It has been shown that as the fruit ripens the amounts of essential oils and monoterpene hydrocarbons in its peel and in the leaves increase. From the period of forced dormancy to flowering, the quantitative levels of the monoterpenoids in the leaves scarcely change.

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THE STRUCTURE OF A NEW GERMACRANOLIDE — SHONACHALIN C — FROM Artemisia fragrans

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UDC: 633.82/88

The structure of the new germacranolide shonachalin C ($C_{15}H_{22}O_4$, mp 203-205°C) isolated from Artemisia fragans has been established on the basis of spectroscopic (IR, ^1H and ^{13}C NMR) results.

Continuing a study of the sesquiterpene lactones of Artemisia fragrans Willd. collected in the village of Shona-chala, Lerik region, Azerbaidzhan SSR, by means of chromatography on a column of alumina we have isolated a crystalline substance with the composition $C_{15}H_{22}O_4$, mp 203-205°C (hexane—ether). The molecular weight, determined mass-spectrometrically, was 266.

In the region of characteristic frequencies of the IR spectrum there were bands of OH groups (3250 cm^{-1}), of the CO of a γ-lactone ring (1770 cm^{-1}), and of double bonds (1675 cm^{-1}).

The presence of two hydroxy groups was shown by acetylation. This gave a diacetyl derivative with the composition $C_{19}H_{26}O_2$, mp 149-151°C (hexane—ether) the IR spectrum of which contained absorption bands at 1770 cm^{-1} (CO of a γ-lactone ring), 1740, 1245, and 1230 cm^{-1} (CO of acetyl groups), and 1670 cm^{-1} (double bonds). There was no band of OH groups.

On comparing the physiochemical properties of the lactone under investigation with those of known sesquiterpene lactones, we came to the conclusion that it was new and we have called it shonachalin C.

In the ^{13}C NMR spectrum of shonachalin C taken with complete suppression of spin-spin coupling, 15 signals corresponding to the 15 carbon atoms of the molecule of the compound were detected, and in the off-resonance spectrum (here and below where the multiplicity of a signal is given, what is in view is the form of the signal under conditions of incomplete uncoupling from protons) these appeared in the form of the two quadruplets, four triplets, six doublets, and three singlets.

Doublets at 124.81 and 128.69 ppm, and singlets at 138.51 and 139.25 ppm observed in the spectrum of the region of sp^2-hybridized carbon atoms showed the presence of two trisubstituted double bonds in the molecule of the substance.

In the region of sp^3-hybridized carbon atoms, in addition to signals of carbon atoms bearing hydroxyls (69.26 ppm, triplet, and 73.90 ppm, doublet), there were three doublets in the spectrum at 41.80, 55.33, and 77.31 ppm relating to methine carbon atoms. Of these, the

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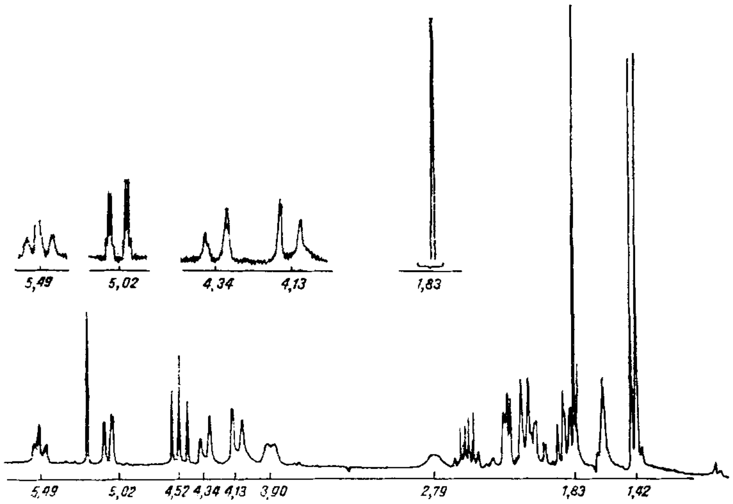


Fig. 1. NMR spectrum of shonachalin C.

