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Synthetic Transformations of Higher Terpenoids: XXXII.* Synthesis of 16-Alkenyl-Substituted Labdatrienes by Oxidative Coupling of Methyl Phlomisoate with Alkenes

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Abstract—Reactions of methyl phlomisoate with methyl acrylate, phenyl acrylate, methyl vinyl ketone, phenyl vinyl ketone, or N-substituted acrylamides catalyzed by $Pd(OAc)_2$ in the presence of $Cu(OAc)_2$, *p*-benzoquinone in the mixture of propionic acid and acetonitrile proceed regio- and stereoselectively with the formation of (*E*)-16-vinyl labdatrienoates. The oxidative coupling under these conditions of the methyl phlomisoate with styrene results in a mixture of 15,16-distyryl-, 16-styryl-, and 16-(1-phenylvinyl)-derivatives of furanolabdanoid.

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We formerly demonstrated by an example of the oxidative coupling of methyl phlomisoate (**I**) with styrene (**II**) (2 equiv) or with excess methyl acrylate (**III**) the possibility to modify labdanoid **I** at the furan fragment with the introduction of an alkenyl substituent in the positions C^{15} and C^{16} labdane skeleton. The reaction with styrene (**II**) in the presence of 0.1 equiv of $Pd(OAc)_2$, 0.5 equiv of $Cu(OAc)_2$, and 0.1 equiv of 1,4-benzoquinone (BQ) in a mixture of propionic acid and ether, 1 : 1 (35°C, 10 h) in an oxygen atmosphere afforded methyl (*E*)-15,16-distyryl-15,16-epoxylabdatrienoate (**IV**) (yield 63%) (Scheme 1) [2]. The yield of the products of the Pd-catalyzed cross-coupling reaction of the substituted furans with styrene (**II**) and the other alkenes is considerably affected by the nature of the solvent [3, 4] and by the composition of the oxidizing system [5, 6]. It seemed therefore reasonable to investigate the effect of the cosolvent, the composition of the oxidation system, and the alkene nature on the yield and the composition of the products of the oxidative coupling of methyl phlomisoate acid (**I**) with terminal alkenes and to obtain new alkenyl-substituted furanolabdanoids.

The reaction of compound **I** with styrene (**II**) in a mixture of propionic acid and acetonitrile, 1 : 1, in the presence of $Pd(OAc)_2/Cu(OAc)_2/BQ/O_2$ (35°C, 10 h) led to the formation of a mixture of methyl 15,16-distyryl- (**IV**), 16-(1-phenylvinyl)- **(V)**, and 16-styryl-15,16-epoxylabdatrienoates **(VI)** in a ratio 1 : 4.5 : 1. Compounds **IV** (yield 4%) and **VI** (yield 4%) were isolated in an individual state. The main reaction product **V** (yield 18%, according to ^1H NMR data) suffered further transformations in the course of the column chromatography. At the reaction in the mixture of the propionic acid and DMF, 1 : 1, (35°*C,* 15 h) the conversion reached 68%, compounds **IV** and **VI** were isolated in an individual state (yield 5 and 7% respectively).

The replacement of the cosolvent made it possible to change the selectivity of the reaction between labdatriene **I** and methyl acrylate (**III**). Whereas at the reaction of compounds **I** and **III** in the mixture of propionic acid and ether, 1 : 1, (35°C, 80 h) in the presence of 0.1 equiv of $Pd(OAc)_2$, 0.5 equiv of $Cu(OAc)_2$, 0.1 equiv of (BQ) in the atmosphere of O_2 methyl ethers were isolated of 15,16-bis(2-methoxycarbonylvinyl)- (**VII**), 16-(2-methoxycarbonylvinyl)- (**VIII**), and 15-(2-methoxycarbonylvinyl)-15,16-epoxylabdatrien-18-oic acid (**IX**) (yield 27, 17, and 7%, respectively) [2], the reaction carried out in the solvents mixture propionic acid–acetonitrile, 1 : 1, afforded com-

* For Communication XXXI, see [1].

† Deceased.

pounds **VIII** and **VII** (yield 54 and 5%).

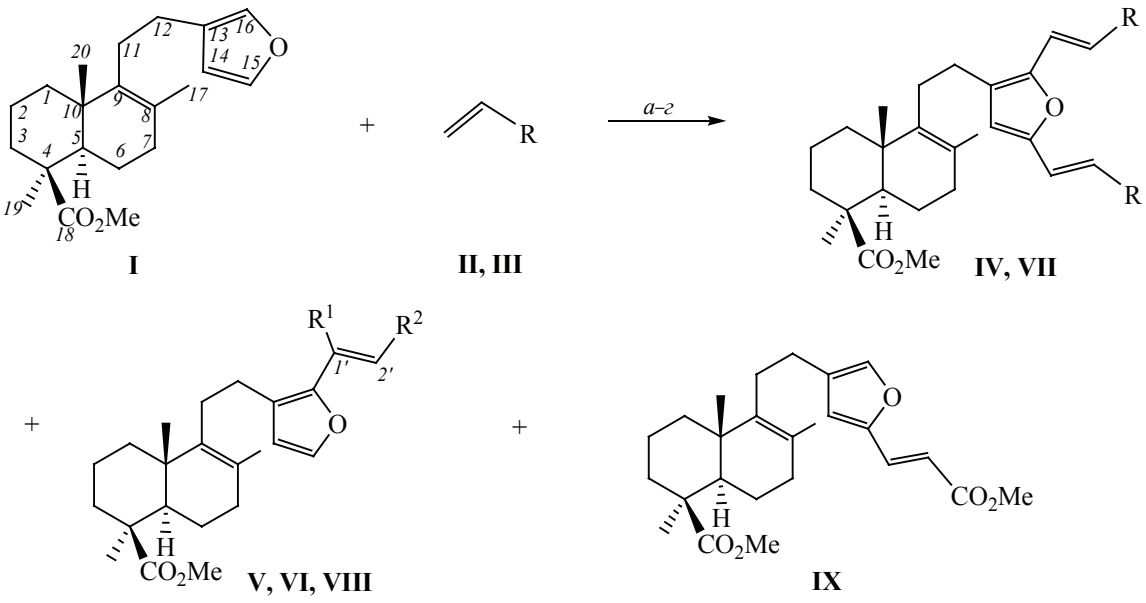
By an example of the reaction of furanolabdanoid **I** with methyl acrylate (**III**) we found the significant effect of the composition of the oxidative system on the products yield and the selectivity of the reaction. The reaction of compound **I** with 1 equiv of methyl acrylate (**III**) in the mixture of propionic acid and ether in an argon atmosphere in the presence of 0.05 equiv of $Pd(OAc)_2$, 2 equiv of $Cu(OAc)_2$, and 0.1 equiv of BQ resulted in the formation of the alkenyl derivatives **VII, VIII, IX** in the ratio 1 : 5 : 1. The replacement of the cosolvent (ethyl ether for acetonitrile) the regioselectivity of the reaction increased. Under the identical experimental conditions (40°*C,* 80 h) 18-methyl-16-(2-methoxycarbonylvinyl) labdatrienoate (**VIII**) was obtained as a single reaction product (yield 34% after the column chromatography; besides, 7% of initial compound **I** was isolated).

The oxidative coupling of compound **I** with phenyl acrylate (**X**), methyl vinyl ketone (**XI**), or phenyl vinyl ketone (**XII**) in the presence of 0.05 equiv of $Pd(OAc)_2$, 2 equiv of $Cu(OAc)_2$, and 0.1 equiv of BQ in propionic acid and acetonitrile, 1 : 1, (35°C, 80 h) led to the formation of 18-methyl-16-(*E*)-(2-R-carbonylvinyl)labdatrienoates **XIII–XV** in 29–54% yield (Scheme 2). Compound **XIV** was obtained previously [7] in a comparable yield (calculated with respect of two stages) by the formylation of methyl phlomisoate (**I**) followed by the condensation of 16-formyllabdatrienoate with acetone.

We explored the reaction of labdanoid **I** with acrylamides **XVI–XXI**. The corresponding 18-methyl-16-(*E*)-[3-(R-amino)-3-oxoprop-1-en-1-yl]labdatrienoates **XXIII–XXVII** were isolated as individual substances by column chromatography on silica gel. The maximum yield was obtained by the oxidative coupling of furanolabdanoid **I** with *N*-arylacrylamides **XVI, XVII**; the yield of compounds **XXII, XXIII** was 59 and 42%. In the reactions of diterpenoid **I** with amides prepared from the methyl esters of amino acids **XIX–XXI,** and also with *N*-acryloylmorpholine (**XXVIII**) the considerable decrease in the yield was observed of the products of 16-alkenylation **XXV–XXVII, XXIX (**16–25 and 8%). The replacement of the cosolvent in the reaction of compound **I** with amides **XIX–XXI** did not result in the increase of the overall yield of the reaction products.

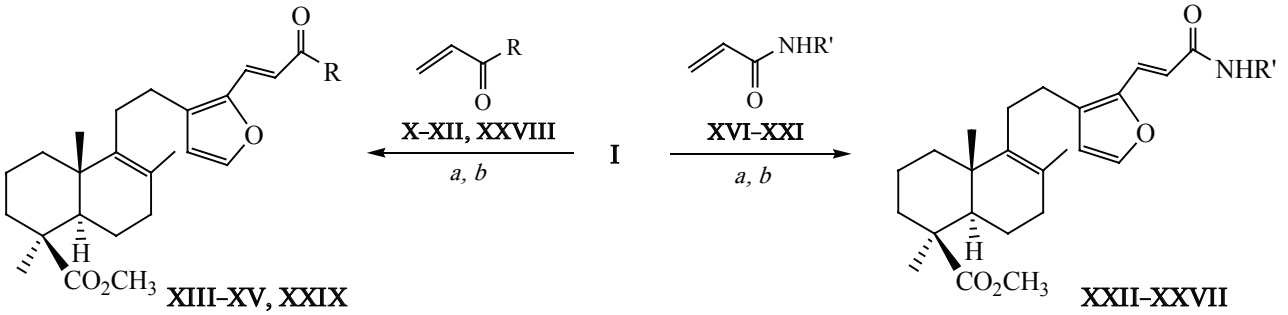
Taking into consideration valuable pharmacological properties of 2,5-dialkenylfurans [8, 9], we investigated the possibility of successive introducing vinyl groups into labdanoid derivatives with various alkenyl substituents. The reaction of 16-(2-methoxycarbonylvinyl)labdatrienoate (**VIII**) with styrene (**II**) in the presence of 0.1 equiv of

Scheme 1.



