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Reactions of Caryophyllene, Isocaryophyllene, and Their Epoxy Derivatives with Acetonitrile under Ritter Reaction Conditions

O.I. Yarovaya, D.V. Korchagina, T.V. Rybalova, Yu.V. Gatilov, M.P. Polovinka, and V.A. Barkhash

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences
Novosibirsk, 630090 Russia
e-mail: ooo@nioch.nsc.ru

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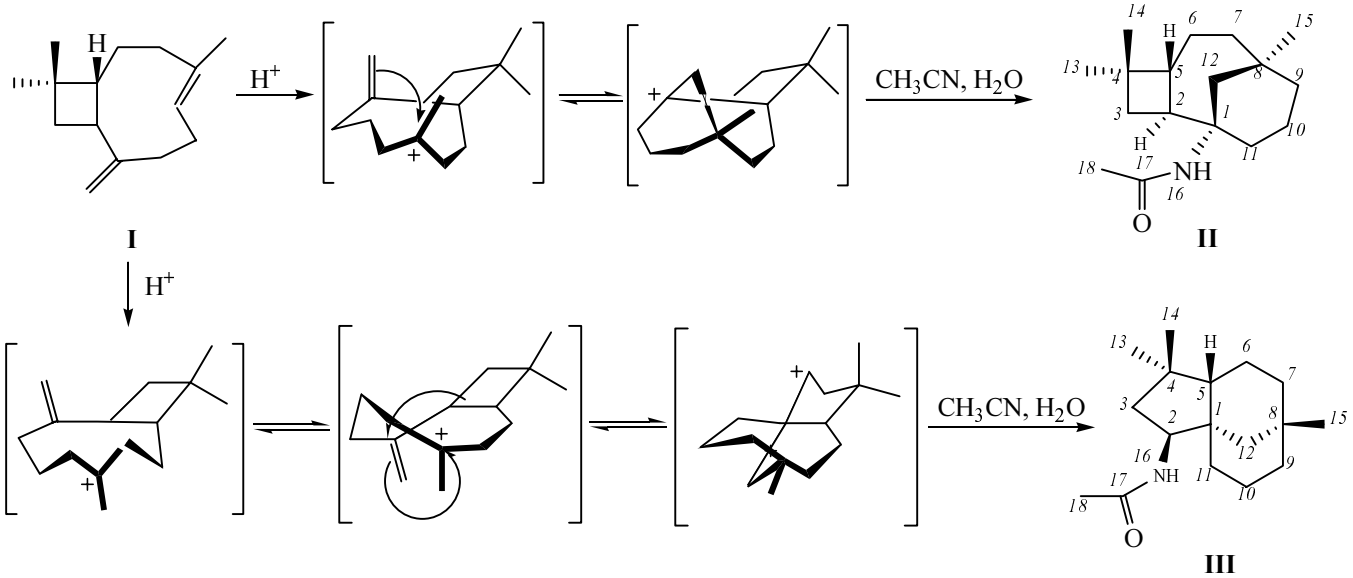
Abstract— Acid-catalyzed reactions between acetonitrile and caryophyllene, isocaryophyllene, caryophyllene 4β,5α-epoxide, and isocaryophyllene 4β,5β-epoxide affording optically active amides with a tricyclic skeleton were investigated.

The study of acid-catalyzed reactions of epoxy derivatives from terpene series and their comparison with the reactions of original terpenoids opens the way to understanding the effect of cation center formation on the final result of transformations. We formerly demonstrated that dissolution of a mixture of citral 6,7-epoxides in a system acetonitrile–sulfuric acid (Ritter reaction conditions) resulted in formation of substituted oxazolines [1]. The formation of 2-oxazolines from epoxides and nitriles is known [2], but we did not find any publications on the use of terpene epoxides as reagents for synthesis of compounds with an oxazoline ring; the preparation of diamides by Ritter reaction with α-pinene epoxide was reported in [3].

