ALKALOIDS OF Stephania hernandifolia

VIII. METHYLHERNANDINE

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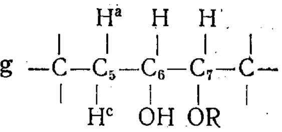
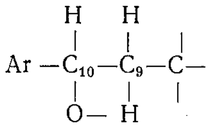
Continuing an investigation of the alkaloids of the epigeal part of Stephania hernandifolia, through the sparingly ethanol-soluble hydrochloride we have isolated a base with the composition $C_{20}H_{27}O_6N$ which we have called methylhernandine (I).

The IR spectrum of the base (Fig. 1) exhibits two absorption bands of OH groups (3250 and 3525 cm^{-1}), one of which is alcoholic and the other phenolic, as is confirmed by the preparation of a diacetyl derivative (IR spectrum: 1730 and 1775 cm^{-1}).

The NMR spectrum of the compound (Fig. 2) shows the presence in its structure of a $N-CH_3$ group (2.48 ppm, singlet, 3 H) and three methoxy groups, one of them aromatic (3.38, 3.48, and 3.72 ppm, singlets, 3 H each).

The molecule also contains a number of structural fragments that are present in other alkaloids of Stephania hernandifolia (hernandifoline [1] and hernandine [2]) and which possess similar spectral characteristics. Thus, the NMR spectrum of methylhernandine has the signals of two equivalent aromatic ortho protons (6.50 ppm, singlet, 2H), of the grouping  $-\overset{|}{\underset{|}{C}}-\overset{H^a}{\underset{H^c}{C_5}}-\overset{H}{\underset{OH}{C_6}}-\overset{H'}{\underset{OR}{C_7}}-\overset{|}{\underset{|}{C}}-$ (C_5-H^a: 1.93 ppm, quartet, J = 14.8 and 2.9 Hz; C_5-H^e: 3.00 ppm, quartet, J = 14.8 and 3.4 Hz; C_6-H: 4.05 ppm, multiplet; C_6-OH: 2.24 ppm, doublet, J = 9.8 Hz; C_7-H: 3.62 ppm, doublet, J = 4.1 Hz); and the grouping  $Ar-\overset{H}{\underset{O-}{C_{10}}}-\overset{H}{\underset{H}{C_9}}-\overset{|}{\underset{|}{C}}-$ ($C_{10}-H$: 4.81 ppm, doublet, J = 6.2 Hz; $H-C_9-H$: 1.45 ppm, doublet, J = 10.8 Hz, 1 H; and 2.63 ppm, quartet, J = 10.8 and 6.2 Hz, 1 H). The chemical shifts and the coupling constants were determined by using double resonance (see Fig. 2).

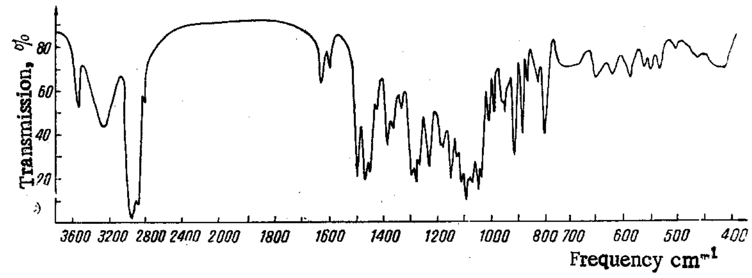


Fig. 1. IR spectrum of methylhernandine (paraffin oil).

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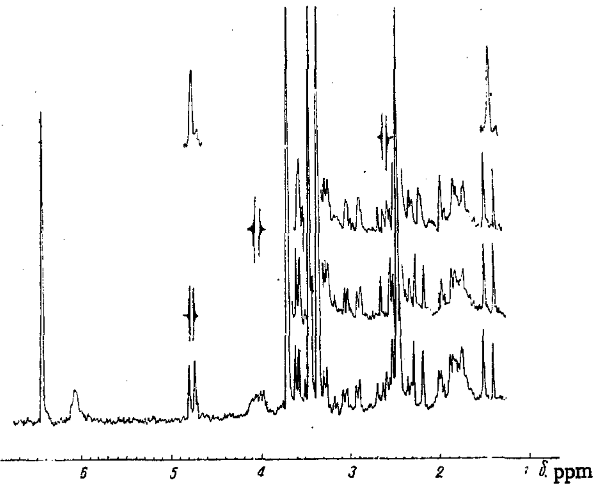


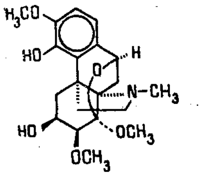
Fig. 2. NMR spectrum of methylhernandine in $CDCl_3$ (sections of the double-resonance spectra are shown above, the position of the beats coinciding with the position of the irradiated signal).

The results obtained show that the base considered has the structural formula of the methylamino alcohol from hernandifoline [1].

The results of a comparison of the IR spectra of the alkaloid and of the methylamino alcohol from hernandifoline and the absence of a depression of the melting point of a mixed sample confirmed the identity of these compounds.

By comparing the spectra and chemical behavior of methylhernandine and hernandifoline [1] and also their derivatives we can propose for methylhernandine a spatial structure which is in good agreement with biogenetic considerations and also with recently published information on stephisoferuline [4].

Consequently, the structural formula of methylhernandine is



EXPERIMENTAL

The IR spectrum was taken on a UR-10 instrument (paraffin oil), and the NMR spectrum on an HA-100D spectrometer (in $CDCl_3$ with HMDS as internal standard, the sample having been degassed).

Methylhernandine (I). After the first portions of eluate, containing only hernandoline [3] had been obtained, ether eluted from the column a mixture of hernandoline and methylhernandine. The eluate was evaporated and the residue was dissolved in ethanol containing hydrogen chloride. After some time, a crystalline hydrochloride with mp 199-201° C deposited.

Found %: C 55.40; 55.41; H 7.28; 7.35; N 3.26; 3.41; OCH_3 21.75. $C_{20}H_{27}O_6N \cdot HCl \cdot H_2O$. Calculated%: C 55.62; H 6.99; N 3.24; 3 OCH_3 21.75.

The base obtained from the hydrochloride softened at 107-109° C and melted at 152-153° C (ether–methanol), $[\alpha]_D$ + 125° (c 0.4; ethanol).

Found %: C 63.50; 63.35; H 7.29; 7.35; N 3.80; 3.83; Mol. wt. 377 (mass-spectrometically). $C_{20}H_{27}O_6N$. Calculated%: C 63.66; H 7.16; N 3.71. Mol. wt. 377.

Diacetylmethylhernandine. A mixture of 0.07 g of methylhernandine, 1 ml of pyridine, and 0.5 ml of acetic anhydride was left at room temperature for 24 h. By the usual method, 0.05 g of reaction product was isolated, and its hydrochloride with mp 161-162° C (ethanol–ether) was obtained.

SUMMARY

A new hasubanan alkaloid with the composition $C_{20}H_{27}O_6N$, mp 152-153° C (ether–methanol) has been isolated from the herb Stephania hernandifolia and has been called methylhernandine. The alkaloid has been shown to be identical with the methylamino alcohol obtained in the hydrolysis of hernandifoline.

LITERATURE CITED

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