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DELCORININE, A NEW ALKALOID FROM *Delphinium corymbosum*

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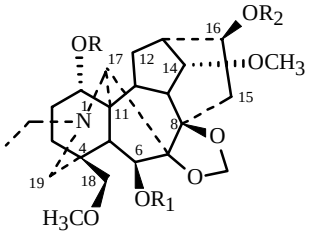
The aerial part of D. corymbosum *yielded delcoridine and a new C_{19}-norditerpenoid alkaloid delcorinine. The structure of delcorinine was established using spectral data and correlation with delcorine and delsoline.*

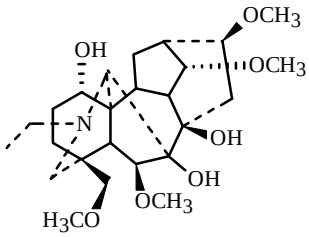
Key words: *Delphinium corymbosum*, new C_{19}-norditerpenoid alkaloid delcorinine.

Separation of the total alkaloids ($CHCl_3$) of the aerial part of *D. corymbosum* collected during flowering near Pokatilovka (Republic of Kazakhstan, Dzhungarskii Alatau) [1] yielded delcoridine and a new base $C_{24}H_{37}NO_7$ (**1**), mp 226-228°C (acetone), called delcorinine. The IR spectrum of **1** contains absorption bands at 3470, 3330 (OH), and 1090 cm^{-1} (C–O ether). The PMR spectrum exhibits signals for N-ethyl (1.07, t, J = 7.0 Hz, 3H), two methoxyls (3.31 and 3.33, s, 3H each), and methylenedioxy group (5.07 and 5.12, s, 1H each). The mass spectrum of **1** gives peaks with *m/z* 451 [M^+ (46)], 436 (33), 434 (100), 421 (87), 406 (33), 404 (25), 395 (17), 392 (50), 390 (25), 378 (19), 376 (25), 374 (8), 364 (19), 362 (17), 360 (8), 332 (4).

The composition and spectral data indicate that **1** is a C_{19}-norditerpenoid alkaloid with the lycoctonine skeleton and the following structural formula: $C_{19}H_{21}(N–C_2H_5)(OH)_3(OCH_3)_2(–O–CH_2–O–)$.

A comparison of the structural formulas of **1** and delcorine (**2**) [3] (four methoxyls and one hydroxyl) indicates that they differ in the number of methoxyls and hydroxyls whereas the total number of these substituents is the same. Methylation of **1** by methyliodide in dioxane in the presence of NaH gave the dimethyl ether **3**, M^+ 479, and 6-O-methyldelcorine (**4**) [4]. Reaction of **3** with H_2SO_4 (10%) afforded the known alkaloid delsoline (**5**) [5]. The correlation confirms the presence of the lycoctonine skeleton in **1** and reveals the position and configuration of the substituents, indicating a OH on C-1 and methylenedioxy group on C-7 and C-8. The relative position of the remaining substituents was solved as follows.





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1: R = R_1 = R_2 = H
2: R = R_2 = CH_3; R_1 = H
3: R = H; R_1 = R_2 = CH_3
4: R = R_1 = R_2 = CH_3
6: R = R_1 = R_2 = $COCH_3$

Acetylation of **1** by acetic anhydride in pyridine gave the triacetyl derivative **6**. The PMR spectrum of **6** has a 1H singlet at δ 5.42. This signal for **1** appears at δ 4.32, which is characteristic for H-6α [6], and places the second hydroxyl on C-6. Furthermore, a 1H triplet with J = 5.0 Hz for H-14β appears at δ 3.66 in the PMR spectrum of **6** [7], which indicates that one of the methoxyls occurs on C-14.

The mass spectrum of **1** contains peaks for $[M - 56]^+$ and $[M - 87]^+$, which is due to the locations of the α-hydroxyl

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and methoxyl at the 1- and 18-positions, respectively [8]. Therefore, the 16-position is the only one possible for the third hydroxyl. Thus, delcorinine has structure **1**.