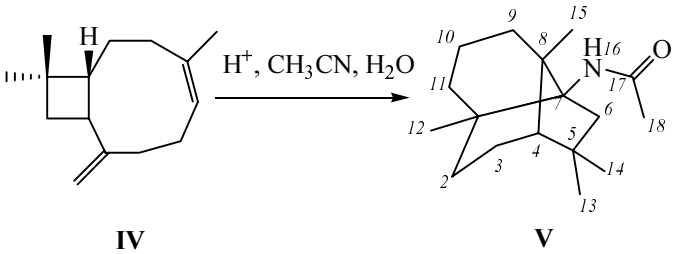
We explored in this study the behavior of caryophyllene, isocaryophyllene, and their monoepoxy derivatives under conditions of Ritter reaction. The dissolution of caryophyllene (I) in a system acetonitrile–sulfuric acid followed by treating with anaqueous sodium hydrogen carbonate afforded optically active tricyclic amides II and III with caryolane and clovane skeletons at a ratio 3:1 respectively (Scheme 1).*

Scheme 1.

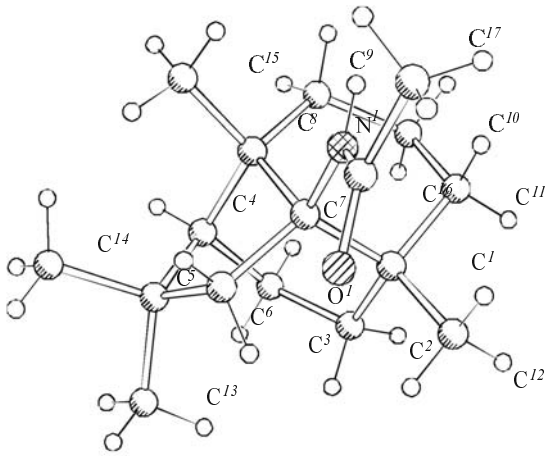


* The atoms in compounds on Schemes are numbered analogously to their notation in the NMR spectra.

Scheme 2.

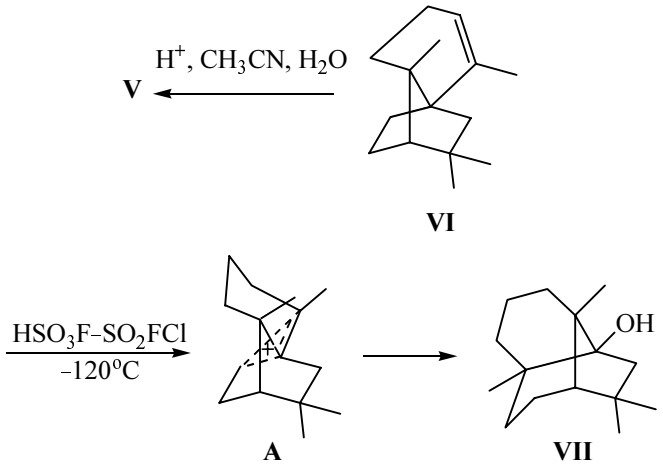


IV **V**



Structure of compounds **V** molecule according to x-ray diffraction data.

Scheme 3.



The dissolution of isocaryophyllene (**IV**) under the same conditions furnished mainly optically active compound **V** whose structure was established by X-ray diffraction analysis. The structure of molecule **V** is presented on the figure. The six-membered rings in the molecule are in the *chair* conformation, and the five-membered one has an *envelope* form with deviation of atom C^8 by 0.738(9) E from the plane where are located the other atoms. The same ring conformation in a bicyclo[5.4.0.$0^{4,8}$]undecane was observed in ginseng derivatives [4, 5], in the rearrangement products of nerolidol [6] and neoclovene [7]. In the crystal of compound **V** the molecules are connected by hydrogen bonds NH···O into screw-like chains twisted (1D-motive) around screw axis of the fourth order. The parameters of the hydrogen bonds $N^1H\cdots O^1$ are as follows: N–H 0.86, H···O 2.05, N···O 2.889(6) Å, angle NHO 165°.

