CORPAINE FROM Corydalis paczoskii

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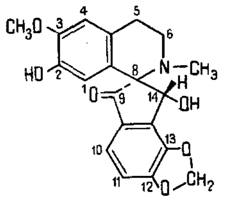
Isolation of a base with the composition $C_{22}H_{25}O_7N$, mp 202-203°C, $[\alpha]_D$ −194°, called "coryline," from the epigeal part of Corydalis paczoskii, has been reported previously [1].

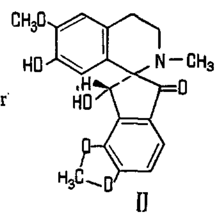
We have established that coryline is a mixture of two substances, one of which, $C_{20}H_{19}O_6N$, mp 204°C (absolute ethanol), mol. wt. 369 (mass spectrometry), is present in a predominant amount. This compound proved to be a new alkaloid, which we have named "corpaine."

A spectroscopic study of corpaine suggests one of two structural variants I or II.



I

or



II

The UV spectrum of corpaine is similar to the spectra of the spirobenzylisoquinoline alkaloids [2-7]. The IR spectrum of corpaine in $CHCl_3$ (Fig. 2) shows that its molecule contains two hydroxy groups (3560 and 3260 cm^{-1}), the carbonyl group of an α,β-unsaturated ketone (1707 cm^{-1}), and aromatic rings (1633, 1601, and 1516 cm^{-1}). At least one of the hydroxy groups is phenolic, according to the shift in the absorption band in the UV spectrum of the substance in ethanolic alkali (see Fig. 1).

The NMR spectrum of corpaine (Fig. 3) is similar to the NMR spectra of corydaine [2], sibiricine [3], ochrobirine [4], fumariline [5], and other spirobenzylisoquinoline alkaloids [6-10]. The signals of the protons of ring A are found at 6.19 ppm (H_1) and 6.58 ppm (H_4). The ortho protons of ring D give two doublets with δ 7.45 (J = 8.0 Hz) and δ 6.98 (J = 8.0 Hz) (H_{10} and H_{11} in structure I or H_{12} and H_{13} in structure II). The spectrum also has the signals of an aromatic methoxy group (3.87 ppm) and of a methylenedioxy group (quadruplet, δ 6.16 and 6.20 ppm, J = 1.2 Hz). The chemical shift of the latter shows that it is attached to ring D. Consequently, the methoxy group and one of the hydroxy groups occupy positions 2 and 3 of ring A. An analysis of the information in a series of papers [5-10] shows that the signal from a C_2-OCH_3 is present in the 3.37-3.62 ppm range, and that from C_3-OCH_3 in the 3.68-3.87 ppm range. In the spectrum of corpaine the signal of the methoxy group is present at 3.87 ppm, which shows that this group is located at C_3. Consequently, the phenolic hydroxyl occupies position 2.

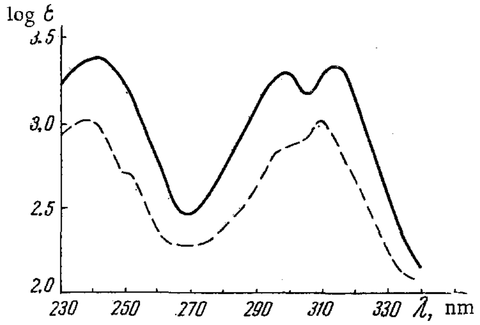


Fig. 1. UV spectrum of corpaine in acidified ethanol (full curve) and in 0.05 N ethanolic alkali.

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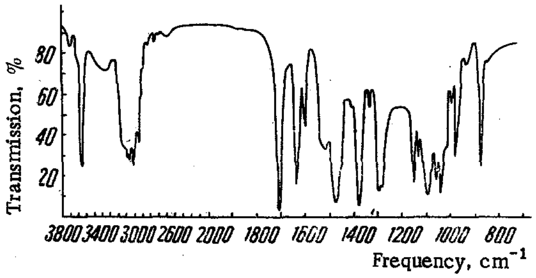


Fig. 2. IR spectrum of corpaine.

