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Original article

Esters and amides of maslinic acid trigger apoptosis in human tumor cells and alter their mode of action with respect to the substitution pattern at C-28

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ABSTRACT

Cancer is one of the most commonly diagnosed diseases worldwide; its mortality rate is high, and there is still a demand for the development of antitumor active drugs. Triterpenoic acids show many pharmacological effects, among them antitumor activity. One of these, maslinic acid-1 is of interest because of its antitumor profile. It is not only cytotoxic but also triggers apoptosis in various human tumor cell lines. To improve the cytotoxicity of parent **1** we set out to synthesize a series of esters and amides differing in structure and lipophilicity. These compounds were tested in a sulforhodamine B assay for cytotoxicity, and screened for their ability to induce apoptosis using an acridine orange/propidium iodide assay, DNA laddering and cell cycle experiments. Esters containing small-chain, lipophilic residues increased the cytotoxicity whereas amides as well long-chain esters led to a decrease in activity. The antitumor activity seems to be independent from the substitution pattern at position C-28 for esters and amides but alters their mode of action.

1. Introduction

Cancer is one of the most commonly diagnosed diseases worldwide. Recent research results [1–5] correlate the low cancer mortality rate in Mediterranean countries to a diet rich in olives. The triterpenoic compounds maslinic acid (**1**, Scheme 1) and oleanolic acid seem to be the main antitumor active ingredients of olives (*Olea europea* L.) [1,3,6–8]. Thus, for **1** an inhibitory activity for glycogen phosphorylases [9,10], protein tyrosine phosphatase 1B [11] as well as an anti-HIV-1 activity [12] were reported. Both triterpenoic acids can be extracted in high amounts from waste [13] of the olive oil production ("olive pomace"), hence underlining an economical interest connected with the investigation of the pharmaceutical effects attributed to these natural products.

Consequently, several groups investigated the effects of maslinic acid onto cancer cell lines [1,6,8,14–16]. Among others, Reyes et al. [8,14,15] could demonstrate that **1** is able to induce cell death by apoptosis in the colon cancer cell lines HT29 and in Caco-2. In 2007, **1** was reported to be cytotoxic for the breast cancer cell line MCF7 [17], and quite recently these initial findings were confirmed by several groups [3,18–21]. Furthermore, compound **1** exhibits [22] some selectivity between malignant and non-malignant cell lines, and selective parasitostatic activities of **1** were established in mice [23,24].

Structural modifications of triterpenoids have a high impact onto their biological activity [25]. As compared to other triterpenoids, for maslinic acid only a limited number of derivatives is known, and even less of them have been investigated with respect to their antitumor activity. Recent studies [26] gave evidence for an apoptotic effect of **1**. To the best of our knowledge, however, only one report [26] has been published showing a correlation between the ability to induce apoptosis as a function of structural modifications – but unfortunately no IC_{50} values have been reported. In that study, Parra et al. [26] demonstrated that the ability for inducing apoptosis increases by "simple" modifications of **1**: Thus, especially amide and benzyl maslinoates induce apoptosis in >90% of the tumor cells – thus making these compounds interesting candidates for further development. For betulinic acid several structure–activity relationships have been deduced but almost nothing is known for compound **1** and derivatives thereof [27–29]. Hence, we became interested in a more systematic investigation on maslinic acid derivatives: Several esters and amides of **1** were prepared, characterized and their cytotoxicity (IC_{50} values from photometric sulforhodamine B protein (SRB) assays) were determined.

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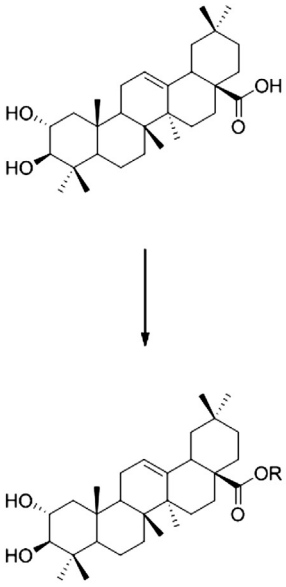


R =		
H	Maslinic acid	**1**
CH_3	Methyl	**2**
CH_2CH_3	Ethyl	**3**
CH_2CH_2OH	2-Hydroxyl-ethyl	**4**
CH_2CH_2Cl	2-Chloro-ethyl	**5**
$CH_2CH_2CH_3$	Propyl	**6**
$CH_2CH{=}CH_2$	Prop-2-enyl	**7**
$CH_2C{\equiv}CH$	Propargyl	**8**
$CH_2CH_2CH_2OH$	3-Hydroxy-propyl	**9**
$CH_2CH_2CH_2Cl$	3-Chloro-propyl	**10**
$CH_2CH_2CH_2Br$	3-Bromo-propyl	**11**
$CH_2CH_2CH_2I$	3-Iodo-propyl	**12**
$CH_2CH_2CH_2CH_3$	Butyl	**13**
$CH_2CH_2CH{=}CH_2$	But-3-enyl	**14**
$CH_2CH_2C{\equiv}CH$	But-3-inyl	**15**
$CH_2CH_2CH_2CH_2Cl$	4-Chloro-butyl	**16**
$CH_2CH_2CH_2CH_2Br$	4-Bromo-butyl	**17**
(*Z*)-$CH_2CH{=}CHCH_2Cl$	(Z)-4-Chloro-but-2-enyl	**18**
$CH_2CH_2C{\equiv}CCl$	4-Chloro-but-2-inyl	**19**
$CH_2(CH_2)_4CH_3$	Hexyl	**20**
$CH_2(CH_2)_{10}CH_3$	Dodecyl	**21**
$CH_2(CH_2)_{16}CH_3$	Octadecyl	**22**
CH_2Cy	Cyclohexylmethyl	**23**

Scheme 1. Synthesis of the esters **2**–**23** from maslinic acid **1**: using DMF, K_2CO_3, 25 °C, 30 min followed by the addition of Hal-R, 25 °C, 12 h.

2. Chemistry

Maslinic acid-1, a triterpenoic acid, carries three different functional groups: two hydroxyl groups in ring A, a double bond in ring C and a carboxylic group (C-28). Antitumor screening of derivatives of betulinic acid, oleanolic or ursolic acid revealed the presence of a C=O moiety to be essential for obtaining good antitumor activity [25–29].

Firstly, we prepared several esters at position C-28. This carboxyl group is remarkably unreactive, and, Fischer esterification protocols failed. The esters were obtained by treating **1** in *N*,*N*-dimethylformamide (DMF) or acetone with alkyl bromides in the presence of freshly grounded potassium carbonate. An aqueous work-up using 5% cold aqueous hydrochloric acid facilitated the isolation of the products by destroying some byproducts [30]. Thus, following this general procedure, aliphatic esters (Scheme 1) were synthesized in good to excellent yields (75–99%), and esters containing side chains of different lengths (**2**,**3**,**6**,**13**,**20**–**21**) as well as halogenated (**5**, **10**–**12**, **16**–**19**) and hydroxylated (*e.g.* **4**) esters were obtained.

The structures of the esters **2**–**23** were confirmed by extensive analysis. Thus, the mass spectrometric analysis revealed for all esters the presence of a characteristic methyl oleanoate decomposition signal $m/z = 203$ [31,32]. Also, the elimination of two molecules of water followed by a subsequent splitting off of two molecules of alcohol was observed ($m/z = 409$). All ^{13}C NMR signals for the triterpenoic skeleton in this series of compounds were similar with exception of the signal for C-28 (and the additional signals for the alcohol part of the ester). For C-28 a shift to higher field for the esters was observed as compared to parent **1** ($\delta = 180.2$ ppm for **1** to $\delta = 177.8 \pm 0.47$ ppm for the esters). In addition, for the alkynic derivatives **8** and **15** in the IR spectra the typical bands for alkynes were found at $\nu = 3314$ and 3296 cm^{-1}, respectively.

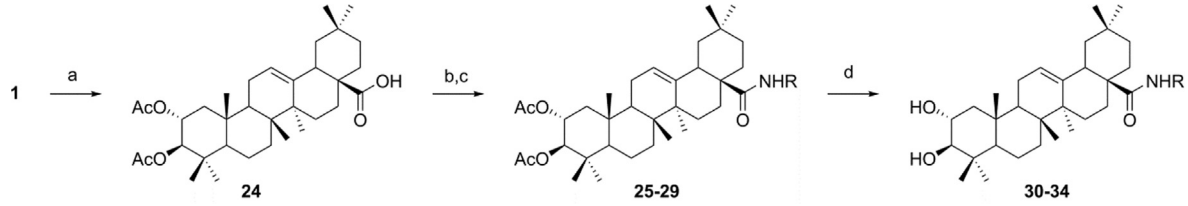
Consecutively, a series of homologous amides was synthesized (Scheme 2) to investigate the influence of a nitrogen substituent. Starting from **1**, diacetylation furnished a diacetate **24** whose treatment with thionylchloride followed by the reaction with amines yielded diacetylated amides **25**–**29** whose de-acetylation with potassium carbonate in MeOH gave amides **30**–**34** in 61–82% isolated yield.

3. Biology

Photometric SRB assays [33] were performed, the results of which are compiled in Table 1. Thus, IC_{50} values (Table 1) were determined for six different human cancer cell lines and non-malignant mouse fibroblasts (NIH 3T3).

By and large, esterification of parent **1** results in an increase of cytotoxicity. As shown for three different human cancer cell lines [A2780 (ovarian carcinoma), HT29 (colon adenocarcinoma) and MCF7 (breast adenocarcinoma)] short alkyl esters of **1** up to a maximum length of six carbons possess a higher cytotoxicity than parent **1** (Fig. 1). Activity is lost, however, for long chain esters (*e.g.* **20**–**22**).

The allyl ester of 2-cyano-3,12-dioxooleana-1,9(11)dien-28-acid (CDDO) has previously been shown to possess a five-fold higher inhibitory activity for the production of nitric oxide NO in mouse macrophages than a homologous butyl ester, whereas a significant drop in activity was determined for the corresponding CDDO ethyl ester [34]. Recently, we were able to show for several derivatives of glycyrrhetinic acid that unsaturated esters exhibit higher cytotoxicity towards several human tumor cell lines as compared to their saturated analogs. However, comparison of the IC_{50} values from the SRB tests using the estrogen receptor positive breast cancer cell line MCF7 showed no significant differences in the cytotoxicity for the allyl (**7**), propargyl (**8**) or but-3-enyl (**14**) ester as compared to parent **1**. A drop in activity was observed for the alkynyl ester **15**.



Scheme 2. a) Ac_2O, pyridine, TEA b) DCM/THF, $SOCl_2$, 0 °C → 25 °C, 30 min c) DCM, RNH_2, 25 °C, 12 h d) K_2CO_3, MeOH, 25 °C, 8 h; R′ = H (**25**), ethyl (**26**), propyl-27, propenyl (**28**), propargyl-29; R = H (**30**), ethyl (**31**), propyl (**32**), propenyl (**33**), propargyl (**34**).

Following these observations we assumed that the improvements in cytotoxicity following the introduction of an ester moiety might be explained by differences in the transport of the compounds through the cell membrane. In addition, the overall lipophilicity of the C-28 ester seems to be more important for activity than individual modifications at this functional group. Thus, the IC_{50} values of several halogenated analogs of the propyl **6** as well as of the butyl ester **13** are similar; these substituents exhibited no strong impact onto the cytotoxicity of the compounds. By and large, these halogenated analogs showed similar cytotoxicity as their non-halogenated analogs. Interestingly, introducing additional polar groups (as exemplified in the 2-hydroxyethyl ester **4**) resulted in a complete loss of activity in melanoma cells (518A2), thyroid carcinoma (8505C) and lung cancer (A549) cells. The same is true for the butinyl analog **19**. Promising results could be seen for the 4-chloro-butyl compound **16** whereas a drop of activity was observed for the chlorobutinyl derivative **19**.

Several amides of **1** [26] are able to induce apoptosis; this parallels previous findings for CDDO derivatives [34]. Contrary to the results for the esters, introduction of a lipophilic moiety resulted in a significant loss of cytotoxicity for the amides. The propyl derivative **32** was shown to be significantly more potent than the ethyl derivative **31**. Introducing moieties containing C=C double bonds led to a decrease in activity. It seems that esters exhibit a 2–3 fold higher cytotoxicity than the amides. These findings may be the result either of different transport mechanisms of the compounds through the membrane or of a different integration into the cell membrane [35,36]. The effects of several analogs of betulinic acid onto the membrane of erythrocytes has been studied several years ago [37]. Compounds possessing a hydrogen bond donor group (for example COOH, $CONH_2$ or CHOH) at position C-28 acted echinocytogenic, whereas esters, aldehydes and lupeol resulted in the formation of stomatocytes. The latter were formed when the incorporation took place predominantly into the inner leaflet. The amides **30**–**34**, parent **1** as well as inactive **4** and **9** carry a hydrogen bond donor group whereas all of the active compounds of our study are devoid of this function.

The amide **30** exhibited IC_{50} values comparable to those of **1** employing the malignant human tumor cell lines A549 (human lung carcinoma) and HT29. This compound showed a significantly higher cytotoxicity towards tumor cell lines than towards the non-malignant mouse fibroblasts. Furthermore, the introduction of a saturated, bulky cyclohexylmethyl residue (as in **23**) led to promising results; for example for the ovarian cancer cell line an IC_{50} value of 3.6 μM was observed.

The IC_{50} values from the SRB assays show the cytotoxicity of a compound but these tests don't indicate whether the cell death occurs *via* apoptosis or necrosis. To investigate the compounds for their ability to induce apoptosis or for a stop of cell growing, additional cell cycle investigations (after incubation periods of 24 and 48 h) were performed.

Treatment of a cell population with a specific and proportionally DNA-binding fluorescence dye allows measuring the distribution of the cell cycle by FACS-analysis [38]. These experiments revealed (Fig. 2) that the compounds induced a significant G1/G0 arrest in the living, adherent growing cells after 24 h. After 48 h, a further increase of cells in the G1/G0 phase with a total reduction of cells in the S as well as the G2/M phase was observed. Hence, these analogs of **1** are potent cell proliferation stopping agents.

Controlled dying of cells is characterized by an intact cell membrane until the middle phases of the death process [39–42]. The combination of a cell impermeable dye (*e.g.* propidium iodide, PI) and a permeable dye (*e.g.* acridine orange, AO) [42] in a fluorescence microscopy based assay allows quantitative information concerning the different modes of cell death. In this AO/PI assay the cells were treated with maslinic acid derivatives possessing a three carbon chain in the ester or amide moiety, and a green fluorescence (Fig. 3) was observed; hence a controlled cell death had been induced. A hallmark of apoptosis is the activation of caspase-activated DNAse (CAD) by caspase 3 [43]. As a result, DNA is cut into several smaller pieces of 178 bps length. Using gel

Table 1
Cytotoxicity (IC_{50} values in microM, from SRB assays after 96 h of treatment; the values are averaged from at least 3 independent experiments; confidence interval = 95%, individual positive (upper value) and negative (lower value) errors are given in the supplementary part; n.D. not detected) for maslinic acid derivatives **1**–**23**, **30**–**34** and betulinic acid (**BA**, as a standard) using a panel of various cancer cell lines (518A2, 8505C, A2780, A549, HT29 and MCF7) and non-malignant mouse fibroblasts NIH 3T3.