R = Ph (**II, IV**), CO_2Me (**III, VII**); R^1 = Ph, R^2 = H (**V**); R^1 = H, R^2 = Ph (**VI**), CO_2Me (**VIII**); *a*. $Pd(OAc)_2$, $Cu(OAc)_2$, BQ, O_2, $EtCO_2H–Et_2O$, 1 : 1; *b*. $Pd(OAc)_2$, $Cu(OAc)_2$, BQ, O_2, $EtCO_2H–MeCN$, 1 : 1; *c*. $Pd(OAc)_2$, $Cu(OAc)_2$, BQ, $EtCO_2H–Et_2O$, 1 : 1; *г*. $Pd(OAc)_2$, $Cu(OAc)_2$, BQ, $EtCO_2H–MeCN$, 1 : 1.

Scheme 2.

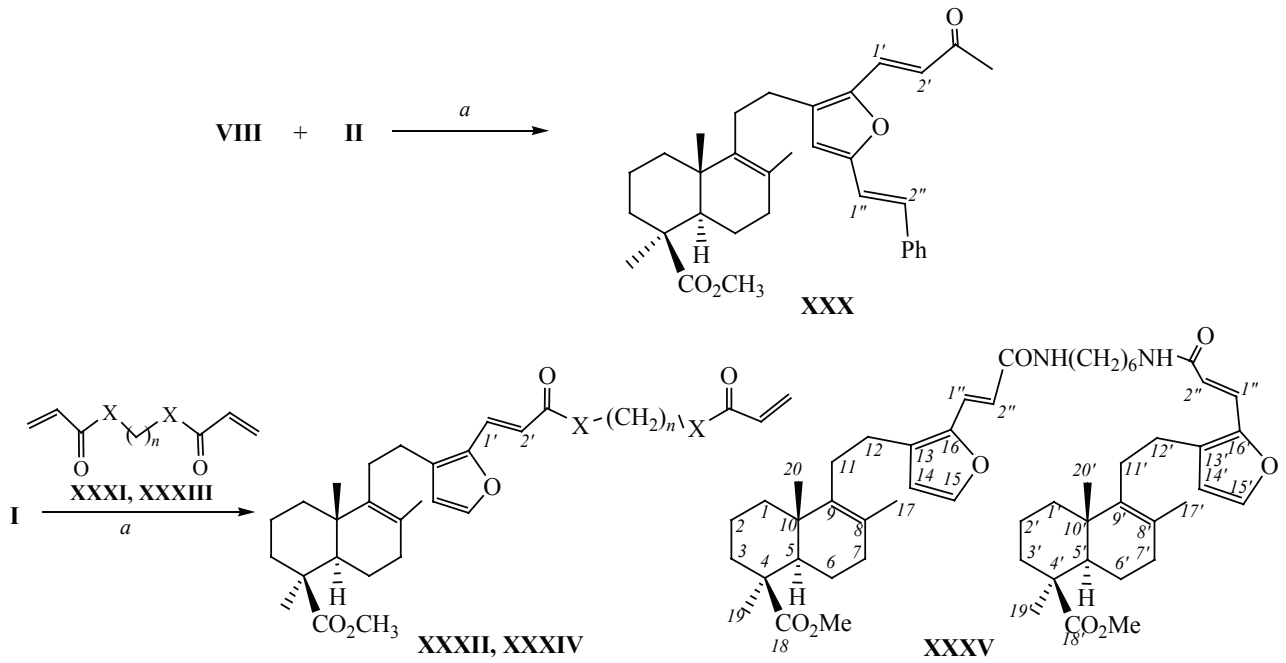


R = OPh (**X, XIII**), Me (**XI, XIV**), Ph (**XII, XV**), morpholin-4-yl (**XXVIII, XXIX**); R' = Ph (**XVI, XXII**), 4-MeC_6H_4 (**XVII, XXIII**), Bn (**XVIII, XXIV**), CH(Me)CO_2Me (**XIX, XXV**), CH(Ph)CH_2CO_2Me (**XX, XXVI**), CH(Et)CO_2Me (XXI, XXVII); *a*. $Pd(OAc)_2$, $Cu(OAc)_2$, BQ, $EtCO_2H$–MeCN, 35°C; *b*. $Pd(OAc)_2$, $Cu(OAc)_2$, BQ, O_2, $EtCO_2H$–Et_2O, 35°C.

$Pd(OAc)_2$, 0.5 equiv of $Cu(OAc)_2$, and 0.1 equiv of BQ in the mixture of propionic acid and ether, 1 : 1, (35°C, 80 h) in the atmosphere of O_2 furnished 15-styryl-16-(2-methoxycarbonylvinyl)labdatrienoate (**XXX**) (yield 10%) (Scheme 3). The conversion of compound **VIII** was 50%. As seen, the presence of an acceptor substituent in the position *2* of the furan ring imparts the subsequent introduction of a substituent into the position *5*.

The reaction of methyl phlomisoate (**I**) with 1 equiv of pentane-1,5-diyl diacrylate (**XXXI**) in the presence of 0.1 equiv of $Pd(OAc)_2$, 0.5 equiv of $Cu(OAc)_2$, and 0.1 equiv of BQ in the mixture of propionic acid and ether, 1 : 1, (35°C, 80 h) in the oxygen atmosphere led to the formation of monocoupling product **XXXII** isolated by column chromatography in 10% yield. The reaction of diterpenoid **I** with *N*,*N*′-hexane-1,6-diyl(bisacrylamide) (**XXXIII**) under similar conditions gave besides 16-acryloylamino derivative **(XXXIV)** (yield 26%) a coupling

Scheme 3.



X = O, *n* = 5 (**XXXI, XXXII**); X = NH, *n* = 6 (**XXXIII, XXXIV**); *a*. $Pd(OAc)_2$/BQ/$Cu(OAc)_2$/O_2, $EtCO_2H$/Et_2O, 35°C.

product by both double bonds **XXXV** (yield 2%).

The structure and composition of compounds synthesized were confirmed by IR, UV, NMR, and mass spectra and by elemental analysis. The introduction of alkenyl substituents into the furan ring of labdanoids **VI, XIII, XXII–XXIV, XXVII, XXX** results in the appearance in the UV spectra of two absorption bands with the maxima in the regions 236–285 and 307–334 nm.

^{1}H and ^{13}C NMR spectra of compounds **V, VI, XIII, XV, XXII–XXVII, XXIX, XXX, XXXII, XXXIV** are in complete agreement with their assumed structure and contain a single set of the characteristic signals of the furanolabdane scaffold and of the corresponding substituent. The position of substituents at the atom C^{16} in the monosubstituted labdanoids **V, VI, VIII, XIII–XV, XXII–XXVII, XXIX, XXXII, XXXIV, XXXV** is confirmed by the data of ^{1}H NMR spectra containing the proton signals of the furan ring [δ 6.31–6.42 ppm (H^{14}) and 7.31–7.40 ppm (H^{15}), *J* 1.6–1.9 Hz]. The presence of the (1-phenyl)vinyl substituent in the position C^{16} of compound **V** is indicated by the doublet signals of the protons of the terminal vinyl group H$^{2'A,2'B}$ (δ 5.44 and 5.51 ppm, *J* 1.1 Hz). These data unambiguously prove the regioselectivity of the reaction.

The protons of the double bond H$^{1',2'}$ in the ^{1}H NMR spectra of compounds **XIII–XV, XXII–XXVII, XXIX, XXXII, XXXIV,** and also the protons H$^{1'',2''}$ of compound **XXXV** appear as doublets in the region δ 7.35–7.55 and 6.20–6.68 ppm respectively. The value *J*(H$^{1'}$, H$^{2'}$) [*J*(H$^{1'',2''}$)] in the 16-substituted labdanoids equals 14.8–15.8 Hz indicating the *trans*-position of the protons. The protons of the double bond H$^{1',2'}$ in the spectrum of compound **VI** are observed at δ 7.00 and 6.91 ppm respectively (*J* 16.1 Hz). The characteristic features of the ^{1}H NMR spectrum of 13,15,16-substituted furanolabdanoid **XXX** are a singlet signal of the proton H^{14} (δ 6.39 ppm) and two pairs of doublet proton signals from the double bonds of 3-oxobut-1-ene [δ 6.66 m (H$^{2'}$), δ 7.30 ppm (H$^{1'}$), *J* 15.4 Hz] and styrene substituents [δ 6.83 (H$^{2''}$), δ 7.17 ppm (H$^{1''}$), *J* 16.4 Hz]. The reported data prove the (*E*)-configuration of the double bond C$^{1'}$=C$^{2'}$ in compounds **VI–IX, XIII–XV**, **XXII–XXVII, XXIX, XXXII, XXXIV** and C$^{1'}$=C$^{2'}$, C$^{1''}$=C$^{2''}$ in compounds **XXX, XXXV**. The relative simplicity of the ^{1}H and ^{13}C NMR spectra of compound **XXXV** containing a single set of proton and carbon signals of the labdane scaffold and the *trans*-double bond of the acrylamide substituent demonstrates the symmetry of the molecule. The ratio of the integral intensities of the protons of the hexane linker in the ^{1}H NMR spectrum and the proton signals of the 16-(*N*-alkenyl)furanolabdane fragment in the product of double coupling **XXXV** equals 1 : 2.

Hence based on the oxidative coupling of methyl phlomisoate with the activated alkenes we synthesized diverse 16-(*E*)-alkenyl-substituted furanolabdanoids. Performing the reaction in the presence of the catalytic system $Pd(OAc)_2/Cu(OAc)_2$/BQ and the application of acetonitrile as the cosolvent results in the increased regioselectivity of the reaction of methyl phlomisoate with methyl acrylate or styrene The largest yields of the oxidative coupling products were obtained in the reactions of the furanolabdanoid with vinyl ketones and acrylamides.

The interest to the development of methods of preparation furan derivatives containing alkenyl fragments in the positions *2* and *5* is due to the valuable biological properties of a number of inaccessible furan metabolites [10].

