ALKALOIDS OF Corydalis vaginans

1-O-METHYLCORPAINE

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Continuing an investigation of the composition of the alkaloids of Corydalis vaginans Royle, family Papaveraceae, introduced into the Botanical garden of VILR [All-Union Scientific-Research Institute of Medicinal Plants] [1], we have additionally isolated and identified by IR, UV, NMR, mass spectra and the results of a direct comparison with authentic samples *l*-cheilanthifoline, dihydrosanguinarine, d-bulbocapnine, *l*-scoulerine, d-bicuculline, and *l*-adiumine.

We have isolated a base $C_{20}H_{17}O_6N$ with mp 189-189.5°C (ether), $[\alpha]_D^{22}$ +145° (c 1.3; chloroform) identical in its IR, UV, NMR, and mass spectra with corydaine [2]. However, in view of the absence of information on the relative angle of specific rotation in the literature, we have called it d-corydaine.

Crystallization of the combined alkaloids from methanol also yielded a new base $C_{21}H_{21}O_6N$ with mp 220-221°C, $[\alpha]_D^{22}-36.7°$ (c 0.44; chloroform). Its IR spectra showed absorption bands at 1710 cm^{-1} (−C=of an α, β-unsaturated five-membered ketone) and 3260 cm^{-1} (OH) (chloroform). UV spectrum: $\lambda_{max}^{ethanol}$ 204, 240, 291, and 313 nm (log ε 4.80, 3.94, 3.91, 3.99). The NMR spectrum of the base is similar to those of the spirobenzylisoquinoline alkaloids (Table 1). In its spectrum there are the signals of the aromatic protons of ring A at 6.06 ppm [H_1] and 6.53 ppm [H_4]. The ortho proteins of ring D give two doublets at 7.3 ppm (J = 8.0 Hz) and 6.94 ppm (J = 8.0 Hz). The signals of the protons of the methylenedioxy groups are present at 6.2 ppm and those of two methoxy groups at 3.72 and 3.82 ppm, while there is a three-proton singlet of a $N-CH_3$ group at

TABLE 1. Comparative Chemical Shifts of the Protons of Spirobenzylquinoline Alkaloids taken in $CDCl_3$ (δ scale)

Proton	Sibericine	Corydaine	Corpaine	O-Methylledebourine	O-Methylcorpaine*
$C_{(1)}-H$	6,04	6,01	6,14	6,03	6,06
$C_{(4)}-H$	6,54	6,50	6,53	6,66	6,58
$C_{(10)}-H$	7,51	7,40	7,40	7,53	7,32
$C_{(11)}-H$	7,01	6,94	6,93	7,01	6,93
$C_{(2-3)}O_2CH_2$	5,84	5,77	—	—	—
$C_{(12-13)}O_2CH_2$	6,12	6,14	6,15	6,18	6,2
$C_{(14)}-H$	5,57	4,97	5,04	5,55	5,08
$C_{(3)}-OCH_3$	—	—	3,82	3,77	3,82
$C_{(2)}-OCH_3$	—	—	—	3,45	3,72
$N-CH_3$	2,43	2,23	2,30	2,31	2,25

*0 − TMS; in the other cases − HMDS.

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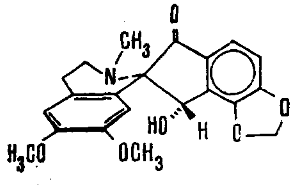
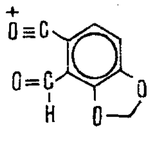
2.25 ppm. The signal of a methine proton geminal to a hydroxy group, ArC (OH)$\underline{H}$, which is located at 5.08 ppm, shows a configuration similar to that of corpaine [3-5].

The mass spectrum of the compound, in addition to the molecular peaks M^+383 (100%) and M^{++} (191.5), shows the peaks of the ions M − 15 (368), M − 45 (338), and 206 (6,7-dimethoxy-2-methyl-3,4-dihydroisoquinoline) (a), 206 − CH_4 (190), and M − 206 (177) of fragment (b). Thus, it may be concluded that the substance is 1-O-methylcorpaine (I):



I



b

LITERATURE CITED

1. N. N. Margvelashvili, O. E. Lasskaya, A. T. Kir'yanova, and O. N. Tolkachev, Khim. Prirodn. Soedin., 813 (1974).
2. Kh. Sh. Baisheva, D. A. Fesenko, B. K. Rostotskii, and M. E. Perel'son, Khim. Prirodn Soedin., 456 (1970).
3. Kh. Sh. Baisheva, D. A. Fesenko, M. E. Perel'son, and B. K. Rostotskii, Khim. Prirodn. Soedin., 574 (1970).
4. D. A. Fesenko and M. E. Perel'son, Khim. Prirodn Soedin., 166 (1971).
5. I. A. Israelov, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 268 (1975).

A NEW ALKALOID FROM Spirea japonica

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From the combined alkaloids of Spirea japonica (Japanese spirea) by chromatography on alumina we have isolated an alkaloid with composition $C_{20}H_{25}O_2N$ (I), mp 280-282°C, m/e 311 (M^+) the IR spectrum of which contains bands at 1710 cm^{-1} (C = O group), 3100 cm^{-1} (OH group), and 1655 cm^{-1} (double bond). The NMR spectrum of the alkaloid shows the presence of a quaternary methyl group (3H, singlet at 1.33 ppm) and of an exocyclic methylene group [singlets at 4.73 ppm (1H) and 4.87 ppm (1H)]. The presence of the latter was confirmed by the catalytic hydrogenation of the alkaloid in ethanol, which led to a dihydro derivative $C_{20}H_{27}O_2N$ (II), mp 290-292°C, m/e 313 (M^+), in the NMR spectrum of which the signal of a secondary methyl group appeared (doublet at 0.93 ppm, J = 5 Hz) in place of the signals of the exocyclic methylene group. On treatment with methyl iodide in methanol, the alkaloid gave a crystalline product $C_{20}H_{25}O_2N \cdot CH_3I$ the space group of which, $P2_12_12_1$, and the parameters of the elementary cell of which, a = 14.04 Å, b = 15.88 Å, c = 8.55 Å, were determined from an x-ray diagram obtained on a Weissenberg equi-inclination x-ray goniometer.

These facts make it possible to identify the alkaloid isolated as spiradine A [1].

In addition to spiradine A we isolated a new alkaloid $C_{22}H_{27}O_3N$ (III), mp 163°C, m/e 353 (M^+), which we have called spiredine. Its IR spectrum has bands at 1720 cm^{-1} (C = O group in an unstrained ring) and 1690 cm^{-1} (C = O group in a transannular position with respect to nitrogen). By means of the NMR spectra of the

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