# CORYDAINE FROM CORYDALIS PACZOSKII

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Khimiya Prirodnykh Soedinenii, Vol. 6, No. 4, pp. 456–459, 1970.
UDC 547.92

From the herb Corydalis paczoskii N. Busch. we have isolated a new base $C_{20}H_{17}O_6N$, mp 184° C (absolute ethanol), mol wt 367 (mass spectrometry), which we have called "corydaine." The UV spectrum of corydaine, $\lambda_{max}$ (ethanol) 236, 290, and 314 mμ (log ε 4.49, 4.04, and 4.03), is similar to the spectra of the benzylisoquinoline alkaloids [1]. The IR spectrum of corydaine (Fig. 1) has absorption bands with $\nu_{max}$ (paraffin oil), $cm^{-1}$, at 3200 (OH), 3050 (aromatic C—H), 1710 (CO of an α,β-unsaturated five-membered ketone), and 1638 and 1610 (skeletal vibrations of aromatic rings).

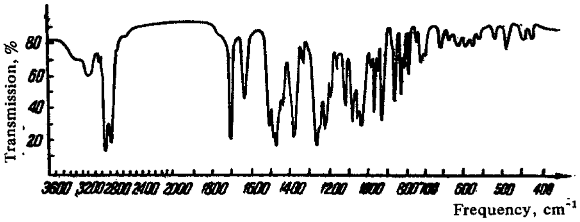


Fig. 1. IR spectrum of corydaine (mull in paraffin oil).

Bases which are tetrahydroisoquinoline derivatives and have a carbonyl group in their structure include alkaloids of the phthalide isoquinoline, protopine, and cularine types. The phthalide isoquinoline alkaloids contain the carbonyl of an α,β-unsaturated γ-lactone (1775–1735 $cm^{-1}$). The frequency of the vibrations of the carbonyl group of the protopine alkaloids is lower (1675–1650 $cm^{-1}$) because of conjugation with the aromatic ring and the transannular interaction of the CO group with the unshared pair of the nitrogen. The absorption band of the ester group of the cularine alkaloids is found in the 1740–1750 $cm^{-1}$ region [2].

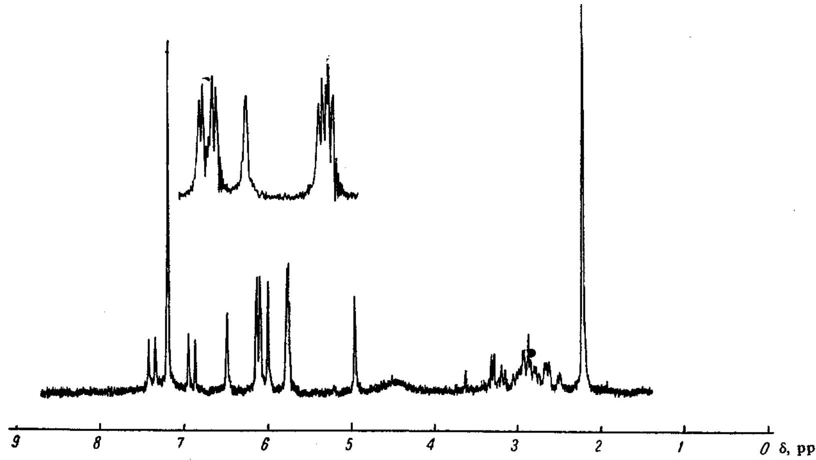
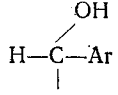


Fig. 2. NMR spectrum of corydaine (in $CDCl_3$).

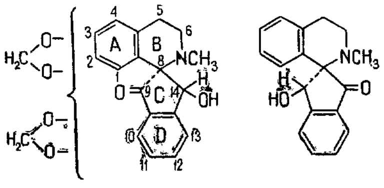
The NMR spectrum of corydaine in $CDCl_3$ (Fig. 2) has the signals of two aromatic ortho protons (doublets at 7.45 and 6.99 ppm, J = 8.0 Hz), of two aromatic para protons (singlets at 6.55 and 6.06 ppm), and of two aromatic methylenedioxy groups (doublets at 6.19 and 6.16 ppm, J ≈ 1.2 Hz, and 5.82 ppm, narrow multiplet consisting of six poorly resolved lines), the proton of the



$\mathrm{H{-}\overset{\overset{\large OH}{/}}{\underset{|}{C}}{-}Ar}$

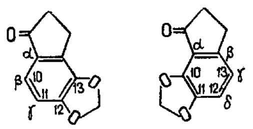
fragment (5.02 ppm) and an N-methyl group (2.28 ppm). These facts show that corydaine belongs to the spirobenzylisoquinoline group of alkaloids [3–8].

Taking into account the two possible positions of the oxo group, the skeleton of the alkaloid may be represented in the following forms.



