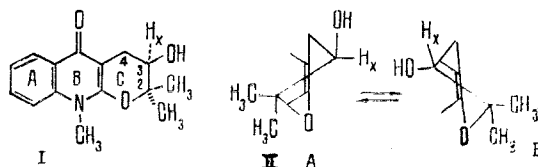


# THE CONFORMATIONAL MOBILITY OF THE DIHYDROPYRAN RING OF THE ALKALOID FOLIFINE

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UDC 547.944.1.92

The structure of the alkaloid folifine (I) isolated from *Haplophillum bucharicum* [1] has proved to be identical with that of the alkaloid ribalinine [2]. The conformational mobility for the dihydropyran ring C of folifine can be represented in form (II) (A and B).



In the NMR spectrum of folifine at room temperature (+24°C) the signals of the protons of the two methyls of the gem-dimethyl group are nonequivalent and give two three-proton singlets at  $\tau$  8.54 and 8.76 ppm with a difference between their chemical shifts of  $\Delta\nu = 22.1$  Hz (Fig. 1a; spectra taken on a JNM-4H-100/100 MHz instrument,  $\text{CDCl}_3$ , HMDS as internal standard,  $\tau$  scale). The free protons at  $\text{C}_3$  and  $\text{C}_4$  form a system of the ABX type the outer lines of the AB part of which are of low intensity because of the closeness of the chemical shifts (CSSs) of  $\text{C}_4\text{-H}_2$  and are lost in the noise and it is therefore impossible to determine the geminal SSCC

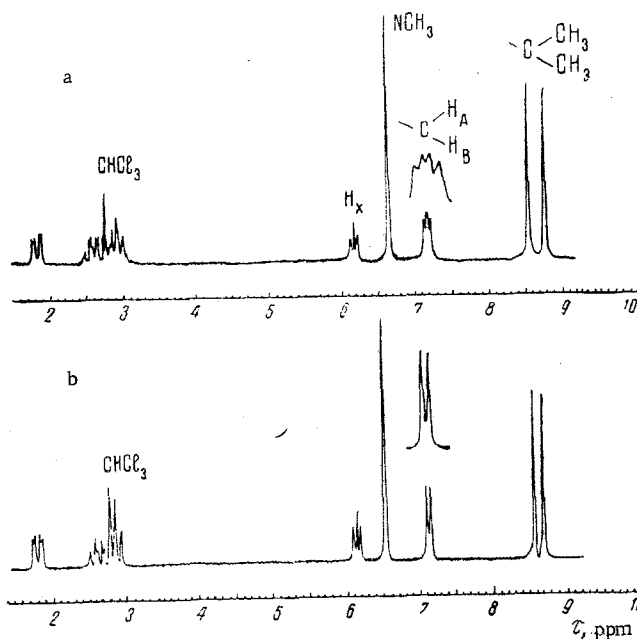


Fig. 1. NMR spectra of folifine in  $\text{CDCl}_3$  at +24°C (a) and +60°C (b).

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$J_{AB}$  from the remaining spectrum – a quartet with its center at about 7.20 ppm. The X part of the ABX spectrum (signal of the proton geminal to the OH group at  $C_3$ ) appears in the form of a one-proton triplet at 6.20 ppm with  $\frac{1}{2}[J_{AX} + J_{BX}] = 5.0$  Hz.

A characteristic feature of the NMR spectrum of folifine is that with a rise in the temperature the difference in the CSs of the signals of the protons of the methyls of the gem-dimethyl group decrease: at +45°C this difference  $\Delta\nu = 15.0$  Hz at +60°C  $\Delta\nu = 12.8$  Hz. Furthermore, the AB part (quartet) of the folifine spectrum (Fig. 1a) is converted, with a rise in the temperature, into a doublet with its center at 7.15 ppm,  $J = 5.0$  Hz, i.e., on heating, the protons of the methylene group at  $C_4$  become magnetically equivalent and together with the  $H_X-C_3OH$  proton they form a spin system of the  $A_2X$  type with  $J_{AX} = 5.0$  Hz (Fig. 1b).

Thus, the observed temperature dependence of the CSs of the protons of the gem-dimethyl groups and the SSC of  $H_X-COH$  and  $CH_2$  show that with a rise in the temperature the rate of conversion of the dihydropyran ring C from one half-chair conformation (Scheme II, A) to the other (B) rises. With the rapid conversion of ring C, of course, reorientation of the hydroxy group and the proton geminal to it from the equatorial (A) to the axial (B) orientation takes place, which, in its turn, leads to the magnetic equivalence of the protons of the methylene group and to the equalization of the SSCs of the  $CH_2-H_X-COH$  protons.

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#### THE STRUCTURE OF DIPHTHOCARPAMINE

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Continuing an investigation of the alkaloids of *Diphthyocharpus strictus*, we have studied the structure of diphthocarpamine (I) with mp 100–101°C,  $[\alpha]_D^{28} -58.21^\circ$  [1].

On the basis of the results of elementary analysis and mass spectroscopy, the composition  $C_{11}H_{24}N_2O_2S$ ,  $M^+ 248$  has been proposed for (I), and it has  $R_f$  value 0.40 in a thin layer of silica gel in the chloroform–methanol (9:1) system.

The alkaloid is stable to the action of acids and alkalis and is not reduced by the Adams method, since the sulfur present in the base poisons the catalyst. The base gives a positive biuret reaction for urea derivatives. The oxidation of (I) with chromium trioxide in an acid medium gave acetone in the form of its 2,4-dinitrophenylhydrazone. Consequently, diphthocarpamine contains an isopropyl group.

The IR spectrum of (I) shows the absorption band of active hydrogen (3365 and 3330  $cm^{-1}$ ), the band of an amide carbonyl (1630  $cm^{-1}$ ), and an intense band at 1045  $cm^{-1}$  ( $S \rightarrow O$ ).

The NMR spectrum (JNM-4H-100/100 MHz in  $CDCl_3$  with HMDS as internal standard) shows a doublet at  $\delta$  1.1 ppm [6H,  $-HC(CH_3)_2$ ], a singlet (3H) from a  $S-CH_3$  group at 2.5 ppm, a quartet (2H;  $CH_2-N=$ ) at 3.04 ppm, a multiplet (1H) from  $=CH-N=$  at 3.76 ppm, and a one-proton doublet and a triplet from two NH groups capable of undergoing deuterium substitution at 5.64 and 5.45 ppm.

Mass spectrum:  $m/e$  248 ( $M^+$ ), 233 ( $M-15$ )<sup>+</sup>, 218 ( $M-30$ )<sup>+</sup>, 190 ( $M-58$ )<sup>+</sup>, 185 ( $M-63$ )<sup>+</sup>, 171, 162, 61, 58, 44.

The reduction of (I) with lithium tetrahydroaluminate or with zinc in hydrochloric acid gave an optically inactive substance (II) with mp 108–109°C,  $M^+ 232$ .

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