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometers Bruker AV-300 [operating frequencies 300.13 (^{1}H) and 75.47 MHz (^{13}C)], Bruker AV-400 [operating frequencies 400.13 (^{1}H) and 100.78 MHz (^{13}C)], Bruker AV-600 [operating frequencies 600.30 (^{1}H) and 150.96 MHz (^{13}C)] from solutions of compounds in $CDCl_3$, reference TMS. In the description of ^{1}H and ^{13}C NMR spectra the numeration of the labdane scaffold corresponds to that shown for structure **I**. The assignment of NMR signals was performed using various 2D proton-proton and proton-carbon correlation spectra (COSY, COXH, COLOC). The multiplicity of signals in the ^{13}C NMR spectra was established by registering spectra in the *J* modulation mode.

Recording of mass spectra, the determination of the molecular mass and elemental composition of compounds was carried out using high-resolution mass spectrometer DFS Thermo Scientific (EI 70 eV, vaporizer temperature 230–280°C). Elemental analysis was performed on a CHN-analyzer Carlo Erba 1106.

The values of specific rotation $[\alpha]_D^{20}$ were measured on a polarimeter poLAAr 3005 at room temperature (20–23°C). IR spectra were recorded on a spectrophotometer Vector-22 from pellets with KBr. UV absorption spectra were taken on a spectrophotometer HP 8453 UV Vis in ethanol (c 10^{-4} mol L^{-1}).

The monitoring of the reaction progress and checking the purity of compounds obtained was performed by TLC on Silufol UV-254 plates, eluents: chloroform–ethanol, 3 : 1; petroleum ether–ethyl acetate, 10 : 1. The spots visualization was carried out by spraying on the plates 10% aqueous H_2SO_4 followed by heating to 100°C or by UV irradiation.

Methyl phlomisoate (**I**) was obtained by procedure [11], $Pd(OAc)_2$, by method [12]. Commercially availably reagents styrene (**II**), methyl acrylate **(III)**, and methyl vinyl ketone (**XI**) were used in the study without additional purification. Phenyl acrylate (**X**) [13], vinyl phenyl ketone (**XII**) [14], *N*,*N*′-(hexane-1,6-diyl)bisacrylamide (**XXXIII**) [15] were prepared by known procedures. The physicochemical characteristics of *N*,*N*′-(hexane-1,6-diyl)bisacrylamide (**XXXIII**) were consistent with the published data [16].

Amides XVI–XXI, XXVIII and pentane-1,5-diyl diacrylate (XXXI). General procedure. To a solution of 10.0 mmol of amine (pentane-1,5-diol) and 15.0 mmol of acryloyl chloride in 20 mL of dichloromethane at 0°C under an argon atmosphere was added dropwise while stirring 30.0 mmol of triethylamine in 10 mL of dichloromethane. The reaction mixture was warmed to room temperature and stirred for 6 h. The solvent was removed in a vacuum, the residue was diluted with 20 mL of ether, the precipitated salt $Et_3N{\cdot}HCl$ was filtered off. The mother liquor was evaporated in a vacuum, as the residue were obtained the corresponding amides **XVI–XXI, XXVIII** or pentane-1,5-diyl diacrylate (**XXXI**) in 60–90% yields. The physicochemical constants of anilide of acrylic acid **(XVI)**, *N*-(*p*-tolyl)acrylamide **(XVII)**, *N*-benzylacrylamide **(XVIII),** methyl 2-(acryloylaminopropanoate **(XIX),** 4-acryloylmorpholine (XXVIII), and pentane-1,5-diyl diacrylate (**XXXI**) are published in [16–21].

Methyl 3-acryloylamino-3-phenylpropanoate (XX). Oily substance. ^{1}H NMR spectrum, δ, ppm: 2.81 d.d (1H, CH_2, *J* 15.9, 5.9 Hz), 2.92 d.d (1H, CH_2, *J* 15.9, 5.9 Hz), 3.55 s (3H, OCH_3), 5.46 t (1H, CH, *J* 5.9 Hz), 5.59 d.d (1H, CH_2=, *J* 10.2, 1.6 Hz), 6.11 d.d (1H, CH=, *J* 16.9, 10.2 Hz), 6.24 d.d (1H, CH_2=, *J* 16.9, 1.6 Hz), 7.22 m, 7.26 m (5H, Ph).

Methyl 2-acryloylaminobutanoate (XXI). Oily substance. ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, *J* 7.3 Hz), 1.72 m, 1.89 m (2H, CH_2), 3.71 s (3H, OCH_3), 4.61 m (1H, CH), 5.63 d.d (1H, CH_2=, *J* 10.0, 1.6 Hz), 6.14 d.d (1H, CH=, *J* 17.1, 10.0 Hz), 6.27 d.d (1H, CH_2=, *J* 17.1, 1.6 Hz).

Reaction of methyl phlomisoate with styrene. *a.* To a solution of 1.00 g (3.03 mmol) of methyl phlomisoate **(I)** in a mixture of 4 mL of propionic acid and 4 mL of acetonitrile while stirring was added in succession 0.35 mL (3.03 mmol) of styrene (**II**), 0.046 g (0.15 mmol) of $Pd(OAc)_2$, 0.275 g (1.51 mmol) of $Cu(OAc)_2$, and 0.03 g (0.30 mmol) of 1,4-benzoquinone. The reaction mixture was stirred in an oxygen flow at 35°C for 10 h, then it was cooled and poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 40mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 10 : 1). The elution provided in succession 0.29 g (22%) of a mixture of methyl esters of **16-(1-phenylvinyl)-** (**V**) and **16-[(*E*)-styryl]-15,16-epoxy-8(9),13(16),14-labdatrien-18-oic acids** (**VI**) in a ratio 4.5 : 1 as showed ^{1}H NMR data (fraction 1), and 0.065 g (4%) of **methyl 15,16-bis[(*E*)-styryl]-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate** (**IV**). The repeated chromatography of the fraction 1 on a column with silica gel afforded **methyl (1S,4aS,8aR)-5-(2-{2-[(*E*)-styryl]-furan-3-yl}ethyl)-1,4a,6-trimethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate {methyl 16-[(*E*)-styryl)]-15,16-epoxy-8(9),13(16),14-labdatrie-18-oate}** (**VI**), oily substance. IR spectrum, cm^{-1}: 3433, 2955, 2932, 2873, 1723, 1602, 1459, 1381, 1235, 1153, 974, 956, 847, 753, 694. UV spectrum, λ_{max}, nm (logε): 285 (3.95), 334 (3.78). ^{1}H NMR spectrum, δ, ppm: 0.80 s (3H, $C^{20}H_3$), 1.06 d.t (1H, H^3, *J* 13.7, 4.2 Hz), 1.23 s (3H, $C^{19}H_3$), 1.28 m (1H, H^1), 1.38 d.d (1H, H^5, *J* 12.7, 1.7 Hz), 1.59 m (1H, H^2), 1.70 s (3H, $C^{17}H_3$), 1.75 d.d (1H, H^6, *J* 12.7, 6.8 Hz), 1.80–1.92 m (1H, H^2), 1.94–2.01 m (3H, $H^{1,7,6}$), 2.04–2.14 m (2H, $H^{7,11}$), 2.22–2.29 m (2H, $H^{3,11}$), 2.55 m (2H, $H^{12,12}$), 3.64 s (3H, OCH_3), 6.35 d (1H, H^{14}, *J* 1.7 Hz), 6.91 d (1H, $H^{2'}$, *J* 16.1 Hz), 7.00 d (1H, $H^{1'}$, *J* 16.1 Hz), 7.23 t.m (1H, $H^{4''}$, *J* 7.6 Hz), 7.34 t (3H, H^{15}, $H^{3'',5''}$, *J* 7.6 Hz), 7.49 d.d (2H, $H^{2'',6''}$, *J* 7.6, 1.2 Hz). ^{13}C NMR spectrum, δ, ppm: 17.69 q (C^{20}), 19.55 t (C^2), 19.82 q (C^{17}), 20.75 t (C^6), 25.58 t (C^{12}), 28.36 q (C^{19}), 29.27 t (C^{11}), 34.21 t (C^7), 37.23 t (C^1), 37.64 t (C^3), 39.54 s (C^{10}), 43.82 s (C^4), 51.03 q (OCH_3), 53.43 d (C^5), 112.55 d (C^{14}), 114.51 d ($C^{1'}$), 124.09 s (C^{13}), 125.42 d ($C^{2'}$), 125.99 d ($C^{6'',2''}$), 127.17 d ($C^{4''}$), 127.49 s (C^8), 127.31 d ($C^{3''}$), 128.59 d ($C^{5''}$), 137.34 s ($C^{1''}$), 138.51 s (C^9), 141.47 d (C^{15}),

148.17 s (C^{16}), 177.96 s (C^{18}). Found, %: C 80.22; H 8.65. $C_{29}H_{36}O_3$. Calculated, %: C 80.52; H 8.39.

Methyl (1*S*,4a*S*,8a*R*)-5-{2-[2-(1-phenylvinyl) furan-3-yl]ethyl}-1,4a,6-trimethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate (V) we failed to isolate as individual substance due to its instability during chromatographic separation. ^{1}H NMR spectrum of compound **V** (extracted from the spectrum of the mixture of compounds **V** and **VI**), δ, ppm: 0.80 s (3H, $C^{20}H_3$), 1.06 d.t (1H, H^3, *J* 13.7, 4.2 Hz), 1.23 s (3H, $C^{19}H_3$), 1.28 m (1H, H^1), 1.38 d.d (1H, H^5, *J* 12.7, 1.7 Hz), 1.59 m (1H, H^2), 1.69 s (3H, $C^{17}H_3$), 1.75 d.d (1H, H^6, *J* 12.7, 6.8 Hz), 1.80–1.92 m (1H, H^2), 1.94–2.01 m (3H, $H^{1,7,6}$), 2.04–2.14 m (2H, $H^{7,11}$), 2.22–2.29 m (2H, $H^{3,11}$), 2.55 m (2H, $H^{12,12}$), 3.62 s (3H, OCH_3), 5.44 d (1H, $H^{2'A}$, *J* 1.1 Hz), 5.51 d (1H, $H^{2'B}$, *J* 1.1 Hz), 6.38 d (1H, H^{14}, *J* 1.6 Hz), 7.23 t.m (1H, $H^{4''}$, *J* 7.6 Hz), 7.34 m (3H, H^{15}, $H^{3'',5''}$, *J* 7.6 Hz), 7.49 d.d (2H, $H^{2'',6''}$, *J* 7.6, 1.2 Hz).

b. To a solution of 1.00 g (3.03 mmol) of methyl phlomisoate **(I)** in a mixture of 4 mL of propionic acid and 4 mL of DMF while stirring was added in succession 0.35 mL (3.03 mmol) of styrene (**II**), 0.046 g (0.15 mmol) of $Pd(OAc)_2$, 0.275 g (1.51 mmol) of $Cu(OAc)_2$, and 0.03 g (0.30 mmol) of 1,4-benzoquinone. The reaction mixture was stirred in an oxygen flow at 35°C for 10 h, then it was cooled and poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 40mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 10 : 1). The successive elution afforded 0.09 g (7%) of compound **VI** and 0.08 g (5%) of compound **IV**.