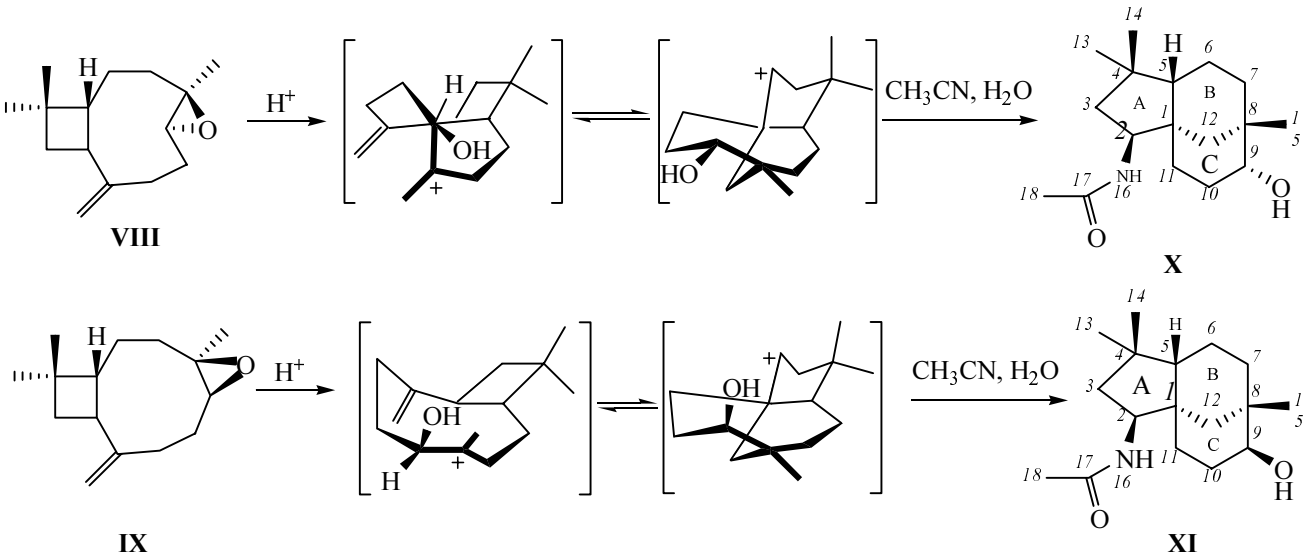
The skeleton of compound **V** is identical to that of compound **VII** [7] obtained by quenching with water a solution of ion **A** salt generated by dissolving neoclovene (**VI**) in a system HSO_3F–SO_2FCl at–120°C (Scheme 3). Nonclassic σ-delocalized structure of ion **A** was proved using NMR spectral data.

The neoclovene is known to be one of the principal products of acid-catalyzed cyclization of the isocaryophyllene. The above cited findings suggest that the formation mechanism of tricyclic compound **V** involves isocaryophyllene (**IV**) isomerization into the neoclovene followed by rearrangement into cation **A**, trapping of the latter by acetonitrile and subsequent reaction with water resulting in compound **V**. Actually, the dissolution of neoclovene (**VI**) in the system acetonitrile–sulfuric acid afforded compound **V** as the only reaction product thus confirming our assumptions on the reaction mechanism.

In order to extend the number of natural epoxy compounds brought into Ritter reaction we investigated reaction of acetonitrile catalyzed by sulfuric acid with 4β,5α-epoxide of caryophyllene (**VIII**) and 4β,5β-epoxide of isocaryophyllene (**IX**). It was shown that amides **X** and **XI** formed in a good yield (Scheme 4). Cations arising on the epoxy ring opening suffered the known rearrangements [8] resulting in ions with the clovane-type skeleton. These ions were trapped by acetonitrile molecules, and the subsequent hydrolysis provided the corresponding N-alkylamides. The optically active compounds **X** and **XI** differ from each other only by the configuration of the hydroxy group.

It should be noted that transformations of caryophyllene, its isomers, and oxygen-containing derivatives are well documented [9]. Inasmuch as caryophyllene is a polyfunctional and conformationally labile compound, its acid-catalyzed rearrangements afford with rare exception [10] complex mixtures of substances. Therefore we demonstrated that the nucleophilic addition of nitriles to carbocations known as "Ritter reaction" provided a convenient method for investigation of multistage rearrangements, since the presence in the reaction mixture of a weak nucleophile (nitrile) gave a

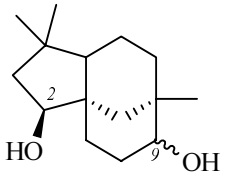
Scheme 4.



possibility, on the one hand, to stabilize carbocations arising in the course of the reaction; on the other hand, the most labile and short-lived cations had not enough time to react with the weak nucleophile. Thus the reaction either furnished relatively simple product mixtures or individual substances obtained from highly reactive and polyfunctional compounds like terpenoids. All amides prepared in this study were unknown before.

