STRUCTURE OF SEVERIDININE

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A new alkaloid, severidinine, with mp 145-147°C $[\alpha]_D$ −50.2°, $C_{19}H_{45}NO_6$, has been isolated from the epigeal part of *Koralkowia sewerzowii* Regel. On the basis of the IR, PMR, and mass spectra of severidinine and its transformation products, and also passage to the known alkaloids severidine, the structure of 3α-acetylseveridine has been established for severidinine.

We have studied the structure of an alkaloid with mp 145-147°C isolated from the epigeal part of *Koralkowia sewerzowii* Regel [1-4]. The alkaloid proved to be new and we have called it severidinine (I).

Severidinine is an optically active base with the composition $C_{29}H_{45}NO_6$ which forms a hydrochloride. The IR spectrum of (I) contains absorption bands at (cm^{-1}) 3460 (OH), 2960-2815 ($-CH_3$; $-CH_2-$); 2780 (trans-quinolizidine); 1730, 1260 (ester C=O); 1710 (C=O). The mass spectrum of (I) shows the peaks of ions with m/z 98, 111, 112, 124, 125, 138, 139, 140, 162, 164, 166, 178, 180, 196, 233, 238, 250 (100%), 251, 276, 400, 411, 420, 442, 444, 460, 470, 486, 503 M^+, which are characteristic for the 11,12-seco-cevanine alkaloid severidine [4].

When compound (I) was saponified, an amino alcohol with mp 200-202°C, shown to be identical with severidine (mixed melting point, IR spectra), was obtained. Acetic acid was detected in the acid part of the hydrolysate by paper chromatography.

The acetylation of (I) with acetic anhydride in pyridine gave diacetylseveridinine, identical with triacetylseveridine.

When severidinine was oxidized with chromium trioxide in pyridine, the ketone severidininone (II) with mp 149-150°C was obtained. In the IR spectrum of (II) absorption bands were observed at (cm^{-1}) 3450 (OH); 1740, 1240 (ester C=O); 1715 (C=O).

The acetylation of (II) gave acetylseveridininone (III). The IR spectrum of (III) had no absorption bands of hydroxy groups but had absorption bands at (cm^{-1}) 1740, 1240 (ester C=O), 1710 (C=O). On methanolysis, (III) gave severidininone. The characteristics of the PMR spectra of (I-III) are given below (chemical shifts, ppm, δ scale):

	19-CH_3, singlet	3CH−CH_3, doublet	$OCOCH_3$, singlet	H, HC−$COCH_3$, multiplet
I	0.69	0.77, 0.80 (6H)	2.01	5.18
II	1.08	0.75, 0.80, 0,91	1.97	5.36
III	1.04	0.79 (6H), 0.87	1.96 2.01	5.34

The identity of the aminoalcohol with severidine and of diacetylseveridinine with triacetylseveridine shows that severidinine is a monoacetyl derivative of severidine. The acetic acid residue may be present in the amino alcohol severidine in one of two possible positions: at C_1 or C_3. The C_{13} position for the acetic acid residue is excluded on the basis of the presence in the PMR spectra of (I) of the signal of a geminal proton at 5.18 ppm.

In the PMR spectrum of triacetylseveridine, a multiplet from a proton geminal to an acetoxy group at 5.05 ppm is assigned to C_3β-H and one at 4.85 ppm to C_1β-H [4-6]. In severidinine, a proton geminal to an acetoxy group gives a signal at 5.18 ppm. It follows from this that only the C_3 position is possible for the acetic acid residue in the molecule of

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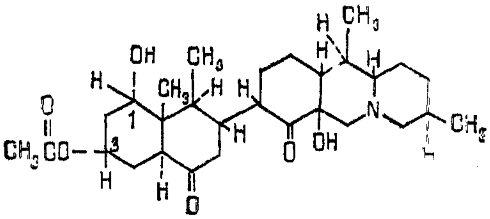
(I). This was confirmed by the downfield displacement of the signal of the 19-CH_3 protons in the PMR spectrum of severidininone (II) by 48 Hz as compared with that for severidinine [4, 7].

On the basis of the facts given above, it has been established that severidinine has the structure of 3α-acetylseveridine [3α-acetyl-1S,13R-dihydroxy-(20R,25R)-11,12-secocevanine-6,12-dione].



EXPERIMENTAL

Thin-layer chromatography (TLC) was carried out in a fixed layer of KSK silica gel (90 μm) in the solvent system chloroform–methanol (10:0.5). IR spectra were recorded on a UR-20 spectrometer (KBr), PMR spectra on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard (the values are given in the δ scale), and mass spectra on a MKh-1303 instrument.

Severidinine. It crystallized from a mixture of acetone and petroleum ether (1:5) with mp 145-147°C, $[\alpha]_D$ −50.2° (c 0.777; chloroform), R_f 0.24 [1-4].

Severidinine Hydrochloride. The addition of an ethanolic solution of hydrogen chloride to 0.34 g of the base yielded severidinine hydrochloride with mp 198-200°C (ethanol–acetone (1:5)).

