ALKALOIDS OF FAR-EASTERN SPECIES OF *Thalictrum*. IV

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Continuing a study of far-eastern species of *Thalictrum* [1], we have investigated *Th. amurense*, *Th. contortum*, *Th. filamentosum*, and *Th. minus*.

There is no information in the literature on the alkaloid composition of *Th. amurense*. We have established that all the organs of the plant contain alkaloids, the total amounts of bases varying between 0.01 and 0.76%. In the present paper we give the results of a study of the combined bases of the flowers and seeds of *Th. amurense*.

Ordinary chloroform extraction of the flowers gave the total bases consisting practically of a single compound which was identified by a comparison of R_f values and of mass and NMR spectra, and also by a mixed melting point with an authentic sample, as β-allocryptopine (I). On TLC, the mixture of bases from the seeds showed the presence of two compounds. By preparative separation we obtained substance (I) and base (II) with mp 262-263°C (decomp.). UV spectrum: λ_{max} 287 nm (log ε 3.83). The mass spectrum of (II) showed the peaks of ions with m/e 353 (M^+), 269, 206 (100%), 192, 164, and 150. Methylation of (II) with diazomethane gave β-allocryptopine. The facts given show that base (II) is thalictrisine. Thalictrisine has been isolated previously only from the roots of *Th. simplex* [2].

The alkaloid composition of *Th. contortum* has now been studied for the first time. We investigated the epigeal part, the flowers, the roots, and the rhizomes. In the specimens investigated, the amount of total alkaloids was very low. The mixture of bases from the flowers was chromatographed on a column of alumina. The alkaloids were eluted with benzene, ether, and chloroform. The chloroform eluate yielded β-allocryptopine. Below we give information on the amounts of alkaloids in *Th. amurense* and *Th. contortum* collected in Maritime Territory in 1974:

Site and date of collection	Plant organ	Total alkaloids, % on the weight of the air-dry raw material
	Th. amurense	
Khasan region, July 26	Epigeal part	0.014
The same, August 17	Flowers	0.76
The same, August 17	Roots	0.142
The same, October 5	Roots	0.11
The same, October 5	Seeds	0.65
Kirovskii region, July 24	Rhizomes	0.105
	Th. contortum	
Khasan region, July 4	Epigeal part	0.003
The same, August 19	Roots	0.13
The same, October 5	Roots	0.06
The same, July 4	Rhizomes	0.07
Partizanskii region, June 23	Flowers	0.005

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Th. minus is widely distributed over the whole globe and is the most completely studied of the alkaloid-bearing representatives of the genus *Thalictrum* [3]. Some alkaloids (thalicarpine [4], thalidasine [5], etc.) possess valuable physiological properties [6] and therefore *Th. minus* from new growth sites is of great interest. We investigated *Th. minus* growing in the Shkotovo region of Maritime Territory:

Plant organ	Date of collection (1973)	Total alkaloids, % on the weight of the air-dry raw material
Epigeal part	June	0.006
Leaves	June	0.011
Seeds	October 2	0.04
Roots	October 6	0.15
Rhizomes	October 6	0.29

The combined ether-soluble bases from the roots were chromatographed on a column of alumina. A benzene eluate yielded a crystalline base with mp 135-137°C which was identified by a comparison of R_f values and mass and NMR spectra as argemonine. From the aqueous alkaline mother solution after the separation of the tertiary bases we obtained magnoflorine (III) and from the combined bases of the rhizomes we obtained (III) and berberine. The alkaloids berberine and magnoflorine are characteristic for *Thalictrum* roots, but this is the first time that argemonine has been isolated from this species.

There is no information in the literature on the alkaloid composition of *Th. filamentosum*. We investigated the roots and epigeal part of the plant. From the epigeal part collected in the environs of Vladivostok on May 25, 1974, we obtained 0.008%, and from the roots collected on August 28, 1974, 0.18% of combined bases. From the mixture of alkaloids of the roots by chromatography on a column of alumina followed by preparative separation we isolated glaucine and thalicsimidine.

EXPERIMENTAL

Extraction of the Flowers of *Th. amurense*. The comminuted air-dry flowers (1420 g) were wetted with a 5% aqueous solution of sodium carbonate and were extracted with chloroform. The chloroform extract was evaporated to dryness and the residue was treated with 10% sulfuric acid. The acid extract was washed with ether and then with chloroform, the precipitate that had formed was separated off, and it was made alkaline with 25% ammonia solution and the bases were extracted with ether and chloroform. This gave 4.96 g (0.35%) of ethereal extract and 1.04 g (0.072%) of chloroform extract.

