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14-METHYLISOTALATISIDINE – A NEW ALKALOID FROM Delphinium confusum

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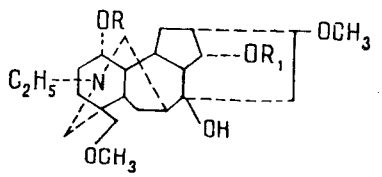
The known alkaloids isotalatisidine, nevadensine, delcosine, delsoline, and isobaldine have been isolated form the epigeal part of Delphinium confusum M. Pop., collected in the flowering period, and also a new alkaloid with the composition $C_{24}H_{39}NO_5$, mp 136-137°C (acetone), for which the structure of 14-methylisotalatisidine has been established on the basis of spectral characteristics and of passages from condelphine and isotalatisidine. This is the first time that the alkaloids nevadensine, delcosine, delsoline, isobaldine, and 14-methylisotalatisidine have been isolated from this plant.

From the epigeal part of Delphinium confusum M. Pop., collected in the flowering period in the upper reaches of the R. Talas, in addition to the condelphine, virescenine, 14-acetylvirescenine, and 14-acetylkarakoline isolated previously [1], we have isolated isotalatisidine [2], nevadensine [3], delcosine [4], delsoline [5], and isobaldine [6], and a new base (V) with the composition $C_{24}H_{39}NO_5$, M^+ 421, mp 136-137° (acetone).

Its IR spectrum contained absorption bands of hydroxy groups at 3210 and 3560 cm^{-1} and of ester bonds at 1120 cm^{-1}. According to its PMR spectrum, the alkaloid contained an N-ethyl group (three-proton triplet with J = 7 Hz at 1.06 ppm) and three methoxy groups (singlets at 3.28, 3.30, and 3.36 ppm, 3 H each). Its mass spectrum contained, in addition to the peak of the molecular ion, the peaks of ions with m/z M^+ –15 (30%), M^+ –17 (100%), M^+ –56 (2.5%), and M^+ –87 (15%).

The mass spectrum of the alkaloid was characteristic for C_{19} diterpene alkaloids and had as its maximum peak that of the M^+ –17 ion, which showed the presence of an α-hydroxy group at C-1 [7]. This was confirmed by the presence in the mass spectrum of a peak due to the M^+ –56 ion [8]. The medium intensity of the peak of the M^+ –87 ion was due to the presence of a methoxymethyl group at C-4 [8].

In the mass spectrum of the alkaloid, the peak of the M^+ –15 ion amounted to 30% of the maximum peak, which is characteristic for α-1,8-dihydroxy C_{19} diterpene alkaloids [8]. A two-proton signal at 3.68 ppm was probably due to H-14α and H-1β atoms, geminal to methoxy



I.	R=H;	R_1=Ac
II.	R=Ac;	R_1=Ac
III.	R=Ac;	R_1=H
IV.	R=Ac;	R_1=CH_3
V.	R=H;	R_1=CH_3
VI.	R=H;	R_1=H

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and hydroxy groups, respectively [9]. The facts given made it possible to suggest for the alkaloid the structure of 14-methylisotalatisidine (V).

To confirm the structure of the alkaloid, we effected a passage from condelphine to 14-methylisotalatisidine. Condelphine (I) was acetylated with acetic anhydride in the presence of pyridine, and 1-acetylcondelphine (II) was obtained [9]. The saponification of (II) with 5% methanolic KOH at room temperature for 20 min led to 1-acetylisotalatisidine (III) [10]. The methylation of (III) with methyl iodide in dioxane in the presence of sodium hydride gave 1-acetyl-14-methylisotalatisidine (IV). After the saponification of (IV) with 5% methanolic KOH at a boil for 5 h, a base with mp 135-136°C (acetone) was obtained which, according to TLC, a mixed melting point, and its IR spectrum, was identical with the sample isolated from the plant.

14-Methylisotalatisidine was also obtained by the selective methylation of isotalatisidine (VI).