	518A2	8505c	A2780	A549	HT29	MCF7	NIH 3T3
BA	11.9	6.7	11.0	14.9	n.d.	14.8	10.0
1	13.7	17	19.5	23.4	28.8	24.4	16.6
2	15.6	14.7	17.3	17.8	12.8	16.3	21.4
3	11.1	12.2	12.6	13.7	12	8.8	12.1
4	32.5	>30	13.4	32.5	24.1	24	>30
5	16.9	18.9	10.2	19	14.9	17.8	14
6	13.9	13.8	14.1	13.2	12.8	13.5	13.4
7	14.2	12.4	n.d	14.2	14.7	15.1	15.1
8	20.4	14.9	7.8	17.3	12.6	14.3	18.1
9	31.6	37.3	18.1	30.3	30.9	36	32.6
10	12.4	11.6	12.1	14	11.4	13.8	17.3
11	19.4	22.2	n.d.	20.6	16.4	21.1	21.6
12	12.8	13.5	11.7	13.8	14.3	13.4	12.3
13	12.2	13.7	17.7	17.5	11.5	13.1	16
14	13.3	7.1	8	12.8	10.1	12.7	14.1
15	22.7	26.3	10.1	18.6	9.8	19.7	26.1
16	8.4	8.5	6.5	12.2	8.9	8.6	12.9
17	13.1	13.2	5.9	12.7	n.D	12.8	12.9
18	27.9	29.1	22.5	27.4	20.5	23.4	33.1
19	12.4	9.2	8.5	9.9	8.5	7.7	12.6
20	12.4	7.2	13	14.4	13.3	13	14.1
21	111	141.3	80.3	135.6	107	67.7	>120
22	38.5	>90	93.8	104.1	75.7	123.4	56.9
23	8	5.9	3.6	10.5	9.3	8.2	11.9
30	41.2	61.3	29.7	>60	43.7	81.1	47.8
31	42.1	45.2	27.4	37.3	37.7	29.1	14.2
32	29.1	28.1	18.3	23.4	25.2	13.9	17.6
33	39.3	42.5	25.8	37	37.6	28.2	24.8
34	24.5	27.7	21.9	29.8	29.5	24.6	26.1

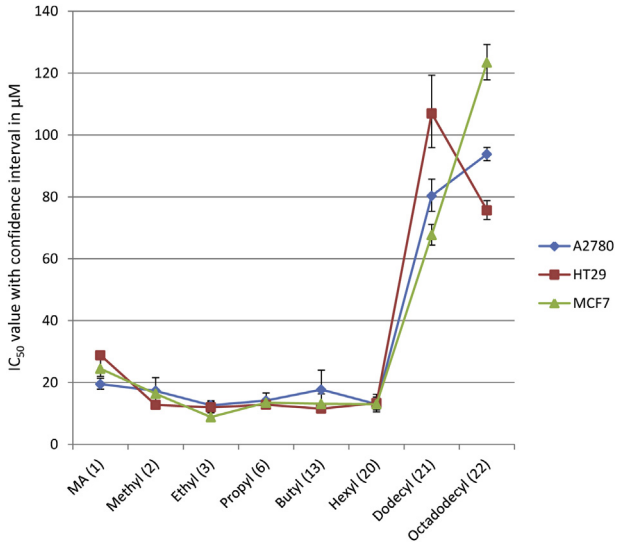


Fig. 1. Comparison of IC_{50} values (from SRB assays after 96 h of incubation with several human tumor cell lines, confidence interval = 95%) for compounds **1**–**3**, **6**, **13**, **20**–**22**.

electrophoresis and staining, the typical "DNA-ladders" are found. The results from these DNA-laddering experiments are depicted in Fig. 3, too. These assays, however, do not allow quantifications. Hence, an annexin-V/PI assay was performed [44]. In these experiments, the whole cell population was treated with fluorescence labeled phosphatidyl-serine specific binding protein annexin-V and PI. Quantitative FACS analysis allowed to distinguish vital from necrotic or apoptotic or secondary necrotic cells. As a result, most of the dead cells showed secondary necrosis after having been incubated for 6 h. Hence, the outer leaf of the membrane carries the phosphatidyl-serine (as expected for an apoptosis), and the integrity of the membrane is lost (as typical for late apoptotic events). These results suggest that either apoptosis is induced slowly or the integrity of the cell membrane might be altered upon incubation of the cells with the compounds.

To investigate whether the apoptotic process is caspase-dependent an extra colorimetric assay [42] was applied. The cell lysate collected from treated as well as untreated cell populations was reacted with *p*-nitroaniline-containing tetra-peptides. The changes in the optical density (Fig. 4) were measured after 12 h of incubation. In this experiment, a high concentration of an aspartate specific cutting caspase correlates with a high optical density. For **1** a low optical density was found after an incubation period of 12 h. For compounds **1** and **8** caspases 3, 8 and 9 were shown to be activated.

Triterpenoic acids are known to intercalate into isolated membranes [35,36,38]. These intercalation processes take place either in the upper or deeper fatty acid regions of the cell membrane depending on the log *P* value of the intercalants. Hence, the entering of PI into cells might occur *via* gaps in the membrane being formed by an intercalation between compounds and the membrane.

4. Summary

Starting from industrial waste a series of different esters and amides of maslinic acid was synthesized. Biological screening of these compounds showed for esters containing small-chain, lipophilic residues an increase in cytotoxicity whereas for amides as well as for long-chain esters a decrease was observed. Results from a dye exclusion assay, from DNA laddering experiments, from a caspase assay as well from annexin-V binding studies indicate that the cytotoxicity seems to be independent from the substitution pattern at position C-28 for esters and amides; modifications at this position determine their mode of action. Of special interest is ethyl ester **3** due to its pronounced cytotoxicity for HT29 cells whereas compounds **8** and **14** exhibited good cytotoxicity against the human ovarian cancer cell line A2780.

5. Experimental

5.1. General

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 using the Varian spectrometers Gemini 2000 or Unity 500 (δ given in ppm, *J* in Hz, internal Me_4Si), IR spectra (film or KBr pellet) on a Perkin–Elmer FT-IR spectrometer Spectrum 1000. MS spectra were taken on a Finnigan MAT TSQ 7000 (electrospray, voltage 4.5 kV, sheath gas nitrogen) instrument. Optical rotations were taken on a Perkin–Elmer 341 polarimeter (1 cm micro cell, 20 °C) and UV–vis spectra on a Perkin–Elmer unit, Lambda 14. Elemental analyses were measured on a Foss–Heraeus Vario EL unit and correct elemental analyses were obtained for all compounds (C, H, and N where appropriate, max. deviation from theoretical value < 0.3%). TLC was performed on silica gel (Merck 5554, detection by UV absorption). The solvents were dried according to usual procedures. The purity of the compounds was >95% as checked by HPLC. Atoms were numbered according to usual IUPAC numbering for triterpenoids. The assignments of the NMR signals attribution was realized using a combination of several 2D NMR techniques (H, H-COSY, H, H-NOESY, gHMBC and gHSQC). Carbon shifts for all compounds are summarized in Tables 2–4.

5.2. Biological assays

5.2.1. SRB-assay

SRB-Assays were prepared according to ref [33]. The cell lines 518A2, 8505C, A549, A2780, HT29, MCF7 and NIH 3T3 were amplified with a starting cell number of 2000, 2500, 1500, 1000, 2000, 2000 and 2500, respectively and counted with an automatic cell counter (Invitrogene™ countess®). IC_{50} values were calculated from semi logarithmic dose response curves by non-linear regression applying a two parametrical Hill-slope equation [45]. Values are given with a confidence interval CI = 95% (cf. Supplementary material).

5.2.2. Acridine orange/propidium iodide dye exclusion assay

Approximately 500,000 cells (HT29) were seeded in cell culture flasks and were allowed to grow for 1 day. After removing of the medium, the substance loaded medium was added, and the flasks were incubated for about 24–48 h. The supernatant medium was collected and centrifuged; the cell pellet was suspended in PBS and centrifuged again. Equal amounts of a PI/AO solution (1:1, 100 µg/ml) and a suspension of the cell pellet in PBS (w/o Ca^{2+} and Mg^{2+}) were softly mixed. Visual analysis was performed under a fluorescence microscope (Axioskop II (Carl Zeiss, Jena). While green fluorescence shows apoptosis, a deep colored nucleus indicates necrotic cells; weak orange dots mark lysosomes [39,40].

5.2.3. Cell cycle investigations

Approximately 1,000,000 cells (HT29) were seeded in cell culture flasks and were allowed to grow for 1 day. After removing of the medium, the substance loaded medium was added, and the flasks were incubated for about 24–48 h. The living cells were collected by centrifugation (1200 rpm, 5 min) and washed twice (PBS, w/o). After careful fixation with ice cold ethanol (70%, min. 2

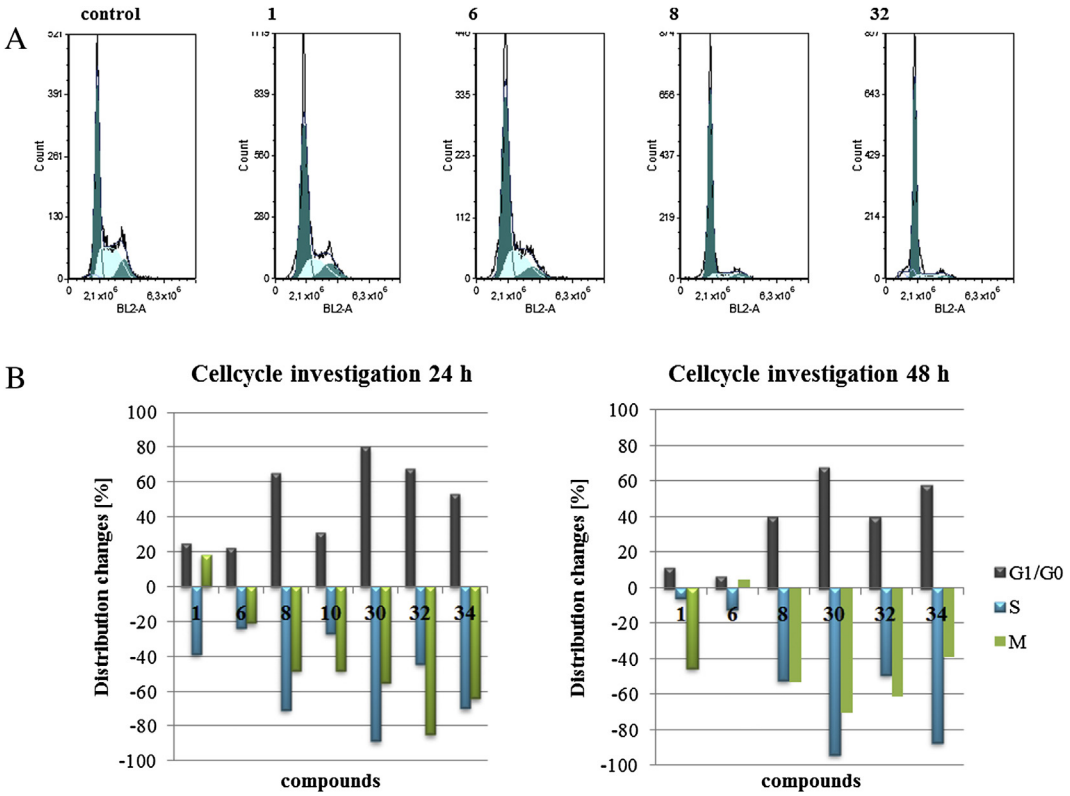


Fig. 2. Upper part: Cell cycle distribution after 24 h treatment of HT29 cells with maslinic acid **1** or derivatives **6**, **8** and **32**. Lower part: Relative changes in the cell cycle of HT29 colon cancer cells after treatment for 24 h and 48 h respectively with MA (**1**, 30 μM), propyl maslinoate (**6**, 15 μM), propargyl (**8**, 30 μM), 3-chloropropyl (**10**, 15 μM), maslinic amide (**30**, 60 μM), propyl amide (**32**, 60 μM) and propargyl amide (**34**, 60 μM).

h), the cells were centrifuged (1200 rpm, 5 min) again, washed twice with staining buffer (PBS (w/w), fetal bovine, sodium azide) and treated with RNAse (100 μL, 100 μg/mL, 30 min) at 37 °C. Then, at room temperature PI (1 mg/ml, 30 min) was added in the dark. Analysis was performed with using an AB™ Attune FACS machine and calculated with FCS express using the method described by Dean [46].

5.2.4. Annexin V/PI assay

Approximately 1,000,000 cells (HT29) were seeded in cell culture flasks and were allowed to grow for 1 day. After removing of the medium, the substance loaded medium was added, and the flasks were incubated for about 6 h. All cells were harvested, centrifuged (1200 rpm, 5 min) and washed twice (PBS, w/w). Approximately 100,000 cells were washed with annexin V bounding buffer (BD) and treated in the dark with propidium iodide (5 μL, life technologies™) for 15 min at room temperature. After adding of the annexin V bounding buffer (400 μL), the suspension was subjected to a FACS measurement. Calculation of the data was performed as described in the suppliers (BD Biosciences®) manual.

5.2.5. General procedure for the synthesis of the esters (method A)

Compound **1** (1 equiv) was dissolved in dry DMF (5 mL), and finely grounded potassium carbonate (5 equiv) was added. After stirring for 1 h at room temperature, the alkyl bromide (2 equiv) was added, and stirring was continued for another 18 h. The mixture was poured into an ice cold solution of aq. hydrochloric acid (5%, 50 mL), and the white precipitate was filtered off. Its chromatographic purification (silica gel, *n*-hexane/ethyl acetate, 7:3) and recrystallization (ethanol) yielded the product in an analytically pure form.

5.2.6. General procedure for the synthesis of the diacetylated amides (method B)

To a solution of **24** (1 equiv) in dry DCM/THF (50 mL, 1:1, v/v), thionyl chloride (1.1 equiv) and triethylamine (1.3 equiv) were added at 0 °C, stirring at 0 °C was continued for 20 min. After stirring at 25 °C for several hours (until TLC showed completion of the reaction), the solvents were removed under reduced pressure, the residue was dissolved in DCM, and the corresponding amine (1.3 equiv) and triethylamine (1.3 equiv) were added. After completion of the reaction (as checked by TLC), the mixture was poured into ice water, the precipitate was filtered off, washed with cold water and purified by chromatography (silica gel, *n*-hexane/ethyl acetate).

5.2.7. General procedure for deacylation (method C)

The diacetylated amides were dissolved in methanol, and KOH (1.2 equiv) was added; the mixture was stirred at room temperature until TLC showed completion of the reaction. Usual workup followed by chromatography (silica gel, *n*-hexane/ethyl acetate mixtures) yielded the amides.

*5.2.7.1. Maslinic acid (**1**).* Maslinic acid was isolated from olive pomace as reported in Refs. [47]; after recrystallization from ethyl acetate **1** was obtained as a colorless solid; m.p. 263–267 °C, (lit.: 266–269 °C [9]); R_F = 0.22 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D = +55°$ (*c* 0.42, $CHCl_3$) (lit.: $[\alpha]_D = +60°$ (*c* 0.1, $CHCl_3$) [48]). MS (ESI, MeOH): *m/z* = 471.5 (43%, $[M - H]^-$), 517.0 (100%, $[M + HCO_2]^-$), 943.1 (62%, $[2M - H]^-$).

*5.2.7.2. Methyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**2**).* Obtained from **1** (100 mg, 0.21 mmol) by method **A** as fine colorless needles; yield: 88%; m.p. 229–231 °C (lit.: 214–216 °C [49]); $R_F = 0.4$ (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D = 60.9°$ (*c* 6.5, $CHCl_3$); IR

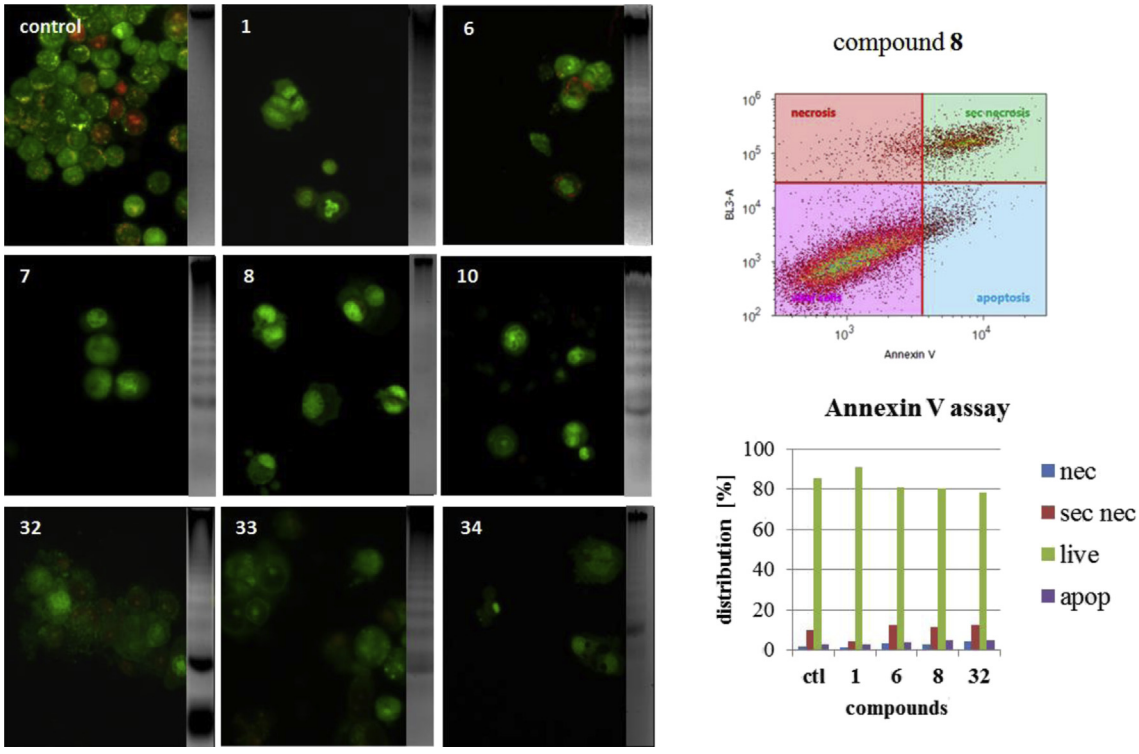


Fig. 3. Left part: Dye exclusion assay and DNA-ladder (HT29, colon cancer cell line): Cells were treated with **1** (30 μM), **6** (15 μM), **7** (30 μM), **8** (30 μM), **10** (15 μM), **32** (60 μM), **33** (60 μM), **34** (60 μM). Right part: Annexin V assay (HT29, colon cancer cells): Cells were treated for 6 h with **1** (30 μM), **6** (15 μM), **8** (30 μM) and **32** (60 μM).

