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NEW ALKALOIDS OF Corydalis ledebouriana

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Continuing the separation of the combined alkaloids of the epigeal part of Corydalis ledebouriana collected in the Tashkent oblast [1], we have isolated two new bases (I) and (II).

Base (I), with mp 219-220°C (methanol+chloroform), $[\alpha]_D \pm 0°$ has the composition $C_{21}H_{23}O_6N$. The IR spectrum of (I) shows absorption bands at (cm^{-1}) 3540, 3520 (hydroxy group), 1515 (aromatic ring), and 1040, 930, and 920 (methylenedioxy group). The mass spectrum of (I) contains the peaks of ions with m/e 385 (M^+), 370, 367, 352, 338, 324, 308, and 206. According to its NMR spectrum, base (I) contains a N-methyl group, two methoxy groups, and a methylenedioxy group (see below). The spectral characteristics are identical with those of d-raddeanine [2]. To confirm this, we reduced dl-raddeanone (III) [2], which we isolated from the same plant (shown to be identical with an authentic sample by Prof. T. Kametani, Japan), with sodium tetrahydroborate and obtained dihydroraddeanone with mp 218-219°C, $[\alpha]_D \pm 0°$C, a direct comparison of which with (I) showed their identitiy. Thus, base (I) is dl-raddeanine.

Base (II) with mp 140-141°C, $[\alpha]_D$ +114° (c 0.28; methanol), which we have called ledebouridine, has the composition $C_{20}H_{21}O_6N$, mol. wt. 371 (mass spectrometrically). The IR spectrum of (II) has absorption bands at (cm^{-1}) 3540, 3430 (OH), 1600, 1500 (aromatic ring), and 1030 and 920 (CH_2O_2). The NMR spectrum of (II) (see below) shows the signals of N-methyl, methoxy, and methylenedioxy groups. The mass spectrum contains, in addition to the peak of the molecular, peaks of ions with m/e 356, 353, 338, 324, 308, 294, 192, 190, 177. The facts given show that ledebouridine belongs to the group of spirobenzylisoquinoline alkaloids containing two hydroxy groups in the five-membered ring [2-4].

The PMR spectra were taken on a JNM-4H-100/100 MHz instrument with HMDS as internal standard. Below we give the chemical shifts (δ scale, CDC-$_3$):

	d-Raddeanine [2]	dl-Raddeanine (I)	O-Methylledebouridine	Ledebouridine (II)
C_1—H	6,16	6,11	6,12	6,19
C_4—H	6,55	6,61	6,61	6,59
C_{10}—H	6,76 (d, 8 Hz)	6,76 (d, 8 Hz)	6,76 (d, 8 Hz)	6,77
C_{11}—H	6,80	6,88	6,86	6,77
C_{14}—H	5,42	5,39	5,36	5,33
C_9—H	5,21	5,19	5,15	5,11
C_2—OCH_3	3,40	3,35	3,35	—
C_3—OCH_3	3,81	3,78	3,78	3,75
N—CH_3	2,60	2,56	2,55	2,50
CH_2O_2	5,97	5,94	5,91	5,91

The presence in the mass spectrum of (II) of the peak of an ion with m/e 192 shows that in the isoquinoline part of the molecule of the base there is a methoxy group and a hydroxy group. The methylation of ledebouridine with diazomethane gave O-methylledebouridine with mp 204-205°C (acetone), $[\alpha]_D$ +107° (c 0.18;

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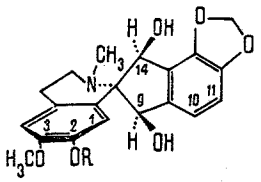
methanol), the properties of which agree well with those of d-raddeanine [2]. The hydroxy group in ledebouridine is present at C_2, since in its NMR spectrum the methoxy group gives a signal at 3.75 ppm, and in the product of its methylation signals at 3.35 and 3.78 ppm [1]. On the basis of the facts given, the following structure (II) may be proposed for ledebouridine:



I. R=CH_3
II. R=H
III. C_9=O, R=CH_3

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INDOLE ALKALOIDS OF A CALLUS CULTURE OF Vinca rosea

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There is contradictory information concerning the capacity of callus tissue of Vinca rosea (Madagascar periwinkle) for synthesizing alkaloids. Some workers [1] have obtained tissue capable of biosynthesizing monomeric and dimeric alkaloids, while others [2] have found only monomeric bases in such tissues. This is the first time that information on the chemical composition of the tissue has been published.

Callus tissue which we obtained in 1974 was grown in modified Murashige-Skoog medium in the dark at −27°C and at a humidity of 70%.

By standard methods we showed the capacity of the tissues for synthesizing indole alkaloids. Depending on their origin and the times of their growth we isolated 0.10-0.20% of combined alkaloids. By chromatographic methods in extracts from the tissues we detected alkaloids with R_f 0.18, 0.29, 0.35, 0.51, 0.60, 0.64, 0.67, 0.76, and 0.90 (TLC on alumina, benzene–ethanol (9:1) system). The combined alkaloids consisted of a complex mixture of bases which it was difficult to separate by the usual methods.

We separated the combined material into several fractions [3]. By chromatographing them in various systems and treating the chromatograms with specific reagents (1% solution of cerium ammonium sulfate in 85% orthophosphoric acid) we were unable to achieve a good separation and staining of the alkaloids, and therefore some of them contained a considerable amount of pigments. By chromatographing these fractions on a column containing inactivated alumina [4] followed by preparative separation on "Silufol" plates we obtained five individual substances. Their melting points, R_f values in various systems, color reactions, UV spectra, and a comparison with literature information [5] permitted the conclusion that they were ajmalicine, catharanthine, vindoline, lochnericine, and vinblastine. The other alkaloids could not be obtained in the pure form and be identified. Apart from the known alkaloids, seven bases the R_f values and color reactions of which corresponded to no compounds given in the literature were isolated.

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