Let us consider some details of establishing the structure of compounds synthesized. The β-configuration to the methylene group $C^{12}H_2$ in compound **II** we assigned on comparison of the ^1H and ^{13}C NMR spectra of the compound with the corresponding spectra of kindred compounds with 12α- and 12β-methylene bridges [11]. Note also that the chemical shifts of carbon atoms in the ^{13}C NMR spectra of compound **V** have values close to those in the spectra of hydroxy derivative **VII** taking into account the different effect of OH and $NHCOCH_3$ groups on the chemical shifts of the adjacent atoms [7].

The β-orientation of substituents at C^2 in compounds **III, X,** and **XI** was assigned basing on the published data for clovane-2,9-diols prepared from 4β,5α-epoxide of caryophyllene and 4β,5β-epoxide of isocaryophyllene [12]. Similar values of the chemical shifts and identical coupling constants of proton H^2 signals prove their identical α-orientation. As suggest the values of the vicinal coupling constants of H^9 protons and the protons of the contiguous methylene groups $C^{10}H_2$, in compound **X** proton H^9 is in the equatorial position, and in compound **XI** the respective proton is in the axial position. Inasmuch as the C rings exist in the *chair* conformation, consequently the hydroxy group is α-oriented in compound **X** and β-oriented in compound **XI**. It should also be mentioned that the analysis of the ^{13}C NMR spectra of clovane-type compounds with 9α- and 9β-hydroxy groups shows the characteristic feature of the chemical shifts of C^{12} atoms, and therefore the latter can be applied to assignment of the 9-hydroxy group configuration. In the compounds with the α-OH group the C^{12} carbon signals appear in the region ~35–37 ppm and in the compounds with the β-OH group the similar signal is located at ~42–44 ppm [8, 13]. Note that the chemical shifts in the ^{13}C NMR spectra of compounds **X** and **XI** and related substances **XIIa, b** have close values except of the peaks of the C^2 atoms.



XIIa, b

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-400 (400.13 and 100.61 MHz respectively) from samples dissolved in $CDCl_3$. As internal reference served the chloroform signals (δ_H 7.24, δ_C 76.90 ppm). The structure of compounds was elucidated from NMR spectral data basing on analysis of coupling constants in the double resonance ^1H–^1H spectra and from ^{13}C NMR spectra registered with selective and off-resonance proton decoupling, from two-dimensional

correlation ^{13}C-^{1}H spectra on direct (COSY, using $^{1}J_{C,H}$ 135 Hz) and long-range (COLOC, $^{2,3}J_{C,H}$ 10 Hz) coupling, and from one-dimensional correlation ^{13}C-^{1}H spectra on long-range coupling (LRJMD, $^{2,3}J_{C,H}$ 10 Hz). The structure of compound **V** was established by X-ray diffraction analysis. The X-ray study was carried out on diffractometer Bruker P4 (MoK_α-radiation, graphite monochromator, room temperature, θ/2θ-scanning). Crystals of compound V tetragonal: $a = b = 10.1572(18)$, c 15.656 A, V 1615.2(7) Å^3, space group $P4_3$. $C_{17}H_{29}NO$. M 263.41, Z 4, d_c 1.083 g/cm^3, μ 0.066 mm^{-1}, crystal habit $1.20 \times 0.09 \times 0.05$ mm, $2\theta < 50°$. The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation till wR_2 0.1908, S 1.054 for 1578 independent reflections (R 0.0588 for 951 $F > 4\sigma$) with the use of software package SHELX-97. Hydrogen atoms were placed from geometric considerations. The corrections for extinctions were not taken into account. The atomic coordinates can be available from the authors.

The purity of initial compounds was checked and the reaction products were analyzed by GLC on a chromatograph Biokhrom-1 equipped with various columns: (a) a glass capillary column 53000×0.26 mm, stationary phase XE-60; b) a quartz capillary column 13000×0.22 mm, stationary phase SE-54, flame-ionization detector, carrier gas helium.

The reagents used in the study were as follows: caryophyllene (**I**) separated from clove oil, $[\alpha]_{580}^{20}$ –13.8° (*C* 4.3, $CHCl_3$), isocaryophyllene (**IV**), $[\alpha]_{580}^{20}$ –20.0° (*C* 5.4, $CHCl_3$) obtained by caryophyllene(**I**) isomerization by procedure [14], 4β,5α-epoxide of caryophyllene (**VIII**), $[\alpha]_{580}^{20}$ – 46.4° (*c* 5.6, $CHCl_3$), and 4β,5β-epoxide of isocaryophyllene (**IX**), $[\alpha]_{580}^{20}$ –11.3° (*c* 12.4, $CHCl_3$) prepared by treating the original sesquiterpenes with monoperphthalic acid by method [15].