(KBr) ν = 3571, 3300, 2947, 1739, 1461, 1386, 1363, 1262, 1229, 1190, 1162, 1124, 1052, 1037, 984, 958, 921 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.28 (dd, J = 3.4, 3.4 Hz, 1H, H-12), 3.72–3.65 (m, 1H, H-2), 3.61 (s, 3H, CH_3-31), 3.00 (d, J = 9.4 Hz, 1H, H-3), 2.85 (dd, J = 13.8, 4.1 Hz, 1H, H-18), 2.21 (br, 2H, OH), 1.97 (dd, J = 10.4, 3.9 Hz, 1H, H_a-1), 1.96–1.83 (m, 3H, H_a-16 + $H_{a,b}$-11), 1.68 (ddd, J = 13.9, 13.9, 4.4 Hz, 1H, H_a-7), 1.64–1.56 (m, 4H, H-9 + H_a-19 + H_a-15 + H_b-16), 1.55–1.52 (m, 1H, H_a-6), 1.50 (ddd, J = 14.0, 3.4, 3.4 Hz, H_a-22), 1.43 (m, 1H, H_b-7), 1.38 (ddd, J = 12.4, 12.4, 2.5 Hz, H_b-6), 1.29 (ddd, J = 13.8, 9.6, 2.7 Hz, 1H, H_a-21), 1.29–1.27 (m, 1H, H_b-22), 1.16 (ddd, J = 14.0, 4.2, 4.2 Hz, 1H, H_b-21), 1.15–1.11 (m, 1H, H_b-19), 1.12 (s, 3H, CH_3–C27), 1.06–1.02 (m, 1H, H_b-15), 1.02 (s, 3H, CH_3-23), 0.97 (s, 3H, CH_3-25), 0.92 (s, 3H, CH_3-30), 0.92–0.87 (m, 1H, H_b-1), 0.89 (s, 3H, CH_3-29), 0.84–0.82 (m, 1H, H-5), 0.82 (s, 3H, CH_3-24), 0.71 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): m/z = 487.4 (48.8%, $[M + H]^+$), 504.5 (53.4%, $[M + NH_4]^+$), 509.5 (100%, $[M + Na]^+$), 541.2 (22.0%, $[M + Na + MeOH]^+$), 741.5 (14.6%, $[3M + Na + H]^{2+}$), 749.6 (73.2%, $[3M + K + H]^{2+}$), 992.8 (48.8%, $[4M + K + H]^{2+}$).

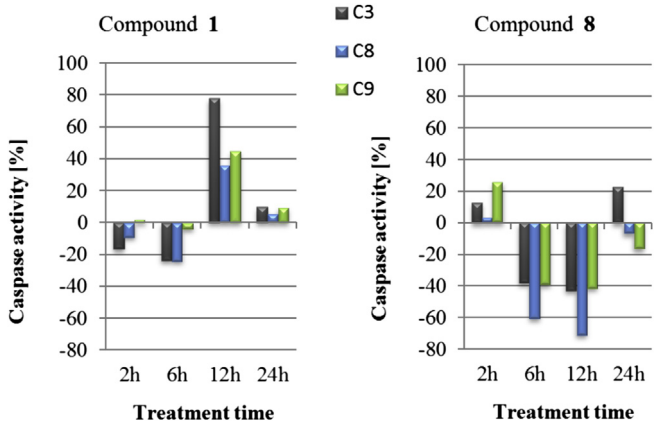


Fig. 4. Relative activity of caspases 3, 8 and 9 after treatment of HT29 colon-cancer cells with 30 μM of **MA**(**1**) or propargyl maslinoate (**8**) for 6, 12 and 24 h, respectively.

*5.2.7.3. Ethyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**3**).* Obtained from **1** by method **A** as a colorless solid; yield: 86%; m.p. 223–224 °C; R_F = 0.4 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D$ = +201.5° (*c* 6.2, $CHCl_3$); IR (KBr) ν = 3609, 3363, 2948, 1723, 1463, 1387, 1365, 1320, 1302, 1258, 1180, 1161, 1126, 1098, 1081, 1050, 1037 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.26 (dd, J = 3.4, 3.4 Hz, 1H, H-12), 4.06 (m, 2H, CH_2-31), 3.67 (m, 1H, H-2), 2.98 (d, J = 9.3 Hz, 1H, H-3), 2.84 (dd, J = 13.8, 4.1 Hz, 1H, H-18), 2.10–2.00 (br, 2H, OH), 1.95 (dd, 1H, J = 14.8, 3.2 Hz, H_a-1), 1.95–1.82 (m, 3H, H_a-16 + $H_{a,b}$-11), 1.68 (ddd, J = 13.7, 13.7, 4.3 Hz, 1H, H_a-7), 1.64–1.54 (m, 4H, H-9 + H_a-19 + H_a-15 + H_b-16), 1.54–1.47 (m, 1H, H_a-6), 1.50–1.43 (m, 1H, H_b-7), 1.44–1.40 (m, 1H, H_a-22), 1.38–1.33 (m, 1H, H_b-6), 1.32–1.24 (m, 2H, H_a-21 + H_b-22), 1.24–1.15 (m, 1H, H_b-21), 1.20 (t, J = 7.1 Hz, 3H, CH_3-32), 1.16–1.10 (m, 1H, H_b-19), 1.11 (s, 3H, CH_3-27), 1.06–1.00 (m, 1H, H_b-15), 1.01 (s, 3H, CH_3-23), 0.96 (s, 3H, CH_3-25), 0.90 (s, 3H, CH_3-30), 0.92–0.86 (m, 1H, H_b-1), 0.88 (s, 3H, CH_3-29), 0.84–0.82 (m, 1H, H-5), 0.80 (s, 3H, CH_3-24), 0.72 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): m/z = 523.6 (100%, $[M + Na]^+$), 555.1 (19.5%, $[M + Na + MeOH]^+$), 770.5 (75%, $[3M + K + H]^{2+}$), 1020.8 (38.7%, $[4M + K + H]^{2+}$), 1024.2 (36.4%, $[4M+2Na + H]^{2+}$)).

*5.2.7.4. 2-Hydroxyethyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**4**).* Obtained from **1** by method **A** as a colorless solid; yield: 84%; m.p. 224–226 °C; R_F = 0.08 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D$ = 57.1° (*c* 3.5, $CHCl_3$); IR (KBr) ν = 3422, 2948, 2866, 1706, 1048, 1458, 1034, 1176, 1718, 754,1262, 1162, 1388, 1080, 1364 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.30 (dd, J = 3.4, 3.4 Hz, 1H, H-12), 4.19 (ddd, J = 11.7, 5.8, 3.8 Hz, 1H, H_a-31), 4.13 (ddd, J = 11.8, 5.4, 3.6 Hz, 1H, CH_b-31), 3.79 (dd, J = 5.3, 3.8 Hz, 2H, CH_2-32), 3.68 (ddd, J = 10.7, 10.7, 3.6 Hz, 1H, H-2), 2.99 (d, J = 9.3 Hz, 1H, H-3), 2.87 (dd,

Table 2
^{13}C NMR shifts (100 MHz, $CDCl_3$) for compounds **1**–**12**.

	1	2	3	4	5	6	7	8	9	10	11	12
C-1	46.6	46.3	46.3	46.5	47.0	46.5	46.6	46.3	48.4	46.5	46.5	46.5
C-2	68.6	68.9	68.9	69.1	69.1	69.1	69.1	68.9	69.5	69.1	69.0	69.1
C-3	83.8	84.0	84.0	84.0	84.2	84.1	84.1	84.0	84.5	84.1	84.0	84.1
C-4	39.8	39.1	39.1	39.3	39.3	39.3	39.3	39.1	40.5	39.3	39.3	39.3
C-5	55.9	55.3	55.3	55.4	55.5	55.4	55.4	55.3	55.7	55.4	55.4	55.4
C-6	18.8	18.3	18.3	18.5	18.5	18.5	18.5	18.3	19.5	18.5	18.5	18.5
C-7	33.2	32.5	32.3	32.7	32.6	32.6	32.4	32.4	33.5	32.6	32.6	32.6
C-8	39.8	39.3	39.3	39.5	39.6	39.6	39.6	39.4	40.7	39.6	39.5	39.6
C-9	48.1	47.6	47.6	47.7	47.8	47.7	47.8	47.6	48.6	47.7	47.7	47.8
C-10	38.5	38.3	38.3	38.4	38.5	38.4	38.5	38.3	39.3	38.5	38.4	38.5
C-11	23.9	23.0	23.0	23.8	23.8	23.1	23.8	23.0	24.6	23.8	23.6	23.7
C-12	122.4	122.1	122.1	122.3	122.6	122.3	122.6	122.2	123.7	122.5	122.4	122.4
C-13	144.8	143.8	143.8	144.3	143.7	144.0	143.6	143.8	145.1	144.0	143.9	143.9
C-14	42.4	41.6	41.6	42.0	42.0	41.9	41.9	41.7	42.9	41.5	41.5	41.5
C-15	28.3	27.6	27.6	27.7	27.8	27.7	27.8	27.6	28.7	27.8	27.7	27.8
C-16	23.7	23.4	23.4	23.2	26.7	23.6	23.1	23.4	24.0	23.2	23.1	23.2
C-17	47.7	46.7	46.7	47.1	47.0	46.8	46.9	46.7	47.1	47.0	46.9	47.0
C-18	42.0	41.2	41.2	41.6	41.4	41.4	41.4	41.3	42.8	41.9	41.9	41.9
C-19	46.4	45.8	45.8	45.9	46.0	46.0	46.0	45.8	48.1	45.9	45.9	45.9
C-20	30.9	3.7	30.7	30.8	30.9	30.9	30.8	30.7	31.6	30.9	30.8	30.9
C-21	34.2	33.8	33.8	34.0	33.2	34.1	34.0	33.9	33.7	34.0	34.0	34.0
C-22	33.2	32.3	32.5	32.6	32.6	32.8	32.8	32.6	34.8	31.9	32.8	32.8
C-23	29.3	28.6	28.6	28.8	28.8	28.8	28.8	28.6	29.3	28.8	28.4	28.4
C-24	17.6	16.7	16.7	17.2	17.2	16.9	17.3	16.7	17.8	17.3	16.9	16.9
C-25	17.4	16.5	16.6	16.8	16.8	16.8	16.9	16.6	17.1	16.8	16.7	16.8
C-26	16.8	16.9	16.9	16.9	16.9	17.2	16.8	17.0	17.4	16.9	17.2	17.4
C-27	26.2	25.9	25.9	26.0	26.0	26.0	26.0	25.9	26.4	26.1	26.0	26.0
C-28	180.2	178.2	178.2	178.3	177.6	177.9	176.8	177.3	179.5	177.6	177.7	177.7
C-29	33.3	33.1	33.1	33.2	33.3	33.2	33.1	33.2	33.5	33.2	33.2	33.1
C-30	23.8	23.6	23.6	23.6	23.8	23.6	23.6	23.7	23.9	23.7	23.8	23.6
C-31		51.5	51.5	66.2	64.0	66.0	51.8	64.8	62.6	62.0	61.0	63.8
C-32				61.8	41.7	22.2	78.3	132.5	32.7	31.9	31.8	32.6
C-33						10.8	74.5	177.7	59.6	29.7	41.4	1.9

J = 13.6, 3.9 Hz, 1H, H-18), 2.16 (brs, 3H, O*H*), 1.97 (ddd, J = 13.9, 13.9, 4.3 Hz, 1H, H_a-16), 1.96–1.93 (m, 1H, H_a-1), 1.93–1.87 (m, 2H, $H_{a,b}$-11), 1.72 (ddd, J = 13.8, 13.8, 4.4 Hz, 1H, H_a-7), 1.65–1.59 (m, 4H, H-9 + H_a-15 + H_a-19 + H_b-16), 1.53 (m, 2H, H_a-6 + H_b-7), 1.44 (ddd, J = 10.1, 10.1, 2.7 Hz, 1H, H_a-22), 1.39–1.27 (m, 3H, H_b-6 + CH_2-21), 1.22–1.14 (m, 2H, H_b-22 + H_b-19), 1.14 (s, 3H, CH_3-27), 1.10–1.05 (m, 1H, H_b-15), 1.02 (s, 3H, CH_3-23), 0.97 (s, 3H, CH_3-25), 0.92 (s, 3H, CH_{3-30}), 0.90 (s, 3H, CH_3-29), 0.85–0.81 (m, 1H, H-5), 0.81 (s, 3H, CH_3-24), 0.74 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): m/z = 539.6 (100%, $[M + Na]^+$), 1055.2 (36%, $[2M + Na]^+$).

*5.2.7.5. 2-Chloroethyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**5**).* Obtained from **1** by method **A** as a colorless solid; yield: 56%; m.p. 169–170 °C; R_F = 0.37 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D$ = +34° (*c* 1.3, $CHCl_3$); IR (KBr): ν = 3430, 2944, 2926, 2852, 1730, 1634, 1462, 1434, 1384, 1366, 1302, 1262, 1238, 1196, 1174, 1160, 1124, 1108, 1094, 1082, 1050, 1034 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.32 (dd, J = 3.4, 3.4 Hz, 1H, H-12), 4.31 (ddd, J = 11.6, 5.7, 5.7 Hz, 1H, H_a-31), 4.24 (ddd, J = 11.6, 5.6, 5.6 Hz, 1H, CH_b-31), 3.68 (ddd, J = 10.2, 9.4, 4.7 Hz, 1H, H-2), 3.66 (dd, J = 5.7, 5.7 Hz, 2H, CH_2-32), 3.01 (d, J = 9.4 Hz, 1H, H-3), 2.88 (dd, J = 14.1, 4.4 Hz, 1H, H-18), 2.03–1.88 (m, 4H, H_a-1 + H_a-16 + $H_{a,b}$-11), 1.74 (dd, J = 13.7, 13.7, 4.2 Hz, 1H, H_a-7), 1.68–1.50 (m, 6H, H-9 + H_a-15 + H_a-19 + H_b-16 + H_a-6 + H_b-7), 1.49–1.44 (m, 1H, H_a-22), 1.43–1.20 (m, 5H, CH_2 (21) + H_b-6 + H_b-22 + H_b-19), 1.23–1.15 (m, 1H, H_b-15), 1.14 (s, 3H, CH_3-27), 1.07 (m, 1H, H_b-1), 1.03 (s, 3H, CH_3-23), 0.98 (s, 3H, CH_3-25), 0.93 (s, 3H, CH_3-30), 0.91 (s, 3H, CH_3-29, 0.84 (m, 1H, H-5), 0.83 (s, 3H, CH_3-24), 0.74 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): m/z = 557.3 (100%, $[M + Na]^+$), 1091.3 (90%, $[2M + Na]^+$).

