BISBENZYLISOQUINOLINE ALKALOIDS OF *Thalictrum sultanabadense*

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Hernandezine, thalidezine, thalbadensine, and hernandezine N-oxide have been isolated from the epigeal part of *Thalictrum sultanabadense* Stapf. [1, 2]. Continuing a study of the alkaloid composition of this plant, we have investigated roots collected at the end of the vegetation period in the gorge of the R. Shagun' (Hissar range, Uzbek SSR) on June 3, 1978.

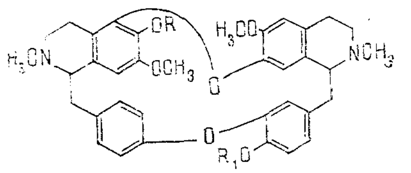
The comminuted air-dry raw material was moistened with 8% ammonia solution and extracted with chloroform. The combined bases were obtained from the chloroform extract in the usual way and were separated into nonphenolic (fraction A) and phenolic (fraction B) parts. From fraction A a crystalline nitrate was isolated with mp 221-223°C (acetone or ethanol). The composition of the latter yielded an amorphous optically active base (I), $[\alpha]_D$ −33° (methanol).

Analysis of the UV, mass, and PMR spectra showed that base (I) belonged to the group of bisbenzylisoquinoline alkaloids of the thalmine type [3]. A comparison of our results and literature information enabled (I) to be identified as thalictine, which has been isolated previously only from *Th. thunbergii* DC [4]. The CD spectrum of (I) (in methanol) showed a positive Cotton effect (CE) in the 290 nm region and a mixed one at 200-220 nm, which confirmed the S,S configuration of thalictine [5].

Such a configuration was suggested previously on the basis of the results of a study of the products of the reactive cleavage of O-methyl- and O-ethylthalictine with sodium in liquid ammonia [4]. The mother liquor after the separation of thalictine was chromatographed on a column of silica gel. The column was washed with benzene and then with chloroform. The chloroform eluate yielded compound (II).

Base (II) was amorphous with $[\alpha]_D$ −43° (methanol). UV spectrum of (II): $\lambda_{max}^{ethanol}$ 285 nm. PMR spectrum: 2.10 and 2.58 (singlets, 3 H each, 2 × NCH_3); 3.60 (singlet, 3 H), 3.78 (singlet, 3 H), 3.81 (singlet, 6 H) (4 × OCH_3); 5.76 and 5.98 (two one-proton singlets, H-8 and H-8'); 6.49-6.85 (8 × ArH). The mass spectrum of (II) showed the peaks with ions with m/z 622 (M^+), 621, 396, 395, 198, 190, 175, and 174.

Analysis of the CD spectrum showed that base (II) likewise had the S,S configuration. The results of a comparison of the UV, mass, PMR, and CD spectra of (II) with those of thalmine (III) [6, 7], thalbadensine (IV), O,O-dimethylthalbadensine [1], and thalictine [4] permitted us to suggest for (II) the structure of O-methylthalmine, and this was confirmed by a comparison with an authentic sample of O-methylthalmine (R_f, $[\alpha]_D$, and IR, mass, and PMR spectra). It must be mentioned that O-methylthalmine has been obtained previously by synthesis [6], but this is the first time that it has been isolated from plant raw material.



I $R = CH_3$; $R_1 = H$

II $R = R_1 = CH_3$

III $R = H$; $R_1 = CH_3$

IV $R = R_1 = H$

Thus, six bases have been isolated from *Th. sultanabadense* of which thalbadensine, thalictine, and O-methylthalmine belong to the very small thalmine group of bisbenzylisoquinoline alkaloids, amounting at the present time to only eight bases.

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ALKALOIDS OF *Nitraria komarovii*.

IX. STRUCTURE OF KOMAROINE

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Continuing a study of the alkaloids of the epigeal part of the plant *Nitraria komarovii* Iljin et Lava [1], collected in June, 1978, in the environs of Krasnovodsk, the ethereal material of the pH 4 fraction from the polybuffer separation of the mixture of bases has been subjected to chromatographic separation. Chloroform, and then mixtures of chloroform and methanol in various proportions were used to elute the substances from the column. The chloroform eluate yielded a new alkaloid with the composition $C_{28}H_{18}N_2$, mp 144-145°C (petroleum ether—CH_2Cl_2), which has been named komaroine (I).

The mass spectrum of (I) contained, in addition to others, the peaks of ions with m/z 286 (M^+), 271 (M — 15), 257 (M — 29), and 243 (M — 43), showing the presence of a propyl group in the molecule.

The PMR spectrum of the alkaloid contained, in addition to the signals in the aromatic region, signals at 0.85 ppm (triplet, 3 H, $-CH_2-C\underline{H}_3$), 2.58 ppm (triplet, 2 H, $Ar-C\underline{H}_2-CH_2-$), and 1.58 ppm (multiplet, 2 H, $-CH_2-C\underline{H}_2-CH_3$). These results permitted the conclusion that (I) contained a N-propyl group bound to an aromatic ring.

The UV spectrum of (I) taken in ethanol exhibited absorption maxima with λ_{max} 215, 235, 235, 280, 290, 350 nm (log ε 4.44, 4.42, 4.12, 4.12, 3.81), which in an acid medium underwent bathochromic shifts to λ_{max} 216, 255, 265, 310-318, 382 nm. This behavior of the spectrum and the region of appearance of the maxima are characteristic for β-carboline derivatives.

The IR spectrum of (I) contained absorption bands of the bonds of a o-disubstituted benzene ring (750 cm^{-1}), of an indole nucleus (1460, 1505, 1570, 1630 cm^{-1}), and of saturated C—H bonds (2860, 2870, 2930, and 2965 cm^{-1}).

When the dehydrogenation reaction of the alkaloid nitrarine (II) was studied, among the products a compound identical with komaroine was detected. It has been shown previously that the dehydrogenation of (II) with selenium takes place with the cleavage of the N_4-C_{21} bond in the initial stages of the reaction [2]. There is information in the literature that the dehydrogenation of decahydroquinolines takes place in some cases with the cleavage of the piperidine ring and the ejection of ammonia [3]. It is easy on the basis of these facts to explain the formation of komaroine from nitrarine when the latter is dehydrogenated with selenium or sulfur.

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