Reaction of methyl phlomisoate with methyl acrylate. *a*. To a solution of 2.00 g (6.06 mmol) of methyl phlomisoate (**I**) in a mixture of 8 mL of propionic acid and 8 mL of acetonitrile while stirring was added in succession 0.56 mL (6.06 mmol) of methyl acrylate (**III**), 0.09 g (0.30 mmol) of $Pd(OAc)_2$, 0.50 g (3.03 mmol) of $Cu(OAc)_2$, and 0.07 g (0.60 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an oxygen atmosphere at 40°C for 80 h, it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 4 : 1). The successive elution afforded 1.08 g (54%) of methyl esters of **16-(3-methoxy-3-oxoprop-1-yl)- (VIII)** and 0.45 g (5%) of **15,16-bis(3-methoxy-3-oxoprop-1-en-1-yl)-15,16-epoxy-8(9),13(16),14-labdatrien-18-oic VII) acids**.

b. To a solution of 2.00 g (6.06 mmol) of methyl phlomisoate **(I)** in a mixture of 8 mL of propionic acid and 8 mL of ethyl ether while stirring was added in succession 0.56 mL (6.06 mmol) of methyl acrylate (**III**), 0.09 g (0.30 mmol) of $Pd(OAc)_2$, 2.20 g (12.1 mmol) of $Cu(OAc)_2$, and 0.07 g (0.60 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue consisted of a mixture of compounds **VII, VIII**, and **IX** in a ratio 1 : 5 : 1.

c. To a solution of 2.00 g (6.06 mmol) methyl phlomisoate **(I)** in a mixture of 8 mL of propionic acid and 8 mL of acetonitrile while stirring was added in succession 0.56 mL (6.06 mmol) of methyl acrylate (**III**), 0.09 g (0.30 mmol) of $Pd(OAc)_2$, 2.20 g (12.1 mmol) of $Cu(OAc)_2$, and 0.07 g (0.60 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 4 : 1). The successive elution afforded 0.13 g (7%) of initial diterpenoid **I** and 0.68 g (34%) of compound **VIII.**

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-(2-{2-[(E)-3-oxo-3-phenoxyprop-1-en-1-yl]furan-3-yl}-ethyl)-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate [methyl 16-(3-oxo-3-phenoxyprop-1-en-1-yl)-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate] (XIII). To a solution of 0.50 g (1.52 mmol) of methyl phlomisoate **(I)** in a mixture of 2 mL of propionic acid and 2 mL of acetonitrile while stirring was added in succession 0.22 g (1.52 mmol) of phenyl acrylate (**X**), 0.02 g (0.08 mmol) of $Pd(OAc)_2$, 0.55 g (3.03 mmol) of $Cu(OAc)_2$, and 0.016 g (0.15 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, on cooling it was poured into 30 mL of

water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1 : 1). The successive elution afforded 0.18 g (36%) of initial diterpenoid **I** and 0.18 g (29%) of compound **XIII**. Oily substance, $[\alpha]_D^{27}$ +42.51° (*c* 0.89, $CHCl_3$). IR spectrum, cm^{-1}: 3525, 2947, 2862, 1705, 1633, 1459, 1434, 1351, 1256, 1194, 1152, 1117, 1102, 1087, 1063, 1011, 617. UV spectrum, λ_{max}, nm (logε): 250 (3.83), 332 (3.88). ^{1}H NMR spectrum, δ, ppm: 0.77 s (3H, $C^{20}H_3$), 1.02 d.t (1H, H^3, *J* 13.5, 4.3 Hz), 1.20 c (3H, $C^{19}H_3$), 1.25 m (1H, H^1), 1.34 d.d (1H, H^5, *J* 12.4, 1.6 Hz), 1.55 m (1H, H^2), 1.64 s (3H, $C^{17}H_3$), 1.74 d.t (1H, H^6, *J* 12.4, 5.6 Hz), 1.87 m (1H, H^2), 1.90 m, 1.94 m, 1.98 m (3H, $H^{1,6,7}$), 2.05–2.14 m (2H, $H^{7,11}$), 2.22 m (2H, $H^{3,11}$), 2.58 m (2H, $H^{12,12}$), 3.62 s (3H, OCH_3), 6.42 d (1H, H^{14}, *J* 1.8 Hz), 6.44 d (1H, $H^{2'}$, *J* 15.6 Hz), 7.14 m (2H, $H^{2'',6''}$), 7.24 m (1H, $H^{4''}$), 7.38 m (4H, $H^{3'',5''}$, $H^{15,1'}$). ^{13}C NMR spectrum, δ, ppm: 17.19 q (C^{20}), 18.96 t (C^2), 19.31 q (C^{17}), 20.19 t (C^6), 25.14 t (C^{12}), 27.81 q (C^{19}), 28.48 t (C^{11}), 33.70 t (C^7), 36.70 t (C^1), 37.06 t (C^3), 38.99 c (C^{10}), 43.28 s (C^4), 50.50 q (OCH_3), 52.83 d (C^5), 112.33 d (C^{14}), 112.74 d ($C^{2'}$), 120.92 d, 120.97 d ($C^{2'',6''}$), 125.02 d ($C^{1'}$), 125.25 d ($C^{4''}$), 128.77 d, 128.86 d ($C^{3'',5''}$), 127.48 s (C^8), 131.48 s (C^{13}), 137.63 s (C^9), 144.20 d (C^{15}), 145.82 s (C^{16}), 150.14 s ($C^{1''}$), 170.54 s (CO), 177.44 s (C^{18}). Found, %: C 76.51; H 7.41. $C_{30}H_{36}O_5$. Calculated, %: C 75.60; H 7.61.

Methyl (1*S*,4a*S*,8aR)-1,4a,6-trimethyl-5-(2-{2-[(*E*)-3-oxobut-1-en-1-yl]furan-3-yl}ethyl)-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate [methyl 16-(3-oxobut-1-en-1-yl)-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate] (XIV). To a solution of 1.00 g (3.03 mmol) of methyl phlomisoate **(I)** in a mixture of 4 mL of propionic acid and 4 mL of acetonitrile while stirring was added in succession 0.6 mL (3.03 mmol) of methyl vinyl ketone (**XI**), 0.05 g (0.15 mmol) of $Pd(OAc)_2$, 1.10 g (6.06 mmol) of $Cu(OAc)_2$, and 0.033 g (0.30 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an oxygen atmosphere at 40°C for 80 h, it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 4 : 1). Yield 0.68 g (54%). Oily substance, $[\alpha]_D^{20}$ +60.7° (*c* 0.34, $CHCl_3$). Found %: C 75.76; H 8.53. $C_{25}H_{34}O_4$. Calculated %: C 75.34; H 8.60. The data of IR, UV, and NMR spectra were analogous to the data published in [7].

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-(2-{2-[(*E*)-3-oxo-3-phenylprop-1-en-1-yl]furan-3-yl}-ethyl)-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate [methyl 16-(3-oxo-3-phenylprop-1-en-1-yl)-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate] (XV). To a solution of 0.50 g (1.52 mmol) of methyl phlomisoate **(I)** in a mixture of 2 mL of propionic acid and 2 mL of acetonitrile while stirring was added in succession 0.25 g (1.75 mmol) of vinyl phenyl ketone (**XII**), 0.03 g (0.09 mmol) of $Pd(OAc)_2$, 0.83 g (3.5 mmol) of $Cu(OAc)_2$, and 0.035 g (0.3 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1 : 1). Yield 0.22 g (44%). Oily substance, $[\alpha]_D^{20}$ +23.67° (*c* 0.54, $CHCl_3$). IR spectrum, cm^{-1}: 3300, 2953, 1724, 1663, 1460, 1370, 1236, 1138, 1021, 969, 889, 758, 656. ^{1}H NMR spectrum, δ, ppm: 0.77 s (3H, $C^{20}H_3$), 1.04 d.t (1H, H^3, *J* 13.2, 4.3 Hz), 1.21 s (3H, $C^{19}H_3$), 1.24 m (1H, H^1), 1.35 d.d (1H, H^5, *J* 13.2, 1.7 Hz), 1.55 m (1H, H^2), 1.64 s (3H, $C^{17}H_3$), 1.74 d.t (1H, H^6, *J* 13.2, 5.6 Hz), 1.86 m, 1.92 m, 1.99 m (4H, $H^{1,6,7,2}$), 2.03–2.15 m (2H, $H^{7,11}$), 2.21 m (2H, $H^{3,11}$), 2.60 m (2H, $H^{12,12}$), 3.62 s (3H, OCH_3), 6.34 d (1H, H^{14}, *J* 1.7 Hz), 6.60 d (1H, $H^{2'}$, *J* 15.2 Hz), 7.38 d (1H, H^{15}, *J* 1.7 Hz), 7.44–7.50 m (2H, $H^{3'',5''}$), 7.55 m (1H, $H^{4''}$), 7.65 d (1H, $H^{1'}$, *J* 15.2 Hz), 7.95 m (2H, $H^{2'',6''}$). ^{13}C NMR spectrum, δ, ppm: 17.58 q (C^{20}), 19.35 t (C^2), 19.71 q (C^{17}), 20.57 t (C^6), 25.58 t (C^{12}), 28.19 q (C^{19}), 28.85 t (C^{11}), 34.05 t (C^7), 37.16 t (C^1), 37.43 t (C^3), 39.34 s (C^{10}), 43.64 s (C^4), 50.85 q (OCH_3), 53.17 d (C^5), 113.36 d (C^{14}), 117.42 d ($C^{2'}$), 127.82 d, 128.10 d, 128.37 d, 128.42 d ($C^{2'',6'',3'',5''}$), 132.54 s (C^8), 132.34 d ($C^{1'}$), 133.13 d ($C^{4''}$), 136.37 s (C^{13}), 137.97 s ($C^{1''}$), 138.11 s (C^9), 144.29 d (C^{15}), 147.10 s (C^{16}), 177.75 s (C^{18}), 189.51 s (CO). Found, %: C 77.89; H 8.04. $C_{30}H_{36}O_4$. Calculated, %: C 78.23; H 7.88.

