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DELTERINE — A NEW DITERPENE ALKALOID FROM *Delphinium ternatum*

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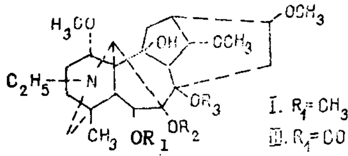
From the epigeal part of *Delphinium ternatum* Huth., collected in the vegetation phase in the basin of the R. Varzob, in addition to known bases [1, 2], we have isolated the new base delterine (I), $C_{25}H_{41}NO_7$, mp 73-75°C (ether—hexane) and base (II) with mp 116-118°C (ether—hexane).

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 signelts 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 lycoctonine 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).



I. $R_1 = CH_3$; $R_2 = R_3 = H$
III. $R_1 = COCH_3$; $R_2 + R_3 = CH_2$
IV. $R_1 = H$; $R_2 + R_3 = CH_2$
V. $R_1 = CH_3$; $R_2 + R_3 = CH_2$

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.

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When (II) was heated in 10% sulfuric acid, a product was obtained the NMR spectrum of which lacked the signal of methylenedioxy group but contained the signal of five methoxy groups.

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INFLUENCE OF VARIOUS DENATURING AGENTS ON THE SOLUBILITY OF GOSSYPULIN

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One of the important factors influencing the solubility of proteins is denaturation [1]. We have previously [2] shown a change in the solubility of gossypulin on acid denaturation, and also with the varying degree of denaturation on chemical modification (with succinic and acetic anhydrides). A disturbance of the quaternary structure of gossypulin with only small changes in the secondary structures led to a rise in the pH maximum of the precipitation (pH 4.3-4.6) of the proteins from dilute solution. The acid-denatured protein precipitated from dilute solution at lower pH values (3.5-3.8) than the native gossypulin (pH 4.0).

In the present communication we give results showing the changes in the solubility of gossypulin under the action of various types of denaturing agents. To study solubility we used the method of turbidimetric titration of dilute solutions, C 0.03% [3]. Table 1 gives the pH values of the precipitation maxima of the denatured proteins under various conditions. Thermal treatment of the protein in 10% NaCl solution and in the absence of salt, and also in 8 M urea solution or in NaOH solution (pH 12.5) at room temperature led to a considerable broadening of the pH range of the precipitation maximum in comparison with that of a native sample of gossypulin and of the acid-denatured protein [2]. At the same time, in spite of the different types of denaturation, the addition of pectin (at a weight ratio of protein to pectin of 4:1) led to a shift of the pH of the precipitation maximum into the more acid region, i.e., it improved its solubility in the neutral region.

TABLE 1. pH Values of the Precipitation Maxima of Denatured Proteins under Various Conditions

Protein sample	Without additives	Apple pectin	Ca^{2+} ions	Ca^{2+} ions + pectin
Gossypulin (with 0.6% of gossypol)	4.0	3,0	4,0—4,5	2,8—2,9
Gossypulin in distilled water (100°C, 15 min)	3,3—4,2	3,0—3,3	3,0—4.5	3,0—3,3
Gossypulin in 10% NaCl solution (100°C, 15 min, after dialysis)	4,0—5,6	3,2—3,8	3,5—5,7	3,2—3,6
Gossypulin in 8 M urea solution (24 h, after dialysis)	4,0—5,5	3,3—3,8	4,0—5,8	3,2—3,6
Gossypulin in NaOH solution (pH 12.5, 60 min, after dialysis)	4,2—5,2	3,2—3,5	4,0—5,5	3,1—3,4

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