*5.2.7.6. Propyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**6**).* Obtained from **1** by method **A** as a colorless solid; yield: 78%; m.p. 167–169 °C; R_F = 0.52 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D$ = +53.8° (*c* 3.0, $CHCl_3$); IR (KBr): ν = 3384, 2946, 1721, 1462, 1386, 1364, 1262, 1162, 1125, 1052, 1032, 958 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.28 (dd, J = 3.3, 3.3 Hz, 1H, H-12), 4.05–3.88 (m, 2H, CH_2-31), 3.68 (ddd, J = 11.1, 11.1, 4.4 Hz, 1H, H-2), 2.99 (d, J = 9.5 Hz, 1H, H-3), 2.88 (dd, J = 13.8, 3.9 Hz, 1H, H-18), 2.21 (brs, 2H, O*H*), 1.97–1.83 (m, 4H, CH_a-1 + H_a-16 + $H_{a,b}$-11), 1.71 (dd, J = 13.5, 13.5, 4.3 Hz, 1H, H_a-7), 1.71–1.55 (m, 6H, H-9 + H_a-19 + H_a-15 + H_b-16 + CH_2-*32*), 1.52–1.48 (m, 2H, H_a-6 + H_b-7), 1.42 (ddd, J = 12.2, 12.2, 2.7 Hz, 1H, H_a-22), 1.38–1.34 (m, 1H, H_b-6), 1.32–1.24 (m, 2H, H_a-21 + H_b-22), 1.17–1.13 (m, 2H, H_b-19 + H_b-21), 1.13 (s, 3H, CH_3-27), 1.10–1.01 (m, 1H, H_b-15), 1.02 (s, 3H, CH_3-23), 0.97 (s, 3H, CH_3-25), 0.95 (t, J = 7.4 Hz, CH_3 (33)), 0.92 (s, 3H, CH_3-30), 0.92–0.86 (m, 1H, H_b-1), 0.90 (s, 3H, CH_3-29), 0.86 (m, 1H, H-5), 0.82 (s, 3H, CH_3-24), 0.73 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): m/z = 537.6 (100%, $[M + Na]^+$), 792.0 (61%, $[3M + K + H]^{2+}$), 1049.3 (49%, $[4M + K + H]^2$).

*5.2.7.7. 2-Propen-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**7**).* Obtained from **1** by method **A** as a colorless solid; yield: 90%; m.p. 203–205 °C; R_F = 0.49 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D$ = +55.4° (*c* 3.6, $CHCl_3$); IR (KBr): ν = 3406, 2947, 1727, 1648, 1464, 1386, 1363, 1261, 1199, 1178, 1159, 1123, 1051, 1034 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.87 (ddd, 1H, J = 22.7, 10.8, 5.6 Hz, C*H*-32), 5.32–5.25 (m, 1H, CH_a (33)), 5.27 (m, 1H, H-12), 5.18 (dd, J = 10.4, 1.2 Hz, 1H, CH_b (33)), 4.55–4.44 (m, 2H, CH_2-31), 3.65 (ddd, J = 11.1, 9.7, 4.5 Hz, 1H, H-2), 2.98 (d, J = 9.5 Hz, 1H, H-3), 2.86 (dd, J = 13.8, 4.1 Hz, 1H, H-18), 2.03 (br, 2H, O*H*), 2.00–1.84 (m, 4H, $H_{a,b}$-11 + H_a-16 + H_a-1), 1.69 (ddd, J = 13.7, 13.7, 4.3 Hz, 1H, H_a-7), 1.66–1.46 (m, 4H, H_b-16 + H_a-15 + H_a-19 + H-9), 1.55–1.49 (m, 2H, H_b-7 + H_a-6), 1.44 (ddd, J = 15.4, 15.4, 3.8 Hz, 1H, H_a-22), 1.37 (ddd, J = 12.6, 12.6, 2.1 Hz, 1H, H_b-6), 1.33 (m, 1H, H_a-21), 1.28 (m, 1H, H_b-

Table 3
^{13}C NMR shifts (100 MHz, $CDCl_3$) for compounds **13**-**22**.

	13	14	15	16	17	18	19	20	21	22
C-1	46.4	46.4	46.5	45.9	45.8	46.5	46.6	46.5	46.5	46.6
C-2	68.9	68.9	69.1	69.0	68.9	69.1	69.0	69.1	69.1	69.1
C-3	84.0	83.9	84.1	84.0	83.9	84.1	84.1	84.1	84.1	84.1
C-4	39.2	39.2	39.3	39.4	39.2	39.3	39.3	39.3	39.3	39.3
C-5	55.3	55.3	55.4	55.3	55.3	55.4	55.4	55.4	55.4	55.4
C-6	18.3	18.3	18.5	18.4	18.3	18.5	18.5	18.5	18.5	18.5
C-7	32.7	32.4	32.6	32.5	32.3	32.5	32.8	32.6	32.6	32.6
C-8	39.4	39.4	39.6	39.2	41.2	39.6	39.6	39.6	39.6	39.6
C-9	47.5	47.6	47.8	47.6	47.6	47.7	47.7	47.8	47.8	47.7
C-10	38.2	38.3	38.5	38.3	38.3	38.4	38.4	38.4	38.5	38.5
C-11	23.5	22.9	23.7	23.0	23.0	23.6	23.6	23.1	23.6	23.6
C-12	122.3	122.2	122.4	122.3	122.3	122.4	122.6	122.3	122.3	122.3
C-13	144.0	143.8	143.8	143.9	143.8	143.8	143.6	144.0	144.1	144.0
C-14	41.7	41.7	41.9	41.8	41.7	41.9	41.9	41.9	41.9	41.9
C-15	27.6	27.6	27.8	27.6	27.6	27.8	27.8	27.7	27.8	27.8
C-16	23.0	23.4	23.1	23.5	23.5	23.2	23.2	23.6	23.1	23.1
C-17	46.6	46.6	46.9	46.7	46.7	46.9	46.9	46.8	46.8	46.8
C-18	41.3	41.2	41.4	41.3	39.4	41.4	41.4	41.4	41.0	41.4
C-19	45.8	45.8	46.0	46.4	46.4	46.0	46.0	46.0	46.0	46.0
C-20	30.7	30.7	30.9	30.7	30.9	30.8	30.8	30.9	30.9	30.9
C-21	33.9	33.9	34.0	33.9	33.8	34.0	34.0	34.1	34.1	34.1
C-22	32.6	32.6	32.8	32.6	32.6	32.8	32.4	32.8	32.8	32.8
C-23	28.8	28.1	28.3	28.3	28.3	28.8	28.8	28.8	28.8	29.4
C-24	16.8	16.7	17.2	17.1	17.1	17.3	17.2	16.9	17.2	17.2
C-25	16.6	16.6	16.8	16.6	16.6	16.8	16.8	16.7	16.8	16.7
C-26	17.0	17.0	16.9	16.7	16.7	16.9	16.9	17.2	16.9	16.9
C-27	25.9	25.9	26.0	25.9	25.9	26.0	26.0	26.0	26.0	26.0
C-28	177.9	177.6	177.6	177.7	177.7	177.5	177.0	177.9	177.9	177.9
C-29	33.1	33.1	33.2	33.2	33.3	33.2	33.2	33.3	32.1	33.3
C-30	23.6	23.6	23.6	23.6	23.6	23.8	23.8	23.8	29.4	23.8
C-31	64.0	63.3	62.1	63.3	63.2	59.2	51.8	64.5	64.4	66.0
C-32	30.8	33.1	19.1	26.1	27.3	128.4	80.9	28.8	28.8	29.4
C-33	19.2	134.3	69.8	29.4	29.5	129.9	81.3	25.9	26.2	26.2
C-34	13.7	117.0	28.8	44.7	33.0	39.0	30.6	31.6	29.5	
C-36								14.0		
Chain									29.8	29.8
C-42									14.3	
C-35 + C-45										29.5
C-46										32.1
C-48										14.3

22), 1.22–1.07 (m, 2H, H_b-21 + H_b-19), 1.13 (s, 3H, CH_3-27), 1.05 (m, 1H, H_b-15), 1.02 (s, 3H, CH_3-23), 0.97 (s, 3H, CH_3-25), 0.92 (s, 3H, CH_3-30), 0.90 (s, 3H, CH_3-29), 0.91–0.80 (m, 1H, H_b-1), 0.81 (s, 3H, CH_3-24), 0.81–0.79 (m, 1H, H-5), 0.72 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 495.5 (7.3%, $[M + H]^+$), 530.4 (6.1%, $[M + NH_4]^+$), 535.5 (100%, $[M + Na]^+$), 788.5 (36.6%, $[3M + K + H]^{2+}$), 1047.2 (48.8%, $[2M + Na]^+$).

*5.2.7.8. 2-Propyn-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**8**).* Obtained from **1** by method **A** as a colorless solid; yield: 78%; m.p. 225–227 °C (lit.: 233–234 °C [50]); R_F = 0.23 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D$ = +58.6° (*c* 3.0, $CHCl_3$); IR (KBr): ν = 3568, 3406, 3310, 3296, 2946, 2862, 1736, 1466, 1442, 1386, 1364, 1260, 1228, 1196, 1176, 1156, 1118, 1066, 1052, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 4.68 (dd, *J* = 15.6, 2.4 Hz, 1H, CH_a-31), 4.57 (dd, *J* = 15.6, 2.5 Hz, 1H, CH_b-31), 3.69 (ddd, *J* = 11.2, 9.6, 4.5 Hz, 1H, H-2), 3.00 (d, *J* = 9.5 Hz, 1H, H-3), 2.87 (dd, *J* = 13.7, 3.9 Hz, 1H, H-18), 2.41 (dd, *J* = 2.5, 2.5 Hz, 1H, C*H* (33)), 2.10 (brs, 2H, O*H*), 2.02 (ddd, *J* = 12.6, 12.6, 3.5 Hz, 1H, H_a-16), 1.95 (m, 1H, H_a-1), 1.94–1.87 (*m*, 2H, $H_{a,b}$-11), 1.70 (ddd, *J* = 13.7, 13.7, 4.3 Hz, 1H, H_a-7), 1.68–1.49 (m, 6H, H_b-16 + H_b-19 + H_a-15 + H-9 + H_b-7 + H_a-6), 1.49–1.39 (m, 1H, H_a-22), 1.39–1.32 (m, 2H, H_b-6 + H_a-21), 1.29 (m, 1H, H_b-22), 1.24–1.17 (m, 2H, H_b-21 + H_b-19), 1.14 (s, 3H, CH_3-27), 1.07 (ddd, *J* = 9.5, 9.5, 5.3 Hz, 1H, H_b-1), 1.03 (s, 3H, CH_3-23), 0.98 (s, 3H, CH_3-25), 0.93 (s, 3H, CH_3-30), 0.90 (s, 3H, CH_3-29), 0.88–0.78 (m, 1H, H-5), 0.82 (s, 3H, CH_3-24), 0.76 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 533.6 (63%, $[M + Na]^+$), 785.4 (46%, $[3M + K + H]^{2+}$), 1040.8 (100%, $[4M + K + H]^+$).

*5.2.7.9. 3-Hydroxy-prop-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**9**).* Obtained from **1** by method **A** as a colorless solid; yield: 80%; m.p. 119–121 °C; R_F = 0.17 (*n*-hexane/ethyl acetate, 6:4); $[\alpha]_D$ = +51.7° (*c* 1.4, $CHCl_3$); IR (KBr): ν = 3446, 2948, 2878, 2864, 1724, 1706, 1646, 1636, 1458, 1384, 1364, 1262, 1178, 1162, 1050 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OH): δ = 5.33 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 4.19 (ddd, *J* = 12.7, 6.3, 6.3 Hz, 1H, CH_a-31), 4.15 (ddd, *J* = 12.7, 6.3, 6.3 Hz, CH_b-31), 3.68 (ddd, *J* = 6.5, 1.4 Hz, 2H, CH_2 (33)), 3.72–3.64 (m, 1H, H-2), 2.96 (d, *J* = 9.6 Hz, 1H, H-3), 2.95 (dd, *J* = 13.8, 4.5 Hz, 1H, H-18), 2.10 (ddd, *J* = 12.8, 12.8, 3.5 Hz, 1H, H_a-16), 2.03–1.96 (m, 3H, CH_a-1 + $H_{a,b}$-11), 1.95–1.85 (m, 2H, CH_2-32), 1.82–1.67 (m, 2H, H_a-19 + H-7), 1.70–1.60 (m, 3H, H-9 + H_a-15 + H_b-16), 1.63–1.38 (m, 5H, CH_2-6 + H_b-7 + H_a-22 + H_a-21), 1.38–1.33 (m, 1H, H_b-22), 1.25–1.20 (m, 1H, H_b-21), 1.22 (s, 3H, CH_3-27), 1.21–1.08 (m, 2H, H_b-15 + H_b-19), 1.07 (s, 3H, CH_3-23), 1.06 (s, 3H, CH_3-25), 1.00 (s, 3H, CH_3-30), 0.97 (s, 3H, CH_3-29), 0.95–0.88 (m, 2H, H-5 + H_b-1), 0.87 (s, 3H, CH_3-24), 0.82 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 531.1 (8%, $[M + H]^+$), 553.3 (92%, $[M + Na]^+$), 815.9 (70%, $[3M + K + H]^{2+}$), 1083.3 (100%, $[2M + Na]^+$).

*5.2.7.10. 3-Chloro-prop-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**10**).* Obtained from **1** by method **A** as a colorless solid; yield

Table 4
^{13}C NMR shifts (100 MHz, $CDCl_3$) for compounds **23**-**34**.

	23	24	25	26	27	28	29	30	31	32	33	34
C-1	46.6	44.0	44.1	44.1	44.1	44.1	44.1	46.5	48.1	48.1	45.5	48.1
C-2	69.1	70.2	70.1	70.1	70.0	70.1	70.1	69.0	69.5	69.5	69.0	69.5
C-3	84.1	80.8	80.7	80.7	80.7	80.7	80.7	84.7	84.5	84.4	84.1	85.5
C-4	39.3	39.5	39.4	39.5	39.5	39.5	39.5	39.3	40.5	40.5	39.3	40.5
C-5	55.5	55.0	55.0	55.0	55.0	55.0	55.0	55.4	56.6	56.6	55.3	56.7
C-6	18.5	18.3	18.4	18.3	18.3	18.4	18.3	18.5	19.5	19.5	18.4	19.5
C-7	32.8	32.5	32.7	32.6	32.7	32.7	32.4	32.6	34.3	34.4	32.6	34.1
C-8	39.6	39.5	39.5	39.6	39.6	39.6	39.6	39.4	40.7	40.7	39.6	40.8
C-9	47.8	47.7	47.6	47.6	47.6	47.6	47.6	47.7	48.6	48.8	47.7	48.4
C-10	38.5	38.3	38.3	38.2	38.2	38.2	38.2	38.4	39.2	39.2	38.3	39.3
C-11	23.6	23.6	23.9	23.9	23.9	24.0	24.0	24.0	24.6	24.0	23.9	24.7
C-12	122.2	122.4	122.6	122.3	122.3	122.6	122.9	122.8	123.8	123.8	122.8	123.9
C-13	144.0	143.8	145.1	145.4	145.4	145.3	145.0	145.1	145.5	145.5	145.2	145.3
C-14	41.9	41.0	42.3	42.3	42.3	42.1	42.2	42.3	43.0	43.0	42.1	42.9
C-15	27.8	27.8	27.4	27.4	27.4	27.4	27.3	27.5	28.5	28.5	27.4	28.4
C-16	23.1	23.0	23.8	23.7	23.7	23.7	23.8	23.7	24.0	23.6	23.7	24.0
C-17	46.9	46.7	46.6	46.3	46.4	46.5	46.5	46.5	47.4	47.5	46.5	47.5
C-18	41.5	41.7	42.7	42.4	42.4	42.3	42.3	42.7	42.6	42.6	42.4	42.5
C-19	46.0	46.0	46.8	47.0	47.0	46.9	46.8	46.8	47.7	47.7	46.9	47.6
C-20	30.9	30.8	30.9	30.9	30.9	30.9	30.9	30.9	31.6	31.6	30.9	31.6
C-21	34.1	33.9	34.2	34.3	34.3	34.3	34.2	34.1	35.1	35.1	34.3	35.1
C-22	32.7	32.5	32.4	32.3	32.3	32.3	32.3	32.5	33.8	33.8	32.4	33.8
C-23	28.8	28.6	28.6	28.6	28.6	28.6	28.5	28.8	29.3	29.3	28.7	29.3
C-24	16.9	17.3	17.2	17.0	17.0	17.0	17.1	16.9	17.4	17.5	16.9	17.4
C-25	16.8	16.6	16.6	16.6	16.6	16.6	16.6	16.8	17.1	17.1	16.8	17.1
C-26	17.3	17.8	17.8	17.8	17.8	17.8	17.7	17.3	17.9	17.9	17.1	18.1
C-27	26.1	26.0	25.9	25.9	25.9	25.9	25.9	25.9	26.5	26.5	25.9	26.5
C-28	177.9	183.8	181.2	178.1	178.1	178.1	178.0	181.4	180.2	180.2	178.2	180.0
C-29	33.3	33.2	33.1	33.2	33.1	33.1	33.1	33.1	33.5	33.6	33.1	33.5
C-30	23.8	23.7	23.7	23.7	23.7	23.7	23.8	23.7	24.0	24.0	23.7	24.0
C-31	69.6			34.5	41.3	42.3	29.5		35.6	42.5	42.3	29.7
C-32	32.3			14.8	22.8	134.6	71.8		14.9	24.6	134.5	81.0
C-33	26.6				11.6	116.4	70.0			11.9	116.5	71.8
C-34	25.9											
C-35	30.0											
Ac		21.1	21.1	21.1	21.1	21.1	21.0					
Ac		21.3	21.3	21.3	21.3	21.3	21.3					
Ac*C* = O		107.7	170.7	170.7	170.7	170.7	170.7					
Ac*C* = O		171.0	171.0	171.0	171.0	171.0	171.0					