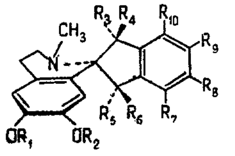
I    II

The location of the methylenedioxy group in ring D was established on the basis of the following considerations. The electron density in ring D must be low because of the electron-accepting influence of the carbonyl group and, as a result, the signals of the ring protons must be present in a weaker field than the signals of the protons of ring A. Literature information confirms this hypothesis [3,5]. Since the quadruplet in the weak field can be ascribed to two ortho protons of ring D, the methylenedioxy group must occupy positions 12 and 13 or 10 and 11.



III    IV

The signals of the protons in the position $\beta,\gamma$ to the carbonyl (structure III), should be in a weaker field than the signals of the protons in the $\gamma,\delta$-position (structure IV). In fact, in the spectrum of fumariline (V) the signals of the protons at $C_{10}$ and $C_{11}$ are at 6.86 and 7.07 ppm, and in the spectrum of the synthetic ketone VI the signals of the protons at $C_{12}$ and $C_{13}$ are at 7.46 and 6.92 ppm [3,5]. Thus, the arrangement of the corresponding doublets in the spectrum of corydaine at 7.45 and 6.99 ppm makes the choice in favor of structure III for ring D unambiguous. The two para protons must be present in ring A and, consequently, they occupy positions 2 and 3.



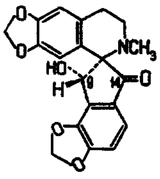
V-X

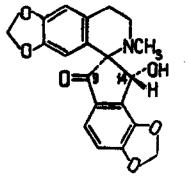
V. $R_1+R_2=CH_2$, $R_3+R_4=0$, $R_5=R_6=R_7=R_8=H$, $R_9+R_{10}=OCH_2O$.
VI. $R_1=R_2=CH_3$, $R_3+R_4=0$, $R_5=R_6=R_9=R_{10}=H$, $R_7+R_8=OCH_2O$.
VII. $R_1+R_2=CH_2$, $R_3=R_7=R_8=H$, $R_4=OH$, $R_5+R_6=0$, $R_9+R_{10}=OCH_2O$
VIII. $R_1=R_2=CH_3$, $R_3=R_5=R_6=R_7=R_8=H$, $R_4=OH$, $R_9+R_{10}=OCH_2O$.
IX. $R_1=R_2=CH_3$, $R_4=R_5=R_6=R_7=R_8=H$, $R_3=OH$, $R_9+R_{10}=OCH_2O$.
X. $R_1+R_2=CH_2$, $R_3=R_6=R_9=R_{10}=H$, $R_4=R_5=OH$, $R_7+R_8=OCH_2O$.

The mass spectrum of corydaine is similar to the mass spectra of spirobenzylisoquinoline alkaloids containing an OH group in ring C [4,5]. Apart from the intensive molecular ion and the peaks M − 15, M − 29, M − 31, and M − 45, the mass spectrum of corydaine has a strong peak with m/e 190. The remaining peaks in the m/e range of 150 are of low intensity. It has been reported [4] that the peak with m/e 190 is a characteristic feature of the mass spectrum of sibiricine (VII). The NMR spectrum shows great similarity to that of VII. The only substantial difference is in the shifts of the protons of the $\mathrm{H{-}\overset{OH}{\underset{|}{C}}{-}Ar}$ group. Literature information [3–8] shows that when the proton at $C_9$ or $C_{14}$ is in a trans position with respect to the $N{-}CH_3$ group its chemical shift is 4.85–4.88 ppm, and when it is in the cis arrangement 5.40–5.60 ppm. The corresponding signal in the spectrum of corydaine is located at 5.02 ppm, which shows its trans arrangement with respect to the N-methyl group.

This is also shown by the IR spectrum of corydaine in $CHCl_3$: the band of the stretching vibrations of the OH group is at 3265 cm$^{-1}$, and when the solution is diluted it does not shift toward higher frequencies, which shows the existence of an intramolecular bond of the —OH...N type. The formation of an intramolecular hydrogen bond between an OH in the position cis to the N-methyl group is shown by the IR spectra of other alkaloids of this group [4,7,8]. In the IR spectrum of fumaricine (VIII), whose OH group is in the trans position, $\nu_{max}$(OH) in CS$_2$ is 3600 cm$^{-1}$, while in IX the OH group is in the cis position and $\nu_{max}$(OH) in CS$_2$ is 3320 cm$^{-1}$. In the IR spectrum of ochrobirine (X) (in CHCl$_3$) one hydroxyl band has $\nu_{max}$(OH) 3585 and the other $\nu_{max}$(OH) 3300 cm$^{-1}$. The frequency of the absorption band of the OH group of sibiricine (VII) (in CHCl$_3$) is 3560 cm$^{-1}$.

These results lead to one of two variants (XI or XII) for the structure of corydaine.


XI


XII

The UV spectrum was taken on an SF-4A spectrophotometer, the IR spectrum on a UR-10 spectrophotometer, the NMR spectrum on a Varian HA-100D spectrometer (0, tetramethylsilane), and the mass spectrum on an MKh-1303 instrument (t$_{ev}$ = 150° C, ionizing voltage 24 V). The microanalyses were performed by E. A. Nikonova.

## CONCLUSIONS

Two variants of the structure of corydaine, a new alkaloid from Corydalis paczoskii, have been proposed.

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20 January 1970

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