3 (C-18), 47.7 (C-4), (C-8), 44.0 (C-20), 43.3 (C-14), 41.1 (C-19), 39.8 (C-1), 37.7 (C-22), 36.7 (C-10), 34.2 (C-2), 32.1 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 26.5 (C-16), 26.4 (C-23), 26.4 (C-15), (C-27), 21.4 (C-24), 18.8 (C-6), 18.5 (C-26), 15.6 (C-25) ppm;
MS (ESI, MeOH): *m/z* = 509.4 (56 %, $[M+H]^+$), 1017.4 (76 %, $[2M+H]^+$), 1039.4 (76 %, $[2M+Na]^+$);
Analysis calcd for $C_{33}H_{48}O_4$ (508.74): C 77.91, H 9.51; found: C 77.80, H 9.73.

**(18β, 20β) Benzyl 3, 11-dioxoolean-12-en-30-oate (34)**
Jones oxidation of **31** (5.0 g, 8.9 mmol) followed by chromatography (silica gel, hexane/ethyl acetate,

8:2) gave **34** (4.38 g, 88%) as a white solid; m.p. 145-147 °C; $R_f$ = 0.35 (hexane/ethyl acetate, 8:2); $[\alpha]_D$ = + 132.2 (*c* = 0.29, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.10); IR (KBr): ν = 3447*s*, 1657*m*, 1456*w* $cm^{-1}$;
$^1$H NMR (400MHz, $CDC1_3$): δ = 7.35 (*m*, 5H, aryl), 5.58 (*s*, 1H, 12-H), 5.20 (*d*, *J* = 12.2 Hz, 1H, 31-H), 5.20 (*d*, *J* = 12.2 Hz, 1H, 31-H), 2.96 (*ddd*, *J* = 13.4, 7.1, 4.0 Hz, 1H 1-H), 2.63 (*ddd*, *J* = 15.9, 11.2, 7.1 Hz, 1H, 2-H), 2.41 (*s*, 1H, 9-H), 2.36 (*ddd*, *J* = 15.8, 6.4, 4.0 Hz, 1H, 2-H), 2.07 (*m*, 1H, 18-H), 2.04 (*m*, 1H, 15-H), 1.99 (*m*, 1H, 21-H) 1.94 (*m*, 1H, 19-H), 1.82 (*ddd*, *J* = 13.6, 13.6, 4.5 Hz, 1H, 16-H*)*, 1.68 (*m*, 1H, 7-H), 1.62, (*m*, 1H, 19-H), 1.57 (*m*, 1H, 6-H), 1.53 (*m*, 1H, 6-H), 1.45 (*m*, 1H, 7-H), 1.42 (*m*, 1H, 1-H), 1.38 (*m*, 1H, 22-H), 1.35 (*s*, 3H, 27-H), 1.31 (*m*, 2H, 22-H + 21-H), 1.28 (*m*, 1 H, 5-H), 1.27 (*s*, 3H, 25-H), 1.21 (*m*, 1H, 16-H), 1.16 (*s*, 3H, 26-H), 1.15 (*s*, 3H, 29-H), 1.10 (*s*, 3H, 23-H), 1.06 (*s*, 3H, 24-H), 1.00 (*m*, 1H, 15-H), 0.75 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 217.1 (C-3), 199.3 (C-11), 176.1 (C-30), 169.5 (CH, C = CH), 136.1 (aryl), 128.6 (aryl), 128.6 (aryl), 128.4 (C-12), 128.3 (aryl), 128.2 (aryl), 66.2 (C-31), 61.0 (C-9), 55.4 (C-5), 48.2 (C-18), 47.7 (C-4), 45.2 (C-8), 44.0 (C-20), 43.3 (C-14), 41.1 (C-19), 39.8 (C-1), 37.6 (C-22), 36.7 (C-10), 34.2 (C-2), 32.1 (C-7), 31.8 (C-17), 31.2 (C-21), 28.4 (C-28), 28.3 (C-29), 26.5 (C-16), 26.4 (C-15), 26.4 (C-23), 23.3 (C-27), 21.4 (C-24), 18.8 (C-6), 18.5 (C-26), 15.6 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 559.3 (80 %, $[M+H]^+$), 581.3 (26 %, $[M+Na]^+$), 1117.2 (68 %, $[2M+H]^+$), 1139.4 (100 %, $[2M+Na]^+$);
Analysis calcd for C37H50O4 (558.80): C 79.53, H 9.02; found: C 79.42, H 9.19.

