SUMMARY

Isotalatisidine, nevadensine, delcosine, delsoline, and isobaldine have been isolated from Delphinium confusum M. Pop., together with a new base for which the structure of 14-methylisotalatisidine has been established on the basis of spectral characteristics and as the result of passages from condelphine and from isotalatisidine.

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STRUCTURE OF A NEW ALKALOID FROM THE FORTUNE VARIETY OF NARCISSUS

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The structure and stereochemistry of a new alkaloid from the Fortune variety of narcissus, which has been called fortucine, have been established.

The isolation of an alkaloid with the composition $C_{16}H_{19}NO_3$ (I) from the leaves of the Fortune variety of narcissus, which was assigned to the lycorine group has been reported previously [1]. In the present communication we give information on the structure of this compound.

A study of the ^1H NMR spectra of (I) and its methylated (II) and acetylated (III) derivatives with the aid of double resonance enabled additional parameters of the spectra to be obtained and permitted a number of signals to be assigned (Table 1). From an analysis of the signals at 4.25, 2.68, and 2.95 ppm it followed that the secondary hydroxy group was present at C-1, occupying the axial position $J_{1,2} \approx J_{1,2'} \approx J_{1,11b} \approx 2.5$ Hz).

The value of the constant $J_{11b,11c} = 6.0$ Hz differs from the constant between the corresponding protons in known compounds of the type under consideration ($J_{11b,11c} = 12.0$ Hz) [2, 3]. A value of the constant of 6.0 Hz for cyclohexenes has been observed in the case of the cis position of substituents present in the α- and β-positions with respect to the double bond [4, 5]. Also in favor of the cis-linkage of rings B and C is the substantial difference in the chemical shifts of the protons at C-7 in (I) and (III). It follows from a consideration of the molecular models that spatial closeness between the C-1 and C-7 centers is possible only if rings B and C are cis-linked.

To find the position of the methoxy group we obtained the spectra of compounds (I) and (II) with additions of the chemical shift reagent (CSR) $Eu(fod)_3$. The rate of shift of the

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TABLE 1. Details of the NMR Spectra of (I), (II), and (III) (parameters of the spectra: δ – chemical shifts, ppm; (J) – SSCCs of the protons between which its value is given, (Hz)

Compound	NH	11c	11b	1	2,2′	3	4	5	7α	7β	8	11	CH_3O	AcO
I	δ	2,63	2,95	4,25	2,3–2,6	5,52	2,3–2,6	2,3–2,6	3,27	3,87	6,53	6,79	3,83	—
	(J)	(6,0)		(2,5) (2,5) (2,5)		(7,0)			(14,0)					
II	δ	2,78	3,00	4,26	2,3–2,6	5,56	2,3–2,6	2,3–2,6	3,32	3,96	6,54	6,82	3,85	
	(J)	(6,0)		(2,5) (2,5) (2,5)		(7,0)			(14,0)					
III	δ	2,6–2,9	2,6–2,9	5,54	2,3–2,6	5,33	2,3–2,6	2,3–2,6	3,53	3,60	6,64	7,08	3,87	1,96
	(J)			(2,5) (2,5) (2,5)										

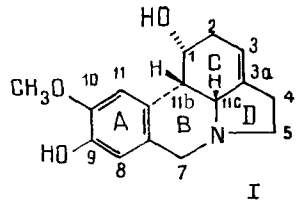
TABLE 2. Mass Spectra of Compounds (I), (II), and (III)

Compound	Relative intensity, %									
	M^+	M–1	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7	Φ_8
Pluviine [16]	237 (100)	286 (52)	243 (68)	242 (84)	269 (15)	268 (48)	266 (16)			
I	273 (99)	272 (100)	229 (17)	228 (23)	256 (12)	254 (5)	252 (22)	242 (8)	244 (22)	
II	287 (99)	286 (100)	243 (30)	242 (27)	270 (20)	268 (8)	266 (9)	256 (10)	258 (27)	
III	315 (75)	314 (74)	229 (12)	228 (24)	255 (49)	254 (100)	252 (12)	242 (15)		226 (18)

signal at 6.79 ppm of one aromatic proton was 1.5 times greater than the rate of shift of the other (at 6.53 ppm). The difference in the rates of shift was due to an additional influence of the complex with respect to the hydroxyl at C-1. It followed from this that the signal in the weak field related to H-11 and that in the strong field to H-8. At the same time, in the initial compound (I) the signal of the proton at 6.53 ppm did not shift on the addition of the CSR. These facts showed that the methoxy group was present at C-10.

A compound (norpluviine) [6] is known with the same arrangement of the functional groups but differing substantially from the compound under consideration of its physicochemical constants. The relative and absolute configurations for the norpluviine described in the literature were established on the basis of the synthesis of its methyl derivative (pluviine) starting from a compound of known structure and stereochemistry in which the linkage of rings B and C was transoid [2, 6-11]. No details of its NMR spectrum have been given.

