

The results given confirm the structure of the base synthesized (I).

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ALKALOIDS OF THE SEEDS OF *Lolium cuneatum*

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UDC 547.944/945

Continuing the separation of the mixture of alkaloids of the seeds of *L. cuneatum* we have isolated two more new alkaloids. By chromatographing the water-soluble fraction of the total alkaloids on a column of alumina, we isolated a base with the composition $C_{10}H_{16}N_2O_3$ (I), oil, $[\alpha]_D^{20} +21.6^\circ$ (c 0.9; methanol), R_f 0.14 [in a thin layer of silica gel in the chloroform-methanol (4:1) system]. The base (I) is readily soluble in ethanol and water and sparingly soluble in organic solvents. In the NMR spectrum of (I) (D_2O , δ scale, JNM 100/100 MHz) there are signals of protons from $=N-COCH_3$ at 2.45 ppm (3H, singlet) and from $=N-CH_3$ at 3.43 ppm (3H, singlet), and other signals characteristic for alkaloids of the loline group [1].

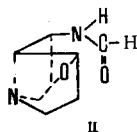
Its good solubility in water and the characteristics of its NMR spectrum show that (I) is probably lolinine N-oxide. The reduction of (I) with zinc in hydrochloric acid gave lolinine and a very small amount of loline. It is possible that in this reaction in addition to the reduction of the $N \rightarrow O$ bond, partial hydrolysis of the lolinine formed took place. The R_f value and the other properties of (I) coincide completely with those of the synthetic N-oxide obtained by oxidizing lolinine with hydrogen peroxide.

When the total alkaloids of the seeds of the introduced plant was separated, we isolated a base $C_8H_{12}N_2O_2$ (II) (M^+ 168), oil $[\alpha]_D^{20} +31.3^\circ$ (c 0.96; acetone); hydrochloride with mp $181^\circ C$, R_f 0.44 [chloroform-methanol (4:1)].

The IR spectrum of (II) showed absorption bands at 1640 cm^{-1} (amide carbonyl) and a broad band at $3300-3360\text{ cm}^{-1}$ (NH).

The mass spectrum of (II) showed the peaks of ions with m/e 168 (M^+), 139 ($M - CHO$), 125, and others characteristic for the alkaloids of this group [2].

Hydrolysis with hydrochloric acid formed norloline, which was identified chromatographically. All these facts permitted the conclusion that our base had the structure of N-formylnorloline. We synthesized N-formylnorloline by the reaction of norloline with ethyl formate. A mixture of the hydrochloride of N-formylnorloline with the hydrochloride of (II) gave no depression of the melting point.



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Thus, the seeds of L. cuneatum have yielded two new alkaloids: lolinine N-oxide and N-formylnorlolinine.

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STRUCTURE OF IOLANTIMINE

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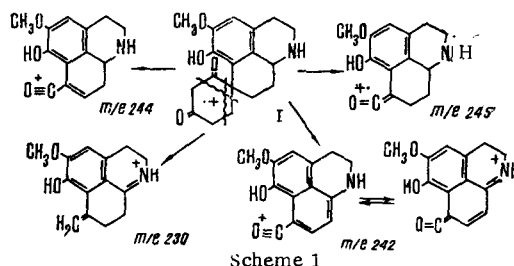
UDC 547.944.6

Continuing an investigation of fractions of the bases of Colchicum kesselringii Rgl. [1] and Merendera iolantae E. Czerniak [2], we have isolated a new base with mp 272-273°C (acetone-methanol), $[\alpha]_D^{25} + 98^\circ$ (c 0.5; methanol) which we have called iolantimine (I).

The base has the composition $C_{18}H_{23}O_4N$ (mass spectrometrically) M^+ 315 148. In its UV spectrum there are absorption maxima at 215 and 287 nm and in the NMR spectrum absorption bands of active hydrogen (3380 cm^{-1}), of a carbonyl group (1640 cm^{-1}), of the $-C=O$ bonds of a benzene ring (1600 cm^{-1}), and of methylene groups (1460 cm^{-1}). The PMR spectrum of (I) shows the resonance signals of one O-methyl group and one isolated hydrogen atom in a benzene ring (three- and one-proton singlets at 3.88 and 6.52 ppm, respectively).

On the basis of the facts given above, compound (I) has been assigned to the group of alkaloids with a homoproaporphine carbon-nitrogen skeleton isolated from colchicine-containing species of plants of the family Liliaceae [3]. At the same time, this base differed sharply from the known representatives of this series by its β -diketone nature (1640 cm^{-1}), by the absence of an N-methyl group, and by a mass spectrum which is uncharacteristic for reduced homoproaporphines [4]. The mass spectrum of (I) has the peaks of ions with m/e 315, 148 (M^+ , 20%), 314 (15%), 287 (100%), 286, 122 (36%), 245, 105 (10%), 244, 098 (28%), 242, 083 (42%), 230, 116 (13%). The action of acetyl chloride on (I) gave an O-acetyl derivative ($\nu_{\max} 1750\text{ cm}^{-1}$). Methylation with methyl iodide in the presence of potassium carbonate yielded a methiodide. The PMR spectrum of the latter in CF_3COOH had the signals of one methoxy group and of the proton of a benzene ring (3.52 and 6.36 ppm, respectively) and of two N-methyl groups (three-proton singlets at 2.50 and 2.96 ppm). The facts given show that (I) contains a hydroxy and an imine group. The diketone nature of the substance was confirmed by the preparation of a dioxime (M^+ 345).

The presence of an imine group in the molecule of (I) is also confirmed by the peaks of ions with m/e 286 (ejection of CH_2NH) and 230 in its mass spectrum. Ions with m/e 245, 244, and 242 show the presence of a carbonyl group in the C_{13} position. On the basis of the facts presented, structure (I) is proposed for iolantimine; this agrees with its fragmentation (Scheme 1), obtained on a high-resolution mass spectrometer (MAT-311) at an energy of the ionizing electrons of 70 eV and a temperature of 40°C.



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