SUMMARY

The roots of Convolvulus subhirsitum have yielded seven known alkaloids and one new one, for which, on the basis of spectral characteristics and a comparative study with known alkaloids of this series, and also by synthesis of (±)-N-isopropyl-3α-veratroyloxynortropone has been established.

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ALKALOIDS OF Petilium raddeana.

V. STRUCTURE OF PETISIDINONE

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From the epigeal part of Petilium raddeana have been isolated the known alkaloids edpetiline and edpetine and the new base petisidinone with mp 217-219°C, $[\alpha]_D$ 0° (c 0.169; chloroform), $C_{27}H_{39}NO_3$ (I). When the known alkaloid petisidine was oxidized, a product identical with petisidinone (I) was obtained. Thus, the structure of (I) has been established as 26,23-nitrilocholestane-3,6,22-trione. Details of the IR, PMR, and mass spectra of (I) are given.

Continuing an investigation of the alkaloids of the epigeal part of Petilium raddeana (Regel) Vved. [1-3], from the chloroform fraction of the total alkaloids we isolated edpetiline and edpetine [4, 5]. The isolation of petisidine and petisine has been reported previously [1]. On the further separation of the mother liquors from these alkaloids, we have isolated a new base, petisidone (I), $[\alpha]_D$ 0° (c 0.169; chloroform), $C_{27}H_{39}NO_3$ M^+ 425).

The IR spectrum of pepisidinone contains strong absorption bands of a carbonyl group at 1710 cm^{-1}, of a α,β-unsaturated ketone at 1690 cm^{-1}, and of a C═N double bond at 1610 cm^{-1}. The PMR spectrum of alkaloid (I) has singlets from tertiary C-methyl groups at 0.60 ppm ($18\text{-}CH_3$) and 0.86 ppm ($19\text{-}CH_3$) and doublets from secondary C-methyl groups at 0.99 ppm (J = 5 Hz) and 1.00 ppm (J = 6 Hz). The mass-spectrometric fragmentation of petisidinone took place similarly to that of petisidine [3]. The maximum peak in the spectrum of compound (I) is that of an ion with m/z 140, which is formed as the result of the cleavage of the C_{17}—C_{20} bond with the migration of hydrogen from C_{15} to the nitrogen atom [6].

On the basis of the facts given above, petisidinone is a typical steroid alkaloid of the tomatillidine group [6]. The difference of two mass units between the petisidinone and petisidine molecular ions and the absence from the IR spectrum of substance (I) of the band of a hydroxy groups permitted the assumption that petisidone may be an oxidized product of petisidine. In actual fact, when the latter was oxidized with chromium trioxide a product identical with petisidinone (mixed melting point, R_f, IR spectra) was obtained.

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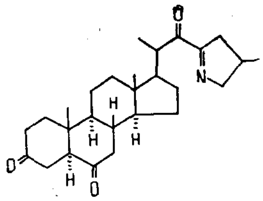
Thus, petisidine has the structure of 26,23-nitrilocholestane-3,6,22-trione (I).



EXPERIMENTAL

For chromatographic purposes we used type KSK silica gel. IR spectra were taken on a UR-20 spectrophotometer in tablets with KBr, the PMR spectrum on a Tesla BS-567 A spectrometer in deuterochloroform (σ, ppm; 0 — HMDS), and the mass spectrum on a MKh-1310 instrument at an ionizing voltage of 50 V and a sample temperature of 100-130°C.

Edpetiline and Edpetine. Part of the combined chloroform-extracted material (10 g) was dissolved in chloroform and the solution was treated with 5-ml portions of 1% sulfuric acid followed by alkalination with ammonia and extraction with chloroform. This gave 16 fractions. Edpetiline was isolated from combined fractions 1-8. The edpetiline (2 g) from the mother liquor was dissolved in 5% sulfuric acid and the solution was made alkaline with ammonia and was extracted with ether and then with chloroform.

The ethereal fraction (0.8 g) was chromatographed on a column of silica gel with elution by chloroform—methanol (9.3:0.7). The eluates were collected in 40-ml fractions. Edpetine was isolated from the first fractions. Edpetiline and edpetine were identified by direct comparison with authentic samples.

Petisidinone (I). The material (3 g) from the mother liquor after the isolation of petisidine and petisine was chromatographed on a column of silica gel. A hexane eluate yielded 0.005 g of petisinone, mp 217-219°C (hexane—acetone (10:1)); R_f 0.50 (hexane—acetone (4:1)).

Mass spectrum of (I): m/z 97, 110, 139, 140 (100%), 149, 397, 410, 425 M^+.

Oxidation of Petisidine. With stirring, 0.055 g of chromium trioxide were added in portions to a mixture of 15 ml of methylene chloride and 1 ml of pyridine. Then a mixture of 0.035 g of petisidine, 10 ml of methylene chloride, and 0.5 ml of pyridine was added to the solution obtained, and stirring was continued at room temperature for another 3 h. After this, the mixture was left to stand for 6 h and was then treated with sodium sulfite. The methylene chloride layer was separated off and the solvent was evaporated off in vacuum. The residue was chromatographed on a column silica gel with elution by hexane—acetone (9:1). The first fractions yielded a base with mp 215-217°C (hexane—acetone (10:1)) identical with petisidinone in terms of temperature, R_f, and IR spectrum.

SUMMARY

1. The known alkaloids edpetiline and edpetine and the new alkaloid petisidinone have been isolated from the epigeal part of Petilium raddeana.

2. The structure of the new alkaloid has been established as 26,23-nitrilocholestane-3,6,22-trione.

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