ALKALOIDS OF Petilium eduardi

IMPERIALINE N-OXIDE

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Continuing the separation of the total alkaloids obtained from the epigeal part of Petilium eduardi [1, 2], the combined ether-soluble bases after the separation of imperialine were dissolved in benzene and the solution was treated with citrate-phosphate buffer solutions with pH values of from 8 to 4 (with intervals of pH 1). The mixture of bases obtained from the pH 7 and 8 fractions was chromatographed on a column of silica, and methanol−chloroform (2 : 8) eluates deposited a base (I) with mp 266-268°C (acetone), $[\alpha]_D$ −48.23° (c 0.68; methanol), composition $C_{27}H_{43}NO_4$, and a base (II) with mp 257-259°C (acetone), $[\alpha]_D$ −33.68° (c 1.187; methanol) and also a mixture of crystals with mp 253-257°C [1]. The latter consisted of bases (III) with mp 247-248°C (ethanol), $[\alpha]_D$ −45.63° (c 0.71; methanol) and (IV) with mp 263-265°C (methanol), $[\alpha]_D$ −15.3° (c 0.39; methanol-chloroform (9 : 1)).

IR spectrum of (I), ν_{max}, cm^{-1}; 3540−3200 (OH), 2937−2878, 1462 (−CH$_2$, CH$_3$), 1705 (C = O), 970, 935, 928 ($>$N→O) [3]. The mass spectrum of (I) had the main peaks of ions with m/e 98, 111, 112 (100%), 114, 124, 125, 138, 140, 150, 154, 155, 156, 162, 164, 230, 372, 384, 386, 410, 411, 413, 429 (M−16)$^+$ (4.3%), which are characteristic for the C-nor-D-homosteroid alkaloids of the imperialine series [4, 5]. In the NMR spectrum of (I) (taken in CD$_3$OD) singlets were observed at 0.71 ppm (19-CH$_3$) and 1.04 ppm (21-CH$_3$), and a doublet at 0.88 ppm (27-CH$_3$) [JNM-4H-100/100 MHz, HMDS, δ scale].

The low intensity of the molecular peaks of (I), in a position corresponding to 16 mass units more than the corresponding peak in the mass spectrum of imperialine, and the absence of a Bohlmann band in the IR spectrum of (I) [6] and its ready solubility in water permit the assumption that base (I) was the N-oxide form of imperialine. The reduction of (I) with zinc in hydrochloric acid gave a substance identical with imperialine (V) [7] (mixed melting point, IR spectrum). Consequently, (I) is imperialine N-oxide. However, (I) was not identical with synthetic imperialine N-oxide [mp 268-270°C (acetone), $[\alpha]_D$ −50.9° (c 0.57; methanol)] (VI) which we obtained by oxidizing imperialine with hydrogen peroxide. The reduction of (VI) also gave imperialine. IR spectrum of (VI), λ_{max}, cm^{-1}: 3350−3170 (OH), 2945−2850, 1500, 1460 (−CH$_2$, CH$_3$), 1710 (C = O), 970, 960, 930 ($>$N→O). The mass spectrum of (VI) showed all the peaks of ions present in the mass spectrum of (I) but with different intensities: ions with m/e 112 (100%) and 445 (M$^+$, 1.9%). The NMR spectrum of (VI) taken in CD$_3$OD showed singlets at 0.71 ppm (19-CH$_3$) and 1.06 ppm (21-CH$_3$), and, a doublet at 1.37 ppm (27-CH$_3$).

On comparing the chemical shift of the protons from the 27-CH$_3$ group in (I) with the corresponding figure for (VI), an upfield shift of the signal by 49 Hz can be seen. This difference in chemical shifts apparently shows that (I) differs from (VI) in the linkage of rings E/F and, correspondingly, in the orientation of the 27-CH$_3$ groups. This means the (I) and (VI) are isomeric N-oxides of imperialine.

Thus, the base (I) is one of the isomers of imperialine N-oxide − the first representative of the N-oxides among the series of steroid alkaloids isolated.

The study of the alkaloids (II), (III), and (IV) is proceeding.

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METHOD FOR THE QUANTITATIVE DETERMINATION OF

DEOXYPEGANINE FROM Peganum harmala

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The epigeal part of Peganum harmala (family Lygophyllaceae) contains a number of alkaloids [1]. We propose a method for the quantitative determination of deoxypeganine in the plant raw material which consists in obtaining the combined alkaloids from this material separating them by chromatography, and determining the deoxypeganine in the eluate by micro nonaqueous titration [2]. The deoxypeganine was separated from the accompanying alkaloids in a thin nonfixed layer of alumina in the chloroform—benzene—acetone (12 : 6 : 9) system. The R_f value for peganine, deoxypeganine, vasicinone, deoxyvasicinone, peganol, harmine, harmaline, peganidine, deoxypeganine and pegamine are, respectively, 0.02, 0.25, 0.10, 0.76, 0.55, 0.40, 0.06, 0.02, 0.07, and 0.04. On elution with chloroform, 98-100% desorption was achieved.

Below we give the characteristics of the statistical treatment of the results of the determination of deoxypeganine (0.5-2.0 mg) by acid—base titration in anhydrous acetic acid using a solution of perchloric acid as the titrant:

h	$\bar{x}$	S^2	S	$S_{\bar{x}}$	a	$t_{a,k}$	E_a	E_{rel}
8	100.40%	2.760	1.661	0.587	0.95	2.365	1.388	1.38 %

The amounts of deoxypeganine in the raw material was found in the following way. A 20-g portion of the comminuted air-dry raw material was wetted with 20 ml of a 10% solution of ammonia, and the alkaloids were extracted exhaustively with chloroform. The extract was concentrated to 25 ml and from 5 ml of this extract the total alkaloids were obtained in the usual way [3] and were dissolved in 5 ml of ethanol. On a plate (13 × 18 cm) with a layer of alumina (activity grade III, particle size 0.2-0.1 mm; layer thickness 1.5 mm, pH of a 10% aqueous suspension 4.2-4.5) was deposited 0.5 ml of the ethanolic solution of the combined alkaloids and chromatography was carried out in the above-mentioned system. A "marker" — 0.5 ml of a 0.5% ethanolic solution of deoxypeganine hydrochloride — was deposited on the same plate, which was treated in the moist state with Dragendorff's reagent. The alkaloids were eluted with 100 ml of chloroform, the resulting solution was evaporated to dryness, and the residue was dissolved in 5 ml of glacial acetic acid and titrated with 0.01 N perchloric acid until the solution acquired a blue color (indicator Crystal Violet). The amount of deoxypeganine in the raw material (x, %), referred to the absolutely dry weight, was calculated from the formula

$$x = \frac{50 \cdot 17.22 \cdot V_1}{p\,(100 - h)},$$

where V_1 is the volume of 0.01 N perchloric acid solution consumed in the titration, ml; p is the weight of the raw material, g; h is the moisture content of the raw material, %; and 1 ml of 0.01 N perchloric acid solution corresponds to 0.001722 g of deoxypeganine. A control experiment was performed in parallel. The method