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-(2-{2-[(*E*)-3-oxo-3-(phenylamino)prop-1-en-1-yl]furan-

3-yl}ethyl)-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate [methyl (*E*)-16-[3-oxo-3-(phenylamino)prop-1-en-1-yl]-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate] (XXII). To a solution of 1.00 g (3.03 mmol) of methyl phlomisoate **(I)** in a mixture of 4 mL of propionic acid and 4 mL of acetonitrile while stirring was added in succession 0.52 g (3.5 mmol) of acrylic acid anilide **(XVI)**, 0.05 g (0.18 mmol) of $Pd(OAc)_2$, 1.60 g (7.00 mmol) of $Cu(OAc)_2$, and 0.004 g (0.04 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1 : 1). Yield 0.59 g (59%). Oily substance, $[\alpha]_D^{20}$ +22.97° (*c* 0.93, $CHCl_3$). IR spectrum, cm^{-1}: 3379, 2922, 1725, 1657, 1626, 1537, 1460, 1436, 1380, 1330, 1235, 1188, 1142, 1031, 972, 691. UV spectrum, λ_{max}, nm (logε): 245 (4.07), 307 (4.53). ^1H NMR spectrum, δ, ppm: 0.75 s (3H, $C^{20}H_3$), 1.03 d.t (1H, H^3, *J* 13.5, 4.4 Hz), 1.20 s (3H, $C^{19}H_3$), 1.25 m (1H, H^1), 1.34 d (1H, H^5, *J* 11.4 Hz), 1.54 m (1H, H^2), 1.62 s (3H, $C^{17}H_3$), 1.71 d.t (1H, H^6, *J* 11.4, 5.0 Hz), 1.85 m (1H, H^2), 1.88–1.97 m (3H, $H^{1,6,7}$), 2.04 m, 2.10 m (2H, $H^{7,11}$), 2.18 m, 2.22 m (2H, $H^{3,11}$), 2.53 m (2H, $H^{12,12}$), 3.61 s (3H, OCH_3), 6.37 d (1H, H^{14}, *J* 1.8 Hz), 6.43 d (1H, $H^{2'}$, *J* 15.2 Hz), 7.08 t (1H, $H^{4''}$, *J* 7.9 Hz), 7.30 t (2H, $H^{3'',5''}$, *J* 7.9 Hz), 7.32 d (1H, H^{15}, *J* 1.8 Hz), 7.55 d (1H, $H^{1'}$, *J* 15.2 Hz), 7.61 d (2H, $H^{2'',6''}$, *J* 7.9 Hz). ^{13}C NMR spectrum, δ, ppm: 17.62 q (C^{20}), 19.42 t (C^2), 19.75 q (C^{17}), 20.65 t (C^6), 25.41 t (C^{12}), 28.26 q (C^{19}), 28.82 t (C^{11}), 34.13 t (C^7), 37.08 t (C^1), 37.50 t (C^3), 39.39 s (C^{10}), 43.75 s (C^4), 50.96 q (OCH_3), 53.28 d (C^5), 112.91 d (C^{14}), 119.80 d ($C^{2'}$), 123.93 d ($C^{1'}$), 126.63 s (C^8), 127.74 d ($C^{6'',2''}$), 128.75 d ($C^{3'',5'',4''}$), 130.15 s ($C^{1''}$), 138.10* s (C^{13}), 138.24* s (C^9), 143.49 d (C^{15}), 146.68 s (C^{16}), 165.29 s (CONH), 178.04 s (C^{18}). Found, %: C 76.07; H 7.83; N 2.78. $C_{30}H_{37}NO_4$. Calculated, %: C 75.76; H 7.84; N 2.94.

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-(2-{2-[(*E*)-3-oxo-3-(*p*-tolylamino)prop-1-en-1-yl]furan-3-yl}ethyl)-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate [methyl (*E*)-16-[3-(*p*-tolylamino)-3-oxoprop-1-en-1-yl]-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate] (XXIII). To a solution of 0.50 g (1.52 mmol) of methyl phlomisoate **(I)** in a mixture of 2 mL of propionic acid and 2 mL of acetonitrile while stirring was added in succession 0.162 g (1.75 mmol) N-(*p*-tolyl)acrylamide **(XVII)**, 0.03 g (0.09 mmol) of $Pd(OAc)_2$, 0.83 g (3.5 mmol) of $Cu(OAc)_2$, and 0.018 g (0.15 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1:1). Yield 0.25 g (42%). Oily substance, $[\alpha]_D^{20}$ +12.75° (*c* 0.53, $CHCl_3$). UV spectrum, λ_{max}, nm (logε): 249 (3.97), 327 (4.41). IR spectrum, ν, cm^{-1}: 3401, 2944, 2837, 1771, 1728, 1663, 1605, 1541, 1439, 1405, 1375, 1325, 1245, 1037, 972, 815, 736. ^1H NMR spectrum, δ, ppm: 0.75 s (3H, $C^{20}H_3$), 1.03 d.t (1H, H^3, *J* 13.0, 4.3 Hz), 1.20 s (3H, $C^{19}H_3$), 1.24 m (1H, H^1), 1.34 d.d (1H, H^5, *J* 12.4, 1.6 Hz), 1.56 m (1H, H^2), 1.63 s (3H, $C^{17}H_3$), 1.71 m (1H, H^6), 1.86 m (1H, H^2), 1.88 m, 1.93 m, 1.97 m (3H, $H^{1,6,7}$), 1.99–2.11 m (2H, $H^{7,11}$), 2.20 d (1H, H^3, *J* 13.0 Hz), 2.20 m (1H, H^{11}), 2.30 s (3H, CH_3), 2.54 m (2H, $H^{12,12}$), 3.62 s (3H, OCH_3), 6.38 d (1H, $H^{2'}$, *J* 15.1 Hz), 6.38 d (1H, H^{14}, *J* 1.6 Hz), 7.11 d (2H, $H^{2'',6''}$, *J* 8.3 Hz), 7.35 d (1H, H^{15}, *J* 1.6 Hz), 7.48 d (2H, $H^{3'',5''}$, *J* 8.3 Hz), 7.54 d (1H, $H^{1'}$, *J* 15.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.67 q (C^{20}), 19.47 t (C^2), 19.85 q (CH_3), 20.70 t (C^6), 20.78 q (C^{17}), 25.50 t (C^{12}), 28.33 q (C^{19}), 28.89 t (C^{11}), 34.19 t (C^7), 37.14 t (C^1), 37.56 t (C^3), 39.46 s (C^{10}), 43.78 s (C^4), 51.01 q (OCH_3), 53.33 d (C^5), 113.00 d (C^{14}), 119.66 d ($C^{2'}$), 126.61 d ($C^{1'}$), 127.81 s (C^8), 138.18 s (C^{13}), 138.71 s (C^9), 129.38 d ($C^{2'',6''}$), 129.62 d ($C^{3'',5''}$), 130.16 s ($C^{4''}$), 133.65 s ($C^{1''}$), 143.54 d (C^{15}), 146.69 s (C^{16}), 163.94 s (CONH), 178.00 s (C^{18}). Found, %: C 75.92; H 7.94; N 2.81. $C_{31}H_{39}NO_4$. Calculated, %: C 76.04; H 8.03; N 2.86.

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-(2-{2-[(*E*)-3-(benzylamino)-3-oxoprop-1-en-1-yl]-furan-3-yl}ethyl)-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate {methyl 16-[3-(benzylamino)-3-oxoprop-1-en-1-yl]-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate} (XXIV). To a solution of 1.00 g (3.03 mmol) of methyl phlomisoate **(I)** in a mixture of 4 mL of propionic acid and 4 mL of acetonitrile while stirring was added in succession 0.48 g (3.5 mmol) of *N*-benzylacrylamide **(XVIII)**, 0.05 g (0.18 mmol) of $Pd(OAc)_2$, 1.60 g

(7.00 mmol) $Cu(OAc)_2$, and 0.035 g (0.3 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1 : 1). Yield 0.30 g (30%). Oily substance, $[\alpha]_D^{20}$ +37.48° (*c* 0.95, $CHCl_3$). IR spectrum, cm^{-1}: 3379, 2926, 1728, 1602, 1537, 1447, 1377, 1330, 1241, 1194, 1161, 1041, 975, 767, 692. UV spectrum, λ_{max}, nm (logε): 243 (4.33), 325 (4.36). ^1H NMR spectrum, δ, ppm: 0.83 s (3H, $C^{20}H_3$), 0.98 d.t (1H, H^3, *J* 13.3, 4.4 Hz), 1.16 s (3H, $C^{19}H_3$), 1.25 m (1H, H^1), 1.35 m (1H, H^5), 1.54 m (1H, H^2), 1.59 s (3H, $C^{17}H_3$), 1.67 m (1H, H^6), 1.81 m (1H, H^2), 1.88 m, 1.92 m, 1.94 m (3H, $H^{1,6,7}$), 1.97–2.08 m (2H, $H^{7,11}$), 2.14 m, 2.18 m (2H, $H^{3,11}$), 2.49 m (2H, $H^{12,12}$), 3.57 s (3H, OCH_3), 4.49 d (2H, CH_2, *J* 5.9 Hz), 6.08 t (1H, NH, *J* 5.9 Hz), 6.23 d (1H, $H^{2'}$, *J* 15.2 Hz), 6.32 d (1H, H^{14}, *J* 1.8 Hz), 7.22–7.36 m (6H, H^{15}, Ph), 7.45 d (1H, $H^{1'}$, *J* 15.2 Hz). ^{13}C NMR spectrum, δ, ppm: 17.65 q (C^{20}), 19.43 t (C^2), 19.80 q (C^{17}), 20.68 t (C^6), 25.44 t (C^{12}), 28.29 q (C^{19}), 28.87 t (C^{11}), 31.79 t (CH_2), 34.18 t (C^7), 37.14 t (C^1), 37.55 t (C^3), 39.44 s (C^{10}), 43.69 s (C^4), 50.97 q (OCH_3), 53.33 d (C^5), 112.87 d (C^{14}), 116.31 d ($C^{2'}$), 126.18 d ($C^{1'}$), 127.32 s (C^8), 127.70 d ($C^{6'',2''}$), 128.53 d ($C^{3'',5'',4''}$), 129.69 s (C^{13}), 138.20 s ($C^{9,1''}$), 143.31 d (C^{15}), 146.62 s (C^{16}), 166.06 s (CONH), 178.00 s (C^{18}). Found, %: C 76.25; H 7.89; N 2.97. $C_{31}H_{39}NO_4$. Calculated, %: C 76.04; H 8.03; N 2.86.

