ALKALOIDS OF *Thalictrum sachalinense*. V

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Continuing a study of Far Eastern species of *Thalictrum* [1], we have investigated for their alkaloid content the roots and epigeal part of *Th. sachalinense* Lecoyer. from two growth sites:

Site and Date of Collection	Plant Organ	Total Alkaloids, % on the Weight of the Air-Dry Raw Material
I. of Kunashir, environs of the village of Mendeleevo, July 23, 1973	Epigeal part	0.02
"	Roots	0.20
I. of Sakhalin, environs of the town of Kholmska, July 15, 1975	Epigeal part	0.27
"	Roots	1.10
"	Rhizomes	0.64

In the present communication we give the results of a study of the total bases of the roots and rhizomes of *Th. sachalinense* growing on Sakhalin. Since a preliminary chromatographic investigation showed that the total materials from the roots and rhizomes were similar in composition, they were combined for separation. By using column and comparative chromatography we obtained seven alkaloids: bases (I), (II), (III), and (IV), glaucine, berberine, and magnoflorine. The UV spectrum of (I) (λ_{max} 285 nm) is characteristic for benzylisoquinoline bases. The mass spectrum of (I) showed the peaks of ions with m/e: 608 (M), 593, 577, 471, 417, 382, 381 (100%), 367, 192.

The NMR spectrum of (I) showed signals at (ppm), 2.26 (s, 3H, NCH_3), 2.43 (s, 3H, NCH_3), 3.72 (s, 3H, OCH_3 at C-6'), 3.87 (s, 6H, 2 × OCH_3), 6.02 (s, 1H, H-8'), and 6.24-7.05 (m, 9 × ArH). The facts given permit (I) to be assigned to the phenolic bisbenzylisoquinoline alkaloids of the berbamine type. The presence in the mass spectrum of a strong peak with m/e 381 (M − 226) showed that the hydroxy group is located in the isoquinoline part of the molecule, and the absence of a strong-field signal in the 3.05-3.25-ppm region shows that it is present at C-7. Since the methoxy group at C-6' appears at 3.72 ppm, (I) must have the RS or the SR configuration [2].

The circular dichroism (CD) curves of (I) and of isotetrandrine coincide completely. Consequently, (I) has the RS configuration and, judging from the results obtained, it must have the structure of 7-demethylisotetrandrine. Such a structure has recently been proposed for the alkaloid thalrugosine isolated from *Th. rugosum* [3]. Then a base with the same structure was isolated under the name thaligine from *Th. poligamum* [4] and under the name of isofangchinoline from *Cuclea barbata* (Menispermaceae) [5]. It has also been isolated recently from *Tiliacora funifera* (Menispermaceae) [6] and *Th. lucidum* [7]. Although the bases isolated from different sources differ sharply in melting point and specific rotation (see below), they all have the same structure (spectral characteristics and passage to isotetrandrine); we propose that only the name thalrugosine should be retained:

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Alkaloid	mp, °C	$[\alpha]_D$ (CH_3OH), deg	Literature
Base (I)	Amorphous	+146	Our results
Thalrugosine	212-214 (d)	+128	3
"	212-215	+162	
		+263*	6
"	216-218	-	7
Isofangchinoline	125-127	+225*	5
Thaligine	153	+ 87	4

Bases (II) and (III), assigned to the benzylaporphine dimeric alkaloids (UV, NMR, and mass spectroscopy), were isolated in very small amounts and have not been studied further.

The UV spectrum of (IV) (λ_{max} 285, 313 nm) is characteristic for the aporphine alkaloids The NMR spectrum shows signals from four three-proton singlets at 3.02 and 3.05 $\left(\overset{+}{N}\begin{matrix}CH_3\\CH_3\end{matrix}\right)$, 3.60, and 3.82 ppm (2 × OCH_3) and a broadened two-proton singlet at 5.84 ppm (CH_2O_2). In the weak-field region there are three one-proton singlets of aromatic protons at 6.64 (H-3), 6.79 (H-8), and 7.70 ppm (H-11). The mass spectrum showed peaks with m/e: 353, 295, 251, 209, and 58 (100%).

The facts given permit the assumption that (IV) was nantenine methiodide, which was confirmed by the formation of thalictuberine [8] when (IV) was subjected to Hofmann degradation. It must be mentioned that nantenine methochloride has been isolated recently from *Th. polygamum* [9].

EXPERIMENTAL

The UV spectra were taken in ethanol on a Hitachi spectrometer, the mass spectra on an MKh-1303 mass spectrometer, and the NMR spectra on a JMN-4H 100/100 MHz instrument in $CDCl_3$ with hexamethyldisiloxane as internal standard (δ scale).

