1.5259, $[\alpha]_D^{20}$ +60.5°) and isopimarinol (n_D^{20} 1.5250, $[\alpha]_D^{20}$ −40.1°). All the compounds isolated were identified by TLC with markers. Alcohols have not previously been found in the oleoresin of the Crimean pine [5].

In the most polar fraction (∿5%) hydroxy esters were detected — methyl 15-hydroxyabietate and methyl 15-hydroxydehydroabietate, present in a ratio of 1:8 (GLC) — and they were identified by additions of authentic samples.

The extremely small amount of oxygen-containing mono- and sesquiterpenoids in the oleoresin of the Crimean pine must be mentioned. 5,8-Germacra-1E,6E-5-ol,* cubebol, epicubebol, δ-cadinol, methyleugenol, and 2,4-dimethoxyallylbenzene were isolated in trace amounts. These components were identified from their PMR spectra.

The acids of the oleoresin were analyzed by GLC in the form of their methyl esters. Pimaric (4.5%), palustric/levopalustric (37%), isopimaric (14%), dehydroabietic (11%), abietic (29.5%), and neoabietic (4%) acids were identified. The quantitative composition of the acids of the oleoresin of the Crimean pine that we studied differs from the figures published previously [6].

In the composition of the terpenoids of its oleoresin the Crimean pine differs from a species close to it — the Scotch pine — by the high content of germacrene D and of diterpene aldehydes.

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BIOMIMETIC CYCLIZATION OF CARYOPHYLLENE TO β-PANASINSENE

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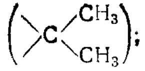
and V. A. Pentegova

UDC 547.91

One of the components of the essential oil of ginseng (*Panax ginseng* C. A. Mayer) — β-panasinsene — is biogenetically linked with neoclovene and, apparently, with caryophyllene. This is shown by the common presence of all these hydrocarbons in the oil mentioned [1]. Although a suggested scheme of the conversion of caryophyllene into neoclovene also includes the intermediate formation of a carbocation with the 1,5,5,8-tetramethyltricyclo$[5.4.0.0^{4,7}]$-undecane skeleton, no hydrocarbons corresponding to this particle were detected among the products of the acid-catalyzed cyclization of caryophyllene [2].

On studying the products of the mercuration-demercuration of caryophyllene under the action of mercury(II) acetate in acetic acid, we found that an 8% yield was formed of a hydrocarbon having the following characteristics: $[\alpha]_D^{23}$ −27.4° (c 3.28; $CHCl_3$); IR spectrum (CCl_4, cm^{-1}): 3092, 1639 and 894 ($>C=CH_2$), 1382 and 1369  $\left(>C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$; PMR spectrum (60 MHz, CCl_4, δ scale, ppm): 0.73, 0.85, and 1.07 (singlets, 3H each); 4.79 and 4.87 (doublets, 1H each, J = 2 Hz); ^{13}C NMR spectrum (50.323 MHz, $CDCl_3$, δ_{TMS}, ppm): quartets at 18.14, 24.78, and 30.56; triplets at 24.65, 25.03, 33.72, 35.62, 35.95, 41.02, and 108.27; doublet at 52.53; singlets at 30.46, 45.53, 52.70, and 153.20; mass spectrum: 204 (M^+, 37%), 189

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(22), 175 (12), 161 (100), 147 (17), 133 (35), 122 (40), 119 (17), 107 (35), 105 (31). On treatment with sulfuric acid in ether, this hydrocarbon was converted into α-neoclovene. On the basis of these facts, we identified the compound obtained as β-panasinsene [1].

Thus, the biomimetic cyclization of caryophyllene into β-panasinsine takes place under the action of mercury(II) acetate.

