# STRUCTURE OF VINERVININE, VINERVINE, VINCANIDINE, AND VINCANICINE

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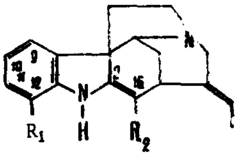
Previously, for the alkaloids vincanidine [1-3], vincanicine [4], vinervine [3, 5], and vinervinine [6], mainly on the basis of their IR spectroscopic characteristics [1], structures I, II, III, and IV, respectively, with the substituent $R_1$ in the benzene ring and $C_{11}$ have been proposed.



I. $R_1$=OH, $R_2$=CHO
II. $R_1$=$OCH_3$, $R_2$=CHO
III. $R_1$=OH, $R_2$=$COOCH_3$
IV. $R_1$=$OCH_3$, $R_2$=$COOCH_3$

To determine the positions of the substituents OH and $OCH_3$ in the aromatic nucleus of (I-IV) we have studied the NMR spectra of (I), (II), and (IV) and some derivatives of (IV) (JNM-4H-100/100 MHz spectrometer, $CDCl_3$, HMDS−10). In the NMR spectra of (I), (II), and (IV) the signals from the three protons of the aromatic ring give a multiplet (3H) in the range $\tau$ 3.2-3.5 ppm. In the spectrum of 2,16-dihydrovinervinine (V) (Fig. 1a), the signals of these protons are also observed in the form of a multiplet. Further, in the NMR spectra of the 11-methoxy substituted $\alpha$-methyleneindoline alkaloids 16-methoxyvincadifformine (ervinceine) and its 2,3-dihydro derivative, as in the spectrum of 16-methoxytabersonine (ervamicine) [7], the signals of the aromatic protons formed a three-spin system of the ABC type the $H_9$ signal in which is located in a relatively weak field as compared with the $H_{10}$ and $H_{12}$ signals.

Moreover, in indoline alkaloids with a substituent in position 11 of the aromatic ring the signal of the $H_{12}$ proton, which has spin−spin coupling with $H_{10}$ (meta constant), shifts by 1.0 ppm and more on the acetylation of the N−H [8, 9]. In the NMR spectrum of N-acetyldihydrovinervinine (VI) (Fig. 1b) the three aromatic protons reveal a pattern of the ABC type, and the signal of one of them appears in the form of a quartet with its center at 2.93 ppm and SSCCs of $J_1 = 8.0$ and $J_2 = 8.5$ Hz. The values of the SSCCs, corresponding to ortho interaction of aromatic protons, show that the quartet with its center at 2.93 ppm must be assigned to the signal of a proton in ortho positions to which there are two other protons. Consequently, the $OCH_3$ group in (VI) and also the substituents $OCH_3$ and OH in the initial alkaloids (I-IV) cannot be located at $C_{11}$ of the aromatic ring, as was considered previously. Substitution at $C_9$ for the OH and $OCH_3$ groups is excluded, since the expected signal of the $H_{12}$ proton (quartet with $J_{ortho} \simeq 8.0$ and $J_{meta} \sim 2.0$) in the spectrum of (VI) is in practically the same position as the CS of $H_{12}$ in the initial spectrum of (V) (see Fig. 1a, b).

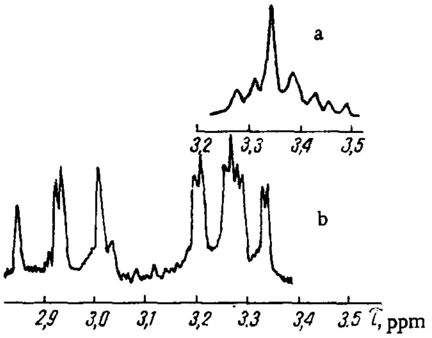


Fig. 1. NMR spectrum of 2,16-dihydrovinervinine (V) (a) and of N-acetyldihydrovinervinine (VI) (b).

Thus, the results of a detailed consideration of the CSs and SSCCs of the signals of the aromatic protons in the NMR spectra of vinervinine and its dihydro and N-acetyldihydro derivatives unambiguously show that the methoxy group in them is located at $C_{12}$. These results show that in vinervine, vincanidine, and vincanicine, likewise, the OH and $OCH_3$ groups are located at $C_{12}$ of the aromatic ring.

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