Extraction of the Roots. The comminuted air-dry roots (625 g) were extracted with methanol. The methanolic extract was evaporated to dryness, and dissolved in 50 ml of 10% sulfuric acid. The acid extract was washed with petroleum ether and then with chloroform. The chloroform was distilled off, giving 5.07 g of residue (AF). The acid solution was made alkaline with concentrated ammonia, and the bases were extracted with chloroform. This gave 2.75 g of combined material (CF).

The alkaline mother solution after the extraction of the tertiary bases was treated with a saturated solution of potassium iodide. The resin that deposited was separated off and it was triturated with methanol to give 4.08 g (0.65%) of crystalline magnoflorine iodide.

Prepurification of the AF and CF Fractions. The total AF (5.07 g) was dissolved in 50 ml of 10% sulfuric acid. The resin that deposited was separated off and it was triturated with methanol to give 0.225 g of berberine. From the acid extract was obtained 0.76 g (AF-1), 0.316 g of ether-soluble material and 0.049 g of chloroform-soluble material (CF-1).

Similarly, from the total CF we obtained 0.164 g of "acid" (AF-2), 0.556 g of ether-soluble, and 1.32 g of chloroform-soluble (CF-2) material and 0.433 g of berberine.

Extraction of the Rhizomes. By the method described above 662 g of rhizomes yielded 3.95 g of AF fraction, 1.5 g of chloroform-soluble fraction (CF), and 3.8 g of magnoflorine iodide (0.57%). The AF fraction yielded 0.169 g of AF-2, 0.167 g of ether-soluble, and 0.048 g of chloroform-soluble material. The CF fraction yielded 0.07 g of AF-2, 0.126 of ether-extractable material, 0.25 g of CF-2, and 0.485 g of berberine.

Nantenine methiodide was obtained by the preparative separation of the methanolic mother liquor (after the isolation of magnoflorine iodide) on plates with a nonfixed layer of Al_2O_3 in the chloroform—methanol (8.5:1.5) system.

Thalictuberine. A solution of 0.028 g of nantenine methiodide in methanol was treated with 0.3 ml of a 30% methanolic solution of KOH. The mixture was heated under reflux for 2 h. Then the methanol was evaporated off, the residue was extracted with ether, giving 0.01 g of thalictuberine.

*In chloroform.

Glaucine and base (III) were obtained by the preparative separation of fraction AF-1 on a fixed layer of SiO_2/gypsum in the chloroform—benzene (8:2) system.

Thalrugosine and Base (II). Fraction CF-2 was chromatographed on a column of Al_2O_3. The bases were eluted with benzene, ether, chloroform, and methanol, the eluate being collected in 50-ml portions. From the first chloroform fraction, by preparative spearation on plates with SiO_2/gypsum in the cyclohexane—ethyl acetate—DEAE (6:2:2) system we obtained 0.04 g of thalrugosine.

Base (II) was obtained by the comparative separation of the second chloroform fraction on plates with SiO_2/gypsum in the chloroform—methanol—concentrated NH_4OH (12.5:3:0.05) system.

SUMMARY

Glaucine, N-methylnantenine, thalrugosine, magnoflorine, berberine, and the unidentified bases (II) and (III) have been obtained from the roots and rhizomes of *Thalictrum sachalinense*. The main alkaloid in the combined bases of the roots and rhizomes was magnoflorine.

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STRUCTURE OF A TRANSFORMATION PRODUCT OF PERFORINE AND HAPLOPHYLLIDINE

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Perforine (I) and haplophyllidine (II) belong to the type of 5,6,7,8-tetrahydrofuranoquinoline derivatives that are found only in the plant *Haplophyllum perforatum* (family Rutaceae) [1]. In their chemical properties, these compounds differ from the furanoquinoline alkaloids. In particular, in contrast to the latter, the methoxy group in position 4 of perforine and haplophyllidine does not undergo saponification when the compounds are heated with strong acids (25% sulfuric or hydrochloric acid), but cyclization followed by elimination of a molecule of methanol, leading to compound (III) is observed.

It has been reported previously [2] that the reaction of perforine and haplophyllidine with concentrated sulfuric acid leads to the same product with the composition $C_{17}H_{15}NO_2$ (IV), mol. wt. 265 (mass spectrometry) [2]. In the present paper we consider the structure of (IV). In its composition, (IV) differs from haplophyllidine by CH_3OH, H_2O, and H_2, and from perforine by CH_3OH, $2H_2O$, and H_2. The two oxygen atoms present in (IV) are contained in a methoxy group, which was determined by the method of Vieböch and Brecher, and a furan ring. The presence of the latter was confirmed by the production, when (IV) was subjected to Adams

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