A characteristic feature of the mass spectra of C(6)-methoxy and C(7)-C(8)-methylenedioxy lycoctonine compounds is the presence of a peak for $[M - 45]^+$, which is due to loss of methyl from C(6)-OCH_3 and formaldehyde from methylenedioxy group [9]. Transformation from **4** to **3** sharply increases the strength of the $[M - 45]^+$ peak whereas that of the peak caused by loss of substituent from C-1 decreases significantly. This indicates that the hydroxyl on C-1 in lycoctonine compounds that have C(6)-methoxy and C(7)-C(8)-methylenedioxy groups enhances formation of $[M - 45]^+$ ions.

EXPERIMENTAL

The purity of the compounds was checked by TLC on KSK silica gel using C_6H_6—CH_3OH (4:1), $CHCl_3$—CH_3OH (20:1, 9:1, 4:1), and $CHCl_3$—C_2H_5OH (9:1), and on aluminum oxide using $CHCl_3$, $CHCl_3$—CH_3OH (50:1), and ether—hexane (3:1). IR spectra were recorded on a UR-20 instrument in KBr pellets; PMR spectra, on a JNM-4H-100/100 MHz spectrometer in $CDCl_3$ with HMDS internal standard; mass spectra, in an MX-1310 instrument equipped with a direct probe into the ion source.

Isolation of Delcorinine (1) and Delcoridine. The total alkaloids ($CHCl_3$) [1] were chromatographed over a column of deactivated Al_2O_3 (1:10) ($CHCl_3$ eluent, 300 mL fraction volume). Fractions 1-15 (8.4 g) were rechromatographed on a column of deactivated Al_2O_3 (1:30) [$CHCl_3$ eluent, fractions 1-45; $CHCl_3$—CH_3OH (100:1), fractions 46-105; fraction volume 200 mL]. Acidification of the alcoholic solution of fractions 9-12 by alcoholic $HClO_4$ (10%) gave delcoridine perchlorate (0.15 g). Fractions 51-59 afforded delcorinine (0.29 g) upon treatment with acetone.

Triacetyldelcorinine (6). A mixture of **1** (0.05 g), acetic anhydride (5.0 mL), and pyridine (0.5 mL) was left at room temperature for 4 d. Usual work up gave **6** (0.056 g), M^+ 577. PMR spectrum: δ 2.0 (9H, 3×$COCH_3$).

Methylation of 1. A mixture of **1** (0.078 g) in dioxane (20.0 mL), CH_3I (2.0 mL), and NaH (0.02 g) was boiled and stirred for 16 h. The NaH was removed. The filtrate was evaporated to dryness. The solid was dissolved in H_2SO_4 (5%), washed with ether, basicified with soda, and shaken with $CHCl_3$. The $CHCl_3$ extracts were dried over Na_2SO_4 and evaporated. The solid (0.082 g) was chromatographed over a column of deactivated Al_2O_3 (1:20) [eluent: hexane—ether (3:1), fraction volume 1.0 mL]. Fractions 17-24 gave 6-O-methyldelcorine (0.012 g), mass spectrum, *m/z*: 493 M^+ (13), 478 (24), 463 (23), 462 (100), 448 (67), 446 (24), 434 (11), 432 (53), 420 (24), 418 (44), 416 (40), 404 (33), 402 (49), 374 (13). Fractions 38-63 gave **3** (0.03 g), mass spectrum, *m/z*: 479 M^+ (16), 462 (56), 449 (12), 434 (100), 432 (20), 423 (14), 420 (12), 418 (80), 406 (24), 404 (72), 402 (32), 392 (16), 390 (48), 388 (28), 360 (24).

Acid Hydrolysis of 3. A solution of **3** (0.025 g) in H_2SO_4 (50.0 mL, 10%) was heated on a water bath for 10 h, cooled to room temperature, diluted with water, and worked up as usual to give delsoline (0.01 g), mp 205-211°C (acetone).

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