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SHONACHALIN B — A NEW EUDESMANOLIDE FROM
Artemisia fragans

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The results are given of an investigation of a new eudesmanolide from *Artemisia fragans* Willd., shonachalin B, with the composition $C_{15}H_{22}O_4$, mp 127-129°C.

Continuing a study of the sesquiterpene lactones of *Artemisia fragans* Willd. [1, 2] growing in various soil and climatic conditions, by chromatography on a column of alumina of an acetone extract of plant material collected in the village of Shona-chala, Lerik region of the Azerbaidzhan SSR, we have isolated 20 mg of a crystalline substance with the composition $C_{15}H_{22}O_4$, mp 127-129°C (ether-hexane). The molecular weight determined by mass spectroscopy was 266.

The IR spectrum of the substance contained, in the region of characteristic frequencies, absorption bands of a γ -lactone ring (1760 cm^{-1}) and of a hydroxy group (3480 cm^{-1}).

The NMR spectrum of the substance showed the singlet of an angular methyl group (1.26 ppm, 3 H, $\text{CH}_3-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-$), and the doublet of a secondary methyl group attached to a lactone ring

(1.28 ppm, $J = 7\text{ Hz}$, 3 H, $\text{CH}_3-\text{CH}<$), one component of the doublet being superposed on the singlet of the angular methyl group. A one-proton triplet at 4.11 ppm ($J = 10\text{ Hz}$) belonged to a gem-hydroxylic proton and indicated the secondary nature of the hydroxy group. The lactone proton appeared in the form of a quartet at 3.78 ppm ($J_1 = 11.5$, $J_2 = 10\text{ Hz}$).

The presence of an OH group in the molecule of the compound was also shown by peak at 248 in the mass spectrum due to the splitting out of one molecule of water ($M - H_2O$).

The substance contained one OH group, as was confirmed by the results of the oxidation of the lactone with chromium dioxide: a keto derivative was formed with the composition $C_{15}H_{20}O_4$, mp 166-168°C (ether-hexane). The IR spectrum of this ketone had the absorption bands of a CO group in a γ -lactone ring (1788 cm^{-1}) and of a ketone ring in a six-membered ring (1725 cm^{-1}). There was no band of an OH group in the spectrum.

The UV spectrum contained a maximum characteristic for an isolated ketone group (λ_{max} 283 nm, $\log \epsilon$ 1.61).

Thus, of the four oxygen atoms present in the molecule of the lactone under consideration two formed the lactone ring, one was present in the form of an OH group, and the fourth formed an oxide ring. The presence of the oxide ring was shown by a three-proton singlet in the NMR spectrum of a methyl group of 1.40 ppm ($\text{CH}_3-\text{C}-\text{O}-$) [3-5] and of a one-proton doublet at 3.66 ppm ($J = 5\text{ Hz}$, $\text{HC}-\text{O}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-$) [6] and the molecular weight of the compound.

On comparing the facts given with literature information, we came to the conclusion that

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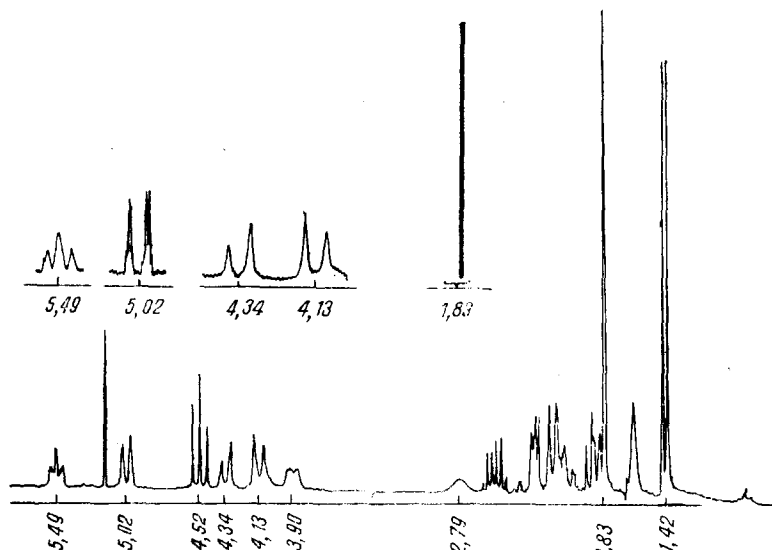
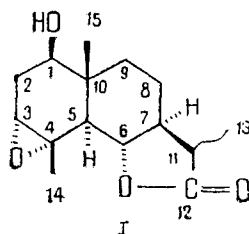


Fig. 1. ^1H NMR spectrum of shonachalin B (in CDCl_3).

the lactone under investigation was new and we have proposed for it the name shonachalin B.

