THE STRUCTURE OF A SESQUITERPENE LACTONE FROM Artemisia fragrans

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UDC 547.913

From the epigeal part of Artemisia fragrans Willd., collected in the village of Alkhanly, Fizuli region of the AzSSR, we have isolated a new sesquiterpene lactone with the composition $C_{15}H_{20}O_4$; mp 201-203°C, R_f 0.63 [Al_2O_3, activity grade II; chloroform–ethanol (100 : 1)] and have named it alkhanin.

The IR spectrum of alkhanin (Fig. 1) has absorption bands of an OH group (3400 cm^{-1}), the CO group of a γ-lactone ring (1775 and 1760 cm^{-1}), of a cyclohexenone CO group (1670 cm^{-1}), and of a double bond (1620 cm^{-1}). The presence of a conjugated ketone group in the molecule of the substance is also shown by a maximum in the UV spectrum at 248 nm (log ε 3.98).

The PMR spectrum of alkhanin contains a singlet at 1.34 ppm $\left(CH_3-\overset{|}{\underset{|}{C}}-,\ 3H\right)$, a doublet with its center at 1.23 ppm, J = 7 Hz, $CH_3-CH{<}$, and a doublet corresponding to the protons of a vinylmethyl group at 2.0 ppm (J = 2 Hz, $CH_3-\overset{|}{C}=$).

A one-proton signal with its center at 3.78 ppm belongs to a proton geminal to a hydroxy group and shows the secondary nature of this hydroxy group. The lactone proton appears in the spectrum in the form of a doublet with its center at 4.72 ppm (J = 10 Hz, 1 H), each component of this doublet being additionally split by 2 Hz. The additional splitting of this signal is apparently the result of long-range spin–spin coupling with a vinylmethyl group. The spin–spin coupling constant for the lactone proton of 10 Hz shows its interaction with only one neighboring proton and the fact that they are in the trans position with respect to one another. Furthermore, in the NMR spectrum there are no signals that could be assigned to olefinic protons. Consequently, the double bond in the molecule of the compound has a tertiary–tertiary nature.

On exhaustive hydrogenation in ethanol with deactivated Raney nickel, alkhanin forms tetrahydroalkhanin with the composition $C_{15}H_{24}O_4$, mp 186-188°C. As already mentioned, alkhanin contains one tetrasubstituted double bond conjugated with the ketone group. The formation of a tetrahydro derivative takes place through the reduction of the keto group.

The IR spectrum of tetrahydroalkhanin shows, in the region of characteristic frequencies, the bands of hydroxy groups (3360 cm^{-1}) and of the carbonyl of a lactone ring (1778 cm^{-1}). The presence in tetrahydroalkhanin of two hydroxy groups was shown by acetylation. This gave a diacetyl derivative with the composition $C_{19}H_{18}O_6$, mp 228-230°C, the IR spectrum of which had bands at 1780 cm^{-1} (CO of a γ-lactone ring) and 1730, 1270, 1250 cm^{-1} (the CO groups of two acetyl residues).

A comparison of the characteristics of the NMR spectra of alkhanin and of α- and β-santonins [1] suggested that, probably, alkhanin differs from α- and β-santonins by the presence of a hydroxy group in place of one double bond. Consequently, the hydroxy group may be present in one of the following positions: C_1, C_2, C_8, or C_9. If it is assumed that the OH group is present at C_1, then, by analogy with ferulidin [2], grossmisin [3], di- and tetrahydrobadkhysin [4], and tetrahydroolgin [5], in the process of acetylation or saponification, even at room temperature, dehydration with the formation of α- or β-santonin would be unavoidable.