**(3 E, 18β, 20β) 3-Hydroxyimino-11-oxoolean-12-en-30-oic acid (35)**
As described above from **28** (5.0 g, 10.68 mmol) and hydroxylammonium chloride (1.5 g, 21.2 mmol) followed by re-crystallization from MeOH compound **35** (4.78 g, 93%) was obtained as a white solid; m.p. 297-299 °C; $R_f$ = 0.49 (hexane/ethyl acetate, 1:1); $[\alpha]_D$ = + 107.3 (*c* = 0.32, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 252 nm (4.01); IR (KBr): ν = 3306*m*, 2971*s*, 1871*s*, 1695*s*, 1649*s*, 1456*s*, 1387*s*, 1367*w*, 1321*m*, 1261*m*, 1227*m*, 1177*m*, 1088*w*, 951*m* $cm^{-1}$;
$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 10.23 (*s*, 1H, NOH), 5.40 (*s*, 1H, 12-H), 2.82 (*ddd*, *J* = 15.2, 4.3, 4.3 Hz, 1H, 2-H), 2.59 (*m*, 1H, 1-H), 2.38 (*s*, 1H, 9-H), 2.09 (*m*, 3H, 18-H + 15-H + 2-H), 1.78 (*m*, 1H, 21-H), 1.71 (*m*, 1H, 16-H, 1.65 (*m*, 3H, 19-H + 7-H), 1.52 (*m*, 1H, 6-H), ), 1.42 (*m*, 1H, 6-H), 1.39-1.31 (*m*, 3H, 22-H + 21-H + 7-H), 1.33 (*s*, 3H, 27-H), 1.25 (*m*, 1H, 22-H), 1.16 (*m*, 1H, 16-H), 1.12 (*s*, 3H, 29-H), 1.09 (*s*, 3H, 23-H), 1.08 (*s*, 3H, 25-H), 1.05 (*s*, 3H, 26-H), 1.03 (*m*, 1H, 5-H), 1.00 (*m*, 1H, 1-H), 0.97 (*s*, 3H, 24-H), 0.95 (*m*, 1H, 15-H), 0.75 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 199.2 (C-11), 178.1 (C-30), 170.3 (C-13), 163.7 (C-3), 127.7 (C-12), 61.0 (C-9), 55.0 (C-5), 48.5 (C-18), 45.3 (C-8), 43.5 (C-20), 43.1 (C-14), 41.1 (C-19), 40.5 (C-4), 38.6 (C-1), 37.9 (C-22), 37.0 (C-10), 32.1 (C-7), 32.0 (C-17), 30.8 (C-21), 28.9 (C-29), 28.3 (C-28), 27.9 (C-23), 26.5 (C-15), 26.2 (C-16). 23.8 (C-27), 23.3 (C-24), 18.7 (C-26), 18.2 (C-6), 16.9 (C-2), 15.9 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 484.4 (100%, $[M+H]^+$), 967.3 (76%, $[2M+H]^+$);
Analysis calcd for $C_{30}H_{45}NO_4$ (483.69): C 74.50, H 9.38, N 2.90; found: C 74.26, H 9.59, N 2.73.