In view of the detection of the singlet of an angular methyl group in the NMR spectrum, it was possible to assume that shonachalin B was based on eudesmane or a pseudoguaiane carbon skeleton. The quartet structure of the lactone proton with a ratio of the intensities of the components of 1:1:1:1 excluded the possibility of a pseudoguaiane carbon skeleton as the basis of shonachalin B.

The $H_{1,2}$, $H_{3,2}$, $H_{5,6}$, and $H_{6,7}$ spin-spin coupling constants (10, 5, 10, and 11.5 Hz, respectively) enabled the orientations of the protons to be determined as $1\alpha\text{H}$, $3\beta\text{H}$, $5\alpha\text{H}$, $6\beta\text{H}$, and $7\alpha\text{H}$. Consequently, shonachalin B is a hydroxyepoxyeudesmanolide with the structure (I).



As we see, shonachalin B has a structure close to that of 11,13-dihydroepoxysantamarin [6]. It may be assumed that shonachalin B is based on the structure of 11,13-dihydrosantamarin in which the double bond at C_3-C_4 is epoxidated. Yoshioka et al. [6] have established on the basis of molecular models that α -epoxidation is sterically more favorable for santamarin. A confirmation of this point of view is the isolation from *Ambrosia confertiflora* of an epoxysantamarin identical with the synthetic epoxy derivative of santamarin [6]. The detection in nature of a stereoisomer of the latter — ludovicin A [7] — suggests that, regardless of the orientation of the OH group at C-1, in the process of epoxidation both in nature and in the laboratory compounds with α -epoxide rings are formed. On the basis of these facts it can be asserted that the epoxide ring in shonachalin B also has the α orientation, all the more since in the NMR spectrum the signal of the H-3 atom appears in the form of a triplet with a spin-spin coupling constant of 5 Hz.

Consequently, shonachalin B is a derivative of 11,13-dihydroepoxysantamarin or differs from it by the orientation of the methyl group at C-11. Since no 11, 13-dihydro derivative has been prepared from epoxysantamarin [6], we have been unable to compare the physicochemical properties of shonachalin B with those of 11,13-dihydroepoxysantamarin.

EXPERIMENTAL

IR spectra were taken in paraffin oil on UR-20 spectrometer, UV spectra of a Specord UV-VIS spectrophotometer in ethanol, and NMR spectra on a JNM-4H-100 MHz spectrometer in

deuterated chloroform solution (with HMDS as internal standard, δ scale), and mass spectra on a MKh-1303 instrument).

Isolation of Shonachalin B. The resin obtained by two extractions with acetone (4 days of each time) of 634 g of the epigeal part of *A. fragans* (35 g) was chromatographed on a column of alumina (122×3 cm, Al_2O_3 , activity grade IV). The volume of each fraction was 100 ml. Elution was performed with hexane (12 fractions), hexane-ether (1:1) (50 fractions), ether (8 fractions), chloroform (15 fractions), and acetone (11 fractions). The chloroform fractions were combined and rechromatographed on a column of alumina (40×1.8 cm, Al_2O_3 , activity grade IV). The volume of each fraction was 50 ml. Elution was performed with ether-chloroform (1:1) (7 fractions) and with chloroform (8 fractions). The first fractions eluted by chloroform yielded 20 mg of a crystalline substance with the composition $\text{C}_{15}\text{H}_{22}\text{O}_4$, mp $127-129^\circ\text{C}$ (ether-hexane).

Oxidation of Shonachalin B. A solution of 10 mg of the substance in 1 ml of acetone was treated with 10 mg of chromium trioxide in 1.5 ml of acetone, and the mixture was left for 3 h. Then it was worked up in the usual way, giving a crystalline substance with the composition $\text{C}_{15}\text{H}_{20}\text{O}_4$, mp $166-168^\circ\text{C}$ (ether-hexane).

SUMMARY

1. The epigeal part of *Artemisia fragans* collected in the Azerbaidzhan SSR has yielded a new eudesmanolide with the composition $\text{C}_{15}\text{H}_{22}\text{O}_4$, mp $127-129^\circ\text{C}$, which has been called shonachalin B.

2. The structure of shonachalin B has been established.

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