In actual fact, the acetylation of alkhanin led to a substance with the composition $C_{15}H_{18}O_3$, mp 170-171°C, R_f 0.69 (Al_2O_3 of activity grade II, solvent – chloroform). The IR and NMR spectra of the substances obtained

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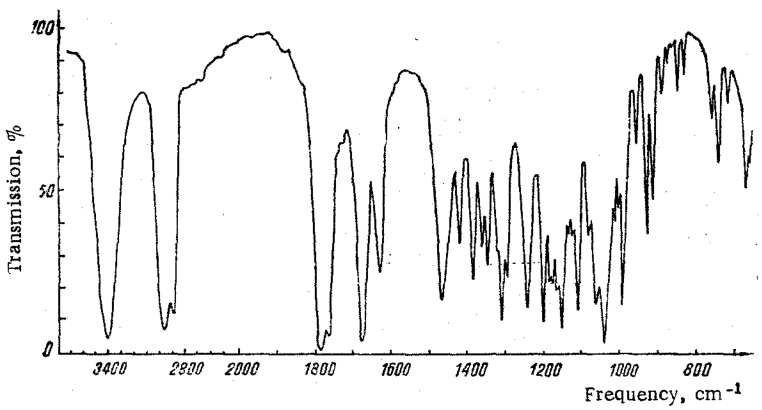
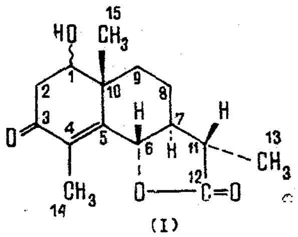


Fig. 1. IR spectrum of alkhanin.

coincided completely with those of α-santonin. A mixture of the samples compared gave no depression of the melting point. Consequently, the stereochemistry of alkhanin at C_6, C_7, C_{10}, and C_{11} is analogous to that of α-santonin.

Thus, alkhanin corresponds to structure I



(I)

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer in paraffin oil, the UV spectra on an SF-4A instrument, and the NMR spectra on a Varian HA-100D spectrophotometer, the chemical shifts being given on the δ scale with TMS as internal standard. The results of microanalysis corresponded to the calculated figures.

Isolation of Alkhanin. The dark green resin (15 g) obtained from the epigeal part of Artemisia fragrans on extraction with acetone was chromatographed on a column, 45 × 3.5 cm, of alumina, (activity grade II). Fractions with a volume of 100 ml were collected. Elution was performed with hexane (15 fractions), hexane–diethyl ether (3 : 2) (eight fractions), (1 : 1) (three fractions), (1 : 2) (five fractions), (1 : 3) (seven fractions), (1 : 4) (six fractions), and ether. Fractions 37-41 yielded a crystalline substance with, after three recrystallizations from ether, had mp 201-203°C.

Hydrogenation of Alkhanin. In solution in 10 ml of ethanol, 0.07 g of alkhanin was exhaustively hydrogenated in the presence of 0.5 g of freshly prepared deactivated Raney nickel. Hydrogenation took 2 h 30 min. The consumption of H_2 was 16 ml (one double bond requires 5.93 ml of H_2). The ethanolic solution was filtered and the solvent was distilled off. The residue consisted of a crystalline substance with the composition $C_{15}H_{24}O_4$ which, after recrystallization from ether had mp 186-188°C.

Acetylation of Tetrahydroalkhanin. A solution of 0.03 g of tetrahydroalkhanin in 1.5 ml of pyridine was treated with 1.5 ml of acetic anhydride. The mixture was left at room temperature for a day and was then evaporated in a watch glass. The residue contained a substance $C_{19}H_{28}O_6$ which crystallized from a mixture of hexane and ether with mp 228-230°C.

Acetylation of Alkhanin. A solution of 0.1 g of the substances in a mixture of 2 ml of pyridine and 2 ml of acetic anhydride was left at room temperature for 24 h. Then it was diluted with water, acidified with dilute sulfuric acid, and extracted with chloroform. The chloroform layer was washed four times with water, dried over Na_2SO_4, and filtered, and the solvent was distilled off. The residue consisted of a crystalline substance with mp 170-171°C (from ethanol).

SUMMARY

From the epigeal part of Artemisia fragrans Willd. a new sesquiterpene lactone $C_{15}H_{20}O_4$ has been isolated which has been called alkhanin.

It has been shown that alkhanin has the structure (I).

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