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NEW ARTEFACTUAL GENINS FROM THE COMBINED HOLOTHURINS OF THE PACIFIC OCEAN HOLOTHURIAN *Holothuria squamifera*

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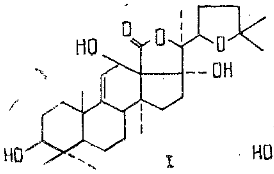
UDC 547.996+593.96

Continuing a study of the triterpene glycosides of holothurians of the family Holothuriidae, we have obtained the combined glycosides from the Pacific Ocean holothurian *Holothuria squamifera*. The native aglycones of the glycosides of the holothurians of the family Holothuriidae are unstable under the conditions for the hydrolysis of glycosidic bonds and are converted into artefactual products [1-3]. In actual fact, the acid hydrolysis (12% HCl, 90°C, 3 h) of the combined glycosides (50 mg) gave the sum of the artefactual genins.

Column chromatography on silica gel in the hexane—ethyl acetate (5:1) system led to the isolation of 10 mg of the completely transformed genin holothurin A, which was found to be identical with the known 22,25-epoxyholosta-7,9(11)-diene-3β,17α-diol [4]. Hexane—ethyl acetate (4:1 and 3:1) systems yielded the minor genins (I) and (II), which, according to ^{13}C and ^{1}H NMR spectroscopy, contained a 12β-hydroxy-9(11)-ene fragment. ^{13}C NMR ($CDCl_3$, ppm): 153.9 (C-9), 117.7 (C-11), 65.9 (C-12). PMR ($CDCl_3$, ppm): 5.16 (C-11, m, 1H), 4.53 (C-12, d, 1H), 3.25 (C-3, m, 1H).

Genins (I) and (II) have not been obtained previously.



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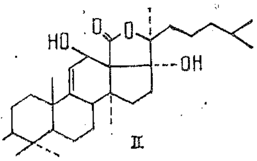

II

22,25-Epoxyholost-9(11)-ene-3β,12α,17α-triol (I), $C_{30}H_{46}O_6$, mp 303-305°C, $[\alpha]_D^{20}$ −24° (c 0.5; $CHCl_3$). Mass spectrum: M^+ 502 m/z. Diacetate of the genin (I): mp 265-276°C, $[\alpha]_D^{20}$ −50° (c 0.42; $CHCl_3$). Mass spectrum, m/z 526 ($M^+ - CH_3COOH$), 466 ($M^+ - 2\ CH_3COOH$), 367.99 (100%); PMR ($CDCl_3$, δ, ppm): 5.73 (C-11, m, 1H, $J_{11,12}$ = 1.7 Hz), 5.06 (C-12, d, 1H), 4.50 (C-3, q, 1H), 4.06 (C-22, t, 1H), 2.08, 2.05 (C-3, C-12 $OCOCH_3$, 2s, 3H, 3H), 1.33 (C-21, s, 3H), 1.25 (C-32, s, 3H), 1.18 (C-19, s, 3H), 1.23, 1.22 (C-26, C-27, s, 3H, 3H), 0.91, 0.89 (C-30, C-31, s, 3H, 3H).

Holost-9(11)-ene-3β,12β,17α-triol (II), $C_{30}H_{48}O_5$, mp 262-264°C, $[\alpha]_D^{20}$ −31° (c 0.2; $CHCl_3$). Mass spectrum, m/z: 488 (M^+). The diacetate of the genin (II) had mp 256-258°C. Mass spectrum, m/z: 512 ($M^+ - CH_3COOH$, 100%), 452 ($M^+ - 2\ CH_3COOH$), 293 ($M^+ - 2\ CH_3COOH - CH_3 - CO_2$). PMR ($CDCl_3$, δ, ppm): 5.75 C-11, m, 1H, $J_{11,12}$ = 1.75 Hz), 5.05 (C-12, d, 1H), 4.50 (C-3, q, 1H), 2.7 (C-8, m, 1H), 2.05, 2.03 (C-3, C-12 $OCOCH_3$, s, 3H, 3H), 1.30 (C-21, s, 3H), 1.23 (C-32, s, 3H), 1.15 (C-19, s, 3H), 0.89 (C-26, C-27, d, 6H), 3H, 3H).

Genin(I) was the product of the partial transformation of the native aglycone holothurin A [5].

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