614 (10.7), 596 (64.3), 554 (27.4), 536 (44.0), 494 (42.9), 476 (21.4), 434 (23.8), 427 (17.9), 367 (35.7), 307 (100), 259 (42.9), 215 (85.7), 199 (64.3). PMR ($CDCl_3$): 0.80 (3H, s, CH_3), 0.87 (3H, d, ^3J = 6 Hz, CH_3-21), 0.89 (3H, s, CH_3), 0.94 (3H, s, CH_3), 1.01 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.89 (3H, s, CH_3COO), 1.95 (3H, s, CH_3COO), 1.99 (6H, s, 2 × CH_3COO), 2.01 (3H, s, CH_3COO), 2.37 and 2.52 (each 1H, d, ^2J = 17 Hz, 2H-12), 4.52 (1H, q, $^3J_1$ = 12 Hz, $^3J_2$ = 5 Hz, H-3), 4.77 (1H; td, $^3J_1$ = $^3J_2$ = 8 Hz, $^3J_2$ = 4 Hz, H-6), 4.98 (1H, q, $^3J_1$ = 11 Hz, $^3J_2$ = 3 Hz, H-24), 5.28 (1H, sx, $W_1/_2$ = kk,5 Hz, H-16).

SUMMARY

The Cotton effect has been determined for 6-oxo- and 11-oxocycloartanes. A 6α-hydroxy group imparts a complex form to the Cotton effect due to a 3-oxo function, separting it into two components: negative at 315-322 nm and positive at 280-290 nm.

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STRUCTURE OF CONVOSINE

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From the roots of the plant Convolvulus subhirsutum Regel et Schmalh. have been isolated seven known alkaloids and one new one, for which, on the basis of spectral characteristics, a comparative study with known alkaloids of the tropane series, and synthesis, the structure of (+)-N-isopropyl-3α-veratroyloxynortropane has been established.

The combined alkaloids have been isolated in an amount of 2.68% on the weight of the air-dry material from the roots of Convolvulus subhirsutum Regel et Schmalh. collected in the environs of Dzhilga, Chimkent province, KazSSR in the phase of the vigorous growth of the plant [4].

By separating the mixture of bases into phenolic and nonphenolic fractions and treatment of the nonphenolic fraction with citrate-phosphate buffer solution, and also by chromatography on a column of alumina, seven bases have been isolated: convolvine and convolamine [1], for the first time from this plant, and phyllalbine, convolidine [3], confoline, convoline [5], and subhirsine [6].

Continuing the separation of the mother liquors from the combined alkaloids by chromatography on a column of alumina, from ethereal eluates we isolated a minor base with mp 103-104°C which differed in its R_f values and spectral characteristics from the bases isolated previously, and we have called it convosine (I). The IR spectrum of convosine contains

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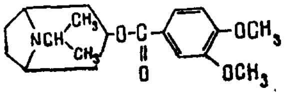
absorption bands of a conjugated ester carbonyl group (1710 cm^{-1}) and of an aromatic ring (1605, 1520 cm^{-1}), and, in the "fingerprint" region, absorption bands at 830 and 885 cm^{-1} that are characteristic for a 1,2,4-trisubstituted benzene ring.

In the mass spectrum of (I), the peak of the molecular ion with m/z 333 was readily detected, together with the peaks of ions having m/z 318, 290, 182, 165, 98, 83.

The presence in the mass spectrum of the peaks of ions with m/z 182, 165, 152, 122, and 98 formed through the splitting out of the acid moiety of the base is diagnostic for 3,4-dimethoxybenzoic acid [6]. It follows from this that the esterifying acid is veratric. The amino alcohol moiety is represented by an unsubstituted tropane nucleus. In view of the molecular weights of the alkaloid (M^+ 333), of the acid moiety of the molecule (182 amu), and of the unsubstituted nitrogen-containing nucleus of tropane, it may be assumed that (I) has substitution at the nitrogen atom and the substituent is a C_3H_7 radical. This may be either n-propyl or isopropyl. In favor of isopropyl is the nature of the mass-spectrometric fragmentation. Thus, the peak with m/z 318, which is one of the strong peaks in the spectrum, corresponds to the splitting out of a methyl group on the basis of the preferential cleavage of a bond at the position of branching of a hydrocarbon chain. In the case of n-propyl substitution at the nitrogen atom, one would expect the presence in the spectrum of a strong peak with m/z 304 corresponding to the splitting out of an ethyl group, which is not in fact observed.

The influence of a saturated tropane ring on the splitting out of the whole isopropyl group is similar to the influence of the branching of a hydrocarbon chain, and we therefore observe the formation of the peak of an ion with m/z 108 in which the isopropyl radical shifts off not from M^+ but from the ion of the amino alcohol moiety with m/z 152 after the preliminary ejection of a veratroyl ion (182 amu) from the molecular ion.

Thus, on the basis of spectral characteristics and a comparative study with alkaloids of the tropane series, for (I) we propose the structure of (±)-N-isopropyl-3α-veratroyloxynortropane.



I

Because convosine was isolated in very small amounts, its NMR spectrum was not recorded, and the proposed structure therefore required confirmation. With this aim, we performed the synthesis of convosine from convoline and isopropyl iodide. The N-isopropylconvoline isolated after appropriate working up corresponded with respect to R_f values and melting point to the natural alkaloid. Their spectral characteristics also coincided (IR and mass spectra).

The NMR spectrum of the synthetic product taken in $CDCl_3$ corresponded to the expected structure. In the 1.1 ppm region a six-proton doublet from a gem-dimethyl group appeared; at 3.90 ppm a six-proton singlet from two aromatic methoxy groups; at 5.22 ppm a multiplet from $C_{3\alpha}H$; at 3.25 and 3.74 ppm the signals of methine protons; and at 7.50 and 6.89 ppm those of aromatic protons.

EXPERIMENTAL

The IR spectrum was taken on a UR-20 spectrophotometer (tablets with KBr), the NMR spectrum on a JNM-100/100 MHz instrument with hexamethyldisiloxane as internal standard (δ scale), and the mass spectrum on a MKh-1303 mass spectrometer.

The isolation of the alkaloids convolvine, convolamine, phyllalbine, convolidine, confoline, convoline, and subhirsine was performed by the method described previously [4].

Synthesis of Convosine. To 0.6 g of convolvine in 5 ml of benzene we added 0.5 ml of isopropyl iodide and 0.4 g of sodium bicarbonate. The mixture was boiled in the water bath for 3 h. The solvent was driven off in vacuum and the residue was dissolved in 8 ml of 5% sulfuric acid. The acid solution was washed with ether and then, after being made alkaline with concentrated ammonia solution, it was extracted with ether. The ethereal extract was dried with potassium carbonate, filtered, and concentrated. This gave crystals with mp 103-104°C (from acetone).

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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