ALKALOIDS OF *Petilium raddeana*.

III. STRUCTURE OF PETISIDININE

I. Nakhatov, A. Nabiev,
R. Shakirov, and S. Yu. Yunusov

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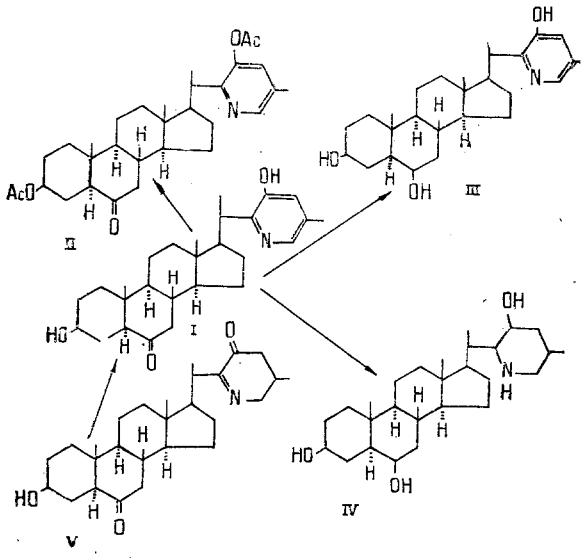
From a mixture of bases from the epigeal part and the bulbs of *Petilium raddeana* (Rgl.) Vved. ex Pazij, a new base petisidinine has been isolated with mp 290-292°C (decomp.), composition $C_{27}H_{39}NO_3$ (I). On the basis of the physicochemical properties of the alkaloid and a correlation with petisine, the structure and configuration of petisidinine have been established as those of 3β-hydroxy-20-(5-hydroxy-3-methylpyridin-6-yl)-5α-pregnan-6-one.

Having continued an investigation of the alkaloids of *Petilium raddeana* (Rgl.) Vved. ex Pazij [1, 2], from the epigeal part and the bulbs we have isolated a new base petisidinine (I) with mp 290-292°C, composition $C_{27}H_{39}NO_3$, M^+ 425. The IR spectrum of (I) has absorption bands at (cm^{-1}) 3400 (OH), 1710 (C=O), 3030, 1610, 1585, 765 (pyridine ring), 2950, 2875 (—CH_2, —CH_3) [3]. The mass spectrum of (I) shows the peaks of ions with m/z 97, 110, 111, 119, 123, 136, 137 (100%), 149, 150, 162, 176, 177, 285, 356, 394, 408, 410, 425 (M^+). The mass-spectrometric fragment of the alkaloid shows that it belonged to the verazine group, like the alkaloids petisine and tomatillidine [4-6].



The PMR spectrum of (I) has singlets at (ppm) 0.60 (18-CH_3, 19-CH_3), 2.16 (—CH_3 attached to an aromatic nucleus), and 6.81 and 7.64 (2 H, aromatic protons), and a doublet at 1.07 (21-CH_3).

The acetylation of (I) gave O,O'-diacetylpetisidine (II) the IR spectrum of which contained absorption bands at (cm^{-1}) 1720, 1740, 1780, and 1250 (ester C=O).

The PMR spectrum of (II) showed signals from the protons of acetoxy groups at 1.97 and 1.98 ppm and a one-proton multiplet at 4.65 ppm from a proton geminal to an acetoxy group.

When (I) was reduced over a platinum catalyst, dihydropetisidinine (III) was formed, while reduction with Na in ethanol gave the octahydro derivative (IV).

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In the mass spectrum of (IV), the maximum peak was that of an ion with m/z 114, which shows the presence of an OH group in ring F [7].

According to the facts given above, petisidinine belongs to the typical steroid alkaloids and contains one secondary and one tertiary hydroxy groups and a carbonyl group, and also a heteroaromatic ring F.

To establish the positions of the functional groups of the configurations of the asymmetric centers, a correlation was carried out with the known alkaloid petisine (V). When petisine [1] was dehydrogenated with palladium, a substance identical with petisidinine (melting point, IR and mass spectra) was isolated from the reaction products.

In petisidinine, the secondary hydroxy group is located at C_{23} and the carbonyl at C_6 and, consequently, it has the structure and configuration of 3β-hydroxy-20-(5-hydroxy-3-methylpyridin-6-yl)-5α-pregnan-6-one (I).

EXPERIMENTAL

To separate mixtures and to identify the alkaloids we used KSK silica gel and alumina (Brockmann activity grade II). IR spectra were taken on a UR-20 spectrometer in tablets with KBr, PMR spectra on a JNM 4H-100/100 MHz instrument ($CDCl_3$:CD_3OD, internal standard HMDS, δ scale), and mass spectra on a MKH-1310 mass spectrometer.

Isolation of Petisidinine. After the usual acid treatment of a chloroform extract obtained from 5.8 g of *Petilium raddeana* bulbs [1], it was neutralized with 25% ammonia and evaporated, and the residue was chromatographed on a column of alumina. Elution with benzene–acetone (3:2) gave 30 fractions. Fractions 21-26 were combined and rechromatographed on a column of silica gel. Elution by chloroform–methanol (95:5) gave 15 fractions. From fraction 10-15 we isolated petisidinine with mp 290-292°C (methanol; decomp.).

The mother liquor from the petisine and petisidine (1 g) from the epigeal part of the plant obtained as described previously [2] was chromatographed on a column of silica gel. On elution with benzene–acetone (3:2), 20 fractions were collected. Fractions 10-19 gave a further small amount of petisidine.