Thus, the structure of the alkaloid (I), which we have called fortucine, differs from that of pluviine by the linkage of rings B and C and can be represented by the following structural formula:



I

It must be mentioned that there is no information in the literature on alkaloids of the lycorine series with the cis-linkage of rings B and C. The available results, including those of x-ray structural analysis, for alkaloids of this group show a transoid linkage of rings B and C [2, 12-14].

The CD spectrum of (I) showed a negative Cotton effect, as in the case of other compounds of the lycorine series [2, 10, 15]. For fortucine $[\theta]_{238}$ +4000, $[\theta]_{282}$ −2000 (c $2.92 \cdot 10^{-4}$ M); for lycorine $[\theta]_{245}$ +4200, $[\theta]_{290}$ −6000 (c $3.12 \cdot 10^{-4}$ M). It follows from a comparison of these figures that the structural differences in the C-11c asymmetric center have little effect on the nature of the CD curves.

The mass spectra of (I), (II), and (III) and pluvine are given in Table 2. O-Methylfortucine (II) showed a mass spectrum close to that of pluviine [16] and differing only by the intensities of the peaks of the ions of the corresponding fragments; in the spectra of compound (I) and (II) additional peaks of ions with, respectively, m/z 242 (8) ($\Phi_3 - CH_2$), 244 (22), 256 (10), and 258 (27) were observed.* In the spectrum of the acetyl derivative (III) there were no peaks of ions containing the acetyl group, which indicates the ease of its elimination in the form of ketene and also as acetic acid.

The IR spectrum of (I) had the band of a free hydroxyl at 3180 cm^{-1}, which disappeared in the spectrum of (III) in which there was the band of an acetyl group carbonyl at 1730 cm^{-1}.

EXPERIMENTAL

The melting points of the substances were determined on a Boëtius instrument. Specific rotations were determined on a Polamat A polarimeter at λ 546 and 578 nm with recalculation for λ 589.3 nm. The IR spectra of (I) and (III) were recorded on a IR-75 spectrophotometer in paraffin oil. UV spectra were taken on a Specord M-40 spectrophotometer in ethanol. NMR spectra were recorded on HA-100D, XL-200, and WM-360 instruments with $CDCl_3$ as solvent, CS-300, internal standard TMS. The chemical shifts are given in the δ scale (ppm) and the coupling constant J in Hz. Electron-impact mass spectra were taken on a Varian CH-8 instrument at an energy of the ionizing electrons of 70 eV. The temperature of the ion source was varied from 60 to 150°C. The CD spectra of (I) and of lycorine were taken on a Roussel Jouan Dichrographe-III instrument using methanol as solvent. The completeness of the methylation and acetylation of (I) were checked by TLC in a fixed layer of KSK silica gel, 5/40 μm, with the addition of 10% of gypsum and 2.5% of soda in the chloroform–ethyl acetate–methanol (2:2:1) solvent system.

*Fragmentation pathways were taken from the literature [16] and [17].

Fortucine (I). IR spectrum, λ_{max} cm^{-1}: 1460, 1510, 1590, 1615, 3180. The methods of isolation and other physicochemical constants of (I) have been given in [1].

Picrate of (I) (prisms) mp 210-212°C (from methanol); hydrochloride of (I) (elongated prisms), mp 208-209°C (from aqueous ethanol), $[\alpha]_D^{20}$ +110.5° (c 0.52; water); methiodide of (I) (prisms), mp 256-257°C (from methanol).

O-Methylfortucine (II) was obtained by the methylation of 0.2 g (I) with diazomethane in ether at +5°C. After the end of the reaction (48 h), the ether was evaporated off, the residue was dissolved in chloroform, and the chloroform solution was washed with 1% caustic soda solution and with water. After drying over sodium sulfate, the chloroform was evaporated off and the dry residue was crystallized twice from ether. This gave 0.09 g of acicular crystals of (II) with M^+ 287, mp 112-113°C, $[\alpha]_D^{20}$ +49.3° (c 1.15; ethanol).

1-O-Acetylfortucine (III) was obtained by the acetylation of 0.1 g of (I) in a mixture of 1 ml of pyridine and 2 ml of acetic anhydride at 20°C. After the end of the reaction (24 h), the solvents were distilled off in vacuum at 60°C. The residue was treated with 5 ml of water and, after being made alkaline with ammonia, the acetylation product was extracted with chloroform. The dried chloroform extract was evaporated to dryness, and the residue was crystallized from methanol. This gave 0.04 g of acicular crystals of (III) with M^+ 315; mp 199-201°C, $[\alpha]_D^{20}$ +9.8° (c 0.28; methanol). UV spectrum, λ_{max}, nm; 285.7, 225.0 (log ε 3.49, 3.90). IR spectrum, λ_{max}, cm^{-1}: 1460, 1520, 1600, 1730.

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SUMMARY

The structure and stereochemistry of a new alkaloid from the Fortune variety of narcissus, which we have called fortucine, have been established.

A distinguishing feature of the stereochemistry of the alkaloid molecule is the cis-linkage of rings B and C.

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