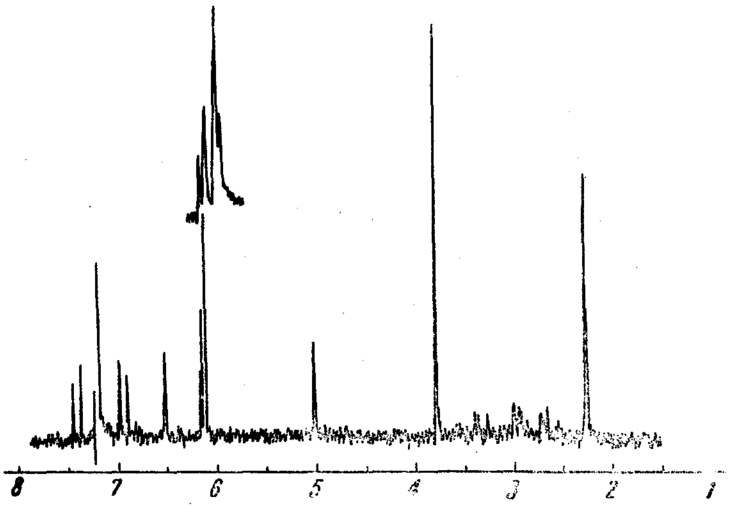
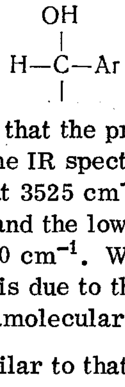


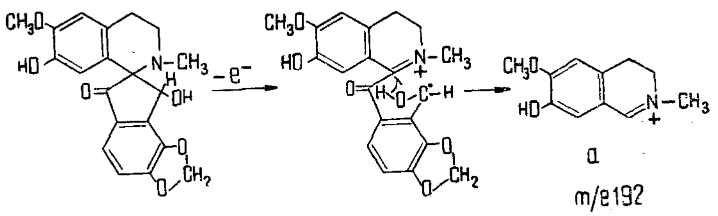
Fig. 3. NMR spectrum of corpaine.

The presence of a $N-CH_3$ group in the structure of corpaine follows from the presence in its NMR spectrum of a somewhat broadened three-proton singlet at 2.35 ppm.

The signal of the methine proton of the  $H-\overset{\overset{\textstyle OH}{|}}{\underset{|}{C}}-Ar$ group is found at 5.09 ppm. As in the case of corydaine [2], its position leads to the conclusion that the proton is in the trans position and the hydroxyl in the cis position relative to the $N-CH_3$ group. The IR spectra confirm this. The bands of the OH groups of the substance in the crystalline state are found at 3525 cm^{-1} and 3400-3235 cm^{-1} (broad). In chloroform the high-frequency band is shifted to 3560 cm^{-1} and the low-frequency band remains in practically the same position, having an absorption maximum at 3260 cm^{-1}. When the solution is diluted, the positions of the bands do not change since the high-frequency band is due to the phenolic OH group and the low-frequency band relates to a tertiary hydroxyl bound by an intramolecular hydrogen bond with a nitrogen atom.

The mass spectrum of corpaine is similar to that of corydaine [2], which shows the structural similarity of these alkaloids. The peak of the ion *a* (see scheme) which is characteristic for the mass spectra of the spirobenzylisoquinoline alkaloids with an OH group in ring C [3], is shifted two units in the region of higher mass numbers in the spectrum of corpaine. This shift confirms the fact that a methylenedioxy group is present in ring D.

Thus, the results obtained lead to structural formula I or II for corpaine.



EXPERIMENTAL

The UV spectra were taken on an SF-4A spectrophotometer, the IR spectra on a UR-10 spectrometer, the NMR spectra on a Varian HA-100D spectrometer (in $CDCl_3$, internal standard, tetramethylsilane), and the mass spectra on an MKh-1303 spectrometer (T_{evap}, 150°C, U_{ion} 24 V).

Fractional crystallization of 0.2 g of coryline from absolute ethanol gave 0.06 g of a resinous substance with R_f 0.49, and 0.12 g of an individual base with the composition $C_{20}H_{19}O_6N$, mp 204°C, R_f 0.32 on a chromatogram in a fixed layer of silica gel–gypsum in a butan-1-ol–acetic acid–water (10 : 1 : 3) system, the spot being revealed with Dragendorff's reagent. Found %: C 65.14, 65.24; H 5.34, 5.32; N 3.78, 3.76; H_{labile} 0.598, 0.581. $C_{20}H_{19}O_6N$. Calculated %: C 65.03; H 5.18; N 3.79; H_{labile} 0.542.

CONCLUSIONS

Two possible structures for corpaine, a new alkaloid isolated from Corydalis paczoskii, have been proposed.

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