O,O'-Diacetylpetisidine (II). A mixture of 0.5 g of petisidinine, 20 ml of pyridine, and 2 ml of acidic anhydride was left at room temperature for a day. The pyridine was evaporated off and the residue was dissolved in ether. The ethereal solution was washed first with 10% ammonia and then with water, and the ether was distilled off. This gave amorphous O,O-diacetylpetisidine with R_f 0.72 [silica gel, benzene–acetone (5:1)], M^+ 509.

Adams Reduction of Petisidine. We reduced 50 ml petisidinine in 2 ml acetic acid for 16 h in the presence of 50 mg platinum oxide until it ceased to absorb hydrogen. The resulting dihydropetisidinine had m.p. 330°C (methanol; decomp.); M^+ 427.

Octahydropetisidinine. Over an hour, 2.5 g of metallic sodium was added to a solution of 0.1 g of petisidinine in 30 ml of absolute ethanol at the boil. The mixture was boiled for another 30 min. Then it was cooled and diluted with water, the ethanol was distilled off in vacuum, and the reduction product was isolated from the aqueous solution with chloroform. This gave an amorphous octahydropetisidinine with mp 152-154°C (acetone), M^+ 433.

Dehydrogenation of Petisine. A mixture of 50 mg of petisine and 0.1 g of 5% palladium on carbon was heated at 210-215°C for 20 min. After cooling, a (2:3) mixture of chloroform and methanol was added, the catalyst was separated off, and the filtrate was distilled. After liquid chromatography of the reaction product on a column of silica gel (eluent: chloroform–methanol (2:3)), the product was isolated with mp 290-292°C (methanol; decomp.). IR spectrum (cm^{-1}): 3400 (OH), 1710 (C=O), 1610, 1585, 765 (pyridine ring); M^+ 425.

A direct comparison of the product obtained with petisidinine showed their identity.

SUMMARY

1. The new base petisidinine has been isolated from the mixture of bases from the epigeal part and bulbs of *Petilium raddeana* (Rgl.) Vved. ex Pazij.

2. On the basis of its physicochemical properties, the structure and configuration of petisidinine have been established as those of 3β-hydroxy-20-(5-hydroxy-3-methylpyridin-6-yl)-5α-pregnan-6-one.

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CONVOLINE — A NEW ALKALOID FROM *Convolvulus krauseanus*

S. F. Aripova, E. G. Sharova,
U. A. Abdullaev, and S. Yu. Yunusov

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A new alkaloid has been isolated from the epigeal part of *Convolvulus krauseanus* Regel. et Schmalh., and its structure has been established as (±)-3-veratroyl-N-hydroxynortropane.

Five alkaloids (convolvine, convolamine, convolidine, phyllalbine, and convolicine) have previously been isolated from the epigeal part of *Convolvulus krauseanus* Regel. et Schmalh. collected in the environs of the village of Bakhmal (Turkestan range) [1]. Continuing the separation of the mother liquors of the combined alkaloids, by chromatography on a column of silica gel the ethereal eluates have yielded a crystalline base with mp 184-185°C, R_f 0.85 [system I: chloroform—methanol—ammonia (8:2:0.1)], which differed from the tropane alkaloids that have been described. We have called it convoline (I).

The IR spectrum of the alkaloid contains the absorption bands of active hydrogen (3245 cm^{-1}), of a conjugated ester carbonyl (1705 cm^{-1}), and of a 1,2,4-trisubstituted benzene ring (830, 885, 1600, 1515 cm^{-1}). The 1,2,4-substitution in the aromatic ring was confirmed by the presence in the PMR spectrum of (I) of the signals from H_a and H_b protons in the 7.70-7.50 ppm region (2 H, m) and from H_c at 6.92 ppm (1 H, d). The spectrum also showed the signals from two aromatic methoxy groups (6 H, s; 3.89 ppm), of a diagnostic proton at CH_3 (1 H, t; 5.06 ppm), of methylene protons at 1.8-2.35 ppm, and of C_1 and C_5 methine protons at 3.55 ppm (2 H, m).

The mass spectrum showed the peaks of the molecular ion (M^+ 307). Ions with m/z 290 $(M - 17)^+$ 182, 165, 142, and 125, which are characteristic for alkaloids of the propane series, were also present. In the mass spectrum of the deuteration product of (I), the M^+ peak and also the peaks of the amino alcohol moiety were displaced by 1 m/z. With acetic anhydride, convoline gave a monoacetyl derivative with mp 130-131°C (M^+ 349), in the IR spectrum of which the band of active hydrogen had disappeared and an additional band of an ester carbonyl group had appeared at 1760 cm^{-1}, which shows the presence of a hydroxy group in the alkaloid. The PMR spectrum of convoline acetate showed at 1.99 ppm a three-proton singlet from the protons of an acetoxy group, and the signals from the C_1 and C_5 protons had undergone a paramagnetic shift by 0.17 ppm.

The facts given above show that convoline is an ester of a substituted tropine and an aromatic acid. The structure of the acid moiety of the molecule was determined by the hydrolysis of the base. From the acid part of the hydrolysate an acid was isolated which was identified by its R_f value and a mixed melting point as veratric acid. The amino alcohol moiety resinified. From the resulting resin by purification was isolated a very small amount of an amorphous substance (II) for which only the spectral characteristics are given.

A characteristic feature of the PMR spectrum of (II) is the upfield shift of the signals of the protons at C_1 and C_5, and also of the C_3-αH [by 3.43 ppm (2 H, m) and 3.82 (1 H, t),

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