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APORPHINE ALKALOIDS OF *Thalictrum baicalense*

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We have previously reported on the isolation from the epigeal part of *Thalictrum baicalense* Turcz. of the new aporphine alkaloids baicaline [1] and baicalidine [2]. We now give the results of a further study of the alkaloid composition of *Th. baicalense*. The phenolic fraction of the combined bases [2] was chromatographed on a column of silica gel. The column was washed with chloroform and with chloroform–methanol.

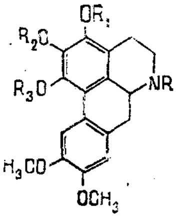
The fraction eluted by chloroform containing 1% of methanol yielded a base (I), and the fraction containing 3% of methanol a base (II). Base (II), $[\alpha]_D$ +61° (methanol). UV spectrum, λ_{max} (C_2H_5OH), nm: 220, 285, 303, 313; λ_{max} ($C_2H_5OH + OH^-$) 325 nm. PMR spectrum ($CDCl_3$, ppm, δ scale, 0 – HMDS): 3.63, 3.81, 3.83, and 3.88 (4 × OCH_3); 6.36 and 7.81 (2 s, 1 H each, 2 × ArH). The mass spectrum of (II) showed the peaks of ions with m/z 357 (M^+), 356, 342, 340, 328 $(M - 29)^+$, 327, 297.

The acetylation of (II) with acetic anhydride in the presence of pyridine yielded a O,N-diacetyl derivative (IIa). IR spectrum, λ_{max} (KBr), cm^{-1}: 1650 ($NCOCH_3$); 1760 ($OCOCH_3$). PMR spectrum, ppm: 3.64 (3 H) and 3.84 (9 H) (4 × OCH_3); 6.67 (s, 1 H) and 7.93 (s, 1 H) (2 × ArH); 2.30 (3 H, $OCOCH_3$); 2.09 and 2.13 (2 s, with a total intensity of 3 H; $NCOCH_3$). Mass spectrum: 441 (M^+), 382, 381, 340, 339, 327, 310, 293.

The facts given above showed that (II) was a new 1,2,3,9,10-pentasubstituted monophenolic noraporphine base. We have called it thalbaicaline. The position of the OH group was established from the results of a study of the mass spectra of (IIa), of N-acetylnorthalicmine (IIb), and N-acetylbaicaline (IIc). The mass spectra of (IIa) and (IIb) had peaks of medium intensity with m/z 381 $(M - 60)^+$ and 365 $(M - 32)^+$, respectively, while in the spectrum of (IIc), as was to be expected, these peaks were not visible. The results obtained indicated that the $OCOCH_3$ group in (IIa) is present at C-3 [3]. Consequently, thalbaicaline has the structure of 3-hydroxy-1,2,9,10-tetramethoxynoraporphine (II).

Base (I) had mp 191-193°C (ethyl acetate), $[\alpha]_D$ +73° (methanol). UV spectrum, λ_{max} (C_2H_5OH): 282, 305, 315 nm; λ_{max} ($C_2H_5OH + OH^-$) 326 nm; mass spectrum, m/z: 371 (M^+), 370, 356, 341, 328 $(M - 43)^+$. PMR spectrum, ppm: 2.46 (s, 3 H, NCH_3); 3.62 (3 H), 3.83 (6 H), and 3.88 (3 H) (4 × OCH_3); 6.65 and 7.77 (2 s, 1 H each, 2 × ArH).

Base (I) was identical with the N-methylthalbaicaline obtained from (II) ($CH_2O/HCOOH$) according to TLC, melting point, and mixed melting point. Thus, base (I) which we have called thalbaicalidine has the structure of 3-hydroxy-1,2,9,10-tetramethoxy-N-methylaporphine.



I. $R = R_2 = R_3 = CH_3$; $R_1 = H$
II. $R = R_1 = H$; $R_2 = R_3 = CH_3$
IIa. $R = R_1 = COCH_3$; $R_2 = R_3 = CH_3$
IIb. $R = COCH_3$; $R_1 = CH_3$; $R_3 + R_2 = CH_3$
IIc. $R = COCH_3$; $R_1 + R_2 = CH_2$; $R_3 = CH_3$

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ALKALOIDS OF *Buxus sempervirens*

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The alkaloids of *Buxus sempervirens* L. (common box) cultivated in the Karachaevo-Cherkeskii autonomous province of Stavropol' krai have not previously been studied.

We determined the alkaloid contents of the various organs of this plant by the chloroform method:

Date of collection (1980)	Plant organ	Total alkaloids, %
May 7	First-year shoots	2.46
	Young roots	2.38
	Leaves and twigs	2.27
	Flowers	2.21
	Roots	2.18
	Perennial twigs	1.02
July 25	First-year shoots	2.34
	Young roots	2.32
	Leaves and twigs	2.01
	Fruit	1.98
	Roots	1.89
	Perennial flowers	0.96

The ethereal fraction of the combined alkaloids isolated from 1.8 kg of twigs and leaves (collected on May 7, 1980) was dissolved in chloroform and separated according to basicities by citrate–phosphate buffer solutions at pH 8.0-2.0 (with a pH interval of 0.5). The fractions of the combined alkaloids with pH 8.0, 7.5, 7.0, and 6.5 were chromatographed separately on a column of alumina (Brockmann activity grade II). Elution was carried out with mixtures of ether and ethanol with increasing concentrations of the latter – 15, 20, 30, 35, and 40%. The fractions indicated yielded cyclobuxine-D, cyclovirobuxine-D, and cycloprotobuxine-A [1-3].

The mother liquor from the cycloprotobuxine-A and the cyclovirobuxine-D was chromatographed on a column of silica gel with elution by hexane–chloroform–ammonia (10:7:0.12). Fractions 25-35 were rechromatographed on a column of alumina with elution by ether–ethanol (5:3) and (5:4).

Fractions 16-23 were treated with acetone. From the acetone-insoluble fraction we isolated a base with mp 233-235°C (ethanol), $C_{26}H_{44}N_2O$ $[\alpha]_D + 113.24°$ (c 0.671; chloroform); M^+ 400. This alkaloid was identified as cyclobuxine-B (from a mixed melting point and also the IR, NMR, and mass spectra of the base and of its derivatives) [4].

The combined alkaloids from the pH 6.0 fraction were treated with acetone. From the acetone-insoluble fraction we isolated a base with mp 245-247°C (petroleum ether). The IR spectrum of the alkaloid contained, in addition to others, the absorption bands of activated hydrogen (3315 cm^{-1}), of a methylcyclopropane ring (30364* and 1458 cm^{-1}), and the mass spec-

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*As in Russian original – Publisher.

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