Transformation of caryophyllene (I) in a system acetonitrile–sulfuric acid . To a solution of 0.5 g of caryophyllene in 10 ml of acetonitrile was added at stirring 0.2 ml of sulfuric acid, after stirring for 5 min the reaction mixture was neutralized with a saturated solution of Na_2CO_3, the reaction products were extracted into dichloromethane, the organic extract was washed with water and dried with $MgSO_4$. The mixture of reaction products (0.48 g, 74%) [compounds (**II**)/(**III**) ratio 3 : 1 (GLC)] was separated by column chromatography on SiO_2 (100–160 μm) (gradient elution with hexane containing from 0.5 to 10% of ethyl ether). We isolated 0.23 g (36%) of compound **II** as colorless fluffy crystals (mp 160–163°C) and 0.11 g (17%) of compound **III**.

(1*S*,2*S*,5*R*,8*S*)-N-(4,4,8-Trimethyltricyclo-[6.3.1.0^{2,5}]dodec-1-yl)acetamide (II). $[\alpha]_{580}^{20}$ 97.0° (*C* 7.0, $CHCl_3$). IR spectrum (CCl_4), ν,cm^{-1}: 1669.0 (C=O), 3439.0 (NH). ^1H NMR spectrum, δ, ppm: 0.83 C ($C^{15}H_3$), 0.93 s ($C^{14}H_3$), 0.94 s ($C^{13}H_3$), 1.00–1.13 m (H^9, H^7), 1.17 d (H^{12a}, $J_{12a,12e}$ 13 Hz), 1.22 d.d (H^3, $J_{3,3'}$ 10, $J_{3,2}$ 10 Hz), 1.24–1.60 m (6H), 1.68 d.d ($H^{3'}$, J 10, $J_{3',2}$ 8 Hz), 1.71 m (H^5, $H^{10'}$), 1.75 d.m (H^{12e}, J 13 Hz), 1.88 c ($C^{18}H_3$), 2.22 d.d.d (H^2, $J_{2,5}$ 12, $J_{2,3}$ 10, $J_{2,3'}$ 8 Hz), 2.28 m ($H^{11'}$), 5.25 br.s (H^{16}). ^{13}C NMR spectrum, δ, ppm: 55.29 s (C^1), 41.05 d (C^2), 37.97 t (C^3), 34.00 s (C^4), 46.01 d (C^5), 22.85 t (C^6), 37.93 t (C^7), 34.06 s (C^8), 37.21 t (C^9), 19.81 t (C^{10}), 35.63 t (C^{11}), 46.03 t (C^{12}), 20.56 q (C^{13}), 30.35 q (C^{14}), 33.89 q (C^{15}), 168.93 s (C^{17}), 24.12 q (C^{18}). Found, *m/z*: 263.22466 $[M]^+$. $C_{17}H_{29}NO$. Calculated M 263.22490.

(3*S*,3*aS*,7*R*,9*aS*)-N-(1,1,7-Trimethyldecahydro-3a,7-methanocyclopentacyclo-oct-3-yl)acetamide (III). $[\alpha]_{580}^{20}$ –38.0° (*C* 4.2, $CHCl_3$). IR spectrum (CCl_4), ν, Cμ^{-1}: 1665.2 (C=O), 3444.8 (NH). ^1H NMR spectrum, δ, ppm: 0.82 s ($C^{15}H_3$), 0.84 s ($C^{13}H_3$), 0.91 d.d.d (H^{9a}, $J_{9a,9e}$ 13, $J_{9a,10a}$ 13, $J_{9a,10e}$ 5 Hz), 0.97 s ($C^{14}H_3$), 0.98 d (H^{12a}, $J_{12a,12e}$ 13 Hz), 1.26 d.d.d (H^{12e}, J 13, 2.5, 2.5 Hz), 1.32 d.d (H^3, $J_{3,2}$ 13, $J_{3,3'}$ 12 Hz), 1.40–1.58 m (2H^{10}), 1.54 d.d ($H^{3'}$, J 12, $J_{3',2}$ 6 Hz), 1.93 s ($C^{18}H_3$), 4.06 d.d.d (H^2, J 13, 6, $J_{2,16}$ 9 Hz), 5.54 br.d. (H^{16}, J 9 Hz), 0.99–1.36 m (8H, other protons). ^{13}C NMR spectrum, δ, ppm: 43.80 s (C^1), 57.79 d (C^2), 45.83 t (C^3), 37.54 c (C^4), 51.07 d (C^5), 20.41 t (C^6), 32.98 t (C^7), 29.99 c (C^8), 40.34 t (C^9), 18.68 t (C^{10}), 33.28 t (C^{11}), 43.17 t (C^{12}), 24.52 q (C^{13}), 30.74 q (C^{14}), 32.62 q (C^{15}), 169.45 s (C^{17}), 23.40 q (C^{18}). Found, *m/z*: 263.22492 $[M]^+$. $C_{17}H_{29}NO$. Calculated M 263.22490

