ALKALOIDS OF Stephania hernandifolia

IX. 3-O-DEMETHYLHERNANDIFOLINE

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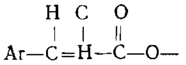
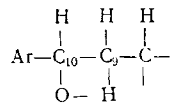
From the methanolic fraction obtained in the chromatography on alumina of a mixture of alkaloids from the herb Stephania hernandifolia we have isolated a base (I) with mp 148-149°C (methanol–ether). In contrast to the hernandifoline [1], hernandine [2], and methylhernandine [3] isolated previously, this substance shows the intensive color reaction with ferric chloride characteristic of oxybiphenols.

In the IR spectrum of (I) (Fig. 1), in the region of the stretching vibrations of OH and NH bonds there is a series of broadened bands at 3560, 3440, and 3200-2700 cm^{-1}. The same spectrum shows the presence in (I) of a carbonyl group (1695 cm^{-1}), a conjugated double bond (1640 cm^{-1}), and an aromatic ring (1612, 1588, 1512, 1489 cm^{-1}).

In the NMR spectrum of (I) (CD_3OD) there are one-proton doublets at 5.35 and 7.00 ppm, J = 15.6 Hz, showing, in association with the 1695-cm^{-1} band in the IR spectrum, the presence of a  $Ar{-}\overset{H}{\overset{|}{C}}{=}\overset{C}{\overset{|}{H}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}$ grouping in the alkaloid. In addition to this, compound (I) contains three methoxy groups, one of which is attached to an aromatic ring (3.89, 3.41, and 3.40 ppm), two aromatic ortho protons (δ = 6.50 and 6.60 ppm, doublets, J = 8.0 Hz), and two fragments characteristic for hasubanan alkaloids with a semiketal bridge at C_8-C_{10} and present in the alkaloids of this type that we have isolated previously [1-3]:



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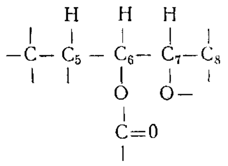

The chemical shifts and the spin–spin coupling constants of the protons of these fragments (Table 1) were determined by the double-resonance method.

The NMR spectrum of one also shows a three-proton singlet at 6.89 ppm analogous to the signal observed in the spectrum of hernandifoline (CD_3OD) and ascribed to the protons of hesperetinic acid [1].

TABLE 1. Features of the NMR Spectrum of the Base (I)*

C_5-H^a	C_5-H^e	C_6-H	C_7-H	$C_{10}-H$	$H-C_9-H$
2,02 ppm. (q; 15,0 Hz; 2,3 Hz)	3,17 ppm (q; 15,0Hz; 4,1Hz)	~5,40 ppm m	3,74 ppm (d; 4,0 Hz)	4,88 ppm (d; 5,8 Hz)	1,85 ppm (d; 10,5Hz) 2,62 ppm (q; 10,5 Hz; 5,8 Hz)

*d – doublet; q – quartet; m – multiple; $CHCl_3$; O – TMS, HA-100D.

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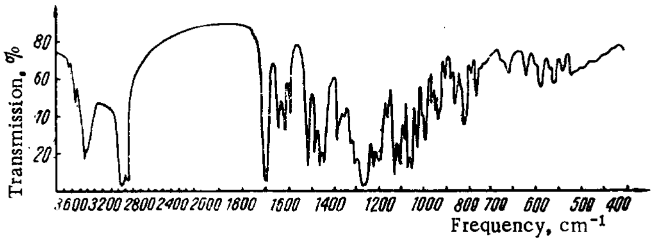
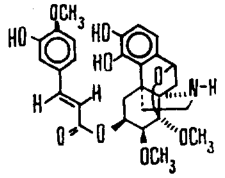


Fig. 1. IR spectrum of 3-O-demethylhernandifoline (mull in paraffin oil).

The saponification of (I) with alcoholic alkali yielded an acid, identified by its melting point, NMR spectrum, and R_f value as hesperetinic acid, and a base with mp 128-129°C giving an intense coloration with ferric chloride. On successive methylation with diazomethane and methyl iodide the base formed a 0,0,N-trimethyl derivative having an R_f value identical with that of the 0,N-dimethylamino alcohol hernandifoline [1].

The acyloxy group in position 6 occupies the quasiaxial position. In actual fact, the maximum value of the coupling constant of C_6-H with the protons at C_5 is 4.1 Hz, which shows its quasiequatorial configuration. This configuration of the C_7-OCH_3 group has been adopted on the basis of the practically equal values of the chemical shifts of the protons at C_7 and the constants of their interaction with C_6-H for (I), hernandifoline (stephisoferuline), hernandine, and methylhernandine [1-4].

The results presented permit the structure of 3-O-demethylhernandofoline, $C_{28}H_{31}O_9N$, to be put forward for (I).



LITERATURE CITED

1. D. A. Fesenko, I. I. Fadeeva, T. N. Il'inskaya, M. E. Perel'son, and O. N. Tolkachev, Khim. Prirodn. Soedin., 7, 158 (1971).
2. T. N. Il'inskaya, D. A. Fesenko, I. I. Fadeeva, M. E. Perel'son, and O. N. Tolkachev, Khim. Prirodn. Soedin., 7, 180 (1971).
3. I. I. Fadeeva, D. A. Fesenko, T. N. Il'inskaya, M. E. Perel'son, and O. N. Tolkachev, Khim. Prirodn. Soedin., 7, 445 (1971).
4. S. M. Kupchan and M. I. Suffness, Tetrahedron Lett., 1970, No. 4975.