Saponification of Severidinine. A mixture of 0.19 g of severidinine in 2 ml of methanol and 18 ml of 5% methanolic caustic potash was heated on the water bath for 30 min, and the solvent was distilled off. The residue was dissolved in water and extracted with chloroform. After the chloroform had been distilled off the dry residue (0.12 g) was treated with acetone. This led to the precipitation of crystals with mp 200-202°C, R_f 0.18, identical with severidine. Acetic acid was detected in the alkaline solution after the separation of severidine by a procedure described previously [1, 8].

Diacetylseveridinine. Using a procedure analogous to that of the acetylation of severidine [2, 4], 0.18 g of (I) was acetylated with 3 ml of acetic anhydride and 2 ml of pyridine. This gave 0.19 g of amorphous diacetylseveridinine with R_f 0.82, identical with triacetylseveridine (IR, PMR, and mass spectra). M^+ 587.

Severidininone. To a solution of 0.1 g of severidinine in 1.5 ml of 80% acetic acid was added 60 mg of chromium anhydride in 3 ml of acetic acid. The mixture was left for a day at +5°C. The solvent was distilled off and the residue was diluted with water and, after being made alkaline with ammonia, it was extracted with chloroform. The chloroform was distilled off and the dry residue was chromatographed on silica gel, benzene–acetone (2:1) eluates giving the ketones severidininone with mp 149-150°C (benzene), R_f 0.34.

Mass spectrum: m/z 98, 111, 112, 124, 125, 140, 149, 162, 164, 178, 180, 196, 233, 234, 250 (100%), 251, 372, 373, 408, 424, 425, 440, 441, 442, 458, 459, 484, 501 M^+.

Acetylseveridininone. A mixture of 70 mg of severidininone, 1 ml of pyridine, and 1.5 ml of acetic anhydride was kept at room temperature for 3 days. After the appropriate working up, amorphous acetylseveridininine was obtained with R_f 0.69.

Methanolysis of Acetylseveridininone. The methanolysis of acetylseveridininone was carried out by the method used for the methanolysis of triacetylseveridine [4]. A substance identical with severidininone was obtained.

SUMMARY

On the basis of its IR, PMR, and mass spectra and its conversion into the known alkaloid severidine, it has been established that severidinine has the structure of 3α-acetylseveridine.

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ALKALOIDS OF *Corydalis stricta*

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The alkaloids of the epigeal part and roots of *Corydalis stricta* have been studied. Of the 23 alkaloids isolated, N-methylcorypalline proved to be new, and its structure has been determined. Stilopine hydroxymethylate and pycnarrhine have been isolated from the genus *Corydalis* for the first time, and cheilanthiofoline isocorypalmine, scoulerine, isoboldine, reticuline, N-methylcoclaurine, coreximine, juziphine, pancorydine, corypalline, wilsonirine, stilopine, adlumidine, dihydrosanguinarine, adlumine, and bicucculine have been isolated from this species of plant for the first time.

We have investigated the alkaloid composition of the epigeal part and roots of the plant *Corydalis stricta* Steph. [1] collected in the flowering period in the environs of the settlement of Rabat (Pamir). d-β-Hydrastine and protopine have been isolated previously from the epigeal part of *C. stricta*, and protopine and sanguinarine from the roots [2]. Chloroform extraction of the epigeal part of *C. stricta* yielded 1.57% of total alkaloids. From the nonphenolic fraction of the total we isolated stilopine, adlumidine, bicucculine, protopine [3], and d-β-hydrastine [4], and from the phenolic part scoulerine, coreximine [4], isoboldine, juziphine, [3], and corypalline [5]. From the quaternary fraction of alkaloids we isolated in the form of iodides stilopine hydroxymethylate [6] and pycnarrhine [7]. All the alkaloids obtained were identified on the basis of spectral characteristics and comparison with authentic samples.

The roots of *C. stricta* collected at the same growth site contained 0.63% of total alkaloids. The separation of this material gave sanguinarine, bicucculine, protopine, wilsonirine, pancorydine, and pancorynine [8]. From the quaternary fraction of total alkaloids we isolated in the form of iodides stilopine hydroxymethylate and a new optically inactive base with mp 238-239°C. Its UV spectrum contained a single absorption maximum at 287 nm (log ε 4.14). Its IR spectrum showed absorption bands at (cm^{-1}) 3370 (hydroxy group), 1530, 1610, and 1620 (aromatic ring). Its mass spectrum had the peaks of ions with m/z 207, 206, 177, 164, 150, 142, 127. The PMR spectrum showed signals in the form of a six-proton singlet at 2.85 ppm from a N-dimethyl group, a three-proton singlet at 3.50 ppm from a methoxy group, and a two-proton singlet at 4.06 ppm from an isolated methylene group. In the aromatic region of the spectrum there were two single-proton singlets at 6.34 and 6.40 ppm, and a four-proton multi-

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