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-[2-(2-{(1*E*)-3-[(4-methoxy-4-oxobutan-2-yl)amino]-3-oxoprop-1-en-1-yl}furan-3-yl)ethyl]-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate (XXV). To a solution of 0.50 g (1.52 mmol) of methyl phlomisoate **(I)** in a mixture of 2 mL of propionic acid and 2 mL of acetonitrile while stirring was added in succession 0.20 g (1.75 mmol) of methyl 2-acryloylaminopropanoate **(XIX),** 0.03 g (0.09 mmol) of $Pd(OAc)_2$**,** 0.83 g (3.5 mmol) of $Cu(OAc)_2$, and 0.018 g (0.15 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1 : 1). The successive elution afforded 0.32 g (64%) of initial diterpenoid **I** and 0.1 g (20%) of compound **XXV**. Oily substance**,** $[\alpha]_D^{20}$ +21.53° **(***c* 0.89, $CHCl_3$). IR spectrum, cm^{-1}: 3435, 2986, 1765, 1632, 1455, 1368, 1228, 1043, 926, 809, 751. ^1H NMR spectrum, δ, ppm: 0.75 s (3H, $C^{20}H_3$), 1.02 d.t (1H, H^3, *J* 13.2, 4.3 Hz), 1.20 s (3H, $C^{19}H_3$), 1.25 m (1H, H^1), 1.33 d.d (1H, H^5, *J* 12.1, 1.4 Hz), 1.45 d (3H, CH_3, *J* 7.3 Hz), 1.52–1.58 m (1H, H^2), 1.63 s (3H, $C^{17}H_3$), 1.73 d.t (1H, H^6, *J* 12.1, 5.7 Hz), 1.85 m (1H, H^2), 1.88 m, 1.89 m, 1.97 m (3H, $H^{1,6,7}$), 2.00–2.10 m (2H, $H^{7,11}$), 2.18 m, 2.21 m (2H, $H^{3,11}$), 2.52 m (2H, $H^{12,12}$), 3.61 s (3H, OCH_3), 3.76 s (3H, CO_2CH_3), 4.71 m (1H, CH), 6.13 d (1H, NH, *J* 7.5 Hz), 6.21 d (1H, $H^{2'}$, *J* 15.1 Hz), 6.37 d (1H, H^{14}, *J* 1.9 Hz), 7.35 d (1H, H^{15}, *J* 1.9 Hz), 7.44 d (1H, $H^{1'}$, *J* 15.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.36 q (C^{20}), 18.25 q (CH_3), 19.14 t (C^2), 19.49 q (C^{17}), 20.37 t (C^6), 25.16 t (C^{12}), 28.00 q (C^{19}), 29.25 t (C^{11}), 33.88 t (C^7), 36.86 t (C^1), 37.25 t (C^3), 39.15 s (C^{10}), 43.47 s (C^4), 47.65 d (CH), 50.65 q (OCH_3), 52.06 q ($CO_2\underline{CH_3}$), 53.03 d (C^5), 112.59 d (C^{14}), 115.62 d ($C^{2'}$), 126.10 d ($C^{1'}$), 127.45 s (C^{13}), 129.62 s (C^8), 137.93 s (C^9), 143.16 s (C^{16}), 146.22 d (C^{15}), 165.05 s (CONH), 173.19 s ($\underline{CO_2}CH_3$), 177.64 s (C^{18}). Found, %: C 69.53; H 7.91; N 2.74. $C_{28}H_{39}NO_6$. Calculated, %: C 69.25; H 8.09; N 2.88.

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-[2-(2-{(1E)-3-[(3-methoxy-3-oxo-1-phenyl пропил)amino]-3-oxoprop-1-ен-1-yl}furan)ethyl]-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate (**XXVI**). To a solution of 0.50 g (1.52 mmol) of methyl phlomisoate (**I**) in a mixture of 2 mL of propionic acid and 2 mL of acetonitrile while stirring was added in succession 0.35 g (1.75 mmol) of methyl 3-acryloylamino-3-phenyl propanoate (**XX**), 0.03 g (0.09 mmol) of $Pd(OAc)_2$, 0.83 g (3.5 mmol) of $Cu(OAc)_2$, and 0.018 g (0.15 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1 : 1). The successive elution afforded 0.18 g (36%) of initial diterpenoid **I** and 0.12 g (25%) of compound **XXVI**. Oily substance, $[\alpha]_D^{20}$ +24.67° (*c* 0.72, $CHCl_3$).

IR spectrum, cm^{-1}: 3300, 2953, 1724, 1663, 1460, 1370, 1236, 1138, 1021, 969, 889, 758, 656. ^{1}H NMR spectrum, δ, ppm: 0.75 s (3H, C^{20}H$_3$), 1.02 d.t (1H, H^3, *J* 13.4, 4.3 Hz), 1.20 s (3H, C^{19}H$_3$), 1.25 m (1H, H^1), 1.33 d.d (1H, H^5, *J* 12.6, 1.3 Hz), 1.52–1.59 m (1H, H^2), 1.62 s, 1.63 s (3H, C^{17}H$_3$), 1.73 d.t (1H, H^6, *J* 12.6, 5.6 Hz), 1.84 m (1H, H^2), 1.90 m, 1.96 m, 1.97 m (3H, H^{1,6,7}), 2.01–2.11 m (2H, H^{7,11}), 2.18 m, 2.22 m (2H, H^{3,11}), 2.52 m (2H, H^{12,12}), 2.88 d.d (1H, CH$_2$, *J* 15.9, 5.9 Hz), 2.99 d.d (1H, CH$_2$, *J* 15.9, 5.6 Hz), 3.62 s (6H, OCH$_3$, CO$_2$CH$_3$), 5.54 m (1H, CH), 6.29 d (1H, H$^{2'}$, *J* 14.9 Hz), 6.37 d (1H, H^{14}, *J* 1.7 Hz), 6.64 d (1H, NH, *J* 8.3 Hz), 7.31 m, 7.32 m (5H, Ph), 7.35 d (1H, H^{15}, *J* 1.7 Hz), 7.45 d (1H, H$^{1'}$, *J* 14.9 Hz). ^{13}C NMR spectrum, δ, ppm: 17.66 q (C^{20}), 19.45 t (C^2), 19.83 q (C^{17}), 20.70 t (C^6), 25.47 t (C^{12}), 28.31 q (C^{19}), 28.91 t (C^{11}), 34.19 t (C^7), 37.13 t (C^1), 37.56 t (C^3), 39.46* s (C^{10}), 39.69* t (CH$_2$), 43.78 s (C^4), 49.56 d (CH), 51.00 q (OCH$_3$), 51.74 q (CO$_2$<u>CH$_3$</u>), 53.34 d (C^5), 112.91 d (C^{14}), 116.35 d (C$^{2'}$), 126.30 d (C$^{1'}$), 126.16 d (C$^{6'',2''}$), 127.47 d (C$^{4''}$), 128.59 d (C$^{3'',5''}$), 127.75 s (C^8), 129.79 s (C$^{1''}$), 138.24 c (C^{13}), 140.50 s (C^9), 143.41 d (C^{15}), 146.60 s (C^{16}), 165.29 s (CONH), 171.59 s (CO$_2$CH$_3$), 177.99 s (C^{18}). Found, %: C 71.89; H 8.02; N 2.32. $C_{34}H_{43}NO_6$. Calculated, %: C 72.70; H 7.72; N 2.49.

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-[2-(2-{(1E)-3-[(1-methoxy-1-oxobutan-2-yl)amino]-3-oxo-prop-1-en-1-yl}furan)ethyl]-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate (XXVII). To a solution of 0.50 g (1.52 mmol) of methyl phlomisoate (**I**) in a mixture of 3 mL of propionic acid and 3 mL of ethyl ether while stirring was added in succession 0.37 g (2.37 mmol) of methyl 2-acryloylaminobutanoate ы (**XXI**), 0.05 g (0.16 mmol) of Pd(OAc)$_2$, 0.14 g (0.79 mmol) of Cu(OAc)$_2$, and 0.02 g (0.16 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an oxygen flow at 40°C for 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with MgSO$_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent chloroform). The successive elution afforded 0.10 g (20%) of initial diterpenoid **I** and 0.15 g (16%) of compound **XXVII**. $[\alpha]_D^{20}$ +66.92° (*c* 1.07, CHCl$_3$). IR spectrum, cm^{-1}: 3364, 3298, 2953, 2878, 2853, 1744, 1726, 1661, 1620, 1533, 1462, 1437, 1377, 1344, 1231, 1204, 1153, 1142, 972, 756. UV spectrum, λ_{max}, nm (logε): 236 (3.53), 309 (4.29). ^{1}H NMR spectrum, δ, ppm: 0.72 s (3H, C^{20}H$_3$), 0.90 t (3H, CH$_2$<u>CH$_3$</u>, *J* 7.5 Hz), 1.00 d.t (1H, H^3, *J* 13.4, 4.4 Hz), 1.17 s (3H, C^{19}H$_3$), 1.22 m (1H, H^1), 1.31 d.d (1H, H^5, *J* 12.8, 1.8 Hz), 1.52 m (1H, H^2), 1.60 s (3H, C^{17}H$_3$), 1.70–1.77 m, 1.88 m, 1.90 m, 1.95 m (7H, H^{1,6,7,2,6}, <u>CH$_2$</u>CH$_3$), 1.98–2.08 m (2H, H^{7,11}), 2.15 m, 2.19 m (2H, H^{3,11}), 2.49 m (2H, H^{12,12}), 3.59 s (3H, OCH$_3$), 3.73 s (3H, CO$_2$CH$_3$), 4.68 m (1H, CH), 6.29 br.s (1H, NH), 6.30 d (1H, H$^{2'}$, *J* 15.0 Hz), 6.34 d (1H, H^{14}, *J* 1.8 Hz), 7.31 d (1H, H^{15}, *J* 1.8 Hz), 7.42 d (1H, H$^{1'}$, *J* 15.0 Hz). ^{13}C NMR spectrum, δ, ppm: 9.08 q (CH$_3$), 17.34 q (C^{20}), 19.12 t (C^2), 19.47 q (C^{17}), 20.36 t (C^6), 25.13 t (C^{12}), 25.33 t (CH$_2$), 27.97 q (C^{19}), 28.56 t (C^{11}), 33.85 t (C^7), 36.82 t (C^1), 37.22 t (C^3), 39.12 s (C^{10}), 43.45 s (C^4), 50.64 q (OCH$_3$), 51.88 q (CO$_2$<u>CH$_3$</u>), 52.94 d (CH), 52.99 d (C^5), 112.58 d (C^{14}), 115.75 d (C$^{2'}$), 125.98 d (C$^{1'}$), 127.41 s (C^{13}), 129.52 s (C^8), 137.90 s (C^9), 143.09 d (C^{15}), 146.25 s (C^{16}), 165.35 s (CONH), 172.59 s (<u>CO$_2$</u>CH$_3$), 177.62 s (C^{18}). Mass spectrum, *m/z* (I_{rel}, %): 499 (2), 267 (12), 252 (11), 251 (70), 189 (15), 175 (10), 173 (15), 135 (18), 134 (100), 133 (10), 119 (14), 107 (11), 105 (10), 91 (10), 58 (23), 41 (11). Found $[M]^+$ 499.2927. $C_{29}H_{41}O_6N$. Calculated m 499.2928.