84%; m.p. 146–147 °C; R_F = 0.3 (*n*-hexane/ethyl acetate, 5:3); $[\alpha]_D = +41.2°$ (*c* 2.1, $CHCl_3$); IR (KBr): ν = 3440, 2948, 2864, 1726, 1654, 1648, 1636, 1628, 1618, 1458, 1438, 1386, 1260, 1176, 1162, 1050, 1034 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.27 (dd, *J* = 3.3, 3.3 Hz, 1H, H-12), 4.17–4.13 (m, 2H, CH_2-31), 3.67 (ddd, *J* = 11.1, 9.5, 4.4 Hz, 1H, H-2), 3.60 (t, *J* = 6.4 Hz, 2H, CH_2 (33)), 2.98 (d, *J* = 9.5 Hz, 1H, H-3), 2.85 (dd, *J* = 13.8, 4.0 Hz, 1H, H-18), 2.49 (brs, 2H, O*H*), 2.09–2.00 (m, 2H, CH_2-32), 1.98–1.87 (m, 4H, $H_{a,b}$-11 + CH_a-1 + H_a-16), 1.70 (ddd, *J* = 13.9, 13.9, 4.3 Hz, 1H, H_a-7), 1.66–1.56 (m, 4H, H_a-19 + H-9 + H_b-16 + H_a-15), 1.55–1.48 (m, 1H, H_a-6), 1.43–1.35 (m, 3H, H_b-6 + H_a-22 + H_b-7), 1.36–1.32 (m, 2H, H_a-21 + H_b-22), 1.22–1.16 (m, 2H, H_b-21 + H_b-19), 1.12 (s, 3H, CH_3-27), 1.08–1.02 (m, 1H, H_b-15), 1.01 (s, 3H, CH_3-23), 0.96 (s, 3H, CH_3-25), 0.91 (s, 3H, CH_3-30), 0.89 (s, 3H, CH_3-29), 0.91–0.84 (m, 2H, H_b-1 + H-5), 0.81 (s, 3H, CH_3-23), 0.72 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 549.1 (11%, $[M + H]^+$), 571.4 (100%, $[M + Na]^+$), 844.6 (10%, $[3M + Na]^{2+}$), 1119.5 (67%, $[2M + Na]^+$).

*5.2.7.11. 3-Bromo-prop-1-yl (2α, 3β)-2,3-dihydroxy-olean-12-en-28-oate (**11**).* Obtained from **1** by method **A** as a colorless solid; yield: 92%; m.p. 117–119 °C; R_F = 0.30 (*n*-hexane/ethyl acetate, 5:3); $[\alpha]_D = +44.4°$ (*c* 4.0, $CHCl_3$); IR (KBr): ν = 3442, 2948, 2864, 1726, 1628, 1458, 1386, 1364, 1302, 1260, 1176, 1162, 1124, 1050, 1034 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.29 (brs, 1H, H-12), 4.17 (dt, *J* = 11.1, 6.9 Hz, 1H, CH_a-31), 4.15 (dt, *J* = 11.1, 6.9 Hz, 1H, CH_b-31), 3.70 (ddd, *J* = 11.0, 9.5, 4.2 Hz, 1H, H-2), 3.46 (t, *J* = 6.6 Hz, 2H, CH_2 (33)), 3.01 (d, *J* = 9.4 Hz, 1H, H-3), 2.86 (dd, *J* = 13.8, 4.0 Hz, 1H, H-18), 2.17 (dtt, *J* = 12.5, 6.3, 6.3 Hz, 2H, CH_2-32), 1.98 (m, 2H, CH_a-1 + H_a-16), 1.85–1.79 (m, 2H, $H_{a,b}$-11), 1.70 (ddd, *J* = 13.8, 13.8, 4.4 Hz, 1H, H_a-7), 1.68–1.59 (m, 4H, H-9 + H_a-19 + H_a-15 + H_b-16), 1.58–1.53 (m, 1H, H_a-6), 1.45 (ddd, *J* = 13.8, 13.8, 4.4 Hz, 1H, H_a-22), 1.41–1.35 (m, 1H, H_b-7), 1.38 (ddd, *J* = 12.5, 12.5, 2.5 Hz, 1H, H_b-6), 1.37–1.28 (m, 2H, H_b-22 + H_a-21), 1.20–1.15 (m, 2H, H_b-1 + H_b-21), 1.13 (s, 3H, CH_3-27), 1.10–1.04 (m, 1H, H_b-15), 1.03 (s, 3H, CH_3-23), 0.99 (s, 3H, CH_3-25), 0.93–0.89 (m, 1H, H_b-1), 0.92 (s, 3H, CH_3-30), 0.90 (s, 3H, CH_3-29), 0.79–0.75 (m, 1H, H-5), 0.75 (s, 3H, CH_3-24), 0.74 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 615.7 (75%, $[^{79}M + Na]^+$), 617.5 (100%, $[^{81}M + Na]^+$), 1209.1 (60%, $[2^{79}M + Na]^+$), 1211.1 (38%, $[2^{81}M + Na]^+$).

*5.2.7.12. 3-Iodo-prop-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**12**).* Obtained from **1** by method **A** as a colorless solid; yield: 92%; m.p. 145–147 °C; R_F = 0.29 (*n*-hexane/ethyl acetate, 5:3); $[\alpha]_D = +47.3°$ (*c* 3.1, $CHCl_3$); IR (KBr): ν = 3424, 2948, 1726, 2864, 1162, 1034, 1050, 1460, 1170, 1384, 1260, 1630, 1124, 1364, 1302 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.28 (dd, *J* = 3.3, 3.3 Hz, 1H, H-12), 4.14–4.10 (m, 2H, CH_2-31), 3.69 (ddd, *J* = 11.3, 9.7, 4.5 Hz, 1H, H-2), 3.23 (ddd, *J* = 6.8, 6.7, 1.0 Hz, 2H, CH_2 (33)), 3.00 (d, *J* = 9.5 Hz, 1H, H-3), 2.85 (dd, *J* = 13.8, 4.2 Hz, 1H, H-18), 2.20–2.01 (br, 2H, O*H*), 2.15–2.07 (m, 2H, CH_2-32), 2.00–1.93 (m, 2H, CH_a-1 + H_a-16), 1.95–1.83 (m, 2H, $H_{a,b}$-11), 1.71 (ddd, *J* = 13.8, 13.8, 4.4 Hz, 1H, H_a-7), 1.64–1.58 (m, 4H, H-9 + H_a-19 + H_a-15 + H_b-16), 1.60–1.55 (m, 1H, H_a-6), 1.53–1.40 (m, 3H, H_b-6 + H_b-7 + H_a-22), 1.39–1.30 (m, 2H, H_b-22 + H_a-21), 1.22–1.14 (m, 2H, H_b-21 + H_b-

19), 1.13 (s, 3H, C*H*$_3$-27), 1.09–1.03 (m, 1H, H$_b$-15), 1.03 (s, 3H, C*H*$_3$-23), 0.98 (s, 3H, C*H*$_3$-25), 0.92 (s, 3H, C*H*$_3$-30), 0.90 (s, 3H, C*H*$_3$-29), 0.92–0.85 (m, 2H, H-5 + H$_b$-1), 0.82 (s, 3H, C*H*$_3$-24), 0.75 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m/z* = 641.1 (20%, $[M + H]^+$), 658.1 (10%, $[M + NH_4]^+$), 663.3 (62%, $[M + Na]^+$), 1303.2 (100%, $[2M + Na]^+$).

*5.2.7.13. Butyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**13**).* Obtained from **1** by method **A** as a colorless solid; yield: 95%; m.p. 149–152 °C; R_F = 0.51 (*n*-hexane/ethyl acetate 1:1); $[\alpha]_D$ = +51.4° (*c* 4.0, $CHCl_3$); IR (KBr): *ν* = 3368, 2950, 2870, 2864, 1720, 1460, 1434, 1386, 1380, 1364, 1304, 1260, 1242, 1176, 1164, 1064, 1052, 1032 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 5.27 (dd, *J* = 3.4, 3.4 Hz, 1H, H-12), 4.00 (m, 2H, C*H*$_2$-31), 3.67 (ddd, *J* = 11.0, 9.5, 4.3 Hz, 1H, H-2), 2.99 (d, *J* = 9.5 Hz, 1H, H-3), 2.94 (br, 2H, O*H*), 2.86 (dd, *J* = 14.0, 4.2 Hz, 1H, H-18), 1.96 (dd, 1H, *J* = 12.6, 3.6 Hz, H$_a$-1), 1.96–1.83 (m, 3H, H$_{a,b}$-11 + H$_a$-16), 1.69 (ddd, *J* = 13.8, 13.8, 4.3 Hz, 1H, H$_a$-7), 1.64–1.54 (m, 3H, H$_a$-19 + H$_a$-15 + C*H*$_b$ (11)), 1.54–1.47 (m, 3H, H-9 + C*H*$_2$-32), 1.52–1.47 (m, 1H, H$_a$-6), 1.45–1.40 (m, 1H, H$_b$-7), 1.43–1.38 (m, 1H, H$_a$-22), 1.38–1.33 (m, 1H, H$_b$-6), 1.37 (m, 2H, C*H*$_2$ (33)), 1.35–1.31 (m, 1H, H$_a$-21), 1.32–1.24 (m, 1H, H$_b$-22), 1.20–1.13 (m, 2H, H$_b$-21 + H$_b$-19), 1.12 (s, 3H, C*H*$_3$-27), 1.05–1.00 (m, 1H, H$_b$-15), 1.01 (s, 3H, C*H*$_3$-23), 0.96 (s, 3H, C*H*$_3$-25), 0.90 (t, *J* = 7.4 Hz, 3H, C*H*$_3$ (36)), 0.91 (s, 3H, C*H*$_3$-30), 0.93–0.86 (m, 1H, H$_b$-1), 0.88 (s, 3H, C*H*$_3$-29), 0.83–0.77 (m, 1H, H-5), 0.80 (s, 3H, C*H*$_3$-24), 0.72 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m/z* = 551.6 (100%, $[M + Na]^+$), 812.5 (20%, $[3M + K + H]^{2+}$), 1079.3 (52.4%, $[2M + Na]^+$).

*5.2.7.14. 3-Buten-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**14**).* Obtained from **1** by method **A** as a colorless solid; yield: 87%; m.p. 149–152 °C; R_F = 0.56 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = +55.4° (*c* 3.2, $CHCl_3$); IR (KBr): *ν* = 3392, 2946, 2864, 1720, 1642, 1460, 1434, 1386, 1364, 1260, 1242, 1176, 1162, 1052, 1032, 992 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 5.78 (ddd, *J* = 17.0, 10.3, 6.7 Hz, 1H, C*H* (33)), 5.27 (dd, *J* = 3.4, 3.4 Hz, 1H, H-12), 5.10 (dd, *J* = 17.2, 1.5 Hz, 1H, C*H*$_a$ (34)), 5.06 (dd, *J* = 10.2, 1.2 Hz, 1H, C*H*$_b$ (34)), 4.07 (ddd, *J* = 13.2, 10.8, 5.4 Hz, 2H, C*H*$_2$-31), 3.69 (ddd, *J* = 11.3, 9.7, 4.5 Hz, 1H, H-2), 3.00 (d, *J* = 9.5 Hz, 1H, H-3), 2.86 (dd, *J* = 13.8, 4.1 Hz, 1H, H-18), 2.47 (br, 2H, O*H*), 2.35 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 2H, C*H*$_2$-32), 1.99–1.91 (m, 4H, H$_{a,b}$-11 + H$_a$-16 + H$_a$-1), 1.69 (ddd, *J* = 13.8, 13.8, 4.3 Hz, 1H, H$_a$-7), 1.66–1.46 (m, 4H, H$_b$-16 + H$_a$-15 + H$_a$-19 + H-9), 1.56–1.47 (m, 2H, H$_b$-7 + H$_a$-6), 1.47 (dd, *J* = 17.3, 3.4 Hz, 1H, H$_a$-22), 1.43–1.38 (m, 1H, H$_b$-6), 1.38–1.27 (m, 2H, H$_a$-21 + H$_b$-22), 1.20–1.14 (m, 2H, H$_b$-21 + H$_b$-19), 1.12 (s, 3H, C*H*$_3$-27), 1.07–1.03 (m, 1H, H$_b$-15), 1.02 (s, 3H, C*H*$_3$-23), 0.97 (s, 3H, C*H*$_3$-25), 0.91 (s, 3H, C*H*$_3$-30), 0.89 (s, 3H, C*H*$_3$-29), 0.91–0.80 (m, 1H, H$_b$-1), 0.82 (s, 3H, C*H*$_3$-24), 0.85–0.79 (m, 1H, H-5), 0.72 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m/z* = 549.6 (83.0%, $[M + Na]^+$), 580.9 (9.8%, $[M + Na + MeOH]^+$), 801.6 (12.2%, $[3M + Na + H]^{2+}$), 810.0 (34.1%, $[3M + K + H]^{2+}$), 1075.3 (100%, $[2M + Na]^+$).

*5.2.7.15. 3-Butyn-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**15**).* Obtained from **1** by method **A** as a colorless solid; yield: 89%; m.p. 168–169 °C; R_F = 0.22 (*n*-hexane/ethyl acetate 1:1); $[\alpha]_D$ = +48.3° (*c* 3.7, $CHCl_3$); IR (KBr): *ν* = 3422, 2942, 2864, 1724, 1636, 1466, 1458, 1386, 1364, 1304, 1260, 1228, 1198, 1178, 1160, 1124, 1088, 1050, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 5.30 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 4.19–4.05 (m, 2H, C*H*$_2$-31), 3.72 (dd, *J* = 14.0, 7.4 Hz, 2H, C*H*$_2$-32), 3.68 (ddd, *J* = 11.3, 9.6, 4.5 Hz, 1H, H-2), 3.00 (d, *J* = 9.5 Hz, 1H, H-3), 2.88 (dd, *J* = 13.8, 4.1 Hz, 1H, H-18), 2.50 (dt, *J* = 6.8, 2.7 Hz, 2H, C*H*$_2$-32), 2.01–1.95 (m, 2H, H$_a$-1 + H$_a$-16), 1.95–1.88 (m, 2H, H$_{a,b}$-11), 1.71 (ddd, *J* = 13.8, 13.8, 4.4 Hz, 1H, H$_a$-7), 1.71–1.50 (m, 6H, H$_a$-19 + H-9 + H$_a$-15 + H$_b$-16 + H$_a$-6 + H$_b$-7), 1.47–1.35 (m, 2H, H$_b$-6 + H$_a$-22), 1.39–1.26 (m, 2H, H$_a$-21 + H$_b$-22), 1.21–1.15 (m, 2H, H$_b$-21 + H$_b$-19), 1.13 (s, 3H, C*H*$_3$-27), 1.11–1.00 (m, 1H, H$_b$-15), 1.03 (s, 3H, C*H*$_3$-23), 0.98 (s, 3H, C*H*$_3$-25), 0.93 (s, 3H, C*H*$_3$-30), 0.90 (s, 3H, C*H*$_3$-29), 0.91–0.81 (m, 2H, H$_b$-1 + H-5), 0.82 (s, 3H, C*H*$_3$-24), 0.74 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m/z* = 525.2 (25%, $[M + H]^+$), 547.4 (81%, $[M + Na]^+$), 806.7 (84%, $[3M + K + H]^{2+}$), 1071.4 (100%, $[2M + Na]^+$).