TABLE 1. ^{13}C Chemical Shifts of Shonachalin C

Carbon atom	Off resonance	INEPT
1	124,81 d	124,73
2	38,15 t	38,13
3	73,91 d	73,85
4	138,51 s	—
5	128,69 d	128.70
6	77,31 d	77.30
7	55,33 d	55,29
8	25,31 t	25.30
9	35,23 t	35,21
10	139,25 s	—
11	41,80 d	41.75
12	179,32 s	—
13	16,45 q	16.47
14	17,25 q	17,30
15	69,26 t	69,24

last (77.31 ppm) belongs to the carbon atom of a lactone ring (C-6) and the other two to C-11 and C-7, respectively.

With the presence in the ^{13}C NMR spectrum of four doublet signals characterizing methine groups and three triplets due to three cyclic methylene carbon atoms (Table 1), in addition to the presence of two trisubstituted double bonds, shonachalin C can be based only on a germacrane carbon skeleton. The presence of a germacrane skeleton as the basis of the compound under investigation was also confirmed by the results of the INEPT ^{13}C NMR spectrum where 12 signals were found of which four belonged to three cyclic methylene and one hydroxymethyl carbon atoms.

According to the ^{13}C NMR spectrum, shonachalin C contains two methyl groups (quadruplets at 16.45 and 17.25 ppm). As the ^{1}H NMR spectrum (Fig. 1) shows, one of the methyl groups is secondary (doublet at 1.42 ppm, J = 6.84 Hz) and the other is a vinyl methyl group (doublet at 1.83 ppm; J = 1.22 Hz).

If shonachalin C contains a germacrane carbon skeleton, two trisubstituted double bonds, and one secondary hydroxy group the spectrum should show only three triplet signals in the region of sp^3-hybridized carbon atoms. However, the spectrum shows four triplets: at 25.31, 35.23, 38.15, and 69.26 ppm. As can be seen, one of the triplets is strongly shifted in the downfield direction. Such a signal may be caused by the presence of anhydroxymethyl group in the molecule of the compound under investigation. The correctness of this point of view is confirmed by the presence in the ^{1}H NMR spectrum, on the one hand, of only two signals of methyl groups and, on the other hand, of the signals of a hydroxymethyl group appearing in the form of one-proton doublets at 4.12 ppm (J = 12.5 Hz) and 4.34 ppm (J = 12.5 Hz). These signals are somewhat shifted downfield, which is due to the presence of a double bond in the α position with respect to the CH_2OH group.

The lactone ring in the shonachalin C molecule is located at C_6-C_7. This shown by a triplet signal in the proton spectrum at 4.52 ppm (J_1 = J_2 = 10 Hz) with a 1:2:1 ratio of the intensities of its components. The spin-spin coupling constant (SSCC) of 10 Hz shows the trans position of the H-5, H-6, and H-7 protons relative to one another.

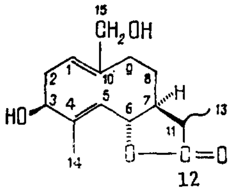
The positions of the double bonds in the shonachalin C molecule were established on the basis of the fact that in the ^1H NMR spectrum the signals from one olefinic proton and the lactone proton appeared in the form of a doublet (at 5.02 ppm) and a triplet with equal SSCCs (10 Hz). Each component of the doublet of the olefinic proton is additionally split into quadruplets with SSCCs of 1.22 Hz because of allyl interaction with a vinyl methyl group. The signal of the vinyl methyl group is also split into a doublet with a constant of 1.22 Hz, and therefore one of the double bonds is located at C_4-C_5.

The olefinic proton of the second double bond appears in the spectrum in the form of a triplet at 5.49 ppm (J = 6.84 Hz) the ratio of the intensities of the components of which corresponds to 1:2:1. Consequently, the double bond may be present at C_1-C_{10} or C_9-C_{10}, and the hydroxymethyl group at C-10. From the aspect of biogenesis [1], the position of the double bond at C_1-C_{10} is more likely.