Methyl (1*S*,4a*S*,8a*R*)-1,4a,6-trimethyl-5-(2-{2-[(1*E*)-3-(morpholin-4-yl)-3-oxoprop-1-ен-1-yl]-furan-3-yl}ethyl)-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate {methyl 16-[3-(morpholin-4-yl)-3-oxoprop-1-ен-1-yl]-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate} (XXIX). To a solution of 0.50 g (1.52 mmol) of methyl phlomisoate (**I**) in a mixture of 2 mL of propionic acid and 2 mL of acetonitrile while stirring was added in succession 0.13 g (1.75 mmol) of 4-acryloylaminomorpholine (**XXVIII**), 0.03 g (0.09 mmol) of Pd(OAc)$_2$, 0.8 g (3.5 mmol) of Cu(OAc)$_2$, and 0.018 g (0.15 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an argon flow at 40°C for 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with MgSO$_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 1 : 1). The successive elution afforded 0.14 g (28%) of initial diterpenoid **I** and 0.04 g (8%) of compound **XXIX**. Oily substance, $[\alpha]_D^{20}$ +34.79° (*c* 0.13, CHCl$_3$). IR spectrum, cm^{-1}: 3303, 2948, 1724, 1667, 1463, 1369, 1235, 1134, 1022.

^{1}H NMR spectrum, δ, ppm: 0.75 s (3H, C^{20}H$_3$), 1.02 d.t (1H, H^3, *J* 13.7, 4.3 Hz), 1.19 s (3H, C^{19}H$_3$), 1.23 m (1H, H^1), 1.33 d (1H, H^5, *J* 12.1 Hz), 1.55 m (1H, H^2), 1.63 s (3H, C^{17}H$_3$), 1.68–1.75 m (1H, H^6), 1.85 m (1H, H^2), 1.91–1.97 m (3H, H^{1,6,7}), 1.99–2.10 m (2H, H^{7,11}), 2.20 d (1H, H^3, *J* 13.7 Hz), 2.20 m (1H, H^{11}), 2.53 m (2H, H^{12,12}), 3.61 s (3H, OCH$_3$), 3.70 br.s (8H, CH$_2$), 6.38 d (1H, H^{14}, *J* 1.6 Hz), 6.68 d (1H, H$^{2'}$, *J* 14.8 Hz), 7.35 d (1H, H^{15}, *J* 1.6 Hz), 7.52 d (1H, H$^{1'}$, *J* 14.8 Hz). ^{13}C NMR spectrum, δ, ppm: 17.67 q (C^{20}), 19.47 t (C^2), 19.85 q (C^{17}), 20.70 t (C^6), 25.50 t (C^{12}), 28.34 q (C^{19}), 28.97 t (C^{11}), 34.20 t (C^7), 37.16 t (C^1), 37.58 t (C^3), 39.46 s (C^{10}), 43.79 s (C^4), 51.01 q (OCH$_3$), 53.35 d (C^5), 66.78 t (4CH$_2$), 112.06 d (C^{14}), 113.04 d (C$^{2'}$), 127.78 s (C^8), 127.90 d (C$^{1'}$), 129.92 s (C^{13}), 138.24 s (C^9), 143.37 d (C^{15}), 146.95 s (C^{16}), 165.59 s (CON), 177.98 s (C^{18}). Found, %: C 71.47; H 8.22; N 2.57. $C_{28}H_{39}NO_5$. Calculated, %: C 71.61; H 8.37; N 2.98.

Methyl (1*S*,4a*S*,8a*R*)-5-(2-{2-[(1*E*)-3-oxobut-1-en-1-yl]-5-[(*E*)-phenylethenyl)furan-3-yl}ethyl)-1,4a,6-trimethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate {methyl 16-[(*E*)-3-oxobut-1-ен-1-yl]-15-[(*E*)-styryl]-15,16-epoxy-8(9),13(16),14-labdatrien-18-oate} (XXX). To a solution of 0.50 g (1.25 mmol) of methyl ester **VIII** in a mixture of 4 mL of propionic acid and 4 mL of ethyl ether while stirring was added in succession 0.22 mL (1.88 mmol) of styrene (**II**), 0.038 g (0.13 mmol) of Pd(OAc)$_2$, 0.11 g (0.63 mmol) of Cu(OAc)$_2$, and 0.014 g (0.13 mmol)of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an oxygen atmosphere at 35°C over 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 40mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with MgSO$_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 4 : 1). The successive elution afforded 0.27 g of initial labdanoid **VIII** and 0.06 g (10%) of compound **XXX**, $[\alpha]_D^{20}$ +40.21° (*c* 1.00, CHCl$_3$). IR spectrum, cm^{-1}: 3435, 2953, 2876, 2853, 1769, 1722, 1684, 1665, 1620, 1609, 1566, 1468, 1449, 1433, 1379, 1360, 1345, 1232, 1192, 1161, 1142, 1099, 1038, 978, 947, 893, 756, 710. UV spectrum, λ_{max}, nm (logε): 281 (3.63), 329 (3.79). ^{1}H NMR spectrum, δ, ppm: 0.77 s (3H, C^{20}H$_3$), 1.04 d.t (1H, H^3, *J* 13.6, 4.4 Hz), 1.21 s (3H, C^{19}H$_3$), 1.25 m (1H, H^1), 1.35 d.d (1H, H^5, *J* 12.5, 1.7 Hz), 1.58 m (1H, H^2), 1.65 s (3H, C^{17}H$_3$), 1.73 d.d (1H, H^6, *J* 12.5, 5.4 Hz), 1.84 m (1H, H^2), 1.89 m, 1.94 m, 1.99 m (3H, H^{1,7,6}), 2.01–2.14 m (2H, H^{7,11}), 2.22 d.m (1H, H^3, *J* 13.6 Hz), 2.22 m (1H, H^{11}), 2.33 s (3H, CH$_3$), 2.54 m (2H, H^{12,12}), 3.62 s (3H, OCH$_3$), 6.39 s (1H, H^{14}), 6.66 d (1H, H$^{2'}$, *J* 15.4 Hz), 6.83 d (1H, H$^{2''}$, *J* 16.4 Hz), 7.17 d (1H, H$^{1''}$, *J* 16.4 Hz), 7.28 d.t (1H, Ph, *J* 7.3, 2.2 Hz), 7.30 d (1H, H$^{1'}$, *J* 15.4 Hz), 7.35 t (2H, Ph, *J* 7.3 Hz), 7.48 d.m (2H, Ph, *J* 7.3 Hz). ^{13}C NMR spectrum, δ, ppm: 17.79 q (C^{20}), 19.59 t (C^2), 19.91 q (C^{17}), 20.78 t (C^6), 25.80 t (C^{12}), 28.03* q (C^{19}), 28.43* q (CH$_3$), 29.02 t (C^{11}), 34.28 t (C^7), 37.33 t (C^1), 37.66 t (C^3), 39.61 s (C^{10}), 43.88 s (C^4), 51.13 q (OCH$_3$), 53.44 d (C^5), 112.39 d (C^{14}), 115.49 d (C$^{1''}$), 122.14 d (C$^{2'}$), 126.55 d (C$^{2''}$), 128.63 d (2C, Ph), 128.22 d (Ph), 128.03 s (C^8), 128.79 d (2C, Ph), 130.07 d (C$^{1'}$), 134.82 s (C^{13}), 136.40 s (Ph), 138.17 s (C^9), 146.18 s (C^{15}), 154.99 s (C^{16}), 178.00 s (C^{18}), 197.59 s (CO$\underline{\text{C}}$H$_3$). Found, %: C 79.07; H 7.87. $C_{33}H_{40}O_4$. Calculated, %: C 79.16; H 8.05.