*5.2.7.16. 4-Chloro-but-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**16**).* Obtained from **1** by method **A** as a colorless solid; yield: 72%; m.p. 134–136 °C; R_F = 0.41 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = +49.0° (*c* 3.3, $CHCl_3$); IR (KBr): *ν* = 3396, 2945, 1723, 1462, 1387, 1261, 1161, 1124, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 5.22 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 3.98 (t, *J* = 6.2 Hz, 2H, C*H*$_2$-31), 3.62 (ddd, *J* = 11.0, 9.8, 4.6 Hz, 1H, H-2), 3.49 (t, *J* = 6.5 Hz, 2H, C*H*$_2$ (34)), 2.98 (d, *J* = 9.4 Hz, 1H, H-3), 2.80 (dd, *J* = 13.5, 3.9 Hz, 1H, H-18), 1.91 (dd, *J* = 12.5, 4.4 Hz, 1H, H$_a$-1), 1.89–1.81 (m, 3H, H$_a$-16 + H$_{a,b}$-11), 1.80–1.75 (m, 2H, C*H*$_2$ (33)), 1.74–1.67 (m, 2H, C*H*$_2$-32), 1.64 (ddd, *J* = 13.9, 13.9, 4.4 Hz, 1H, H$_a$-7), 1.61–1.44 (m, 6H, H$_a$-19 + C*H*$_2$ -9 + C*H*$_b$-11 + H$_b$-7 + H$_b$-16 + H$_a$-15 + H$_a$-22), 1.38 (ddd, *J* = 14.0, 11.1, 3.4 Hz, 1H, H$_a$-21), 1.30 (ddd, *J* = 11.3, 9.6, 2.9 Hz, 1H, H$_a$-21), 1.27–1.22 (m, 1H, H$_b$-21), 1.16–1.02 (m, 2H, H$_b$-21 + H$_b$-19), 1.07 (s, 3H, C*H*$_3$-27), 1.03–0.97 (m, 1H, H$_b$-15), 0.96 (s, 3H, C*H*$_3$-23), 0.91 (s, 3H, C*H*$_3$-25), 0.86 (s, 3H, C*H*$_3$-30), 0.84 (s, 3H, C*H*$_3$-29), 0.83–0.77 (m, 2H, H$_b$-1 + H-5), 0.76 (s, 3H, C*H*$_3$-24), 0.66 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m/z* = 585.5 (21%, $[M + Na]^+$), 1147.2 (100%, $[2M + Na]^+$).

*5.2.7.17. 4-Bromo-but-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**17**).* Obtained from **1** by method **A** as a colorless solid; yield: 55%; m.p. 151–155 °C; R_F = 0.25 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = +45.0° (*c* 4.1, $CHCl_3$); IR (KBr): *ν* = 3385, 2947, 1725, 1464, 1386, 1260, 1178, 1161, 1051, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 5.26 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 4.02 (t, *J* = 6.2 Hz, 2H, C*H*$_2$-31), 3.66 (ddd, *J* = 11.2, 9.6, 4.5 Hz, 1H, H-2), 3.40 (t, *J* = 6.7 Hz, 2H, C*H*$_2$ (34)), 2.97 (d, *J* = 9.5 Hz, 1H, H-3), 2.84 (dd, *J* = 12.9, 3.2 Hz, 1H, H-18), 2.03–1.95 (m, 1H, H$_a$-1), 1.95–1.86 (m, 5H, C*H*$_2$ (33) + H$_a$-16 + H$_{a,b}$-11), 1.79–1.72 (m, 2H, C*H*$_2$-32), 1.72–1.69 (m, 2H, H-7 + H-19)), 1.63–1.48 (m, 5H, H-9 + H$_b$-16 + H$_a$-15 + H$_a$-6 + H$_b$-7), 1.48–1.33 (m, 2H, H$_a$-22 + H$_b$-6), 1.32–1.25 (m, 2H, H$_b$-22 + H$_a$-21), 1.20–1.09 (m, 2H, H$_b$-19 + H$_b$-21), 1.11 (s, 3H, C*H*$_3$-27), 1.07–1.02 (m, 1H, H$_b$-15), 1.00 (s, 3H, C*H*$_3$-23), 0.96 (s, 3H, C*H*$_3$-25), 0.90 (s, 3H, C*H*$_3$-30), 0.88 (s, 3H, C*H*$_3$-29), 0.83–0.77 (m, 2H, H$_b$-1 + H-5), 0.80 (s, 3H, C*H*$_3$-24), 0.70 (s, 3H, C*H*$_{3-26}$) ppm; MS (ESI, MeOH): *m/z* = 629.3 (15%, $[M + Na]^+$), 1237.1 (100%, $[2M + Na]^+$).

*5.2.7.18. (2Z) 4-Chlorobut-2-en-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**18**).* Obtained from **1** by method **A** as a colorless solid; yield: 78%; m.p. 148–149 °C; R_F = 0.27 (*n*-hexane/ethyl acetate, 5:3); $[\alpha]_D$ = +46.9° (*c* 3.2, $CHCl_3$); IR (KBr): *ν* = 3422, 2948, 2864, 1726, 1636, 1460, 1386, 1364, 1260, 1230, 1196, 1176, 1160, 1122, 1050, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 5.82 (dddd, *J* = 10.8, 7.7, 7.7, 1.3 Hz, 1H, C*H* (33)), 5.71 (ddd, *J* = 10.8, 6.8, 6.8 Hz, C*H*-32), 5.29 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 4.66 (ddd, *J* = 13.1, 6.9, 1.2 Hz, 1H, C*H*$_a$-31), 4.59 (ddd, *J* = 13.1, 6.7, 1.2 Hz, 1H, C*H*$_b$-31), 4.15 (ddd, *J* = 11.9, 7.7, 0.9 Hz, 1H, C*H*$_a$ (34)), 4.25 (ddd, *J* = 12.0, 7.7, 0.9 Hz, 1H, C*H*$_b$ (34)), 3.69 (ddd, *J* = 11.4, 9.5, 4.5 Hz, 1H, H-2), 3.0 (d, *J* = 9.5 Hz, 1H, H-3), 2.85 (dd, *J* = 13.7, 3.7 Hz, 1H, H-18), 2.11 (brs, 2H, O*H*), 2.03–1.87 (m, 4H, H$_a$-16 + C*H*$_a$-1 + H$_{a,b}$-11), 1.70 (dd, *J* = 13.7, 13.7, 4.4 Hz, 1H, H$_a$-7), 1.68–1.50 (m, 6H, H-9 + H$_a$-19 + H$_a$-15 + H$_b$-16 + H$_a$-6 + H$_b$-7), 1.47–1.40 (m, 2H, H$_b$-6 + H$_a$-21), 1.39–1.27 (m, 2H, H$_b$-22 + H$_b$-21), 1.23–1.15 (m, 2H, H$_b$-21 + H$_b$-19), 1.13 (s, 3H, C*H*$_3$-27), 1.09–1.01 (m, 1H, H$_b$-15), 1.02 (s, 3H, C*H*$_3$-23), 0.98 (s, 3H, C*H*$_3$-25), 0.92 (s, 3H, C*H*$_3$-30), 0.90 (s, 3H, C*H*$_3$-29), 0.89–0.84 (m, 2H, H-5 + H$_b$-1), 0.82 (s, 3H, C*H*$_3$-24), 0.75 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m/z* = 583.3 (100%, $[M + Na]^+$), 584.3

(41%, [M + Na]$^+$), 585.3 (41%, [M + Na]$^+$), 861.9 (6%, [3M + K + H]$^{2+}$), 1038.9 (32%, [4M + K + H]$^{2+}$).

*5.2.7.19. 4-Chloro-but-3-yn-1-yl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**19**).* Obtained from **1** by method **A** as a colorless solid; yield: 72%; m.p. 184–185 °C; R_F = 0.36 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = +53.6° (*c* 3.1, $CHCl_3$); IR (KBr): ν = 3430, 2944, 2862, 1734, 1466, 1458, 1388, 1364, 1262, 1174, 1158, 1118, 1052, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.30 (dd, *J* = 3.3, 3.3 Hz, 1H, H-12), 4.71 (ddd, *J* = 15.7, 1.9, 1.9 Hz, 1H, C*H*$_a$-31), 4.64 (ddd, *J* = 15.7, 1.9, 1.9 Hz, 1H, C*H*$_b$-31), 4.14 (dd, *J* = 1.9 Hz, 2H, C*H*$_2$ (34)), 3.70 (ddd, *J* = 11.2, 9.5, 4.4 Hz, 1H, H-2), 2.99 (d, *J* = 9.5 Hz, 1H, H-3), 2.86 (dd, *J* = 13.7, 3.7 Hz, 1H, H-18), 2.14 (brs, 2H, O*H*), 2.01 (ddd, *J* = 13.3, 13.2, 3.3 Hz, 1H, H$_a$-16), 2.00–1.87 (m, 3H, C*H*$_a$-1 + H$_{a,b}$-11), 1.71 (ddd, *J* = 13.8, 13.8, 4.2 Hz, 1H, H$_a$-7), 1.68–1.50 (m, 6H, H-9 + H$_a$-19 + H$_a$-15 + H$_b$-16 + H$_a$-6 + H$_b$-7), 1.47–1.40 (m, 2H, H$_b$-6 + H$_a$-21), 1.39–1.27 (m, 2H, H$_b$-22 + H$_a$-21), 1.23–1.15 (m, 2H, H$_b$-21 + H$_b$-19), 1.13 (s, 3H, C*H*$_3$-27), 1.06 (ddd, *J* = 14.6, 3.9, 3.9 Hz, 1H, H$_b$-15), 1.02 (s, 3H, C*H*$_3$-23), 0.98 (s, 3H, C*H*$_3$-25), 0.92 (s, 3H, C*H*$_3$-30), 0.90 (s, 3H, C*H*$_3$-29), 0.89–0.84 (m, 2H, H-5 + H$_b$-1), 0.82 (s, 3H, C*H*$_3$-24), 0.75 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 581.5 (100%, [M + Na]$^+$), 858.4 (24%, [3M + K + H]$^{2+}$), 1038.9 (54%, [4M + K + H]$^{2+}$).

*5.2.7.20. Hexyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**20**).* Obtained from **1** by method **A** as a colorless solid; yield: 81%; m.p. 161–163 °C; R_F = 0.24 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = +53.2° (*c* 6.2, $CHCl_3$); IR (KBr): ν = 3418, 2950, 2861, 1725, 1466, 1386, 1364, 1302, 1262, 1200, 1178, 1161, 1124, 1051, 1034, 996 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.27 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 4.00 (dt, *J* = 6.5, 3.0 Hz, 2H, C*H*$_a$-31), 3.68 (ddd, *J* = 11.2, 9.5, 4.4 Hz, 1H, H-2), 2.99 (d, *J* = 9.5 Hz, 1H, H-3), 2.87 (dd, *J* = 13.8, 4.1 Hz, 1H, H-18), 2.25 (brs, 1H, O*H*), 2.21 (brs, 1H, O*H*), 2.00–1.87 (m, 4H, C*H*$_a$-1 + H$_a$-16 + H$_{a,b}$-11), 1.70 (ddd, *J* = 13.8, 13.8, 4.4 Hz, 1H, H-7), 1.68–1.55 (m, 6H, *H-9* + H$_a$-19 + C*H*$_2$-32 + H$_a$-15 + H$_b$-16), 1.58–1.50 (m, 2H, H$_b$-7 + H$_a$-6), 1.41–1.35 (m, 1H, H$_b$-6), 1.34–1.26 (m, 8H, H$_a$-21 + C*H*$_2$-35 + C*H*$_2$-33 + C*H*$_2$-34 + H$_a$-22), 1.16–1.08 (m, 2H, H$_b$-21 + H$_b$-19), 1.12 (s, 3H, C*H*$_3$-27), 1.08–1.00 (m, 1H, H$_b$-15), 1.02 (s, 3H, C*H*$_3$-23), 0.97 (s, 3H, C*H*$_3$-25), 0.92 (s, 3H, C*H*$_3$-30), 0.90 (s, 3H, C*H*$_3$-29), 0.92–0.85 (m, 1H, H$_b$-1), 0.89 (t, *J* = 6.8 Hz, 3H, C*H*$_3$-36), 0.85–0.79 (m, 1H, H-5), 0.82 (s, 3H, C*H*$_3$-24), 0.73 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 557.3 (14.6%, [M + H]$^+$), 579.6 (100.0%, [M + Na]$^+$), 607.5 (34.1%, [M + NH$_4$+MeOH + H]$^+$), 855.0 (26.9%, [3M + K + H]$^{2+}$), 1135.3 (85.3%, [2M + Na]$^+$).

*5.2.7.21. Dodecyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**21**).* Obtained from **1** by method **A** as a colorless solid; yield: 99%; M.p. 141–142 °C; R_F = 0.5 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = +45.7° (*c* 2.9, $CHCl_3$); IR (KBr): ν = 3326, 2926, 2854, 1726, 1704, 1466, 1460, 1438, 1386, 1382, 1362, 1262, 1200, 1180, 1160, 1124, 1052, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (dd, *J* = 3.4, 3.4 Hz, 1H, H-12), 4.06–3.94 (m, 2H, C*H*$_2$-31), 3.68 (ddd, *J* = 10.8, 9.5, 4.1 Hz, 1H, H-2), 3.00 (d, *J* = 9.4 Hz, 1H, H-3), 2.87 (dd, *J* = 13.7, 4.1 Hz, 1H, H-18), 2.20–2.10 (br, 2H, O*H*), 2.98 (dd, *J* = 12.2, 4.0 Hz, 1H, H$_a$-1), 1.97–1.88 (m, 3H, H$_a$-16 + H$_{a,b}$-11), 1.71 (ddd, *J* = 13.8, 13.8, 4.4 Hz, H$_a$-7), 1.66–1.57 (m, 6H, H-9 + H$_b$-16 + H$_a$-15 + C*H*$_2$ (32) + H$_a$-19), 1.54–1.48 (m, 1H, H$_a$-6), 1.47–1.42 (m, 2H, H$_b$-7 + H$_a$-22), 1.37–1.33 (m, 1H, H$_b$-6), 1.33–1.20 (m, 15H, H$_a$-21 + H$_b$-16 + H$_b$-22 + C*H*$_2$-42 + C*H*$_2$-40) + C*H*$_2$-35 + C*H*$_2$-36 + C*H*$_2$-37 + C*H*$_2$-38), 1.21–1.15 (m, 1H, H$_b$-21), 1.17–1.11 (m, 1H, H$_b$-19), 1.13 (s, 3H, C*H*$_3$-27), 1.08–1.04 (m, 1H, H$_b$-15), 1.03 (s, 3H, C*H*$_3$-23), 0.97 (s, 3H, C*H*$_3$-25), 0.92 (s, 3H, C*H*$_3$-30), 0.90 (s, 3H, C*H*$_3$-29), 0.91–0.85 (m, 1H, H$_b$-1), 0.86–0.82 (m, 1H, H-5), 0.82 (s, 3H, C*H*$_3$-24), 0.73 (s, 6H, C*H*$_3$ (42) + C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 641.7 (20%, [M + H]$^+$), 663.7 (100%, [M + Na]$^+$), 1303.3 (50%, [2M + Na]$^+$).