Transformation of isocaryophyllene (IV) in a system acetonitrile–sulfuric acid . To a solution of 0.5 g of isocaryophyllene in 10 ml of acetonitrile was added at stirring 0.2 ml of sulfuric acid, after stirring for 5 min the reaction mixture was neutralized with a saturated solution of Na_2CO_3. On storage from the organic layer precipitated colorless needle-like crystals of amide **V**, mp 213–214°C. The reaction product was filtered off, washed with hexane; the separated crystals of compound **V** weighed 0.19 g (30%), and the mother liquor containing according to GLC data ~75 % of amide **V** weighed 0.28 g.

(1*S*,3*aR*,4*R*,7*aS*)-N-(2,2,4,7a-Tetramethyloctahydro-1,4-ethanoinden-3a-yl)acetamide (V). $[\alpha]_{580}^{20}$ –16.4° (*C* 5.0, $CHCl_3$). IR spectrum (CCl_4), ν, cm^{-1}: 1670.1 (C=O), 3440.8 (NH). ^1H NMR spectrum, δ, ppm:

0.80 s ($C^{12}H_3$), 1.03 s and 1.19 s ($C^{13}H_3$, $C^{14}H_3$), 1.10 s ($C^{15}H_3$), 1.12 s (H^{11}), 1.24–1.35 s (2H, H^2, H^9), 1.37 d.d (H^4, $J_{4,3'}$ 3.5, $J_{4,3}$ 2.5 Hz), 1.41–1.64 s (4H, H^{10}, H^3, $H^{11'}$, $H^{2'}$), 1.75–1.93 s (3H, $H^{10'}$, $H^{9'}$, $H^{3'}$), 1.94 s ($C^{18}H_3$), 2.28 d and 2.36 d (2H^6, $J_{6,6'}$ 15 Hz), *AB* system, 5.45 br.s (H^{16}). ^{13}C NMR spectrum, δ, ppm: 40.15 c (C^1), 33.62 t (C^2), 25.86 t (C^3), 56.08 d (C^4), 36.41 s (C^5), 45.05 t (C^6), 68.07 s (C^7), 45.83 s (C^8), 33.68 t (C^9), 21.43 t (C^{10}), 34.88 t (C^{11}), 26.85 q (C^{12}), 28.16 q and 34.07 q (C^{13}, C^{14}), 30.52 q (C^{15}), 169.48 s (C^{17}), 24.26 q (C^{18}). Found, *m/z*: 263.22516 $[M]^+$. $C_{17}H_{29}NO$. Calculated *M* 263.22490.

Reaction of caryophyllene 4β,5α-epoxide with acetonitrile under conditions of Ritter reaction. To a solution of 0.45 g of caryophyllene 4β,5α-epoxide (**VIII**) in 4.5 ml of acetonitrile was added at stirring 0.2 ml of concn. sulfuric acid, after stirring for 5 min the reaction mixture was neutralized with a saturated solution of Na_2CO_3, the reaction products were extracted into dichloromethane, the organic extract was washed with water and dried with $MgSO_4$. The crude reaction product (0.46 g) containing according to GLC predominantly compound **X** was washed from compurities with hexane and ethyl ether (acetamide **X** was sparingly soluble in these solvents). We isolated 0.31 g (56%) of compound **X**.

