STRUCTURE AND CONFIGURATION OF ARSANIN

B. Akyev, Sh. Z. Kasymov,
and G. P. Sidyakin

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We have continued a study of the structure and configuration of the sesquiterpene lactone arsanin isolated previously [1].

The action on arsanin (I) of 50% sulfuric acid gave anhydroarsanin (II) with the composition $C_{15}H_{20}O_3$, mp 138-139°C (from ethanol). The same product is formed by the action of a 15% solution of hydrochloric acid in methanol, dehydration beginning at an even lower concentration of acid.

To determine the configuration, we investigated the NMR spectrum of arsanin and its acetyl derivative (III). In the NMR spectrum of (I) (Fig. 1), the lactone proton at C_6 is expressed in the form of a triplet at δ 3.94 ppm (J = 10 Hz, 1H). This proton is in the trans position with respect to the protons at C_5 and C_7. An unresolved multiplet at δ 3.55 ppm (W = 25 Hz, 2H) is due to the proton of a hydroxy group at C_1 and its geminal proton. In acetylarsanin, the proton at C_1 is represented in the form of a quartet at δ 4.74 (J_1 = 6 Hz and J_2 = 10 Hz) because of spin–spin coupling with the C_2 protons. The spin–spin coupling constant [2] shows the axial arrangement of this proton. Consequently, the hydroxy group has the equatorial orientation.

The stereochemistry of the other asymmetric centers of arsanin (C_4, C_5, C_6, C_7, and C_{11}) was elucidated by its conversion to α-tetrahydrosantonin [3]. The catalytic dehydrogenation of (II) gave a substance (IV) with the composition $C_{15}H_{22}O_3$ identified as 3-oxo-4β,5α,6β,7α (H),11β(H)-eudesman-6,7-olide [4].

In the IR spectrum of (IV) there are absorption bands in the 1770-cm^{-1} region (γ-lactone carbonyl) and the 1700-cm^{-1} region (cyclohexanone). A mixture of the α-tetrahydrosantonin obtained from α-santonin (V) and the product of the hydrogenation of anhydroarsanin gave no depression of the melting point. The IR spectra of the two substances were identical: α-tetrahydrosantonin was obtained by isomerizing γ-tetrahydrosantonin [5] with perchloric acid.

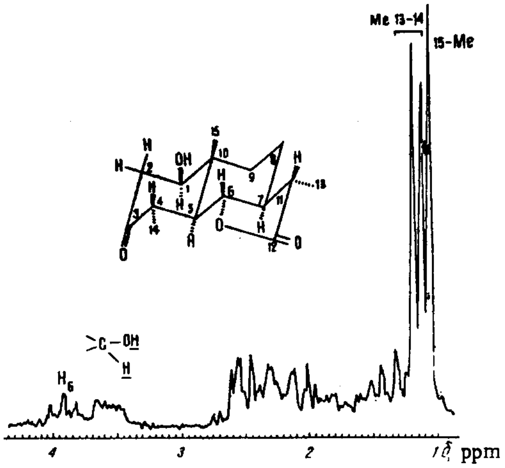

Fig. 1. NMR spectrum of arsanin.

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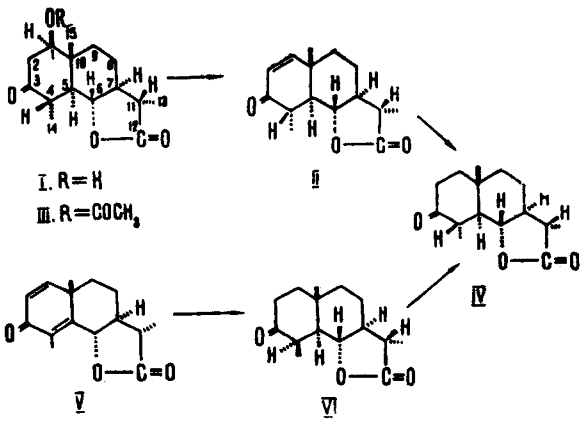
Thus, arsanin is 1β-hydroxy-3-oxo-4β,5α,6β,7α (H),11β(H)-eudesman-6,12-olide (I).



EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer (tablets with KBr), the mass spectra on an MKh-1303 mass spectrometer, and the NMR spectrum on a JNH-4 H-100 MHz instrument (in $CDCl_3$ with HMDS as internal standard).

Anhydroarsanin. A mixture of 0.1 g of arsanin and 4 ml of a 15% solution of HCl in methanol was left for 1 h and was then diluted with a small amount of water and was shaken with ether five times. From the residue after the evaporation of the solvent a substance was obtained with the composition $C_{15}H_{20}O_3$, mp 138-139°C (from ether), mol. wt. 248 (mass spectrometry). Yield 0.08 g.

Hydrogenation of Anhydroarsanin. To a solution of 0.08 g of anhydroarsanin in 4 ml of ethanol was added 0.04 g of catalyst (Pd/C), and hydrogenation was performed for 3 h. The residue after the elimination of the catalyst and the solvent deposited crystals with the composition $C_{15}H_{24}O_3$, mp 153-154°C (from ether), mol. wt. 250 (mass spectrometry). A mixture with a sample of α-tetrahydrosantonin showed no depression of the temperature. Their IR spectra were identical.

γ-Tetrahydrosantonin (VI). To a solution of 0.15 g of α-santonin in 6 ml of ethanol was added 0.08 g of catalyst (Pd/C), and hydrogenation was performed for 3 h. After the catalyst had been removed, γ-tetrahydrosantonin was obtained with mp 145-146°C (from ether), $C_{15}H_{24}O_3$, mol. wt. 250 (mass spectrometry).

Isomerization of γ-Tetrahydrosantonin. A solution of 0.1 g of γ-tetrahydrosantonin was treated with 70% ethanolic perchloric acid and the mixture was left for 15 h. Then it was diluted with water and extracted with ether, and the ethereal solution was washed with water. After evaporation of the solvent, α-tetrahydrosantonin was obtained with mp 153-154°C (from ether); composition $C_{15}H_{24}O_3$, mol. wt. 250 (mass spectrometry).

SUMMARY

It has been established that the sesquiterpene lactone arsanin from Artemisia santolina Schrenk is 1β-hydroxy-3-oxo-4β,5α,6β,7α (H),11β (H)-eudesman-6,12-olide.

LITERATURE CITED

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