*5.2.7.22. Octadecyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**22**).* Obtained from **1** by method **A** as a colorless solid; yield: 82%; m.p. 119–120 °C; R_F = 0.5 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = 37.2° (*c* 3.4, $CHCl_3$); IR (KBr): ν = 3572, 3314, 3150, 2922, 2852, 1726, 1468, 1386, 1362, 1262, 1228, 1200, 1180, 1160, 1124, 1052, 1036 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (dd, *J* = 3.3, 3.3 Hz, 1H, H-12), 4.06–3.93 (m, 2H, C*H*$_2$-31), 3.72–3.64 (m, 1H, H-2), 3.00 (d, *J* = 9.3 Hz, 1H, H-3), 2.87 (dd, *J* = 13.8, 4.1 Hz, 1H, H-18), 2.14 (brs, 2H, O*H*), 2.00–1.87 (m, 4H, H$_{a,b}$-11 + H$_a$-16 + H$_a$-1), 1.69 (ddd, *J* = 13.8, 13.8, 4.4 Hz, 1H, H$_a$-7), 1.65–1.50 (m, 6H, H-9 + H$_a$-19 + H$_a$-15 + C*H*$_2$-32 + H$_b$-16), 1.50–1.43 (m, 1H, H$_a$-6), 1.42–1.30 (m, 3H, H$_b$-7 + H$_a$-22 + H$_b$-6), 1.37–1.22 (m, 27H, H$_a$-21 + C*H*$_2$-33 + C*H*$_2$-47 + H$_b$-22 + C*H*$_2$-46 + C*H*$_2$-(36–44)), 1.22–1.11 (m, 2H, H$_b$-19 + H$_b$-21), 1.13 (s, 3H, C*H*$_3$-27), 1.08–1.00 (m, 1H, H$_b$-15), 1.02 (s, 3H, C*H*$_3$-23), 0.97 (s, 3H, C*H*$_3$-25), 0.91 (s, 3H, C*H*$_3$-30), 0.90 (s, 3H, C*H*$_3$-29), 0.88 (t, *J* = 7.0 Hz, 3H, C*H*$_3$-48), 0.86–0.75 (m, 2H, H-5 + H$_b$-1), 0.82 (s, 3H, C*H*$_3$-23), 0.73 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH, source CID): *m*/*z* = 725.5 (36%, [M + H]$^+$), 747.6 (100%, [M + Na]$^+$), 1107.2 (32%, [3M + K + H]$^{2+}$), 1471.5 (85%, [2M + Na]$^+$).

*5.2.7.23. (Cyclohexyl)-methyl (2α, 3β) 2,3-dihydroxy-olean-12-en-28-oate (**23**).* Obtained from **1** by method **A** as a colorless solid; yield: 74%; m.p. 198–200 °C; R_F = 0.43 (*n*-hexane/ethyl acetate, 1:1); $[\alpha]_D$ = +46° (*c* 3.2, $CHCl_3$); IR (KBr): ν = 3424, 2928, 1725, 1615, 1451, 1385, 1261, 1161, 1051, 1034 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.21 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 3.78–3.70 (m, 2H, C*H*$_2$-31), 3.62 (ddd, *J* = 11.1, 11.0, 4.5 Hz, 1H, H-2), 2.93 (d, 1H, *J* = 9.5 Hz, H-3), 2.81 (dd, *J* = 13.8, 4.2 Hz, 1H, H-18), 1.91 (dd, *J* = 12.5, 4.7 Hz, 1H, H$_a$-1), 1.89–1.81 (m, 3H, H$_a$-16 + H$_{a,b}$-11), 1.69–1.50 (m, 10H, C*H*-32 + C*H*$_a$-33 + C*H*$_a$-34 + C*H*$_2$-35 + H$_a$-7 + H$_a$-19 + H$_b$-16 + H$_a$-15 + H-9), 1.50–1.35 (m, 4H, H$_a$-22 + C*H*$_2$-6 + H-7), 1.30 (ddd, *J* = 14.6, 10.8, 3.2 Hz, 1H, H$_a$-21), 1.25–1.07 (m, 3H, H$_b$-21 + H$_b$-22 + H$_b$-34 + H$_b$-33), 1.12 (dd, *J* = 14.9, 4.8 Hz, 1H, H$_b$-19), 1.06 (s, 3H, C*H*$_3$-27), 0.96 (s, 3H, C*H*$_3$-23), 1.01–0.89 (m, 2H, H$_b$-1 + H$_b$-15), 0.91 (s, 3H, C*H*$_3$-25), 0.86 (s, 3H, C*H*$_3$-30), 0.83 (s, 3H, C*H*$_3$-29), 0.82–0.77 (m, 1H, H-5), 0.76 (s, 3H, C*H*$_3$-24), 0.66 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m*/*z* = 569.5 (18%, [2M + H]$^+$), 1159.3 (100%, [2M + Na]$^+$).

*5.2.7.24. (2α, 3β) 2,3-Di-O-acetyl-maslinic acid (**24**).* Acetylation of **1** (1.2 g; 2.54 mmol) in dry dichloromethane (50 mL) with acetic anhydride (0.96 mL, 10.16 mmol) and triethylamine (0.96 mL, 10.16 mmol) for 12 h at 24 °C followed by aqueous work-up and recrystallization from ethanol gave **24** as a colorless solid; yield: 88%; m.p. 170–173 °C, (lit.: 175–180 °C [51]); $[\alpha]_D$ = +30° (*c* 8.3, $CHCl_3$); R_F = 0.61 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); IR (KBr): ν = 2949, 1748, 1694, 1464, 1369, 1252, 1183, 1156, 1045 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.18 (dd, *J* = 3.4, 3.4 Hz, 1H, H-12), 5.01 (ddd, *J* = 11.4, 9.8, 4.7 Hz, 1H, H-2), 4.66 (d, *J* = 10.4 Hz, 1H, H-3), 2.73 (dd, *J* = 13.8, 4.1 Hz, 1H, H-18), 1.96 (s, 3H, C*H*$_3$-32), 1.92 (dd, *J* = 11.3 Hz, 4.3 Hz, 1H, H$_a$-1), 1.91–1.90 (m, 1H, C*H*$_a$ (11)), 1.89 (s, 3H, C*H*$_3$ (33)), 1.84 (ddd, *J* = 12.5, 9.9, 3.5 Hz, 1H, H$_a$-16), 1.80–1.72 (m, 2H, H$_b$-16 + C*H*$_b$ (11)), 1.68 (ddd, 1H, *J* = 14.1, 10.8, 4.5 Hz, H$_a$-7), 1.65–1.62 (m, 1H, H$_a$-15), 1.60 (dd, *J* = 11.8, 4.1 Hz, 1H, H-9), 1.56–1.48 (m, 2H, H$_b$-7 + H$_a$-19), 1.48–1.45 (m, 1H, H$_a$-6), 1.41–1.32 (m, 2H, H$_a$-22 + H$_b$-6), 1.27 (ddd, *J* = 11.7, 11.7, 1.9 Hz, 1H, H$_a$-21), 1.19–1.09 (m, 2H, H$_b$-21 + H$_b$-22), 1.06 (ddd, *J* = 13.9, 4.5, 2.0 Hz, 1H, H$_b$-19), 1.03 (s, 3H, C*H*$_{3-27}$), 1.01–0.86 (m, 4H, C*H*$_2$-15 + H$_b$-1 + H-5), 0.96 (s, 3H, C*H*$_3$-23), 0.84 (s, 3H, C*H*$_3$-25), 0.83 (s, 3H, C*H*$_3$-30), 0.82 (s, 3H, C*H*$_3$-29), 0.81 (s, 3H, C*H*$_3$-24), 0.65 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m*/*z* = 557.4 (49%, [M + H]$^+$),

574.5 (100%, $[M + NH_4]^+$), 579.5 (51%, $[M + Na]^+$), 1135.2 (100%, $[2M + Na]^+$).

*5.2.7.25. (2α, 3β) 2,3-Dihydroxy-28-oxo-olean-12-en-28-amide (**25**).* Obtained from **24** by method **B** as a colorless solid; yield: 61%; m.p. 292–295 °C, (lit.: 160–162 °C [25]); R_F = 0.21 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +52° (*c* 3.7, $CHCl_3$), (lit.: +60°, *c* 1.0, $CHCl_3$/MeOH 2:1 [25]); IR (KBr): ν = 3456, 2946, 1660, 1596, 1463, 1364, 1191, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.81 (brs, 2H, N*H*$_2$), 5.31 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 3.63 (ddd, *J* = 11.3, 9.9, 4.5 Hz, 1H, H-2), 2.94 (d, *J* = 9.5 Hz, 1H, H-3), 2.46 (dd, *J* = 13.1, 3.9 Hz, 1H, H-18), 2.02–1.92 (m, 2H, H$_a$-16 + H$_a$-1), 1.90–1.81 (m, 2H, H$_{a,b}$-11), 1.80–1.71 (m, 2H, H$_a$-19 + H$_a$-7), 1.65–1.52 (m, 5H, H-9 + H$_b$-7 + H$_a$-15 + H$_b$-16 + H$_a$-6), 1.52–1.30 (m, 3H, H$_b$-6 + H$_a$-21 + H$_a$-22), 1.24–1.12 (m, 5H, H$_b$-22 + H$_b$-19 + H$_b$-21), 1.11 (s, 3H, C*H*$_3$-27), 1.07–0.98 (m, 1H, H$_b$-15), 0.97 (s, 3H, C*H*$_3$-30), 0.92 (s, 3H, C*H*$_3$-23), 0.85–0.77 (m, 1H, H$_b$-1), 0.85 (s, 3H, C*H*$_3$-29), 0.85 (s, 3H, C*H*$_3$-24), 0.84–0.82 (m, 1H, H-5), 0.76 (s, 3H, C*H*$_3$-25), 0.76 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m*/*z* = 943.5 (22%, $[2M + H]^+$), 965.4 (100%, $[2M + Na]^+$).

*5.2.7.26. Ethyl (2α, 3β) 2,3-di-O-acetyl-28-oxo-olean-12-en-28-amide (**26**).* Obtained from **24** by method **B** as a colorless solid; yield: 81%; m.p. 146–149 °C; R_F = 0.41 (toluene/ethyl acetate/*n*-heptane/HCOOH, 80:25:30:4); $[\alpha]_D$ = +16° (*c* 3.1, $CHCl_3$); IR (KBr): ν = 3432, 2947, 1745, 1662, 1517, 1368, 1252, 1044 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.82 (dd, *J* = 5.1, 5.1 Hz, 1H, N*H*), 5.36 (dd, *J* = 3.4, 3.4 Hz, 1H, H-12), 5.09 (ddd, *J* = 11.4, 11.4, 4.6 Hz, 1H, H-2), 4.74 (d, *J* = 10.3 Hz, 1H, H-3), 3.38–3.30 (m, 1H, C*H*$_a$-31), 3.19–3.03 (m, 1H, C*H*$_{2-31}$), 2.50 (dd, *J* = 12.8, 3.4 Hz, 1H, H-18), 2.05 (s, 3H, C*H*$_3$ (Ac)), 2.02 (ddd, *J* = 12.5, 12.5, 4.7 Hz, 1H, H$_a$-16), 1.98 (s, 3H, C*H*$_3$ (Ac)), 1.96–1.87 (m, 3H, H$_{a,b}$-11 + H$_a$-1), 1.75 (m, 1H, *J* = 13.4, 13.4 Hz, H$_a$-19), 1.70–1.61 (m, 3H, H-9 + H$_b$-16 + H$_a$-7), 1.60–1.47 (m, 4H, H$_b$-7 + H$_a$-22 + H$_a$-15 + H$_a$-6), 1.44 (ddd, *J* = 11.9, 11.9, 2.3 Hz, 1H, H$_b$-6), 1.38–1.25 (m, *2*H, H$_b$-22 + H$_a$-21), 1.22–1.16 (m, 1H, H$_b$-21), 1.17–1.08 (m, 1H, H$_b$-19), 1.15 (s, 3H, C*H*$_3$-27), 1.10 (t, *J* = 7.3 Hz, C*H*$_3$-32), 1.06 (s, 3H, C*H*$_3$-25), 1.05–0.98 (m, 2H, H$_b$-15 + H$_b$-1), 0.90 (m, 13H, H-5 + C*H*$_3$-23 + C*H*$_3$-30 + C*H*$_3$-24 + C*H*$_3$-29), 0.77 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m*/*z* = 584.5 (100%, $[M + H]^+$), 606.4 (34%, $[M + Na]^+$), 1166.9 (14%, $[2M + H]^+$), 1189.2 (48%, $[2M + Na]^+$).

*5.2.7.27. Propyl (2α, 3β) 2,3-di-O-acetyl-28-oxo-olean-12-en-28-amide (**27**).* Obtained from **24** by method **B** as an off-white solid; yield: 61%; m.p. 129–130 °C; R_F = 0.54 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +21° (*c* 2.6, $CHCl_3$); IR (KBr): ν = 3432, 2948, 1744, 1661, 1517, 1368, 1251, 1043 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.88 (dd, *J* = 5.9, 4.9 Hz, 1H, N*H*), 5.36 (dd, *J* = 3.4, 3.4 Hz, 1H, H-12), 5.09 (ddd, *J* = 11.4, 10.3, 4.6 Hz, 1H, H-2), 4.75 (d, *J* = 10.3 Hz, 1H, H-3), 3.34 (dt, *J* = 13.6, 7.1 Hz, 1H, C*H*$_a$-31), 2.95 (dt, *J* = 13.6, 7.2 Hz, 1H, C*H*$_b$-31), 2.51 (dd, *J* = 13.4, 3.3 Hz, 1H, H-18), 2.05 (s, 3H, C*H*$_3$ (Ac)), 2.02 (ddd, *J* = 12.5, 12.5, 4.8 Hz, 1H, H$_a$-1), 1.98 (s, 3H, C*H*$_3$ (Ac)), 1.91–1.86 (m, 3H, H$_a$-16 + H$_{a,b}$-11), 1.77 (dd, *J* = 13.4, 13.4 Hz, H$_a$-19), 1.74–1.59 (m, 3H, H-9 + H$_a$-7 + H$_b$-16), 1.55–1.36 (m, 7H, H$_a$-22 + H$_b$-7 + H$_a$-15 + C*H*$_2$ (32) + C*H*$_2$-6), 1.36–1.24 (m, 2H, H$_a$-21 + H$_b$-22), 1.24–1.16 (m, 1H, C (19)), 1.15 (s, 3H, C*H*$_3$ (17)), 1.11–1.00 (m, 2H, H$_b$-1 + H$_b$-15), 1.06 (s, 3H, C*H*$_3$-25), 1.00–0.94 (m, 1H, H-5), 0.93–0.89 (m, 12H, C*H*$_3$-23 + C*H*$_3$-30 + C*H*$_3$-24 + C*H*$_3$-29), 0.77 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m*/*z* = 598.4 (100%, $[M + H]^+$), 620.5 (39%, $[M + Na]^+$), 1195.0 (28%, $[2M + H]^+$), 1217.3 (68%, $[2M + Na]^+$).

*5.2.7.28. 2-Propen-1-yl (2α, 3β) 2,3-di-O-acetyl-28-oxo-olean-12-en-28-amide (**28**).* Obtained from **24** by method **B** as a colorless solid; yield: 65%; m.p. 158–159 °C; R_F = 0.48 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +11° (*c* 4.2, $CHCl_3$); IR (KBr): ν = 3428, 2948, 1744, 1662, 1517, 1368, 1252, 1043 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.97–5.91 (dd, *J* = 5.3, 5.2 Hz, 1H, N*H*), 5.88–5.78 (m, 2H, C*H*$_2$-31), 5.37 (dd, *J* = 3.3, 3.3 Hz, 1H, *H-12*), 5.16 (dd, *J* = 17.2, 1.4 Hz, 1H, H$_a$-33), 5.12 (dd, *J* = 10.3, 1.3 Hz, H$_b$-33), 5.09 (dd, *J* = 11.2, 10.9, 4.5 Hz, 1H, H-2), 4.75 (d, *J* = 10.3 Hz, 1H, H-3), 4.01 (dddd, *J* = 11.9, 6.0, 5.9, 1.2 Hz, 1H, C*H*$_a$-32), 3.61 (ddd, *J* = 15.6, 5.8, 4.5 Hz, 1H, H$_b$-32), 2.54 (dd, *J* = 12.8, 3.4 Hz, 1H, H-18), 2.06–2.00 (m, 1H, H$_a$-1), 2.05 (s, 3H, C*H*$_3$ (Ac)), 2.03 (ddd, *J* = 12.4, 12.4, 4.7 Hz, 1H, H$_a$-16), 1.98 (s, 3H, C*H*$_3$ (Ac)), 1.96–1.82 (m, 2H, H$_{a,b}$-11), 1.77 (dd, *J* = 13.3 Hz, 1H, H$_a$-19), 1.74–1.69 (m, 1H, H$_a$-7), 1.69–1.61 (m, 2H, H-9 + H$_b$-16), 1.61–1.41 (m, 5H, H$_a$-22 + H$_b$-7 + H$_a$-15 + C*H*$_2$-6), 1.41–1.24 (m, 3H, H$_b$-22 + C*H*$_2$-21), 1.24–1.16 (m, 1H, H$_b$-19), 1.15 (s, 3H, C*H*$_3$-27), 1.09–0.96 (m, 2H, H$_b$-1 + H$_b$-15), 1.05 (s, 3H, C*H*$_3$-25), 0.96 (dd, *J* = 11.9, 1.5 Hz, 1H, H-5), 0.90 (s, 12H, C*H*$_3$-23 + C*H*$_3$-30 + C*H*$_3$-24 + C*H*$_3$-29), 0.75 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m*/*z* = 596.5 (100%, $[M + H]^+$), 618.5 (36%, $[M + Na]^+$), 1191.0 (28%, $[2M + H]^+$), 1213.2 (74%, $[2M + Na]^+$).

