STRUCTURE OF SAMARCANDIN

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One of us has previously given a possible structure for samarcandin [1].

The results of a study of the NMR spectra of samarcandin in $CDCl_3$ solution (JNM-4H-100) have confirmed the main conclusions of the chemical experiments and have enabled the structure of samarcandin to be refined. Thus, the signal of a proton in a secondary hydroxyl group with a center at 3.45 ppm (the chemical shifts are given relative to the signal of TMS, 0 δ, ppm), appears in the form of a singlet (half-width of the line ~5 Hz), which show its probable equatorial orientation [2].

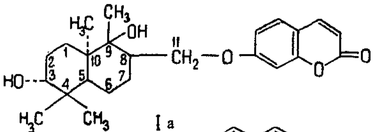
In the 4.1–4.6-ppm region, there are the signals of the protons of a methylene group (see structure Ib) in the fragment $>C_9H—CH_2—O—$ in the form of two quartets ($|J_{gem}| = 11$ Hz, $J_{vic} = 4$ and 6 Hz).

Under double resonance conditions (frequency of the strong radiofrequency field corresponding to the chemical shift of the proton at 1.89 ppm), the signals of the protons of the methylene group of the $>C_9H—CH_2—O—$ fragment are converted into doublets. This enables the signal at 1.89 ppm to be ascribed to the methine proton at C_9. The distance between the extreme peaks of the signal of this proton is 10 Hz. This figure agrees with the sum of the spin-spin coupling constants of the proton at C_9 with the methylene protons of the $>C_9H—CH_2—O—$ group.

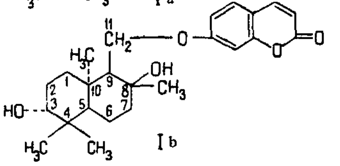
It follows from this that only the methylene protons of the $>C_9H—CH_2—O—$ are present in the position vicinal to the methine proton at C_9.

The presence of two more vicinal protons (see structure Ia) should lead to the splitting of the triplet signal of the methine proton at C_8 and to an increase in the distance between the extreme peaks of this signal by several Hertz.

Thus, on the basis of the NMR spectra structure Ib is probable the one for samarcandin.



I a



I b

This formula has also been proposed by other workers [3].

REFERENCES

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3. A. I. Ban'kovskii, N. E. Ermatov, M. E. Perel'son, A. Bubeva-Ivanova, and N. St. Pavlova, KhPS [Chemistry of Natural Compounds], 6, 173, 1970.

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