**(3 E, 18β, 20β) Methyl 3-hydroxyimino-11-oxoolean-12-en-30-oate (36)**
As described above from **32** (0.68 g, 1.4 mmol) and hydroxylammonium chloride (0.2 g, 2.8 mmol) followed by chromatography (hexane/ethyl acetate, 8:2) compound **36** (0.53 g, 85%) was obtained as a white solid; m.p. 255-259 °C; $R_f$ = 0.40 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = +139.1 (*c* = 0.5, CHCl3); UV-Vis (MeOH): $\lambda_{max}$ (log ε) = 249 nm (3.97); IR (KBr): ν = 3440*s*, 2972*s*, 2941*s*, 2870*m*, 1705*s*, 1659*s*, 1468*m*, 1385*m*, 1314*m*, 1215*s*, 1161*s*, 1090*m*, 1032*w* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDCl_3$): δ = δ = 8.45 (*br*, 1H, NOH), 5.56 (*s*, 1H, 12-H), 3.69 (*s*, 3H, 31-H), 3.07 (*ddd*, *J* = 15.6, 4.8. 3.9 Hz, 1H, 2-H), 2.88 (*ddd*, *J* = 13.4. 5.6. 3.8 Hz, 1H 1-H), 2.40 (*s*, 1H, 9-H), 2.25 (*ddd*, *J* = 15.6, 12.7, 5.7 Hz, 1H, 2-H), 2.00 (*m*, 3H, 21-H + 18-H + 15-H), 1.95 (*ddd*, *J* = 13.5, 3.9, 2.7 Hz, 1H, 19-H), 1.80 (*ddd*, *J* = 13.5, 13.5, 4.3 Hz, 1H, 16-H), 1.70 - 1.55 (*m*, 3H, 19-H + 7-H + 6-H), 1.50 (*m*, 1H, 6-H), 1.42 (*m*, 1H, 7-H), 1.38 (*m*, 1H, 22-H), 1.30 (*s*, 3H, 27-H), 1.29 (*m*, 2H, 22-H + 21-H), 1.26 (*s*, 3H, 25-H), 1.15 (*s*, 3H, 23-H), 1.14 (*m*, 1H, 16-H), 1.13 (*s*, 3H, 29-H), 1.12 (*s*, 3H, 26-H), 1.09 (*s*, 3H, 24-H), 1.06 (*m*, 3H, 15-H + 5-H + 1H), 0.77 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 199.9 (C-11), 177.0 (C-30), 169.5 (C-13), 167.2 (C-3), 128.3 (C-12), 61.5 (C-9), 52.2 (C-31), 55.7 (C-5), 48.0 (C-18), 45.1 (C-8), 44.3 (C-20), 43.3 (C-14), 41.2 (C-19), 40.7 (C-4), 38.8 (C-1), 37.7 (C-22), 37.1 (C-10), 32.6 (C-7), 31.6 (C-17), 31.0 (C-21), 28.6 (C-28), 28.5 (C-29), 27.0 (C-27), 26.9 (C-23) 26.7 (C-15), 26.3 (C-16), 23.0 (C-24), 18.7 (C-26), 18.4 (C-6), 17.3 (C-2), 16.1 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 448.1 (100 %, $[M+H]^+$);
Analysis calcd for $C_{27}H_{45}NO_4$ (447.65): C 72.44, H 10.13, N 3.13; found: C 72.19, H 10.30, N 2.97.

**(3 E, 18β, 20β) Allyl 3-hydroxyimino-11-oxoolean-12-en-30-oate (37)**
As described above from **33** (0.7 g, 1.4 mmol) and hydroxylammonium chloride (0.2 g, 2.8 mmol) followed by chromatography (hexane/ethyl acetate, 8:2) compound **37** (0.62 g, 84%) was obtained as a white solid; m.p. 246-249; $R_f$ = 0.59 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 101.3 (*c* = 0.7, $CHCl_3$);

