DZHEIRANBATANOLIDE — A NEW GUAIANOLIDE FROM *Artemisia fragrans*

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A new guaianolide which has been called dzheiranbatanolide (I), $C_{15}H_{20}O_4$, mp 186-188°C has been isolated from the epigeal part of *Artemisia fragrans* Willd. The oxidation of (I) led to a keto derivative (II) with the composition $C_{15}H_{18}O_4$, mp 247-248°C. The structure of (I) has been established by the chemical and spectral (IR, UV, and ^{13}C NMR) analysis of (I) and (II).

The isolation from *Artemisia fragrans* Willd. of sesquiterpene lactones (erivanin, alkhanin, alkhanol, and others) with the eudesmane carbon skeleton has been reported previously [1-3]. In the present paper we give the results of a study of this plant collected at the end of November, 1981 at Lake Dzheiranbatan.

By column chromatography on alumina of the resin obtained by two acetone extractions of the epigeal part of the species of wormwood we isolated a new sesquiterpene lactone which we have called dzheiranbatanolide.

Dzheiranbatanolide has the composition $C_{15}H_{20}O_4$, mp 186-188°C (from benzene). Its IR spectrum (Fig. 1) shows absorption bands of a CO of a γ-lactone ring (1770 cm^{-1}), of double bonds (1670, 1650 cm^{-1}), and of hydroxy groups (3360 cm^{-1}).

The NMR spectrum of dzheiranbatanolide (Fig. 2) shows the doublet of a secondary methyl group at 1.22 ppm (J = 7 Hz, 3H, $CH_3{-}CH$ at C-11), the singlet of a vinyl methyl group at 1.74 ppm (3H, $CH_3{-}C{=}O$), the triplet of a lactone proton at 4.49 ppm ($J_1 = J_2 = 10$ Hz, H-6), and one-proton singlets at 5.20 and 4.88 ppm due to the protons of an exomethylene group ($CH_2{=}C<$). A triplet at 4.32 ppm (1H, $J_1 = J_2 = 8$ Hz, H-2) and a multiplet at 4.04 ppm (1H, H-8) are due to hemihydroxylic protons. The last signal has a triplet form with a spin-spin coupling constants of 8 Hz, each component of which is additionally split by 2 Hz, which shows interaction with three vicinal protons.

The presence in the spectrum of two one-proton signals characterizing two protons of hemihydroxylic groups indicates the presence of two secondary hydroxy groups in the dzheiranbatanolide molecule.

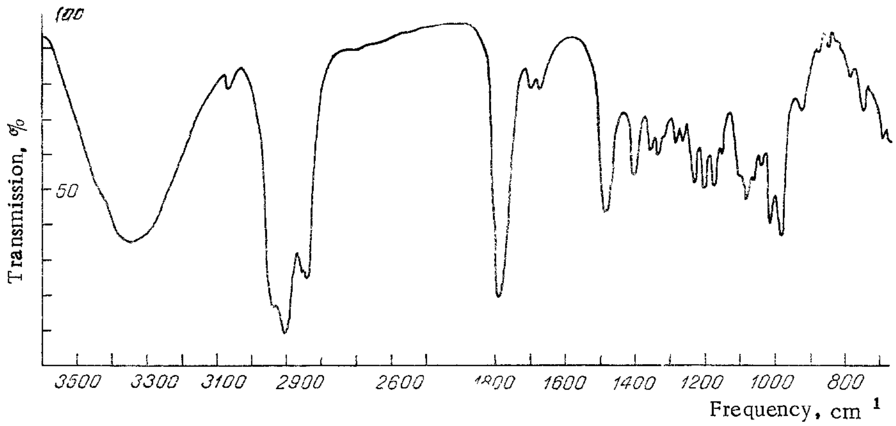

Fig. 1. IR spectrum of dzheiranbatanolide.

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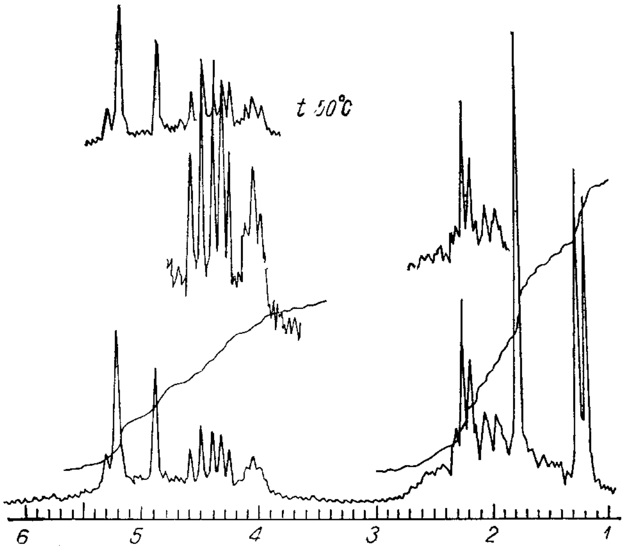


Fig. 2. NMR spectrum of dzheiranbatanolide.

The second double bond is secondary-tertiary, as is shown by the singlet of a vinyl methyl group in the spectrum and the partial overlapping (on a singlet of an exomethylene group at 5.20 ppm) of the doublet of an olefinic proton at 5.25 ppm (J = 8 Hz).

