THE STRUCTURE OF LEDERBOURINE

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From the phenolic fraction of the combined alkaloids of Corydalis ledebouriana K. et K. [1] collected in the Tashkent oblast in the flowering period, we have isolated a new base with mp 184–185°C (chloroform–methanol), which we have called ledebourine (I). UV spectrum: $\lambda_{max}^{ethanol}$ 238, 293, 316 nm (log ε 4.38, 3.98, 3.90). The IR spectrum of the base has absorption bands at (cm^{-1}) 920, 1040 (CH_2O_2), 1600 (aromatic ring), 1705 ($C=O$), and 3450 (OH). According to its NMR spectrum, the base contains N-methyl, methoxy, and methylenedioxy groups. When compound (I) was methylated with diazomethane, ledebourine monomethyl ether (II) was obtained with mp 140–142°C, mol. wt. 383 (mass spectrometrically). The NMR spectrum of (II) had the same pattern as the spectrum of the initial base, but a new signal had appeared at 3.10 ppm from a second methoxy group. The mass spectrum of ledebourine showed, in addition to the peak of the molecular ion with m/e 369, which had the maximum intensity, peaks of ions with m/e 354, 338, 206, 192, and 177. The mass spectra of (I) and (II) are characteristic for spirobenzylisoquinoline alkaloids containing carbonyl and hydroxy groups in the five-membered ring [2]. The facts given above, and also a comparison of the NMR spectrum of ledebourine with those of the alkaloids fumaritine [3], sibiricine [4], corpaine [5], and fumarofine [6] (Table 1), permit it to be assigned to the spirobenzylisoquinoline group and the composition $C_{20}H_{19}O_6N$ and the expanded formula $C_{16}H_9(CH_2O_2)(OCH_3)(OH)_2(N-CH_3)(C=O)$ to be proposed for it.

The presence in the mass spectrum of a strong ion with m/e 192 definitely shows that the methylenedioxy group is present in ring D and the methoxy and hydroxy groups are in ring A [2, 6]. A comparison of the UV and NMR spectra of ledebourine and the spectra of corydaine, corpaine, and sibiricine, in which the methylenedioxy group in ring D is located at C_{12} and C_{13}, confirms this arrangement of the substituents in the rings and, moreover, enables the methylenedioxy group to be located at C_{12} and C_{13} and the methoxy and hydroxy groups at C_2 and C_3. An analysis of the features of the NMR spectra given in a number of papers [3, 5, 8, 9] shows that the signal from C_2-OCH_3 is located in the 3.37–3.61 ppm range and that from C_3-OCH_3 at 3.68–3.87. Because of the poor solubility of ledebourine in chloroform, we recorded its NMR spectrum in trifluoroacetic acid. The signal from the methoxy group appeared at 3.40 ppm (when NMR

TABLE 1. Chemical Shifts (δ scale)

Protons	Sibiricine	Corpaine	O-Methylfumarofine	Fumaritine		Ledebourine*	O-Methylledebourine	
	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	CF_3COOH	CF_3COOH	CF_3COOH	$CDCl_3$
H–1	6,04	6,19	7,29	6,47	6,08	5,70	5,71	6,03
H–4	6,54	6,58	6,61	6,59	6,34	6,31	6,35	6,66
H–10	7,51	7,40	—	6,74	6,40	7,25	7,29	7,53
H–11	7,01	6,98	—	6,68	6,40	6,70	6,73	7,01
H–12	—	—	7.13	—	—	—	—	—
H–13	—	—	7,13	—	—	—	—	—
H–14	5.57	5,04	4,45	5,42	5,54	5,62	5,63	5,55
$N-CH_3$	2,43	2,28	2,53	2,41	2,62	2,67	2,69	2,31
C_2-OCH_3	—	—	3,93	—	—	—	3,10	3,45
C_3-OCH_3	—	3,87	3,87	3,85	3,40	3,40	3,40	3,77
CH_2O_2	5,84; 6,18	6,18	6,18	5,95	5,42	5,70	5,69	6,18

*NMR spectra taken on a JEOL C-60HL instrument with HMDS as internal standard.

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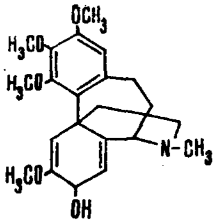
spectra are recorded in CF_3COOH, the HMDS signal shifts upfield by 44 Hz). In view of the fact that the value of the chemical shifts can change on passing from one solvent to another, we compared the NMR spectra of (I) and fumaritine (C_3-OCH_3) taken in trifluoroacetic acid. In both spectra, the methoxy group appeared in the form of a three-proton singlet at 3.40 ppm. Consequently, in ledebourine the OCH_3 group is located at C_3 and the hydroxy group at C_2.

The NMR spectrum of (II) is similar to that of corpaine. The only appreciable difference is observed in the shifts of the protons of the H–C(OH)–Ar group (Table 1). An analysis of literature information [4-6, 10, 11] shows that in the case of the trans arrangement of the C_{14} proton with respect to the nitrogen atom its chemical shift is 4.33-5.04 ppm, and with the cis arrangement it is 5.42-5.57 ppm. The corresponding signal in the spectrum of (II) is found at 5.55 ppm, which shows the cis arrangement of $C_{14}-H$ and the nitrogen atom. On the basis of the facts presented, the following structure can be put forward for ledebourine:



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