*5.2.7.29. 2-Propyn-1-yl (2α, 3β) 2,3-di-O-acetyl-28-oxo-olean-12-en-28-amide (**29**).* Obtained from **24** by method **B** as a colorless solid; yield: 56%; m.p. 226–227 °C; R_F = 0.51 (toluene/ethyl acetate/n-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +1° (*c* 3.8, $CHCl_3$); IR (KBr): ν = 3432, 3250, 2947, 2362, 1744, 1654, 1508, 1369, 1251, 1044 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.04 (dd, *J* = 4.8 Hz, 1H, N*H*), 5.40 (dd, *J* = 3.4, 3.4 Hz, 1H, H-12), 5.08 (ddd, *J* = 11.4, 10.7, 4.6 Hz, 1H, H-2), 4.74 (d, *J* = 10.3 Hz, 1H, H-3), 4.03 (ddd, *J* = 17.6, 5.4, 2.6 Hz, 1H, C*H*$_a$-31), 3.90 (ddd, *J* = 17.6, 4.4, 2.6 Hz, 1H, H$_b$-31), 2.53 (dd, *J* = 12.9, 3.4 Hz, 1H, H-18), 2.20 (dd, *J* = 2.6 Hz, 1H, C≡C*H* (33)), 2.05 (s, 3H, C*H*$_3$ (Ac)), 2.02 (ddd, *J* = 12.4, 12.4, 4.7 Hz, 1H, H$_a$-16), 1.97 (s, 3H, C*H*$_3$ (Ac)), 1.99–1.84 (m, 3H, H$_{a,b}$-11 + H$_a$-1), 1.75 (dd, *J* = 13.3, 13.3 Hz, 1H, H$_a$-19), 1.72–1.67 (m, 1H, H$_a$-7), 1.66–1.51 (m, 4H, H-9 + H$_a$-22 + H$_b$-16 + H$_a$-6), 1.51–1.41 (m, 2H, H$_a$-15 + H$_b$-7), 1.41–1.26 (m, 3H, H$_b$-6 + H$_a$-21 + H$_b$-22), 1.22–1.16 (m, 1H, H$_b$-21), 1.15 (s, 3H, C*H*$_3$-27), 1.14–1.00 (m, 1H, H$_b$-19), 1.06 (s, 3H, C*H*$_3$-25), 1.08–0.99 (m, 2H, H$_b$-1 + H$_b$-15), 0.99–0.94 (m, 1H, H-5), 0.90 (s, 12H, C*H*$_3$ (23) + C*H*$_3$ (30) + C*H*$_3$ (24) + C*H*$_3$-29), 0.79 (s, 3H, C*H*$_3$-26) ppm; MS (ESI, MeOH): *m*/*z* = 594.5 (91%, $[M + H]^+$), 616.5 (39%, $[M + Na]^+$), 1186.9 (24%, $[2M + H]^+$), 1209.2 (100%, $[2M + Na]^+$).

*5.2.7.30. (2α, 3β) 2,3-Dihydroxy-28-oxo-olean-12-en-28-amide (**30**).* Obtained from **25** by method **C** as a colorless solid; yield: 61%; m.p. 292–295 °C (lit.: 160–162 °C [26]); R_F = 0.21 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +52° (*c* 3.7, $CHCl_3$), (lit.: +60°, *c* 1.0, $CHCl_3$/MeOH 2:1 [26]); IR (KBr): ν = 3456, 2946, 1660, 1596, 1463, 1364, 1191, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.81 (brs, 2H, N*H*$_2$), 5.31 (dd, *J* = 3.5, 3.5 Hz, 1H, H-12), 3.63 (ddd, *J* = 11.3, 9.9, 4.5 Hz, 1H, H-2), 2.94 (d, *J* = 9.5 Hz, 1H, H-3), 2.46 (dd, *J* = 13.1, 3.9 Hz, 1H, H-18), 2.02–1.92 (m, 2H, H$_a$-16 + H$_a$-1), 1.90–1.81 (m, 2H, H$_{a,b}$-11), 1.80–1.71 (m, 2H, H$_a$-19 + H$_a$-7), 1.65–1.52 (m, 5H, H-9 + H$_b$-7 + H$_a$-15 + H$_b$-16 + H$_a$-6), 1.52–1.30 (m, 3H, H$_b$-6 + H$_a$-21 + H$_a$-22), 1.24–1.12 (m, 5H, H$_b$-22 + H$_b$-19 + H$_b$-21), 1.11 (s, 3H, C*H*$_3$-27), 1.07–0.98 (m, 1H, H$_b$-15), 0.97 (s, 3H, C*H*$_3$-30), 0.92 (s, 3H, C*H*$_3$-23), 0.85–0.77 (m, 1H, H$_b$-1), 0.85 (s, 3H, C*H*$_3$-29), 0.85 (s, 3H, C*H*$_3$-24), 0.84–0.82 (m, 1H, H-5), 0.76 (s, 3H, C*H*$_3$-25), 0.76 (s, 3H, C*H*$_{3-26}$) ppm; MS (ESI, MeOH): *m*/*z* = 943.5 (22%, $[2M + H]^+$), 965.4 (100%, $[2M + Na]^+$).

*5.2.7.31. Ethyl (2α, 3β) 2,3-dihydroxy-28-oxo-olean-12-en-28-amide (**31**).* Obtained from **26** by method **C** as a colorless solid; yield: 82%; m.p. 170–173 °C; $[\alpha]_D$ = +33° (3.0, $CHCl_3$); R_F = 0.15 (toluene/ethyl acetate/n-heptane/formic acid, 80:25:30:4); IR (KBr): ν = 3422, 2945, 1637, 1525, 1384, 1259, 1050, 1031 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ = 7.25 (dd, *J* = 5.5, 5.5 Hz, 1H, NH), 5.40 (dd, *J* = 3.4,

3.4 Hz, 1H, H-12), 3.66 (ddd, J = 11.4, 9.8, 4.5 Hz, 1H, H-2), 3.30–3.20 (m, 1H, CH_a-31), 3.20–3.12 (m, 1H, CH_b-31), 2.95 (dd, J = 9.6 Hz, 1H, H-3), 2.83 (dd, J = 13.7, 4.1 Hz, 1H, H-18), 2.10 (ddd, J = 13.8, 13.8, 4.0 Hz, 1H, H_a-16), 1.99 (m, 3H, CH_a-1 + $H_{a,b}$-11), 1.82 (dd, J = 13.5, 13.5 Hz, 1H, H_a-19), 1.70–1.52 (m, 7H, H-9 + H_a-15 + H_b-16 + H_a-6 + CH_2-7 + H_a-22), 1.49 (ddd, J = 11.4, 11.4, 3.3 Hz, 1H, H_a-6), 1.43 (ddd, J = 13.9, 13.9, 4.1 Hz, H_a-21), 1.35 (m, 1H, H_b-22), 1.24–1.19 (m, 2H, H_b-19 + H_b-21), 1.21 (s, 3H, CH_3-27), 1.11 (t, J = 7.2 Hz, 3H, CH_3-32), 1.10–1.01 (m, 1H, H_b-15), 1.05 (s, 3H, CH_3-23), 1.05 (s, 3H, CH_3-25), 0.99 (s, 3H, CH_3-30), 0.95 (s, 3H, CH_3-29), 0.97–0.90 (m, 1H, H_b-1), 0.88 (dd, J = 11.3, 0.7 Hz, 1H, H-5), 0.85 (s, 3H, CH_3-24), 0.83 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH): m/z = 500.6 (88%, $[M + H]^+$), 522.7 (20%, $[M + Na]^+$), 999.3 (22%, $[2M + H]^+$), 1021.3 (100%, $[2M + Na]^+$).

*5.2.7.32. Propyl (2α, 3β) 2,3-dihydroxy-28-oxo-olean-12-en-28-amide (**32**).* Obtained from **27** by method **C** as a colorless solid; yield: 80%; m.p. 152–154 °C; R_F = 0.19 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +47° (*c* 4.4, $CHCl_3$); IR (KBr): ν = 3417, 2945, 1639, 1525, 1463, 1384, 1266, 1186, 1050 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ = 5.40 (dd, J = 3.5, 3.5 Hz, 1H, H-12), 3.65 (ddd, J = 11.3, 9.8, 4.5 Hz, 1H, H-2), 3.24–3.16 (m, 1H, CH_a-31), 3.09–3.02 (m, 1H, CH_b-31), 2.94 (d, J = 9.6 Hz, 1H, H-3), 2.83 (dd, J = 13.3, 3.8 Hz, 1H, H-18), 2.10 (ddd, J = 13.1, 13.1, 4.4 Hz, 1H, H_a-16), 2.03–1.94 (m, 3H, CH_a-1 + $H_{a,b}$-11), 1.82 (dd, J = 13.5 Hz, 1H, H_a-19), 1.73–1.50 (m, 9H, H-9 + CH_2-7 + H_a-22 + H_a-15 + CH_2 (32) + H_b-16 + H_a-6), 1.49 (ddd J = 11.8, 11.8, 3.5 Hz, 1H, H_b-6), 1.43 (ddd, J = 13.5, 13.5, 3.9 Hz, 1H, H_a-22), 1.37–1.30 (m, 1H, H_b-21), 1.22 (s, 3H, CH_3-27), 1.25–1.17 (m, 2H, H_b-21 + H_b-19), 1.11–1.03 (m, 1H, H_b-15), 1.05 (s, 3H, CH_3-23), 1.04 (s, 3H, CH_3-25), 0.99 (s, 3H, CH_3-30), 0.95 (s, 3H, CH_3-29), 0.94 (t, J = 7.4 Hz, 3H, CH_3 (33)), 1.00–0.87 (m, 1H, H_b-15), 0.88–0.82 (m, 2H, H-5 + H_b-1), 0.85 (s, 3H, CH_3-24), 0.83 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH): m/z = 514.7 (54%, $[M + H]^+$), 1027.3 (28%, $[2M + H]^+$), 1049.4 (100%, $[2M + Na]^+$).

*5.2.7.33. N-Prop-2-en-1-yl (2α, 3β) 2,3-dihydroxy-28-oxo-olean-12-en-28-amide (**33**).* Obtained from **28** by method **C** as white solid; yield: 62%; m.p. 152–154 °C; R_F = 0.12 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +42° (*c* 3.6, $CHCl_3$); IR (KBr): ν = 3527, 3416, 2945, 1637, 1540, 1469, 1386, 1259, 1050, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.97 (dd, J = 5.0, 5.2 Hz, 1H, N*H*), 5.81 (dddd, J = 16.2, 10.6, 5.8, 5.8 Hz, 1H, C*H*-32), 5.38 (dd, J = 3.5, 3.5 Hz, 1H, H-12), 5.16 (dd, J = 17.3, 3.1, 1.5 Hz, 1H, CH_a (33)), 5.12 (ddd, J = 10.3, 2.7, 1.4 Hz, 1H, CH_b (33)), 4.05–3.97 (m, 1H, CH_a-31), 3.69 (ddd, J = 11.1, 11.1, 4.5 Hz, 1H, H-2), 3.64–3.57 (m, 1H, CH_b-31), 3.00 (d, J = 9.3 Hz, 1H, H-3), 2.54 (dd, J = 13.0, 3.6 Hz, 1H, H-18), 2.18 (brs, 2H, O*H*), 2.00 (ddd, J = 12.6, 12.6, 3.9 Hz, 1H, H_a-16), 1.98–1.91 (m, 3H, CH_a-1 + $H_{a,b}$-11), 1.76 (dd, J = 13.5, 13.5 Hz, 1H, H_a-19), 1.73 (ddd, J = 14.0, 3.6, 3.6 Hz, 1H, H_a-7), 1.68–1.52 (m, 3H, H_b-16 + H_b-7 + H-9), 1.53–1.48 (m, 1H, H_a-6), 1.48–1.42 (m, 1H, H_a-15), 1.42–1.32 (m, 2H, H_b-6 + H_a-22), 1.29–1.17 (m, 4H, CH_2 (21) + H_b-22 + H_b-19), 1.16 (s, 3H, CH_3-27), 1.03 (s, 3H, CH_3-23), 1.02–0.95 (m, 1H, H_b-15), 0.98 (s, 3H, CH_3-25), 0.94–0.87 (m, 1H, H_b-1), 0.91 (s, 6H, CH_3 (30) + CH_3-29), 0.89–0.81 (m, 1H, H-5), 0.83 (s, 3H, CH_3-24), 0.75 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH): m/z = 512.5 (65%, $[M + H]^+$), 534.5 (15%, $[M + Na]^+$), 1023.3 (18%, $[2M + H]^+$), 1045.5 (100%, $[2M + Na]^+$).

*5.2.7.34. N-Prop-2-yn-1-yl (2α, 3β)-2,3-dihydroxy-28-oxo-olean-12-en-28-amide (**34**).* Obtained from **29** by method **C** as a bright yellow solid; yield: 62%; m.p. 181–183 °C; R_F = 0.22 (toluene/ethyl acetate/*n*-heptane/formic acid, 80:25:30:4); $[\alpha]_D$ = +34° (*c* 0.35, $CHCl_3$); IR (KBr): ν = 3418, 2946, 2360, 1646, 1515, 1464, 1387, 1256, 1186, 1050 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 5.40 (dd, J = 3.5, 3.5 Hz, 1H, H-12), 4.0 (dd, J = 17.3, 2.5 Hz, 1H, CH_a-31), 3.91 (dd, J = 17.3, 2.5 Hz, 1H, CH_b-31), 3.66 (ddd, J = 11.3, 9.7, 4.5 Hz, 1H, H-2), 2.95 (d, J = 9.6 Hz, 1H, H-3), 2.84 (dd, J = 13.2, 3.5 Hz, 1H, H-18), 2.54 (d, J = 2.5 Hz, 1H, C*H* (33)), 2.14 (ddd, J = 13.3, 13.3, 3.5 Hz, 1H, H_a-16), 2.06–1.92 (m, 3H, $H_{a,b}$-11 + H_a-1), 1.81 (dd, J = 13.5, 13.5 Hz, 1H, H_a-19), 1.77–1.39 (m, 9H, H-9 + H_a-15 + H_b-16 + CH_2 -6 + CH_2-7 + H_a-22 + H_a-21), 1.37–1.25 (m, 2H, H_b-21 + H_b-22), 1.22 (s, 3H, CH_3-27), 1.29–1.16 (m, 1H, H_b-19), 1.14–1.06 (m, 1H, H_b-15), 1.05 (s, 3H, CH_3-23), 1.05 (s, 3H, CH_3-25), 0.99 (s, 6H, CH_3 (30) + CH_3-29), 0.95 (s, 3H, CH_3-23), 0.91 (s, 3H, CH_3-24), 0.89–0.81 (m, 2H, H_b-1 + H-5), 0.85 (s, 3H, CH_3-26) ppm; MS (ESI, MeOH): m/z = 510.6 (40%, $[M + H]^+$), 1019.2 (10%, $[2M + H]^+$), 1041.3 (100%, $[2M + Na]^+$).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ejmech.2013.10.016.

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