The precipitate obtained in the washing of the acid solution was suspended in ammonia solution and extracted with chloroform. The chloroform extract was evaporated. The addition of ether to the residue led to its crystallization. The yield was 4.9 g (0.34% of the weight of the raw material). Since all three fractions obtained were chromatographically identical, they were combined and, after two recrystallizations from ethanol, β-allocryptopine was obtained with mp 167-169°C.

Extraction of the Seeds of *Th. amurense*. The comminuted seeds (155 g) were defatted with petroleum ether, dried, and extracted with methanol. The methanolic extract was evaporated in vacuum to dryness. By the method described above, 0.82 g (0.53%) of ether extract and 0.20 g (0.13%) of chloroform extract was obtained. By preparative separation on plates with a fixed layer of silica gel/gypsum in the cyclohexane–chloroform–DEA (7:2:1) system we isolated β-allocryptopine and a slightly yellowish amorphous substance. The latter was boiled in methanolic solution with activated carbon for 15 min, and then the solution was filtered through a small layer of silica gel. The solvent was evaporated, giving crystalline thalictrisine with mp 262-263°C (decomp.).

O-Methylthalictrisine (β-Allocryptopine). A solution of 0.01 g of thalictrisine in 10 ml of methanol was treated with an ethereal solution of diazomethane. The reaction mixture was kept in the refrigerator for three days (course of the reaction monitored by TLC). Then the solvent was evaporated off. Recrystallization from methanol gave a crystalline substance with mp 166-167°C which was identified by its melting point, R_f values, and a mixed melting point as β-allocryptopine.

Extraction of the Roots of *Th. minus*. The roots (960 g) were extracted by the method described above. This gave 1.14 g (0.127) of ether extract and 0.37 g (0.037%) of chloroform extract. The material of the ether extract was chromatographed on a column of alumina. The bases were eluted with benzene, and the benzene eluate was evaporated. When ether was added to the residue, argemonine crystallized. The aqueous alkaline mother solution after the isolation of the tertiary bases was evaporated to dryness. The residue was dissolved in a small volume of 10% sulfuric acid, a saturated solution of potassium iodide was added, and the resin that then deposited was separated off. When the resin was treated with methanol, a crystalline substance with mp 242-243°C was obtained. Yield 0.39 g (0.04% of the weight of the roots). After two recrystallizations from methanol, mp 247°C. A mixture with magnoflorine iodide gave no depression of the melting point.

Extraction of the Rhizomes of *Th. minus*. The rhizomes (520 g) were extracted as described above and yielded 1.51 g (0.3%) of combined bases. The chloroform-soluble material was chromatographed on a column of alumina. The alkaloids were eluted with benzene, ether, chloroform, and methanol. The methanolic eluate yielded berberine chloride with mp 197-200°C. Magnoflorine was isolated from the aqueous alkaline mother solution.

Extraction of the Flowers of *Th. contortum*. The comminuted air-dry flowers (250 g) were extracted as described above. This gave 0.011 g (0.005%) of total chloroform extract. This material was chromatographed on a column of alumina. The column was washed successively with benzene, ether, chloroform, and methanol. The benzene and ether fractions gave negative reactions for alkaloids. The chloroform eluate yielded a crystalline substance with mp 164-167°C which was identified as β-allocryptopine.

Extraction of the Roots of *Th. filamentosum*. The comminuted air-dry roots (357 g) were extracted with methanol. The solvent was evaporated off in vacuum to dryness. The dry resin was treated with 10% sulfuric acid and the acid extract was filtered from the insoluble fraction. The filtrate was washed with ether and then with chloroform ("acid" fraction) and was then made alkaline with concentrated NH_4OH and the bases were extracted with ether and chloroform. This gave 0.36 g (0.1%) of "acid" fraction and 0.17 g (0.05%) of combined ether-soluble and 0.12 g (0.033%) of combined chloroform-soluble bases. The "acid" fraction was chromatographed on a column of alumina and the bases were eluted with benzene, giving 0.1 g of an oil fraction. This was separated preparatively on plates with a fixed layer of silica gel/gypsum in the benzene–ethyl acetate–methanol (10:10:1) system. Glaucine and thalicsimidine were isolated.

SUMMARY

The alkaloid composition of four far-eastern species of *Thalictrum* — *Th. amurense*, *Th. contortum*, *Th. filamentosum*, and *Th. minus* — have been studied, for the first time in the case of the first three species. *Th. amurense* contains β-allocryptopine and thalictrisine, and *Th. contortum* contains β-allocryptopine. Glaucine and thalicsimidine have been found in *Th. filamentosum*, and argemonine has been isolated from *Th. minus* for the first time.

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