INFLUENCE OF SOLVENTS ON THE PARAMETERS OF THE NMR SPECTRA OF ALKALOIDS. III

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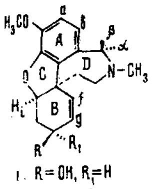
Continuing a study of the influence of solvents on the parameters of the NMR spectra of alkaloids [1, 2], in the present paper we give the results for galanthamine (I) [3], narwedine (II) [4], ungerine (III) [5], dihydrolycorine diacetate (IV), and lycorine diacetate (V) [6]. It has been established for (I) and (II) that the change in the CS of the signal of the OCH_3 protons under the influence of the aromatic solvents C_6D_6 and C_5D_5N ($\Delta\delta = \delta_{CDCl_3} - \delta_{solv}$) is equal to +0.48 and +0.13 ppm, respectively. The values of $\Delta\delta$ for other protons, which are different from one another, we explain by the different structures of rings B of galanthamine and narwedine and also by possible conformational changes of the labile seven-membered ring D. In a study of the influence of highly polar solvents, both diamagnetic and paramagnetic shifts of the signals of the protons of the alkaloids (I) and (II) are observed. Furthermore, it has been established that the changes $\Delta\delta$ in the CSs in trifluoroacetic acid (TFA) for the groups NCH_3, OCH_3, and $H_{\bullet}$ are −0.53, −0.15, and −0.28 ppm, respectively. The changes in the CSs of the protons in polar solvents depend mainly on the effects of the reaction field [7], and in TFA the protonation of the medium has an additional influence. In (III) the most interesting results were obtained in benzene solution for the protons of the aromatic ring. It was found that H_8 undergoes a strong paramagnetic shift of $\Delta\delta = -0.33$ and H_{11} a diamagnetic shift of $\Delta\delta = +0.26$ ppm. This is explained by the fact that benzene can interact by its partially positive peripheral region with the strong electronegative section of the lactone group of ungerine [8]. It has been established that the two protons of the methylenedioxy group of (III) are equivalent in polar solvents and give a signal in the form of a singlet, while in benzene and pyridine they become nonequivalent, forming a typical AB system with $J_{AB} = 1$ Hz.

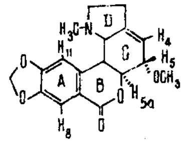
A similar pattern is observed for this group in (IV) in acetone solution.

It has been established for (IV) and (V) that the changes in the CSs of the H_{11}, H_8, and OCH_2O protons in benzene solutions are $\Delta\delta = -0.36$, +0.03, and +0.52 ppm, in pyridine $\Delta\delta = -0.49$, −0.22, and −0.07 ppm, and in TFA $\Delta\delta = -0.32$, −0.27, and −0.17 ppm, respectively.

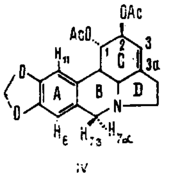
The values of $\Delta\delta$ in polar solvents for these alkaloids are negative.



I. R=OH, R_1=H
II. R+R_1=O



III



IV

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