UV-Vis (MeOH): $\lambda_{max}$ (log ε) = 249 nm (4.04); IR (KBr): ν = 3439*s*, 2970*s*, 2942*s*, 2871*m*, 1705*s*, 1657*s*, 1615*w*, 1467*m*, 1386*m*, 1316*m*, 1217*s*, 1163*s*, 1090*m*, 1031*w*, 982*m*, 920*m* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.35 (*m*, 5H, aryl), 5.56 (*s*, 1H, 12-H, 5.20 (*m*, 1H, 31-H), 5.09 (*m*, 1H, 31-H), 3.05 (*ddd*, *J* = 15.6, 4.8, 3.9 Hz, 1H, 2-H), 2.86 (*ddd*, *J* = 13.4, 5.6, 3.8 Hz, 1H 1-H), 2.36 (*s*, 1H, 9-H), 2.26 (*ddd*, *J* = 15.6, 12.7, 5.7 Hz, 1H, 2-H), 2.02 (*m*, 3H, 21-H + 18-H + 15-H), 1.93 (*ddd*, *J* = 13.5, 3.9, 2.7 Hz, 1H, 19-H), 1.81 (*ddd*, *J* = 13.5, 13.5, 4.3 Hz, 1H, 16-H), 1.69 - 1.57 (*m*, 3H, 19-H + 7-H + 6H), 1.51 (*m*, 1H, 6-H), 1.42 (*m*, 1H, 7-H), 1.36 (*m*, 1H, 22-H), 1.32 (*s*, 3H, 27-H), 1.29 (*m*, 2H, 22-H + 21-H), 1.25 (*s*, 3H, 25-H), 1.17 (*s*, 3H, 23-H), 1.16 (*m*, 1H, 16-H), 1.15 (*s*, 3H, 29-H), 1.13 (*s*, 3H, 26-H), 1.08 (*s*, 3H, 24-H), 1.04 (*m*, 3H, 15-H + 5-H + 1-H), 0.74 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDCI_3$): δ = 199.8 (C-11), 176.0 (C-30), 169.4 (C-13), 167.1 (C-3), 132.2 (C-32), 128.5 (C-12), 118. 4 (C-33), 65.0 (C-31), 61.3 (C-9), 55.6 (C-5), 48.3 (C-18), 45.4 (C-8), 44.0 (C-20), 43.3 (C-14), 41.4 (C-19), 40.4 (C-4), 39.0 (C-1), 37.7 (C-22), 37.0 (C-10), 32.4 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 27.2 (C-27), 27.2 (C-23) 26.5 (C-15), 26.4 (C-16), 23.2 (C-24), 18.6 (C-26), 18.2 (C-6), 17.1 (C-2), 15.7 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 524.3 (86 %, $[M+H]^+$), 1047.3 (100 %, $[2M+H]^+$);
Analysis calcd for $C_{33}H_{49}NO_4$ (523.76): C 75.68, H 9.43, N 2.67; found: C 75.51, H 9.71, N 2.53.

**(3 E, 18β, 20β) Benzyl 3-hydroxyimino-11-oxoolean-12-en-30-oate (38)**
As described above, from **34** (1.5 g, 2.67 mmol) and hydroxylammonium chloride (0.35 g, 5.10 mmol) followed by re-crystallization from MeOH compound **38** (1.29 g, 84%) was obtained as a white solid; m.p. 211-213 °C; $R_f$ = 0.59 (hexane/ethyl acetate, 7:3); $[\alpha]_D$ = + 57.5 (*c* = 0.35, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 249 nm (4.10); IR (KBr): ν = 3441*s*, 2931*m*, 1727*m*, 1654*s*, 1455*m*, 1386*m*, 1150*m*, 1085*w*, 697*m* $cm^{-1}$;
$^1$H NMR (400 MHz, $CDC1_3$): δ = 8.39 (*br*, 1H, NOH), 7.35 (*m*, 5H, aryl), 5.56 (*s*, 1H, 12-H, 5.20 (*m*, 1H, 31-H), 5.09 (*m*, 1H, 31-H), 3.05 (*ddd*, *J* = 15.6, 4.8. 3.9 Hz, 1H, 2-H), 2.86 (*ddd*, *J* = 13.4. 5.6. 3.8 Hz, 1H 1-H), 2.36 (*s*, 1H, 9-H), 2.26 (*ddd*, *J* = 15.6, 12.7, 5.7 Hz, 1H, 2-H), 2.02 (*m*, 3H, 21-H + 18-H + 15-H), 1.93 (*ddd*, *J* = 13.5, 3.9, 2.7 Hz, 1H, 19-H), 1.81 (*ddd*, *J* = 13.5, 13.5, 4.3 Hz, 1H, 16-H), 1.69 - 1.57 (*m*, 3H, 19-H + 7-H + 6-H), 1.51 (*m*, 1H, 6-H), 1.42 (*m*, 1H, 7-H), 1.36 (*m*, 1H, 22-H), 1.32 (*s*, 3H, 27-H), 1.29 (*m*, 2H, 22-H + 21-H), 1.25 (*s*, 3H, 25-H), 1.17 (*s*, 3H, 23-H), 1.16 (*m*, 1H, 16-H), 1.15 (*s*, 3H, 29-H), 1.13 (*s*, 3H, 26-H), 1.08 (*s*, 3H, 24-H), 1.04 (*m*, 3H, 15-H + 5-H + 1H), 0.74 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 199.7 (C-11), 176.2 (C-30), 169.2 (C-13), 166.9 (C-3), 136.1 (aryl), 128.6 (aryl), 128.6 (aryl), 128.5 (C-12), 128.3 (aryl), 128.2 (aryl), 128.2 (aryl), 66.2 (C-31), 61.3 (C-9), 55.6 (C-5), 48.2 (C-18), 45.3 (C-8), 44.0 (C-20), 43.2 (C-14), 41.4 (C-19), 40.4 (C-4), 39.1 (C-1), 37.6 (C-22), 37.0 (C-10), 32.4 (C-7), 31.8 (C-17), 31.2 (C-21), 28.4 (C-28), 28.3 (C-29), 27.1 (C-27), 27.1 (C-23) 26.5 (C-15), 26.4 (C-16), 23.2 (C-24), 18.6 (C-26), 18.2 (C-6), 17.1 (C-2), 16.0 (C-25) ppm;
MS (ESI, MeOH): *m*/*z* = 574.3 (100 %, $[M+H]^+$), 1147.4 (70 %, $[2M+H]^+$);
Analysis calcd for $C_{37}H_{51}NO_4$ (573.82): C 77.45, H 8.96, N 2.44; found: C 77.37, H 9.15, N 2.29.