(3*S*,3*aS*,6*R*,7*R*,9*aS*)-N-(6-Hydroxy-1,1,7-trimethyldecahydro-3a,7-methanocyclopentacyclooct-3-yl)acetamide (X). $[\alpha]_{580}^{20}$ –50.2° (*c* 4.1, $CHCl_3$). IR spectrum (CCl_4), ν, cm^{-1}: 1664.8 (C=O), 3444.7 (NH). ^{1}H NMR spectrum, δ, ppm: 0.82 s ($C^{13}H_3$), 0.86 s ($C^{15}H_3$), 0.87 m (H^{11e}), 0.94 s ($C^{14}H_3$), 0.97 d.d (H^{12}, $J_{12,12'}$ 13, *J* 2.5 Hz), 0.99 m (H^7), 1.23–1.37 m (5H, H^3, H^{5b}, 2H^6, H^7), 1.42 d.d.d (H^{11a}, $J_{11a,10a}$ 14, $J_{11a,11e}$ 13, $J_{11a,\ 10e}$ 5 Hz), 1.49 d ($H^{12'}$, $J_{12',12}$ 13 Hz), 1.52 d.d ($H^{3'}$, $J_{3',3}$ 12, $J_{3',2a}$ 6 Hz), 1.55 m (H^{10e}, $J_{10e,10a}$ 14, $J_{10e,11a}$ 5, $J_{10e,9e}$ 2.5, $J_{10e,11e}$ 2.5 Hz), 1.87 d.d.d.d (H^{10a}, $J_{10a,10e}$ 14, $J_{10a,11a}$ 14, $J_{10a,11e}$ 5, $J_{10a,9e}$ 3 Hz), 1.90 s ($C^{18}H_3$), 2.16 br.s (OH), 3.19 d.d (H^{9e}, $J_{9e,10a}$ 3, $J_{9e,10e}$ 2.5 Hz), 4.04 d.d.d (H^{2a}, $J_{2a,3}$ 13, $J_{2a,16}$ 9, $J_{2a,3'}$ 6 Hz), 5.67 br.d (H^{16}, $J_{16,2a}$ 9 Hz). ^{13}C NMR spectrum, δ, ppm: 43.32 s (C^1), 57.49 d (C^2), 45.53 t (C^3), 37.33 s (C^4), 50.29 d (C^5), 20.31 t (C^6), 32.85 t (C^7), 34.58 s (C^8), 74.59 d (C^9), 25.31 t (C^{10}), 27.37 t (C^{11}), 35.40 t (C^{12}), 24.33 q (C^{13}), 30.62 q (C^{14}), 28.05 q (C^{15}), 169.64 s (C^{17}), 23.36 q (C^{18}). Found, *m/z*: 279.22026 $[M]^+$. $C_{17}H_{29}NO_2$. Calculated: 279.21982.

Reaction of isocaryophyllene 4β,5β-epoxide with acetonitrile under conditions of Ritter reaction. The reaction was carried under conditions identical to those used in preparation of compound **X**. From 0.3 g of isocaryophyllene 4β,5β-epoxide (**IX**) was isolated 0.21 g (54%) of compound **XI**.