Thus, dzheiranbatanolide contains two secondary hydroxy groups and two double bonds (methylenic and secondary-tertiary).

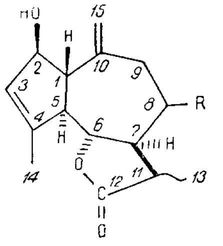
The signals in the NMR spectrum of secondary methyl, vinyl methyl, and exomethylene groups give grounds for considering the presence as the basis of dzheiranbatanolide of a guaiane or germacrane, and not a eudesmane, carbon skeleton. The choice was made on the basis of the results of the ^{13}C NMR spectrum taken with partial suppression of spin-spin coupling. Two quadruplets, two triplets, eight doublets, and three singlets were found in the spectrum.

The singlet signals belonged to the carbon atoms of a lactone carbonyl group (180.76 ppm) and to the quaternary carbons of an olefinic (150.72 ppm) and a methylenic (147.08 ppm) double bonds.

Doublets at 122.36 (J = 158.7 Hz), 75.76 (J = 152.59 Hz), and 75.34 ppm (J = 152.59 Hz) belong to an olefinic and two hemihydroxylic carbon atoms, respectively.

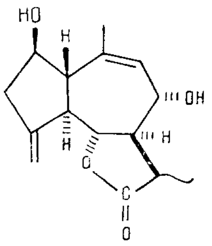
Of the triplet signals in the ^{13}C NMR spectrum of the lactone under investigation, one (at 111.05 ppm, J = 154.2 Hz) was due to the carbon atom of an exomethylene group and the other (at 42.25 ppm) to the carbon of a cyclic methylene group. The signals of two methyl groups $(CH_3{-}CH< \text{ and } CH_3{-}\overset{|}{C}{=})$ of the dzheiranbatanolide molecule were detected in the form of two quadruplets at 12.24 and 28.00 ppm, respectively.

It follows from these facts that dzheiranbatanolide can be based only on a guaiane carbon skeleton. Thus, structure (I) or (II) is likely for dzheiranbatanolide.



I. R = ''''''OH

III. R = =O



II

The choice between the structures presented was made on the basis of the results of the oxidation of the lactone under investigation by chromium trioxide in acetone solution. This gave a substance with the composition $C_{15}H_{18}O_4$, mp 247-248°C (III). The IR spectrum of (III) showed absorption bands of an OH group (3465 cm^{-1}), the CO of a γ-lactone ring (1768 cm^{-1}), a CO in a cyclopentane ring (1720 cm^{-1}), and of double bonds (1670, 1660 cm^{-1}).

Consequently, an OH group in the seven-membered ring (at C-8) was oxidized. This was also shown by the UV spectrum of the oxidized dzheiranbatanolide, in which there was a maximum corresponding to an isolated ketone group (λ_{max} 286 nm; log ε 1.7).

The IR and UV spectra of the oxidized dzheiranbatanolide also showed the presence of two hydroxy groups in the molecule of the lactone under investigation. The spin-spin coupling constants $H_{2,1}$ (8 Hz), $H_{6,5}$ (10 Hz), $H_{6,7}$ (10 Hz), $H_{8,7}$ (8 Hz), and $H_{8,7}$ (8 Hz) permitted the orientations of the protons to be determined as follows: 1βH, 2αH, 5αH, 6βH, 7αH, 8βH. This means that dzheiranbatanolide is represented by structure (I).

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in paraffin oil, the UV spectra on a Specord UV-Vis spectrometer in ethanol solution, the ^1H NMR spectrum on a Varian HA-100D spectrometer in $CDCl_3$ solution + 6 drops of Py-d (internal standard TMS — 0), and the ^{13}C NMR spectrum on a Bruker WP 200 SY 50.32 MHz spectrometer in methanol solution.

Isolation of Dzheiranbatanolide. The air-dry epigeal part of *Artemisia fragrans* (0.5 kg) was twice extracted with acetone, and the extract was filtered and evaporated. This gave 21.5 g (4.3%) of a dark green resin. The resin (20 g) was chromatographed on a column (70 × 2.5 cm) of alumina (activity grade II). Elution was performed with chloroform, 150-ml fractions being collected. Fractions 9-12 yielded a crystalline substance with the composition $C_{15}H_{20}O_4$, mp 186-188°C (from benzene). Yield 0.66%.

Oxidiation of Dzheiranbatanolide. A solution of 0.66 g of the substance in 5 ml of acetone was treated with 0.05 g of chromium trioxide in 5 ml of acetone. The mixture was left in the refrigerator for 18 h. Then it was worked up in the usual way, giving a crystalline substance with the composition $C_{15}H_{18}O_4$, mp 247-248°C (from a mixture of diethyl ether and petroleum ether).

CONCLUSIONS

1. The epigeal part of *Artemisia fragrans* collected at Lake Dzheiranbatan has yielded a new guaianolide with the composition $C_{15}H_{20}O_4$, mp 186-188°C, which has been called dzheiranbatanolide.

2. The structure of dzheiranbatanolide has been established.

LITERATURE CITED

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