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ORGANIC ACIDS FROM MEDICINAL PLANTS. 2. *Ortilia secunda*

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Ortilia secunda (L.) House (Pyrolaceae) is a medicinal plant of Siberian and Far Eastern traditional medicine. Leaves of *O. secunda* are used as an anti-inflammatory, hemostatic, and diuretic agent and are widely applied in gynecological practice [1]. Investigations carried out at the IGEB, SD RAS, found distinct anti-inflammatory and antioxidant activity for extracts of this plant [2]. The chemical composition of *O. secunda* has been little studied. Phenolic glycosides [3], flavonoids [4], and iridoids [5] have been observed in it. Data on the composition of the complex of di- and tricarboxylic acids could not be found.

Using previously published methodological approaches [6-8], we isolated the complex of organic acids (OA) from *O. secunda* leaves and studied their qualitative and quantitative compositions and the dynamics of accumulation of pure components. The total fraction of OA consisted of five compounds, of which three were isolated and identified as citric, malic, and succinic acids. The two unidentified components were amorphous substances that gave positive reactions for carboxylic acid and carbohydrate. We preliminarily classified these as acids of primary sugar oxidation (APSO) [9, 10].

Citric acid, mp 151°C (H_2O), mp of anilide 164°C (dioxane), positive reaction with diphenylamine, ^{13}C NMR (125.7 MHz, DMSO-d_6, ppm) 42.6 (s, CH_2), 72.2 (s, COH), 171.4 (s, COOH), 174.6 (s, COOH).

Malic acid, mp 131°C (H_2O), mp of anilide 197°C (dioxane), positive reaction with β-naphthol, ^{13}C NMR (125.7 MHz, DMSO-d_6, ppm): 40.0 (s, CH_2), 67.2 (s, CHOH), 172.0 (s, COOH), 174.9 (s, COOH).

Succinic acid, mp 188°C (H_2O), mp of anilide 227.3-228.0°C (dioxane), ^{13}C NMR (125.7 MHz, DMSO-d_6, ppm): 41.0 (s, CH_2), 171.2 (s, COOH).

The total content of OA increased during winter dormancy. The investigation of the group composition of OA found that they occurred in leaves primarily in the free state (72-87% of total content) (Table 1). The content of free acids from April to September was practically constant (3.29-3.63%) and slightly decreased toward autumn. The concentration of bound forms of OA was minimal toward the end of flowering (0.53%) and increased during winter dormancy by 2-2.3 times.

TABLE 1. Composition of Acid Complex from *O. secunda* Leaves, %

Group	Vegetation phase				
	start of vegetation (April-May)	budding and flowering (June-July)	end of vegetation, fruiting (July-August)	end of fruiting (October-November)	winter dormancy (December-March)
Group composition of acid complex (calculated for citric acid)					
Total acid content	5.03±0.21	4.58±0.08	3.98±0.20	4.44±0.09	5.34±0.08
Free acids	3.63±0.07	3.53±0.03	3.46±0.05	3.29±0.07	3.87±0.11
Bound acids	1.41±0.02	1.06±0.01	0.53±0.02	1.15±0.03	1.47±0.04
Composition of acid complex					
Citric acid	2.19±0.03	2.09±0.02	1.47±0.04	2.02±0.05	2.32±0.04
Malic acid	0.85±0.02	0.94±0.03	0.92±0.03	0.91±0.04	1.04±0.09
Succinic acid	0.53±0.02	0.67±0.03	0.67±0.03	0.40±0.01	0.40±0.03
APSO	1.46±0.12	0.88±0.10	0.92±0.09	1.11±0.15	1.58±0.12

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The study of the accumulation dynamics of pure OA (Table 1) showed that the content of succinic acid increased during budding-flowering to 0.67% and fell during the start of winter dormancy. The content of citric acid inceased toward autumn to 2%. The content of malic acid remained almost constant (1%) during the whole vegetation period. It should be noted that APSO, which are the form of carbohydrats deposited in plants, also accumulated during winter dormancy.

The dominant component of the acid complex was citric acid (37-46% of the total OA content). It is interesting that a microscopic investigation of *O. secunda* organs found in parenchymal cells numerous crystal druses. Considering this, it can be assumed that these formations were citrates.

OA were isolated for the first time from leaves of *O. secunda*.

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