The position of the secondary hydroxy group was established in the following way. The signal of the gem-hydroxylic proton in the ^1H spectrum is found in the form of a doublet at 3.90 ppm (J = 9.28 Hz) with broadened components. The half-width of each component is 6 Hz. Such a structure of the signal suggests that the gem-hydroxylic proton interacts with two vicinal protons of a methylene group, and therefore the OH group may be present at C-3 or C-9. It is known [2-5] that a hydroxy group present in the vicinal position to a vinylmethyl group and an exocyclic methylene group leads to an appreciable paramagnetic shift of their signals. The signal of the vinyl methyl group of shonachalin C (1.83 ppm) is shifted downfield in comparison with the signal of the CH_3—C group of, for example, tenacin [6] and tanachin [7], which is apparently due to the presence of a hydroxy group at C-3.

One of the triplet signals (at 38.15 ppm, C-2) in the ^{13}C NMR spectrum is more descreened than the other signals of cyclic methylene groups (at 35.23 and 25.31 ppm, C-9 and C-8, respectively). This is probably due to the influence of the OH group at C-3.

Thus, shonachalin C is represented by structure (1).



(1)

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in paraffin oil and the ^1H and ^{13}C NMR spectra on a Bruker WP-200 SY 50.32 MHz spectrometer in $CDCl_3$ solution with TMS (0) as internal standard.

Isolation of Shonachalin C. Chromatography on a column of alumina was carried out in the same way as in the isolation of shonachalin A [8].

The fractions eluted with chloroform—acetone (10:1) yielded 0.08 g of a crystalline substance with the composition $C_{15}H_{22}O_4$, mp 203-205°C (hexane—ether).

Acetylation of Shonachalin C. A solution of 0.03 g of the substance in 1.5 ml of pyridine was treated with 1.5 ml of acetic anhydride. The mixture was heated on the water bath for 20 min and was then left at room temperature for 20 h, after which it was evaporated on the water bath. The residue was dissolved in 5 ml of chloroform and the solvent was distilled off. The residue was dissolved in a mixture of hexane and ether, and, on standing, crystals deposited with the composition $C_{19}H_{26}O_6$, mp 149-151°C.

SUMMARY

A new germacranolide — shonachalin C with the composition $C_{15}H_{22}O_4$, mp 203-205°C — has been isolated from Artemisia fragrans.

A structure has been proposed for shonachalin C.

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CHEMICAL COMPOSITION OF THE OLEORESIN OF Larix kamtschatica

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UDC: 547.913.2

The chemical composition of the oleoresin of the Kamchatka larch has been studied. Mono-, sesqui-, and diterpenoids have been found in it. The monoterpenes were represented by nine components (the main one being 3-carene), and among the sesquiterpene hydrocarbons γ-element, longifolene, and germacrene D predominated. The main oxygen-containing diterpenoid was larixyl acetate. Seven resin acids were determined, the main one being isopimaric and palustric and/or levopimaric.

Continuing a study of the oleoresin of larches growing in the Far East, we have investigated the chemical composition of the oleoresin of Larix kamtschatica (Rupr.) var. kurilensis (Kamchatkan or Kurile Dahurian larch) growing on the Kurile Islands [1, 2].

After the initial oleoresin had been treated by the usual method, about 60% of neutral and 40% of acidic compounds were obtained. The neutral fraction consisted of a mixture of mono-, sesqui-, and diterpene hydrocarbons and their oxygen-containing derivatives. The hydrocarbons (30%) and the oxygen-containing compounds (70%) were separated by the chromatography of the neutral fraction on alumina. The hydrocarbons were separated by vacuum distillation into monoterpenes (24% on the neutral fraction), sesquiterpenes (2.1%), and diterpenes (1.7%).

The monoterpene hydrocarbons were analyzed by the GLC method. Of the nine compounds found — camphene, α- and β-pinenes, 3-carene, limonene, myrcene, β-phellandrene, γ-terpinene, and terpinolene — the main component was 3-carene (78%).

Chromatography of the sesquiterpene fraction on SiO_2 and $SiO_2 + AgNO_3$ led to the isolation of γ-elemene, longifolene, germacrene D, α-, γ-, and δ-cadinenes, and α- and γ-muurolenes. Another 15 hydrocarbons were identified by their retention times in the GLC method. Only three components — germacrene D (25.9%), longifolene (21.8%), and γ-elemene (13.4%) were found in considerable amounts.

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