EXPERIMENTAL

Melting points are uncorrected. Mass spectra were taken on a MKh-1310 instrument fitted with a SVP-5 system for direct introduction into the ion source. The PMR spectrum of the base (V) was taken on a Tesla BS-567A instrument, and the PMR spectra of the other compounds on a JEOL JNM C-60HL instrument in $CDCl_3$ with HMDS as internal standard (values given in the δ scale), while IR spectra were taken on a UR-20 spectrophotometer in tablets with KBr. The homogeneity of the substances was checked by chromatography in a thin layer of type KSK silica gel in the chloroform–methanol (100:1), (50:1), (25:1), and (10:1) systems and on alumina of "for chromatography" grade in the ether–hexane (1:4), (3:1), and (5:1), ether–chloroform (1:1), and chloroform–methanol (100:1) and (50:1) systems.

Acetylation of Condelphine. The acetylation of 1 g of condelphine was carried out by the method described in [9]. This gave 0.97 g of 1-acetylcondelphine with mp 116-117°C (ethanol). M^+ 491; M^+ –59 (100%). PMR spectrum: 1.20 (3 H, t); 2.30 (6 H, s); 3.7 and 3.78 (3 H each, s); 4.78 (1 H, q, J_1 = 7 Hz, J_2 = 10 Hz). IR spectrum, cm^{-1}: 3570, 1720, and 1740, 1100.

Hydrolysis of 1-Acetylcondelphine. A solution of 0.8 g of 1-acetylcondelphine in 10 ml of 5% methanolic KOH was kept at room temperature for 20 min. Then it was diluted with water and the reaction product was extracted with ether. After the solvent had been distilled off, 0.75 g of an amorphous substance was obtained which was chromatographed on a column of alumina. Elution with ether–hexane (5:1) led to the isolation of 0.53 g of chromatographically pure 1-acetylisotalatisidine. M^+ 449; M^+ –59 (100%). PMR spectrum: 1.02 (3 H, t); 3.20 and 3.27 (3 H each, s); 4.04 (1 H, poorly resolved triplet, J ≈ 5 Hz); 4.84 (1 H, q, J_1 = 7 Hz and J_2 = 10 Hz). IR spectrum, cm^{-1}: 3480, 1730, 1110.

Methylation of 1-Acetylisotalatisidine. A solution of 0.2 g of 1-acetylisotalatisidine in 5 ml of dry dioxane was treated with 0.13 g of sodium hydride, and the mixture was stirred for 20 min. Then 0.09 g of freshly distilled methyl iodide was added and stirring was continued for 2 h. After this, the precipitate was filtered off, and the excess of dioxane was eliminated in vacuum. This gave 0.2 g of a product which was chromatographed on a column of alumina. Elution with ether–hexane (1:4) gave 0.12 g of chromatographically pure 1-acetyl-14-methylisotalatisidine with M^+ 463; M^+ –59 (100%). PMR spectrum: 1.03 (3 H, t); 1.95 (3 H, s); 3.20, 3.25, and 3.31 (3 H each, s); 3.57 (1 H, t, J ≈ 4.5 Hz); 4.85 (1 H, q, J_1 = 7 Hz, J_2 = 10 Hz). IR spectrum, cm^{-1}: 3550, 1730, 1110.

Hydrolysis of 1-Acetyl-14-methylisotalatisidine. A solution of 0.05 g of 1-acetyl-14-methylisotalatisidine in 2.5 ml of 5% methanolic KOH was boiled for 5 h. The methanol was evaporated off in vacuum, the residue treated with 10 ml of water, and the reaction product was extracted with ether. The extract was dried over sodium sulfate and, after the solvent had been distilled off, 0.03 g of a base with mp 135-136°C (acetone) was obtained.

Methylation of Isotalatisidine. A solution of 0.2 g of isotalatisidine in 5 ml of dry dioxane was treated with 0.15 g of sodium hydride, and the mixture was stirred at room temperature for 20 min. Then 0.09 g of freshly distilled methyl iodide was added to the reaction mixture and stirring was continued for 2 h. After this, the precipitate was filtered off, and the excess of dioxane was evaporated under reduced pressure. The dry residue was extracted with ether. After the solvent had been distilled off, the residue was treated with acetone, which led to the separation of 0.19 g of base (V) with mp 135-136°C (acetone).

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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