

## ORGANIC ACIDS OF MEDICINAL PLANTS. 1. *Plantago major*

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UDC 582.962+581.192

Plantain (*Plantago major* L., Plantaginaceae) is a medicinal plant that is used widely in medical practice. Its chemical composition is well studied [1]. Fumaric, syringic, vanillic, *p*-hydroxybenzoic, ferulic, *p*-coumaric, gentisic, salicylic, benzoic, and cinnamic acids and methylcaffeate have been isolated from the total organic acids of *P. major* leaves [2]. The content of chlorogenic and neochlorogenic acids has been reported [3]. However, the di- and tricarboxylic acids have not been investigated in detail.

Paper chromatography [PC, 5-7°C; FN-16; isoamyl alcohol (85%):formic acid, 6:4, system I; ethylacetate:formic acid:water, 3:1:1, system II] found that *P. major* leaves contain at least eight organic acids with five compounds in the free state (before ion exchange). We isolated and identified tartaric, citric, malic, malonic, and succinic acids using molecular weights [4]; qualitative reactions [5, 6]; the Buch test [7]; melting points of pure compounds, mixed samples, and acid anilides [4]; chromatographic mobilities (PC, systems I and II), and <sup>13</sup>C NMR spectroscopy.

**Tartaric acid**, 150 g/mol, mp 170.8-171.0°C (H<sub>2</sub>O), mp (anilide) 181.0-182.5°C (dioxane), positive reaction with vanillin, *R<sub>f</sub>* 0.12 (system I), 0.38 (system II), <sup>13</sup>C NMR (125.7 MHz, DMSO-d<sub>6</sub>, ppm): 72.3 (s, CHOH), 173.3 (s, COOH).

**Citric acid**, 192 g/mol, mp 151.5-152.0°C (H<sub>2</sub>O), mp (anilide) 164.0-164.3°C (dioxane), positive reaction with diphenylamine, *R<sub>f</sub>* 0.16 (system I), 0.46 (system II), <sup>13</sup>C NMR (125.7 MHz, DMSO-d<sub>6</sub>, ppm): 42.8 (s, CH<sub>2</sub>), 72.6 (s, COH), 171.4 (s, COOH), 174.6 (s, COOH).

**Malic acid**, 134 g/mol, mp 130.0-130.5°C (H<sub>2</sub>O), mp (anilide) 196.8-197.5°C (dioxane), positive reaction with β-naphthol, *R<sub>f</sub>* 0.23 (system I), 0.53 (system II), <sup>13</sup>C NMR (125.7 MHz, DMSO-d<sub>6</sub>, ppm): 39.5 (s, CH<sub>2</sub>), 67.2 (s, CHOH), 172.1 (s, COOH), 174.9 (s, COOH).

**Malonic acid**, 104 g/mol, mp 133.8-134.5°C (H<sub>2</sub>O), mp (anilide) 223.1-223.7°C (dioxane), positive Kleeman reaction, *R<sub>f</sub>* 0.43 (system I), 0.69 (system II), <sup>13</sup>C NMR (125.7 MHz, DMSO-d<sub>6</sub>, ppm): 40.2 (s, CH<sub>2</sub>), 170 (s, COOH).

**Succinic acid**, 118 g/mol, mp 187.9-188.5°C (H<sub>2</sub>O), mp (anilide) 227.3-228.0°C (dioxane), *R<sub>f</sub>* 0.51 (system I), 0.74 (system II), <sup>13</sup>C NMR (125.7 MHz, DMSO-d<sub>6</sub>, ppm): 41.1 (s, CH<sub>2</sub>), 171.2 (s, COOH).

The spectrum of medicinal agents from plantain leaves is not particularly varied. The most popular preparations are "Plantaglucide" and "Plantain juice" (PJ). The former is the total water-soluble polysaccharides from *P. major* leaves and does not contain organic acids. PJ is a mixture of juices from two plantain species. The organic acids in PJ are analogous to those from *P. major* leaves with the exception that it lacks malic acid. Using a modified method [8], the contents of pure acids in *P. major* leaves and in PJ were found (Table 1). It was found that tartaric and citric acids are the dominant components.

The described compounds were isolated for the first time from *P. major* leaves.

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TABLE 1. Quantitative Content of Pure Acids in *P. major* Leaves and in "Plantain Juice" Preparation, %

Acid	<i>P. major</i> leaves		"Plantain juice"	
	before ion exchange	after ion exchange	before ion exchange	after ion exchange
Tartaric	1.60-1.73	1.80-1.87	0.21-0.28	0.35-0.40
Citric	1.22-1.44	1.44-1.53	0.15-0.18	0.24-0.32
Malic	0.20-0.25	0.40-0.51	-	-
Malonic	0.11-0.15	0.23-0.35	0.11-0.13	0.20-0.25
Succinic	0.25-0.31	0.46-0.55	0.12-0.15	0.19-0.29

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