hus, holothurin A_2 is 3β-[O-(3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-O-β-D-glucopyranosyl-(1 → 4)-O-β-D-quinovopyranosyl-(1 → 2)-{4-(sodium sulfato)-β-D-xylopyranosyloxy}]holost-9(11)-ene-12α,17α-diol.

The determination of the complete structures of two glycosides of the holothurian *H. floridana* — holothurin A_1 [1] and holothurian A_2 — has shown that the holothurians of one species may contain triterpene oligosides with different aglycones but having carbohydrate chains of the same structure.

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ALKALOIDS OF *Petilium raddeanum*.

III. STRUCTURE OF PETISIDINE

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We have continued the separation of the combined alkaloids of the epigeal part and bulbs of *Petilium raddeanum* (Rgl) Vved. [1, 2]. The fraction with pH 4.99 obtained from the epigeal part [1] was separated according to solubilities into ethereal and chloroform fractions. The chromatographic separation of the ethereal fraction on a column of silica gel with elution by chloroform–methanol (9:1) led to the isolation of base with mp 236–239°C (acetone), $[\alpha]_D$ +17° (c 0.50; chloroform), $C_{27}H_{45}NO_3$ (I), M^+ 431.

The physicochemical properties of (I) (melting point, IR, mass, and NMR spectra) coincided with those of isodihydroimperialine [3]. A direct comparison of (I) with an authentic sample of isodihydroimperialine showed their identity.

The material from the mother liquor after the isolation of the alkaloids mentioned in our previous paper [2] was dissolved in benzene, and the bases remaining in it were extracted with 3% acetic acid and then with 5% sulfuric acid. The benzene solution was made alkaline and the solvent was distilled off. The residue was chromatographed on a column of silica gel and, on elution with benzene–acetone (8:2), the initial fractions yielded a base with mp 150–152°C, $C_{27}H_{41}NO_3$, M^+ 427, identical with the petisidine (II) isolated previously from the epigeal part of this plant [1].

The UV spectrum of (II): λ_{max} 285 nm (log ε 2.65). IR spectrum (cm^{-1}): 3380, 1065 (OH), 1691 (C=O), 1615 (N=C).

The mass spectrum of (II) is characterized by the ions with m/z 97 (28%), 110 (19%), 111 (28%), 121 (7%), 124 (9%), 129 (9%), 139 (33%), 140 (100%), 149 (14%), 150 (9%), 164 (9%), 256 (7%), 412 $(M - 15)^+$ (7%), 427 M^+ (33%).

The mass-spectrometric fragmentation of petisidine in the region of low masses was similar to that of tomatillidine [4–6], which permits (II) to be assigned to the steroid alkaloids of the verazine group [3].

The NMR spectrum of (II) shows two singlets at 0.57 ppm, (3 H, 19-CH_3) and 0.66 ppm (3 H, 18-CH_3), and two doublets from secondary methyl groups at 0.99 ppm (J = 6 Hz) and 1.06 ppm (J = 7 Hz).

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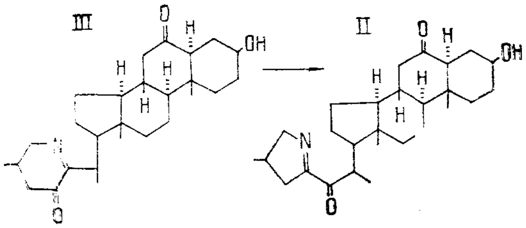
When petisine (III) was deposited on a plate coated with silica gel (KSK), it gradually changed into petisidine (II) (R_f, IR and mass spectra), this transformation taking place to the extent of 5% in the first 40 minutes, 40-50% in a day, and 60% in two days. Isomerization of a similar type has been described by Kusano et al. [5].

The benzene fraction of the combined alkaloids remaining after their separation according to basicity [1], when it was chromatographed rapidly on a silica gel plate showed the spots of substances (II) and (III) similar in size and intensity and therefore excluding the possibility of the conversion of petisine into petisidine in the process of separating the mixture of bases on the silica gel column.

The conversion of petisine to petisidine shows the similar linkages of rings A/B, B/C, and C/D and the position of the OH group at C_3 and of the two carbonyls at C_6 and C_{22}, and the presence of a $\Delta^{23(N)}$ bond.

It follows from the facts given above that petisidine has the structure and partial configuration of 3β-hydroxy-23,26-iminocholest-23(N)-ene-6,22-dione.



Thus, from the epigeal part of *Petilium raddeanum* we have isolated isodihydroimperialine, this being the first time that it has been found in this plant, and from the bulbs petisidine. The structure of the new alkaloid petisidine has been established.

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