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BIOLOGICALLY ACTIVE COMPOUNDS FROM LEAVES OF *Cacalia hastata*. 4. PHENOLIC ACIDS

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We previously isolated and identified from leaves of *Cacalia hastata* polysaccharides [1], photosynthetic pigments [2], and organic acids [3]. Phenolic acids have been detected in leaves of *C. hastata* by investigating the ethylacetate fraction using HPLC (Milichrom A-02, Nucleosil 100-5, C18; 75 × 2 mm; 0.05 M KH_2PO_4:CH_3CN, 95:5).

Pure compounds were isolated by chromatographing over polyamide columns (40 × 200 mm) the ethylacetate fraction obtained by gradient extraction in a Soxhlet apparatus. Phenolic acids were eluted with water. Fractions were concentrated and rechromatographed on paper (PC) (FM-12, BuOH:AcOH:H_2O, 10:8:7, system I; AcOH:H_2O, 15:85, system II). Pure compounds were eluted by ethanol (50%). Recrystallization from ethanol produced three compounds. The purity of the isolated compounds was established using qualitative reactions, melting points, the lack of melting point depression in mixed samples, chromatographic mobility, alkaline destruction products, and UV analysis with diagnostic additives [4].

Compound **1**, mp 197-199°C (EtOH), PC R_f 0.80 (system I), 0.52 (system II), UV spectrum (EtOH, λ_{max}, nm): 328, 300, 230; (AcONa) 310, 278; (MeONa) 362, 251; (H_3BO_3+AcONa) 320, 297; ($AlCl_3$) 358, 310, 240. The alkaline destruction products contained a compound with mp 202-203°C that was chromatographically identical to protocatechuic acid, caffeic acid.

Compound **2**, mp 202-204°C (EtOH), PC R_f 0.65 (system I), 0.62 (system II), UV spectrum (EtOH, λ_{max}, nm): 328, 240; (AcONa) 330; (MeONa) 381, 260; (H_3BO_3) 381, 260; (H_3BO_3); ($AlCl_3$) 360, 215, 238. Alkaline hydrolysis produced caffeic and quinic acids [5]. Compound **2** is chlorogenic acid.

Compound **3**, mp 238-240°C (EtOH), PC R_f 0.60 (system II), UV spectrum (EtOH, λ_{max}, nm): 211, 274; gallic acid.

We also investigated the accumulation dynamics of phenolic acids in leaves of *C. hastata* collected in 2000-2002 in Mukhorshibir Region (Buryatiya Republic) during various vegetative periods. The amounts of caffeic and chlorogenic [6, 7] and gallic [8] acids were determined during different development stages of the leaves (Table 1).

We found that the total amounts of phenolic acids and chlorogenic acid reach a maximum during budding, 1.72 and 0.84%, respectively, and slightly decrease toward autumn. The accumulation dynamics of caffeic and gallic acids are different. Their content increases during plant development and reaches a maximum toward the end of vegetation. The amount of gallic acid remains almost constant during budding with a sharp increase in autumn. This is probably a result of the destruction of hydrolyzed tannins. The content of caffeic acid increases toward the end of vegetation. The correlation between the contents of caffeic and chlorogenic acids is explained by the fact that during autumn the esterase activity increases. This cleaves depside chlorogenic acid to quinic and caffeic acids. The amount of caffeic acid increases as a result.

Caffeic acid and its esters were detected [9] in roots of *C. hastata*. Chlorogenic and gallic acids were isolated from the plant for the first time.

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TABLE 1. Accumulation Dynamics of Phenolic Acids in *C. hastata* L. Leaves, %

Phenolic acid	Start of vegetation (1.06)	Vegetation		Budding (28.07)	Mass flowering (15.08)	Fruiting (28.08)
		(11.06)	(22.06)			
Caffeic	0.10±0.01	0.19±0.04	0.25±0.06	0.34±0.08	0.38±0.08	0.46±0.10
Chlorogenic	0.59±0.13	0.71±0.12	0.94±0.17	1.05±0.16	0.84±0.11	0.70±0.09
Gallic	0.27±0.05	0.28±0.05	0.30±0.04	0.33±0.06	0.39±0.07	0.44±0.06

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