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ORGANIC ACIDS FROM MEDICINAL PLANTS. 4. *Scutellaria baicalensis*

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Little information is available about the organic acids from representatives of the Lamiaceae family. Tartaric acid is known from *Lycopus europaeus* L. [1] and *Salvia deserta* Schang. [2]; citric, *Lagochilus* sp. [3], *Ortosiphon stamineus* Benth. [4], *L. europaeus* [1], and *S. deserta* [2]; fumaric, *Leonurus sibiricus* L. [5]; malic, *L. europaeus* [1], *Panzerina lanata* (L.) Bunge. [6], and *S. deserta* [2]; succinic, *Glehoma hederaceae* L. [7], *Phlomoides tuberosa* (L.) Adyl. [8], and *S. deserta* [2].

Scutellaria baicalensis Georgi. (Lamiaceae) is a valuable medicinal plant that is widely used in Eastern medicine. The presence of phenolic compounds has mainly been investigated [9]. Information on the composition of the organic acids (OA) from the aerial part of *S. baicalensis* has not been published in the open literature. Therefore, we isolated the di- and tricarboxylic acids and pure compounds and studied the OA accumulation features during plant development.

The OA complex was isolated by extracting raw material (200 g) successively with hexane, $CHCl_3$:C_2H_5OH (2:1), and water. The aqueous extract was concentrated, precipitated with acetone, and centrifuged. The precipitate was separated. The supernatant was concentrated and passed successively through columns of KU-2-8 cation exchanger (H^+-form, 0.5 mm, H_2O eluent) and ASD-4-5p anion exchanger (Cl^--form, 0.25 mm, HCOOH eluent, 1 M). The effluent from the anion exchanger was concentrated to a volume of 10-12 mL and separated by preparative PC [FN-16, BuOH:HCOOH (85%), 3:1, system 1, three times to a height of 30 cm]. The preparative separation and recrystallization from water isolated six compounds that were identified as tartaric (Tar), citric (Cit), malic (Mal), malonic (Mln), succinic (Suc), and fumaric acids (Fum). The isolated compounds were identified from the melting points of the starting compound, their anilides, and a mixed sample with authentic samples; molecular weight; specific rotation; chromatographic mobility [PC, system 1, development by a mixture of alcoholic bromcresol green (0.08%) and bromphenol blue (0.03%) with $KMnO_4$ (0.25%) in aqueous Na_2CO_3 (0.5%), 9:9:2], and IR and ^{13}C NMR spectroscopy.

The study of the group composition of the OA complex [10] found that they occurred primarily in the bound form. The coefficients of the forms k^f [11] were always less than unity for all vegetative phases (Table 1). During plant development, the content of free acids decreased from 1.88 to 0.63%. The maximum (12.58%) accumulation of total OA occurred during flowering. The same phenomenon was observed for bound forms of OA (11.48%). The k^f value fell during vegetation, reaching its minimum in senescent plants (0.07).

The individual profile of OA underwent significant changes during development of the aerial part of *S. baicalensis* (Table 2). Only citric acid, the dominant component of the total OA complex (40.43-100% of the total OA content) was observed in the free state in all vegetative phases. The content of tartaric acid was lowest at the start of vegetation. Fumaric acid was not observed. The picture changed during budding. Citric and tartaric acids made up more than 80% of the total content. This tendency persisted during flowering. Fumaric acid was found only during this plant development period. We found tartaric and citric acids in a 1:5-6 ratio during fruiting. Only citric acid was present in senescent plants.

All compounds were isolated from *S. baicalensis* for the first time. Malonic acid was observed for the first time among representatives of the family Lamiaceae.

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TABLE 1. Group Composition of the Acid Complex from the Aerial Part of *S. baicalensis*, % (Calculated for Citric Acid, (min - max)/ $\bar{x}$)

Parameter	Vegetative phase				
	start of vegetation	budding	flowering	fruiting	senescence
X_f	1.61 - 1.97 1.88	1.10 - 1.21 1.13	0.98 - 1.17 1.10	0.73 - 0.91 0.80	0.48 - 0.67 0.63
X_b	3.31 - 3.54 3.38	6.20 - 6.41 6.39	11.37 - 1162 11.48	9.50 - 9.76 9.52	8.22 - 8.51 8.40
X_Σ	5.02 - 5.44 5.26	7.44 - 7.69 7.52	12.41 - 12.70 12.58	10.24 - 10.48 10.32	8.73 - 9.12 9.03
k^f	0.44 - 0.62 0.56	0.15 - 0.21 0.18	0.09 - 0.12 0.10	0.06 - 0.09 0.08	0.05 - 0.07 0.07

$\bar{x}$ is the average; X_f, the content of free forms of acids; X_b, the content of bound forms of acids; X_Σ, the total content of organic acids; k^f, the coefficient of the forms.

TABLE 2. Individual Composition of the Acid Complex from the Aerial Part of *S. baicalensis*, % (min - max/ $\bar{x}$)

Acid	Vegetative phase				
	start of vegetation	budding	flowering	fruiting	senescence
Tartaric	0.51 - 0.70 0.66	1.61 - 1.90 1.82	2.55 - 5.87 2.73	1.44 - 1.71 1.56	-
Citric	2.00 - 2.24 2.13	4.31- 4.67 4.55	5.26 - 5.48 5.35	8.63 - 8.99 8.76	8.17 - 8.52 8.40
Malic	0.80 - 0.89 0.87	0.44 - 0.56 0.45	1.30 - 1.69 1.47	-	-
Malonic	0.72 - 0.82 0.79	0.34 - 0.42 0.39	1.27 - 1.39 1.36	-	-
Succinic	0.77 - 0.87 0.81	0.28 - 0.31 0.30	0.87 - 0.95 0.92	-	-
Fumaric	-	-	0.72 - 0.79 0.76	-	-

$\bar{x}$ is the average.

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