**(3β, 18β, 20β) 3-Amino-11-oxoolean-12-en-30-oic acid (39)**
As described above from **35** (100 mg, 0.21 mmol) followed by chromatography (silica gel, MeOH/$CHCl_3$, 9:1) **39** (42 mg, 43%) was obtained as a white solid; m.p. > 360 °C; $R_f$ = 0.17 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 60.1 (*c* = 0.29, DMSO); UV-Vis (DMSO): $\lambda_{max}$ (log ε) = 255 nm (3.59); IR (KBr): ν = 3428*s*, 2953*m*, 1638*s*, 1384*s*, 1214*w*, 1046*w*, 822*w*, 749*w*, 554*m* $cm^{-1}$;
$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 7.78 (*br*, 2H, $NH_2$), 5.39 (*s*, 1H, 12-H), 2.79 (dd, *J* = 11.8, 4.3 Hz, 1H, 3-H), 2.63 (*m*, 1H, 1-H), 2.36 (*s*, 1H, 9-H), 2.06 (*m*, 2H, 18-H + 15-H), 1.99 (*m*, 1H, 19-H), 1.79 (*m*, 1H, 21-H), 1.76 (*m*, 1H, 16-H), 1.66 (*m*, 3H, 19-H + 7-H + 2-H), 1.55 (*m*, 2H, 6-H + 2-H), 1.41 (*m*, 1H, 6-H), 1.37 (*s*, 3H, 27-H), 1.33 (*m*, 4H, 22-H + 21-H + 7-H), 1.08 (*s*, 3H, 29-H), 1.07 (*m*, 1H, 16-H), 1.04 (*s*, 3H, 126-H), 1.02 (*s*, 3H, 25-H), 1.02 (*m*, 1H, 1-H), 0.89 (*s*, 3H, 23-H), 0.95 (*m*, 1H, 15-H), 0.87 (*s*, 3H, 24-H), 0.76 (*m*, 1H, 5-H), 0.74 (*s*, 3H, 28-H) ppm;
$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 199.5 (C-11), 178.1 (C-30), 170.6 (C-13), 127.5 (C-12), 61.1 (C-9), 59.3 (C-3), 54.0 (C-5), 48.5 (C-18), 45.4 (C-14), 43.5 (C-20), 43.5 (C-8), 41.1 (C-19), 38.7 (C-4), 37.9 (C-1), 36.9 (C-10), 36.8 (C-22), 32.6 (C-7), 31.9 (C-17), 30.8 (C-21), 28.9 (C-29), 29.3 (C-28), 28.0 (C-23), 26.5 (C-16), 26.2 (C-15), 23.8 (C-27), 22.4 (C-2), 18.8 (C-26), 17.3 (C-6), 16.5 (C-25), 16.5 (C-24) ppm;
MS (ESI, MeOH): *m*/*z* = 470.3 (100 %, $[M+H]^+$);
Analysis calcd for $C_{30}H_{47}NO_3$ (469.71): C 76.71, H 10.09, N 2.98; found: C 76.50, H 76.96, N 2.65.

