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14-ACETYLKARAKOLINE — A NEW ALKALOID FROM *Delphinium confusum*

Z. M. Vaisov and M. S. Yunusov

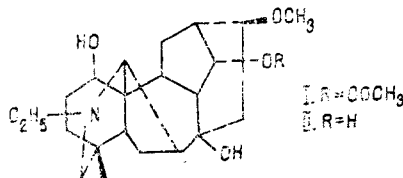
UDC 547.944/945

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 isolated previously [1], we have obtained virescenine, 14-acetylvirescenine [2], and a new base (I) with the composition $C_{23}H_{33}NO_6$, M^+ 419, mp 99-100°C (from acetone). Its IR spectrum had the absorption bands of hydroxy groups at 3460 and 3620 cm^{-1} , of ether bonds at 1100 cm^{-1} , and of an ester carbonyl at 1743 cm^{-1} . According to its PMR spectrum, the alkaloid contained a tertiary C-methyl group (three-proton singlet at 0.83 ppm), an N-methyl group (three-proton triplet with $J = 7$ Hz at 1.06 ppm), a methoxy group (three-proton singlet at 3.22 ppm), and an acetyl group (three-proton singlet at 2.00 ppm).

The mass spectrum of the alkaloid was characteristic for the C_{19} -diterpene alkaloids and had as its maximum peak that of the $(M - OH)^+$ ion, which showed the presence of an α -hydroxy group at C-1 [3]. This was also confirmed by the presence in the mass spectrum of a peak of medium intensity due to the $(M - 56)^+$ ion [4]. A one-proton signal at 4.82 ppm in the form of a triplet with $J = 4.5$ Hz was connected with the presence of an acetoxy group at C-14 [5]. The facts given make it possible to assume for the alkaloid the structure of 14-acetylkarakoline.

In actual fact, when (I) was saponified a base was obtained which, according to TLC, a mixed melting point, and IR spectroscopy was identical with an authentic sample of karakoline (II) [6].

Thus, the alkaloid that we have isolated is 14-acetylkarakoline, which has not been described in the literature.



Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnikh Soedinenii*, No. 6, p. 801, November-December, 1986. Original article submitted July 8, 1986.

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DELTERINE — A NEW DITERPENE ALKALOID FROM *Delphinium ternatum*

A. S. Narzullaev, V. M. Matveev,
S. S. Sabirov, and M. Yu. Yunusov

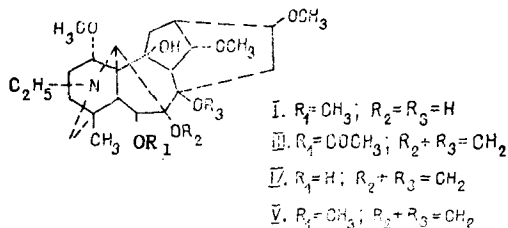
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From the epigeal part of *Delphinium ternatum* Huth., collected in the vegetation phase in the basin of the R. Varzob, in addition to known bases [1, 2], we have isolated the new base delterine (I), $C_{25}H_{41}NO_7$, mp 73–75°C (ether–hexane) and base (II) with mp 116–118°C (ether–hexane).

The IR spectrum of (I) showed absorption bands at 3400 cm^{-1} (hydroxy group) and 1100 cm^{-1} (ether C–O bonds). The NMR spectrum of delterine had signals due to an N-ethyl group (three-proton triplet at 0.99 ppm), to a tertiary methyl group (three-proton singlet at 0.94 ppm), and to four methoxy groups (three-proton singlets at 3.18, 3.26, 3.36, and 3.38 ppm).

In an attempt to acetylate delterine with acetic anhydride in pyridine at room temperature for 20 days, the initial compound was recovered. The deuteration of (I) showed the presence of three active hydrogen atoms. Consequently, the three hydroxy groups present were tertiary.

The results of the mass, NMR, and IR spectroscopy of (I) permitted delterine to be assigned to the diterpene alkaloids with a lycocotinine skeleton and the suggestion for it of the structure of 6-O-methyldemethyleneeldelidine (I). To confirm this suggestion, we made a passage from eldeline (III) to (I). The saponification of (III) in 5% methanolic alkali gave eldelidine (IV), which was methylated with methyl iodide in the presence of sodium hydride. The 6-O-methyleldelidine (V) so obtained, on being heated with 10% sulfuric acid, gave 6-O-methyldemethyleneeldelidine, which was identical with (I) in all respects (TLC, mixed melting point, IR spectra).



The IR spectrum of base (II) showed absorption bands at 1100 cm^{-1} (ether C–O bonds). Its NMR spectrum had signals due to a N-ethyl group (three-proton triplet at 1.00 ppm), to five methoxy groups (three-proton singlets at 3.18, 3.20, 3.30, 3.31, and 3.41 ppm), to a methylenedioxy group (two-proton singlet at 5.07 ppm), and to a tertiary methyl group (three-proton singlet at 0.90 ppm). Attempted deuteration showed the absence of active hydrogens.

Abu Ali ibn Sina [Avicenna] Tadjik State Medical Institute, Dushanbe. Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 6, 802–803, November–December, 1986. Original article submitted July 8, 1986.