Methyl (1*S*,4a*S*,8a*R*)-5-(2-{2-[(*E*)-3-{[5-(acryloylaminooxy)pentyl]oxy}-3-oxoprop-1-en-1-yl]furan-3-yl}ethyl)-1,4a,6-trimethy-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate (XXXII). To a solution of 1.00 g (3.03 mmol) of methyl phlomisoate **(I)** in a mixture of 4 mL of propionic acid and 4 mL of ethyl ether while stirring was added in succession 0.77 mL (3.60 mmol) pentane-1,5-diyl diacrylate (**XXXI**), 0.09 g (0.30 mmol) of Pd(OAc)$_2$, 0.28 g (1.51 mmol) of Cu(OAc)$_2$, and 0.03 g (0.30 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an oxygen flow at 40°C over 80 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with MgSO$_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 4:1). The successive elution afforded 0.55 g (55%) of initial diterpenoid **I** and 0.16 g (10%) of compound **XXXII**. Oily substance, $[\alpha]_D^{20}$ +38.46° (*c* 0.84, CHCl$_3$). IR spectrum, cm^{-1}: 3523, 2946, 2860, 1705, 1631, 1457, 1434, 1352, 1253, 1120, 1156, 1122, 1105, 1079, 1063, 1013, 617. ^{1}H NMR spectrum, δ, ppm: 0.73 s (3H, C^{20}H$_3$), 0.99 d.t (1H, H^3, *J* 13.5, 4.4 Hz), 1.17 s (3H, C^{19}H$_3$), 1.20 m (1H, H^1), 1.31 d.d (1H, H^5, *J* 10.2, 1.8 Hz), 1.42–1.50 m (3H, CH$_2$, H^2), 1.60 s (3H, C^{17}H$_3$), 1.64–1.71 m (6H, 2COCH$_2\underline{\text{CH}}_2$, H^{2,6}), 1.80–1.91 m (3H, H^{1,6,7}), 1.94–2.09 m (2H, H^{7,11}), 2.16 m, 2.19 m (2H, H^{3,11}), 2.50 m (2H, H^{12,12}), 3.58 s (3H, OCH$_3$), 4.14 d.d (4H, 2COCH$_2$, *J* 12.4, 6.5 Hz),

5.76 d.d (1H, CH=, *J* 10.4, 1.7 Hz), 6.10 d (1H, CH_2=, *J* 10.4 Hz), 6.20 d (1H, H$^{2'}$, *J* 15.8 Hz), 6.32 d (1H, CH_2=, *J* 1.7 Hz), 6.34 d (1H, H^{14}, *J* 1.8 Hz), 7.35 d (1H, H^{15}, *J* 1.8 Hz), 7.42 d (1H, H$^{1'}$, *J* 15.8 Hz). ^{13}C NMR spectrum, δ, ppm: 17.34 q (C^{20}), 19.15 t (C^{2}), 19.43 q (C^{17}), 20.35 t (C^{6}), 22.07 t (CH_2), 25.25 t (C^{12}), 27.96 q (C^{19}), 28.67 t (C^{11}), 29.22 t (2COCH$_2$CH$_2$), 33.85 t (C^{7}), 36.88 t (C^{1}), 37.24 t (C^{3}), 39.14 s (C^{10}), 43.42 s (C^{4}), 50.60 q (OCH_3), 52.99 d (C^{5}), 63.60 t (COCH$_2$), 63.83 t (COCH$_2$), 112.71 d (C^{14}), 113.54 d (C$^{2'}$), 127.45 t (CH_2=), 128.10* d (C$^{1'}$), 128.55* d (CH=), 130.01 s (C^{8}), 130.48 s (C^{13}), 137.84 s (C^{9}), 143.76 d (C^{15}), 146.02 s (C^{16}), 165.69 s (CO), 166.87 s (CO), 177.45 s (C^{18}). Found, %: C 70.87; H 7.99. $C_{32}H_{44}O_7$. Calculated, %: C 71.08; H 8.20.

Methyl (1*S*,4a*S*,8a*R*)-5-[2-(2-{(E)-3-[6-(acryloylamino)hexylamino]-3-oxoprop-1-en-1-yl}furan-3-yl)ethyl]-1,4a,6-trimethyl -1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate (XXXIV). To a solution of 1.00 g (3.03 mmol) of methyl phlomisoate **(I)** in a mixture of 4 mL of propionic acid and 4 mL of ethyl ether while stirring was added in succession 0.68 mL (3.03 mmol) of *N*,*N*′-(hexane-1,6-diyl)bisacrylamide (**XXXIII**), 0.09 g (0.30 mmol) of $Pd(OAc)_2$, 0.28 g (1.51 mmol) of $Cu(OAc)_2$, and 0.03 g (0.30 mmol) of 1,4-benzoquinone. The reaction mixture was intermittently stirred in an oxygen flow at 40°C over 60 h, on cooling it was poured into 30 mL of water, the reaction products were extracted with chloroform (3 × 50 mL). The combined organic solutions were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was removed in a vacuum, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ethyl ether, 4:1). The successive elution afforded 0.40 g (40%) of initial diterpenoid **I,** 0.05 g (2%) of compound **XXXV**, and 0.44 g (26%) of compound **XXXIV**.

Compound **XXXIV**. Oily substance. $[\alpha]_D^{20}$ +18.65° (*c* 0.22, $CHCl_3$). IR spectrum, cm^{-1}: 3401, 2939, 2838, 1772, 1728, 1668, 1607, 1542, 1441, 1409, 1372, 1324, 1245, 1035, 971, 820, 738. ^{1}H NMR spectrum, δ, ppm: 0.70 s (3H, C^{20}H$_3$), 0.97 d.t (1H, H^{3}, *J* 13.0, 4.3 Hz), 1.15 s (3H, C^{19}H$_3$), 1.20 m (1H, H^{1}), 1.30 m (5H, CH$_2$CH$_2$, H^{5}), 1.48 m (5H, 2CONCH$_2$CH$_2$, H^{2}), 1.58 s (3H, C^{17}H$_3$), 1.63–1.79 m (2H, H^{2,6}), 1.80–1.93 m (3H, H^{1,6,7}), 1.97–2.05 m (2H, H^{7,11}), 2.13 m, 2.17 m (2H, H^{3,11}), 2.47 m (2H, H^{12,12}), 3.27 m (4H, 2CONCH$_2$), 3.57 s (3H, OCH_3), 5.55 d.d (1H, CH=, *J* 9.4, 2.3 Hz), 6.17 d (1H, CH_2=, *J* 9.4 Hz), 6.21 d (1H, CH_2=, *J* 2.3 Hz), 6.29 d (1H, H$^{2'}$, *J* 15.2 Hz), 6.31 d (1H, H^{14}, *J* 1.3 Hz), 6.49 br.s (1H, NH), 6.61 br.s (1H, NH), 7.31 d (1H, H^{15}, *J* 1.3 Hz), 7.37 d (1H, H$^{1'}$, *J* 15.2 Hz). ^{13}C NMR spectrum, δ, ppm: 17.61 q (C^{20}), 19.43 t (C^{2}), 19.79 q (C^{17}), 20.67 t (C^{6}), 25.41 t (C^{12}), 25.88 t (CH$_2$CH$_2$), 28.29 q (C^{19}), 28.94 t (C^{11}), 29.13 t (CONCH$_2$CH$_2$), 29.33 t (CONCH$_2$CH$_2$), 34.13 t (C^{7}), 37.08 t (C^{1}), 37.52 t (C^{3}), 38.96 t (CONCH$_2$), 39.08 t (CONCH$_2$), 39.41 s (C^{10}), 43.74 s (C^{4}), 51.01 q (OCH_3), 53.28 d (C^{5}), 112.82 d (C^{14}), 117.05 d (C$^{2'}$), 128.35 d (C$^{1'}$), 125.92 t (CH_2=), 127.69 s (C^{8}), 129.26 s (C^{13}), 130.97 d (CH=), 138.16 s (C^{9}), 143.19 d (C^{15}), 146.63 s (C^{16}), 165.81 s (CON), 166.42 s (CON), 178.04 s (C^{18}). Found, %: C 72.02; H 8.71; N 5.27. $C_{33}H_{48}N_2O_5$. Calculated, %: C 71.71; H 8.75; N 5.07.

Dimethyl (1*S*,1'*S*,4a*S*,4a'*S*,8a*R*,8a'*R*)-5,5'-(2,2'-{2,2'-[(1*E*,1'*E*)-3,3'-(hexane-1,6-diyldiimino)bis(3-oxoprop-1-en-1-yl)]bis(furan-3-yl)}bisethyl)-bis(1,4a,6-trimethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalene-1-carboxylate) (XXXV). Oily substance, $[\alpha]_D^{20}$ +7.39° (*c* 0.12, $CHCl_3$). IR spectrum, cm^{-1}: 3405, 2940, 2833, 1764, 1669, 1728, 1611, 1543, 1438, 1372, 1325, 1239, 1037, 976, 821. ^{1}H NMR spectrum, δ, ppm: 0.73 s (6H, C^{20}H$_3$, C$^{20'}$H$_3$), 0.97 m (2H, H$^{3,3'}$), 1.14 s (6H, C^{19}H$_3$, C$^{19'}$H$_3$), 1.20 m (2H, H$^{1,1'}$), 1.30 m, 1.36 m (6H, CH$_2$CH$_2$, H$^{5,5'}$), 1.53 m (6H, 2CONCH$_2$CH$_2$, H$^{2,2'}$), 1.61 s (6H, C^{17}H$_3$, C$^{17'}$H$_3$), 1.65–1.79 m (4H, H$^{2,2',6,6'}$), 1.82–1.94 m (6H, H$^{1,1',6,6',7,7'}$), 2.01–2.06 m (4H, H$^{7,7',11,11'}$), 2.13 m, 2.17 m (4H, H$^{3,3',11,11'}$), 2.50 m (4H, H$^{12,12',12,12'}$), 3.33 m (4H, 2CONCH$_2$), 3.60 s (6H, OCH_3), 6.01 br.s (2H, 2NH), 6.25 d (2H, H$^{2'',2''}$, *J* 15.1 Hz), 6.34 s (2H, H$^{14,14'}$), 7.32 s (2H, H$^{15,15'}$), 7.42 d (2H, H$^{1'',1''}$, *J* 15.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.61 q (C$^{20,20'}$), 19.42 t (C$^{2,2'}$), 19.75 q (C$^{17,17'}$), 20.69 t (C$^{6,6'}$), 25.41 t (C$^{12,12'}$), 25.84 t (2CONCH$_2$CH$_2$), 28.26 q (C$^{19,19'}$), 29.01 t (C$^{11,11'}$), 27.80 t (CH$_2$), 34.15 t (C$^{7,7'}$), 37.11 t (C$^{1,1'}$), 37.52 t (C$^{3,3'}$), 38.54 t (CONCH$_2$), 39.42 s (C$^{10,10'}$), 44.00 s (C$^{4,4'}$), 51.06 q (OCH_3), 53.29 d (C$^{5,5'}$), 112.78 d (C$^{14,14'}$), 116.58 d (C$^{2'',2''}$), 129.03 d (C$^{1'',1''}$), 128.67 s (C$^{8,8'}$), 129.25 s (C$^{13,13'}$), 138.12 s (C$^{9,9'}$), 143.21 d (C$^{15,15'}$), 146.59 s (C$^{16,16'}$), 166.85 s (2CON), 178.02 s (C$^{18,18'}$). Found, %: C 73.42; H 8.75; N 2.94. $C_{54}H_{76}N_2O_8$. Calculated, %: C 73.60; H 8.69; N 3.18.

The signals marked with an asterisk (*) are mutually exchangeable within the description of the same compound.

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