

TERPENOIDS OF *Ferula lapidosa*

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*The chemical compositions of the roots of *Ferula lapidosa* Korov from two growth sites have been studied, and an analysis of literature information has shown a dependence of the chemical composition of the plant on the growth site. A biogenetic interrelationship between germacrane, humulane, and carotane sesquiterpenoids is proposed.*

Continuing a systematic study of the terpenoids of plants of the genus *Ferula* growing in the Republics of Central Asia, we have investigated the components of the roots of *Ferula lapidosa* Korov. (family *Apiaceae*) gathered from two growth sites — in the valleys of the rivers Ulken-sai and Koka-Meren in the Republic of Kyrgystan. By ethanolic extraction followed by chromatographic separation, the roots of the plant gathered in the valley of the river Ulken-sai yield ferocin and ferocinin, which were identified by comparing IR and PMR spectra and by mixed melting points [1].

From an ethanolic extract of the roots gathered in the valley of the R. Koka-Meren, using the above-mentioned method, four compounds were isolated: ferocin, ferocinin, ferolin, and chimganidin [2].

Up to the present time, about 100 species of *Ferula* have been subjected to chemical investigation, but in the majority of cases the influence of the growth site on the qualitative and quantitative compositions of the terpenoids was not taken into account. There are isolated studies where differences in the chemical composition within the limits of a species have been explained by the presence of different chemoforms [3, 4].

Analysis of our experimental results and literature information showed that the qualitative composition of the terpenoids of *Ferula lapidosa* depend on the growth site of the plant. From the roots of *F. lapidosa* gathered in the Susamyr valley, Republic of Kyrgystan, we have previously isolated the germacrane esters ferolin and chimganidin and the camphane ester chimgin [5], while from a sample gathered in the Buam gorge only *l*-chimgin was isolated [6]. From *F. lapidosa* gathered in the Chigirik pass, Republic of Kyrgystan, we have isolated the carotane esters lapidin, lapiferin, lapiferinin, lapidolin, lapidolinin, and lapidolidin [7-11].

The isolation of esters of a monoterpenoid of the camphane type and of sesquiterpenoids of the germacrane, humulane, and carotane types from one plant gathered from different growth sites shows that the chemical composition of *F. lapidosa* depends on the growth site. These results show the existence of a biogenetic interrelationship between sesquiterpenoids of the germacrane, humulane, and carotane types.

It has been established previously that the qualitative and quantitative compositions of the alkaloids of the majority of plants are highly subject to changes according to the growth site [11] and, as can be seen from the facts mentioned above, the chemical composition of *F. lapidosa* corresponds completely to this rule.

EXPERIMENTAL

Conditions for recording the spectra have been given in [7].

Separation of the Extractive Substances of Roots Gathered in the valley of the R. Ulken-Sai. The air-dry comminuted roots of *F. lapidosa* (1 kg) were extracted three times with ethanol. The concentrated ethanolic extract was diluted with water (1:2), and the substances were extracted with ethyl acetate (3 × 0.5 liter). The ethyl acetate extract was washed

with water and dried over anhydrous sodium sulfate, and the solvent was distilled off. This gave 50 g of a viscous brown resinous extract, 20 g of which was deposited on a column of KSK silica gel (3 × 100 cm). The substances were eluted with hexane–ethyl acetate (9:1), 100-ml fractions being collected.

Two substances were isolated: ferocin, C₂₂H₂₈O₃, mp 127-128°C, [α]_D -200° (c 1.0; chloroform), and ferocinin, C₂₃H₃₀O₄, mp 107-108°C, [α]_D -197.4° (c 1.0; chloroform).

Separation of the Total Extractive Substances of the Roots Gathered in the valley of R. Koka-Meren. The extraction of 1 kg of comminuted roots by the method described above gave 63 g of total extractive substances. Of these, 20 g was separated on a column of KSK silica gel (3 × 100 cm). The substances were eluted with hexane–ethyl acetate (9:1), 100-ml fractions being collected. Four substances of ester nature were isolated: ferocin, ferocinin, ferolin, C₂₂H₃₀O₄, mp 190-191°C, [α]_D -91.6° (c 1.0; chloroform), and chinganidin, C₂₃H₃₂O₅, mp 140-141°C, [α]_D -96.7° (c 1.0; chloroform).

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