NMR STUDY OF ALKALOIDS.

VIII. ^{1}H and ^{13}C NMR SPECTRA AND RECONSIDERATION OF THE STRUCTURES OF VINCARICINE AND VINCARININE

M. R. Yagudaev

UDC 547.944.1.92

Structures (I) and (II), respectively, have previously been proposed for the indoline alkaloids vincaricine with mp 187-189°C, $[\alpha]_D$ +0° (c 0.6; chloroform) [1] and vincarinine with mp 178-179°C, $[\alpha]_D$ −81 (c 0.1; methanol) [2], isolated from the plant *Vinca erecta*, mainly on the basis of the results of analysis, and UV, IR, mass, and PMR spectra.

However, the position of the aromatic methoxy group was not strictly shown. We have performed a more detailed analysis of the PMR and ^{13}C NMR spectra of these alkaloids (the PMR spectra were obtained on a Varian XL-200 spectrometer in $CDCl_3$, 0 — TMS; the ^{13}C NMR spectra, on a Varian XL-100-15 instrument in $CDCl_3$, 0 — TMS, $\delta_{TMS} = \delta_{CDCl_3} + 76.91$ ppm).

In the PMR spectrum of vincaricine, the signals of three aromatic protons gave a pattern of the ABC type (Fig. 1), and the signal of one of them shifted downfield to 6.77 ppm relative to the other ($\delta = 6.64$ ppm) has a quartet nature with SSCCs $J_1 = 2$ and $J_2 = 1.2$ Hz, corresponding to meta and para interactions of the protons of a benzene ring. A similar pattern of the signals of the aromatic protons is observed in the PMR spectrum of vincarinine. This fact gives grounds for considering that the methoxy groups in (I) and (II) cannot be located at C-12 of the benzene ring, since this would exclude the appearance of a signal with a constant of para interaction. For the same reason the C-9 position is impossible for OCH_3; consequently only one of two positions — C-10 or C-11 — remains for it. A comparison of the CSs and SSCCs of the aromatic protons at C-10 and C-11 of the methoxy-substituted indoline alkaloids cabuamine [3], o-methylakuammine, cabucraline [4], and vindoline [5] shows that in both cases the H-9 signal is shifted downfield to 6.93 ppm relative to the signals of the other two protons, and a basic criterion of their difference is the value of the SSCC of the weak-field H-9 signal: It is 2-2.5 Hz when OCH_3 is located at C-10 and 8-8.5 Hz when it is located at C-11. Consequently, the SSCC value of the H-9 atom of vincaricine with $\delta = 6.77$ ppm, $J_m = 2$ and $J_p = 1.2$ Hz and that of vincarinine with $\delta = 6.72$ ppm, $J_m = 2.2$ and $J_p = 1.0$ Hz permits the C-10 position for the OCH_3 to be established reliably and demonstrates

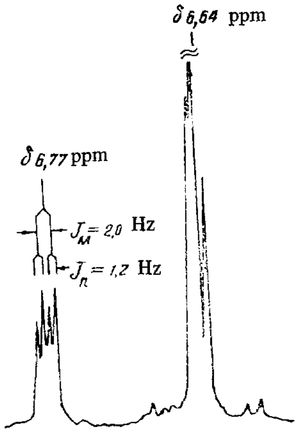


Fig. 1. Signals of the aromatic protons of vincaricine.

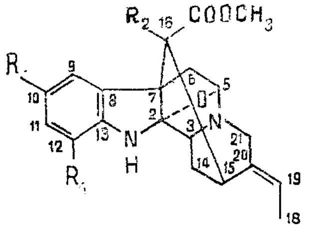
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 129-130, January-February, 1985. Original article submitted June 19, 1984.

0009-3130/85/2101-0131$09.50

structures (Ia) and (IIa), respectively for the alkaloids. These PMR results are confirmed completely by those of an analysis of the ^{13}C NMR CSs of (Ia) and (IIa) (ppm):

Atom	*Ia*	*IIa*	Atom	*Ia*	*IIa*
C-2	107.0	106.7	C-14	25,9	20.5
C-3	51.4	52,9	C-15	31.0	31.6
C-5	87.2	87,4	C-16	51,6	55.9
C-6	40.5	43,4	C-17	—	197.0
C-7	52,0	53,8	C-18	12,6	12.8
C-8	136.2	133.3	C-19	120.2	120.7
C-9	111.2*	113.2*	C-20	136.4	136.2
C-10	154.4	155,0	C-21	46,3	46,5
C 11	112.8*	113,3*	Ar—OCH_3	55.9	55,8
C 12	110.8	111.0	O	172.3	168.0
C-13	141,2	141,5	C—OCH_3	51.4	51,8

The assignment of the signals of the carbon atoms was made on the basis of a comparison of the CSs of the carbon atoms of (Ia) and (IIa) with those of picraline [6] taking into account the increments of the substituent OCH_3 to the CSs of the α-, o-, m-, and p-carbon atoms of the benzene ring [7].



I. $R = R_2 = H, R_1 = OCH_3$

Ia. $R = OCH_3, R_1 = R_2 = H$

II. $R = H, R_1 = OCH_3, R_2 = CHO$

IIa. $R = OCH_3, R_1 = H, R_2 = CHO$

Thus, a detailed analysis of the PMR and ^{13}C NMR spectra of vincaricine and vincarinine enables us to reconsider their structures proposed previously and to show unambiguously that structures (Ia) and (IIa) correspond to them.

LITERATURE CITED

1. D. A. Rakhimov, Kh. T. Il'yasova, V. M. Malikov, and S. Yu. Yunusov, Khim. Prir. Soedin., 327 (1968); 521 (1969).
2. Kh. T. Il'yasova, V. M. Malikov, and S. Yu. Yunusov, Khim. Prir. Soedin., 164 (1971).
3. M. Monsour, L. Le Men-Olivier, J. Levy, and J. Le Men, Phytochemistry, 13, 2861 (1974).
4. L. Douzoua, M. Monsour, M. M. Debray, L. Le Men-Olivier, and J. Le Men, Phytochemistry, 13, 1994 (1974).
5. M. Gorman, N. Neuss, and K. Biemann, J. Am. Chem. Soc., 84, 1058 (1962).
6. N. Petitfrere-Auvray, J. Vercauteren, G. Massiot, G. Lukacs, T. Sevenet, L. Le Men-Olivier, B. Richard, and M.-J. Jacquier, Phytochemistry, 20, 1987 (1981).
7. J. B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York (1972), p. 197.

---

*The assignments of the components of these pairs of signals may be the opposite.