STRUCTURE AND CONFIGURATION OF ARSUBIN

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In the partial structure of arsubin (I) proposed previously, the position of the secondary hydroxy group and the configuration of the lactone itself remained undetermined [1, 2].

In the NMR spectrum of acetylarsubin (III) ($CDCl_3$, all the spectra discussed were taken on a JNM-4H-100 instrument with HMDS as internal standard, using the δ scale), the signal of the proton geminal to the acetyl group forms a quartet with its center at 5.28 ppm ($J_1 = 11$ Hz and $J_2 = 5$ Hz). This nature of the splitting of the signal is due to diaxial and axial–equatorial interactions of the H–C–OAc proton with the protons on the neighboring carbon atom and can be observed if an –OAc(–OH) group with the equatorial orientation is located at the C_1 or C_8 carbon atom. Substitution at C_3 is excluded since the UV spectrum of oxoarsubin (V) lacks the maximum characteristic for an α,β-unsaturated ketone.

It was possible to determine the position of the hydroxy group from a study of the spectra of (I) and (V) in solution in pyridine-d. In the spectra of (V) there is a multiplet with its center at 2.44 ppm (4H) due to the protons in the neighborhood of the carbonyl and exomethylene groups. In substance (I) the signals of these protons appear in a stronger field by 0.47 ppm. In the spectrum of (V) the broadened singlets of the exomethylene group at 5.17 and 5.02 ppm are shifted downfield by 0.15 ppm in comparison with (I). This gives grounds for assuming that the exomethylene group at C_4 and the keto group in (V) are present in the same ring. Consequently, the hydroxy group in arsubin is located at C_1 and occupies the equatorial position.

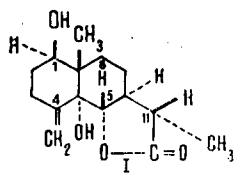
The signal of the lactone proton in the spectrum of (I) appears in the form of a doublet with its center at 4.69 ppm ($J = 10.5$ Hz). The large value of the coupling constant of the H_5 and H_6 protons shows the trans addition of the lactone ring to the C_5 and C_6 atoms.

Thus, compound (I) is a stereoisomer of artemin (VI) [3] and differs from it, possibly, by the configuration of the C_{11} asymmetric center.

Arsubin also has the same skeleton as α-santonin (VII) and β-santonin (VIII). The lactones (VII) and (VIII) differ only by the spatial arrangement of the H–C–CH_3 substituents in the lactone ring. It can be seen from a consideration of models that with the β orientation of the methyl group in (VII) the lactone proton is additionally screened by the C_{11}–CH_3 bond. In the NMR spectrum of (VII), the lactone proton appears in the form of a doublet with its center at 4.81 ppm ($J = 10$ Hz), 0.21 ppm upfield as compared with (VIII) [4].

On comparing the spectra of acetylartemin (IX) and (III) it is possible to see great similarity between them, with the exception of the position of the signals of the lactone proton. In (III) it appears in the form of a sharp doublet with its center at 4.40 ppm ($J = 10$ Hz) and is shifted downfield by 0.23 ppm as compared with (IX).

Consequently, the methyl group at C_{11} in (III) has the same arrangement as in β-santonin, and arsubin has the structure and configuration (I).



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