**(3β, 18β, 20β) Methyl 3-amino-11-oxoolean-12-en-30-oate (40)**
As described above from **36** (1.0 g, 2.06 mmol) followed by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) **40** (748 mg, 74%) was obtained as a white solid; m.p. 290-291 °C (lit.: 206 °C LL15); $R_f$ = 0.36 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 132.4 (*c* = 0.37, $CHCl_3$) (lit.: + 11.8 (*c* = 0.57, $CHCl_3$) LL51);
MS (ESI, MeOH): *m*/*z* = 484.3 (100 %, $[M+H]^+$).

**(3β, 18β, 20β) Allyl 3-amino-11-oxoolean-12-en-30-oate (41)**

As described above from **37** (400 mg, 0.67 mmol), ammonium acetate (1.2 g, 16.0 mmol) and reduction with sodium cyanoborohydride/$TiCl_3$ for 24 h at 25 °C followed by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) **41** (142 mg, 42 %) was obtained as a white solid; m.p. 207-208 °C; $R_f$ = 0.31 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 95.6 (*c* = 0.41, DMSO); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 253 nm (3.94); IR (KBr): ν = 3424*m*, 2949*m*, 1727*m*, 1655*m*, 1384*s*, 1214*w*, 1152*m*, 1084*w*, 1045*w* $cm^{-1}$;

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.45 (*br*, 2H, $NH_2$), 5.92 (*ddt*, *J* = 17.0, 10.5, 5.8 Hz, 1H, 32-H), 5.64 (*s* , 1H, 12-H), 5.33 (*dd*, *J* = 17.2, 1.5 Hz, 1H, 33-H), 5.25 (*dd*, *J* = 10.4, 1.3 Hz, 1H, 33-H), 4.59 (*m*, 2H, 31-H), 3.00 (*m*, 1H, 3-H), 2.89 (*m*, 1H 1-H), 2.35 (*s*, 1H, 9-H), 2.11 (*dd*, *J* = 13.2, 3.6 Hz, 1H, 18-H), 2.03 (*m*, 1H, 15-H), 1.98 (*m*, 1H, 21-H), 1.92 (*m*, 1H, 19-H), 1.87 (*m*, 2H, 2-H), 1.81 (*ddd*, *J* = 13.5, 13.5, 4.1 Hz, 1H, 16-H), 1.72 - 1.65 (*m*, 3H, 19-H + 7-H + 2-H), 1.61 (*m*, 1H, 6-H), 1.46 (*m*, 2H, 6-H), 1.41 (*m*, 1H, 7-H), 1.39 (*s*, 3H, 27-H), 1.31 (*m*, 2H, 22-H), 1.24 (*m*, 1H, 21-H), 1.20 (*m*, 1H, 16-H), 1.17 (*s*, 3H, 29-H), 1.15 (*s*, 3H, 25-H), 1.14 (*s*, 3H, 26-H), 1.13 (*s*, 3H, 23-H), 1.02 (*m*, 2H, 15-H + 1-H), 1.00 (*s*, 3H, 23-H), 0.97 (*s*, 3H, 24-H), 0.95 (*m*, 1H, 1-H), 0.80 (*s*, 6H, 28-H), 0.79 (*m*, 1 H, 5-H) ppm;

$^{13}$C NMR (100 MHz, $CDCI_3$): δ = 199.7 (C-11), 176.0 (C-30), 169.5 (C-13), 132.2 (C-32, CH= $CH_2$), 128.5 (C-12), 118.4 (C-33), 65.1 (C-31), 61.5 (C-9), 60.6 (C-3), 55.1 (C-5), 48.3 (C-18), 45.3 (C-14), 44.0 (C-20), 43.2 (C-8), 41.1 (C-19), 38.7 (C-4), 37.7 (C-1), 37.0 (C-10), 36.8 (C-22), 32.6 (C-7), 31.8 (C-17), 31.1 (C-21), 28.5 (C-28), 28.3 (C-29), 27.8 (C-23), 26.4 (C-16), 26.4 (C-15), 23.4 (C-27), 23.1 (C-2), 18.7 (C-24), 17.5 (C-6), 16.0 (C-26), 15.7 (C-25) ppm;

MS (ESI, MeOH): *m*/*z* = 510.3 (100 %, $[M+H]^+$);

Analysis calcd for $C_{33}H_{51}NO_3$ (509.77): C 77.75, H 10.08, N 2.75; found: C 77.53, H 10.27, N 2.50.