(3*S*,3*aS*,6*S*,7*R*,9*aS*)-N-(6-Hydroxy-1,1,7-trimethyldecahydro-3a,7-methanocyclopentacyclooctan-3-yl)acetamide (XI). $[\alpha]_{580}^{20}$ –46.4° (*c* 5.6, $CHCl_3$). IR spectrum (CCl_4), ν, cm^{-1}: 1665.4 (C=O), 3443.0 (NH). ^{1}H NMR spectrum, δ, ppm: 0.82 s ($C^{13}H_3$), 0.91 s ($C^{15}H_3$), 0.96 s ($C^{14}H_3$), 1.02 d ($H^{12'}$, $J_{12',12}$ 13 Hz), 1.06–1.16 m (4H, 2H^7, 2H^{11}), 1.16–1.25 m (2H, H^{5b}, H^6), 1.29 d.d (H^{12}, $J_{12,12'}$ 13, *J* 2.5 Hz), 1.31 d.d (H^3, $J_{3,2a}$ 13, $J_{3,3'}$ 12 Hz), 1.34 m ($H^{6'}$), 1.42 m (H^{10a}), 1.50 d.d ($H^{3'}$, $J_{3',3}$ 12, $J_{3',2a}$ 6 Hz), 1.64 d.d.m (H^{10e}, $J_{10e,10a}$ 13, $J_{10e,9a}$ 5 Hz), 1.91 s ($C^{18}H_3$), 3.07 d.d (H^{9a}, $J_{9a,10a}$ 11, $J_{9a,10e}$ 5 Hz), 4.08 d.d.d (H^{2a}, $J_{2a,3}$ 13, $J_{2a,16}$ 9, $J_{2a,3'}$ 6 Hz), 5.65 br.d (H^{16}, $J_{16,2a}$ 9 Hz). ^{13}C NMR spectrum, δ, ppm: 43.24 s (C^1), 56.88 d (C^2), 45.69 t (C^3), 37.47 s (C^4), 51.38 d (C^5), 19.94 t (C^6), 26.86 t (C^7), 35.10 s (C^8), 77.34 d (C^9), 27.21 t (C^{10}), 32.24 t (C^{11}), 41.99 t (C^{12}), 24.42 q (C^{13}), 30.65 q (C^{14}), 28.40 q (C^{15}), 169.61 s (C^{17}), 23.26 q (C^{18}). Found, *m/z*: 279.21971 $[M]^+$. $C_{17}H_{29}NO_2$. Calculated *M* 279.21982.

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REFERENCES

1. Yarovaya, O.I., Korchagina, D.V., Salomatina, O.V., Polovinka, M.P., and Barkhash, V.A., *Mendeleev Commun.,* 2003, no. 1, p. 28.
2. Boyd, G.V., in *Comprehensive Heterocyclic Chemistry II*, Katrizky, A.R., Rees, C.W., and Scriven, E.F.V., Eds., Oxford: Pergamon, 1996, vol. 6, p. 229.
3. Koval'skaya, S.S. and Kozlov, N.G., *Zh. Org. Khim.,* 1994, vol. 30, p. 1335.
4. Amigo, C.F.D., Collado, I.G., Hanson, J.R., Hernandez-Galan, R., Hitchcock, P.B., Macias-Sanchez, A.J., and Mobbs, D.J., *J. Org. Chem.,* 2001, vol. 66, p. 4327.
5. Aleu, J., Hernandez-Galan, R., Hanson, J.R., Hitchcock, P.B., Collado, I.G.., *J. Chem. Soc., Perkin Trans. I,* 1999, p. 727.
6. Polovinka, M.P., Korchagina, D.V., Gatilov, Yu.V., Bagrianskaya, I.Yu., Barkhash, V.A., Shcherbukhin, V.V., Zefirov, N.S., Perutskii, V.B., Ungur, N.D., and Vlad, P.F., *J. Org. Chem.,* 1994, vol. 59, p. 1509.
7. Khomenko, T.M., Korchagina, D.V., Gatilov, Yu.V., Bagryanskaya, I.Yu., Rybalova, T.V., Sal'nikov, G.E.,

Mamatyuk, V.I., Dubovenko, Zh.V., and Barkhash, V.A., *Zh. Org. Khim*., 1991, vol. 27, p. 570.

8. Nisnevich, G.A., Korchagina, D.V., Makal'skii, V.A., Dubovenko, Zh.V., and Barkhash, V.A., *Zh. Org. Khim*., 1993, vol. 29, p. 524.
9. Collado, I.J., Hanson, J.R., and Macias-Sanchez, A.J., *Nat. Prod. Rep.,* 1998, vol. 15, p. 187.
10. Fomenko, V.V., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Helv. Shim. Acta,* 2001, vol. 84, p. 3477.
11. Tkachev, A.V., Mamatyuk, V.I., and Dubovenko, Zh.V., *Zh. Org. Khim.,* 1990, vol. 26, p. 1698.
12. Aebi, A., Barton, D.H.R., Burgstahler, A.W., and Lindsey, A.S., *J. Chem. Soc.,* 1954, vol. 12, p. 4659.
13. Collado, I.J., Hanson, J.R., and Macias-Sanchez, A.J., *Tetrahedron,* 1996, vol. 52, p. 7961.
14. Rachlin, S., US Patent 3621070; *Ref. Zh. Khim*., 1971, 192.14, R448.
15. Bombarda, I., Gaydou, E.M., Smadja, J., and Faure, R., *Bull. Soc. Chim.,* 1995, vol. 132, p. 836.