DEHYDROELDELIDINE — A NEW ALKALOID FROM *Delphinium ternatum*

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UDC 547.944/945

Continuing a study of the total alkaloids of the epigeal part and roots of *Delphinium ternatum* Huth., collected in the vegetation (May 12, 1979) and flowering (June 18, 1979) phases in the basin of the R. Varzob, in addition to those isolated previously [1, 2] we have isolated dictyocarpine [3], a base $C_{25}H_{37}NO_7$ (I) with mp 120-122°C (hexane), a base $C_{21}H_{25}NO_4$ (II) with mp 104-109°C (ether), hydrochloride 243.°C;and base B with mp 236-238°C (acetone).

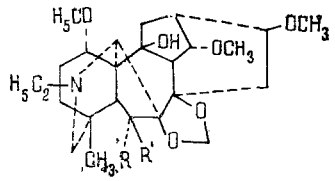
The IR spectrum (KBr) of compound (I) contained absorption bands at (cm^{-1}) 1100 (ether C—O bond), 1745 (carbonyl in a five-membered ring), and 3400-3600 (hydroxy groups). Its NMR spectrum ($CDCl_3$, δ scale) showed signals from a tertiary methyl group (0.88 ppm, singlet, 3 H), from a N-ethyl group (1.02 ppm, triplet, 3 H), from three methoxy groups (3.26, 3.29 and 3.34 ppm, singlets, 3 H each), from a methine group (4.09 ppm, triplet with J ≈ 5 Hz, 1 H), and a methylenedioxy group (5.00 and 5.44 ppm, singlets, 1 H each). The mass spectrum of base (I) contained the peaks of ions with m/z 463 (M^+), 448, 446, 432 (100%), 418, 400, 390, 382, 372, 368. The facts given permit (I) to be assigned to the diterpene alkaloids with a lycotonine skeleton and the following developed formula to be given:

$$C_{16}H_{17}\left(\geq C-CH_3\right),\quad (>N-C_4H_5),\quad (OCH_3)_3\ (CO),\ (CH_2O_2),\ (OH).$$

A comparison of the spectral characteristics and developed formulas of compound (I) and eldelidine (III) and the difference in the molecular weights by two units showed that (I) was dehydroeldelidine. The presence in the PMR spectrum of (I) of a difference in the chemical shifts of the protons of the methylenedioxy group amounting to 44 Hz (in eldelidine, 7 Hz) additionally confirmed the position of the carbonyl group at C_6 and of the methylenedioxy group at C_7 and C_8 [4]. To confirm this hypothesis we oxidized eldelidine with chromium trioxide in acetone and obtained dehydroeldelidine which was shown to be identical with (I) on the basis of IR spectra, thin-layer chromatography, and a mixed melting point [4]. Consequently, the base (I) that we isolated was dehydroeldelidine, and this is the first time that it has been isolated from a plant.

The IR spectrum (KBr) of compound (II) contained absorption bands at 1100 cm^{-1} (ether C—O bonds) and 1600 cm^{-1} (aromatic ring). The NMR spectrum ($CDCl_3$, δ scale) showed the signals of a N-methyl group (2.50 ppm, singlet, 3 H), four methoxy groups (3.60, 3.78, 3.82, 3.88 ppm, singlets, 3 H each), and three aromatic protons (6.53, 6.73, 8.03, singlets, 1 H each).

The mass spectrum of base (II) contained the peaks of ions with m/z 355 (M^+), 354, 340, 324, 312, 297, 281. The UV spectrum showed maxima at 282 and 304 nm (log ε 4.34 and 4.24), which are characteristic for 9,10-substituted aporphines [5]. All the facts given are in harmony with literature information for glaucine [5, 6]. A direct chromatographic comparison with an authentic sample also showed their identity. This is the first time that glaucine has been isolated from plants of the genus *Delphinium*.



I. R = R' = O

II. R = H, R' = OH

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0009-3130/85/2101-0133$09.50

Base B was readily soluble in ethyl acetate and ethanol and more sparingly in acetone, ether, chloroform, ethanol, hexane, and petroleum ether (40-70°C). The IR spectrum (KBr) of base B contained absorption bands at 1100 cm^{-1} (ether C–O bonds), 1710 cm^{-1} (carbonyl group), and 3500 cm^{-1} (hydroxy groups). The mass spectrum had the peaks of ions with *m/z* 415 (M^+, 37%), 397 (25%), 387 (75%), 327 (44%), 309 (100%), 300 (47%), 291 (31%), 280 (44%), 264 (25%).

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CONFORMATIONAL CHANGES OF GOSSYPULIN ON CHEMICAL MODIFICATION.

I. INFLUENCE OF GOSSYPOL

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UDC 547.962

Chemical modification is widely used for regulating the functional properties of food proteins [1]. We have made use of this approach for the study of the interrelationship of the structure of the globulins of cotton seeds with their properties by subjecting the globulins to treatment with such acylating agent as succinic and acetic anhydrides. We have shown previously [2] that the quaternary structure of the 11S globulin (gossypulin) changes appreciably even with a small degree of modification (10-fold excess of agent per 1 mole of lysine). This appears particularly clearly on succinylation. It appeared of interest to investigate the laws in the change of the secondary and tertiary structures at a minimum degree of modification, which would permit a conclusion to be drawn concerning the contribution of particular changes in the structure of the protein, leading to a disturbance of the quaternary structure. It is just with this aim that the minimum excess of acylating agent (tenfold excess per mole of lysine) was taken.

As we have established previously [3], gossypol-free gossypulin can be isolated only from fresh cotton seeds, and in other cases gossypol (the toxic pigment of the cotton plant) is unavoidably present in the protein samples obtained. In view of this, the work was carried out on gossypol-free and gossypol-containing (0.6%) samples of the 11S globulin.

The circular dichroism (CD) spectra of the gossypol-containing and gossypol-free gossypulin differed substantially (Fig. 1), particularly in the region of aromatic absorption (260-280 nm), which indicates differences in their tertiary structures. This, in its turn, affects the conformational stability of the proteins on modification. As can be seen from Fig. 2, which gives the CD spectra of modified gossypol-free proteins, succinylation (degree of modification 25%) and acetylation (degree of modification 13%) caused changes both in the secondary structure (Fig. 2b) and in the tertiary structure (Fig. 2a). In the case of gossypylin containing gossypol (Fig. 3), more substantial changes were observed in 260-280 nm

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Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 132-133, January-February, 1985. Original article submitted June 4, 1984.

0009-3130/85/2101-0134$09.50