**(3β, 18β, 20β) Benzyl 3-amino-11-oxoolean-12-en-30-oate (42)**

As described above from **38** (500 mg) followed by chromatography (silica gel, $CHCl_3$/MeOH, 9:1) **42** (372 mg, 76%) was obtained as a white solid; m.p. 272-274 °C; $R_f$ = 0.28 ($CHCl_3$/MeOH, 9:1); $[\alpha]_D$ = + 132.2 (*c* = 0.38, $CHCl_3$); UV-Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 248 nm (4.04); IR (KBr): ν = 3432*m*, 2951*m*, 1724*m*, 1650*m*, 1537*w*, 1454*w*, 1384*s*, 1293*w*, 1215*w*, 1152*w*, 1087*w* $cm^{-1}$;

$^1$H NMR (400 MHz, $CDC1_3$): δ = 7.43 (*br*, 2H, $NH_2$), 7.36 (*m*, 5H, aryl), 5.54 (*s*, 1H, 12-H), 5.19 (*d*, *J* = 12.2 Hz, 1H, 31-H), 5.08 (*d*, *J* = 12.2 Hz, 1H, 31-H), 2.99 (*m*, 1H, 3-H), 2.88 (*m*, 1H 1-H), 2.33 (*s*, 1H, 9-H), 2.01 (*m*, 3H, 21-H + 18-H + 15-H), 1.92 (*m*, 1H, 19-H), 1.86 (*m*, 2H, 2-H), 1.78 (*m*, 1H, 15-H), 1.71 - 1.60 (*m*, 3H, 19-H + 7-H + 6-H), 1.47 (*m*, 1H, 6-H), 1.43 (*m*, 1H, 7-H), 1.39 (*m*, 1H, 22-H), 1.36 (*m*, 1H, 22-H), 1.35 (*s*, 3H, 27-H), 1.30 (*m*, 1H, 21-H), 1.18 (*m*, 1H, 6-H), 1.16 (*s*, 3H, 29-H), 1.15 (*s*, 3H, 25-H), 1.13 (*s*, 3H, 23-H), 1.11 (*s*, 3H, 26-H), 1.01 (*m*, 2H, 15-H + 1-H), 0.97 (*s*, 3H, 24-H), 0.80 (*d*, *J* = 11.3 Hz, 1H, 5-H), 0.72 (*s*, 3H, 28-H) ppm;

$^{13}$C NMR (100 MHz, $CDC1_3$): δ = 199.6 (C-11), 176.2 (C-30), 169.2 (C-13), 136.1 (aryl), 128.6 (aryl), 128.6 (aryl), 128.4 (C-12), 128.3 (aryl), 128.2 (aryl), 128.1 (aryl), 66.2 (C-31), 61.5 (C-9), 60.6 (C-3), 55.1 (C-5), 48.2 (C-18), 45.3 (C-14), 44.0 (C-20), 43.2 (C-8), 41.0 (C-19), 38.7 (C-4), 37.6 (C-1), 37.0 (C-10), 36.8 (C-22), 32.6 (C-7), 31.8 (C-17), 31.2 (C-21), 28.4 (C-28), 28.3 (C-29), 27.8 (C-23), 26.4 (C-16), 26.4 (C-15), 23.3 (C-27), 23.2 (C-2), 18.7 (C-26), 17.4 (C-6), 16.1 (C-24), 15.7 (C-25) ppm;

MS (ESI, MeOH): *m*/*z* = 560.3 (100 %, $[M+H]^+$);

Analysis calcd for $C_{37}H_{53}NO_3$ (559.84): C 79.38, H 9.54, N 2.50; found: C 79.11, H 9.73, N 2.30.

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