

PHYTOECDYSTEROIDS FROM *Stemmacantha uniflora*

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We have previously studied the seasonal dynamics and general trends in the distribution of **1** in plants of *Stemmacantha uniflora* subspecies *satzyperovii* growing in Primorskii krai [1, 2].

The goal of the present work was to study the dynamics of the phytoecdysteroid content in various plant organs of *S. uniflora* and to compare the composition and content of the edcysteroids 20-hydroxyecdysone (**1**), integristerone A (**2**), 2-deoxy-20-hydroxyecdysone (**3**), and α -ecdysone (**4**) of this species and aerial organs of the pharmacopeic species *S. carthamoides* (Willd.) M Dittrich [*Rhaponticum carthamoides* (Willd.) Iljin].

Compounds **2** and **3** were found in vegetative and generative organs of *S. uniflora* for the first time. Compound **4** was not observed in subterranean and aerial organs of this species. Table 1 gives the content of **1-3** in organs of *S. uniflora* at various development stages.

This species exhibited a sharp gradient in the distribution of **1-3** within a single plant and significant variations in the phytoecdysteroid content in the same organs at various development times.

The content of **1** varied from 0.23 to 8.51 $\mu\text{g}/\text{mg}$ depending on the organ and development phase. Its content was maximum in actively developing organs such as upper stem parts (4.72 $\mu\text{g}/\text{mg}$) during development of generative runner and budding, upper stem leaves (5.14 $\mu\text{g}/\text{mg}$) during mass flowering, root leaves (8.51 $\mu\text{g}/\text{mg}$) during fruiting, and achenes (5.68 $\mu\text{g}/\text{mg}$) when the aerial part was dying.

The results for the content of **1** in *S. uniflora* were compared with those in rhizomes of the pharmacopeic species *S. carthamoides* (0.66 $\mu\text{g}/\text{mg}$). The content of **1** in stems of *S. uniflora* was 7 times greater than in the subterranean organs of *S. carthamoides*; in root leaves, 12 times greater. According to the results, the far eastern species *S. uniflora* is a promising source of **1**.

General trends in the distribution of **1** found for *S. uniflora* were consistent with those for *S. uniflora* subspecies *satzyperovii* [2]. Thus, the content of **1** in these species was maximum in actively growing organs (young leaves or upper stem parts). Toward the end of vegetation, **1** accumulated in achenes. The results indicated that plants collected in Amur oblast have a lower content of **1** than those from Primorskii krai.

The dynamics of the content of minor phytoecdysteroids in vegetative and generative organs of *S. uniflora* during the vegetative period did not reveal any distinct trends in the distribution of **2** and **3** as a function of development phase. The amount of **2** reached a maximum in root leaves (0.30 $\mu\text{g}/\text{mg}$) during fruiting and in middle stem leaves (0.21 $\mu\text{g}/\text{mg}$) during flowering; of **3**, in upper stem leaves (0.25 $\mu\text{g}/\text{mg}$) during budding, in lower stem leaves (0.40 $\mu\text{g}/\text{mg}$) during flowering, in root leaves (0.63 $\mu\text{g}/\text{mg}$) during fruiting, and in achenes (0.59 $\mu\text{g}/\text{mg}$) when the aerial part was dying.

Plants of *S. uniflora* were collected in 2002–2003 near Mokhovaya Pad' of Blagoveshchensk region of Amur oblast.

Plant material was extracted. Samples were prepared and the phytoecdysteroid content was determined by the previously described method [3]. Compounds **1-4** were analyzed in the extracts from various plant organs, rhizomes, stems, leaves (root and stem), buds, flowers, sheaths, pappuses, and achenes. Phytoecdysteroids were identified by GC—MS using chemical ionization at atmospheric pressure and HPLC—UV [3].

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TABLE 1. Content of 20-Hydroxyecdysone (**1**), Integristerone A (**2**), and 2-Deoxy-20-hydroxyecdysone (**3**) in Various Parts of *Stemmacantha uniflora* as Functions of Development Phase*

Phenophase (collection date, plant properties)	Plant organ	Content, µg/mg		
		1	2	3
Developed generative runner and budding (23 May, root leaf rosette formed, flower clusters 1-2 cm in diameter)	Rhizomes	1.30±0.07	0.025±0.001	-
	Root leaf	1.19±0.06	0.065±0.003	-
	Lower stem leaf	0.82±0.04	0.019±0.001	-
	Middle stem leaf	0.83±0.04	-	0.042±0.002
	Upper stem leaf	0.91±0.05	Tr.	-
	Stem (lower part)	0.92±0.05	-	-
	Stem (upper part)	4.72±0.24	0.013±0.001	0.25±0.01
	Bud	0.41±0.02	-	-
	Sheath	1.27±0.06	0.019±0.001	-
	Thalamus	2.98±0.15	0.035±0.002	-
Mass flowering (21 June, generative runner 60-100 cm high; root leaves 30 cm long, 8-10 cm wide; upper leaves of generative runner 4-6 cm long and 1.5-2 cm wide; calathides 3-4.5 cm in diameter)	Rhizome	0.96±0.05	0.028±0.001	-
	Root leaf	3.09±0.15	0.17±0.01	-
	Root leaf petiole	1.27±0.06	Tr.	Tr.
	Lower stem leaf	4.24±0.21	0.16±0.01	0.40±0.02
	Middle stem leaf	4.19±0.21	0.21±0.01	0.38±0.02
	Upper stem leaf	5.14±0.26	0.11±0.01	-
	Stem (lower part)	1.57±0.08	0.027±0.001	-
	Stem (middle part)	1.30±0.07	0.048±0.002	Tr.
	Stem (upper part)	2.48±0.12	0.041±0.002	0.23±0.01
	Flower	0.31±0.02	-	-
	Pappus	0.69±0.03	-	-
	Sheath	0.62±0.03	Tr.	Tr.
	Achene	2.36±0.12	0.014±0.001	-
	Thalamus	3.13±0.16	0.013±0.001	0.33±0.02
	Rhizomes	1.71±0.09	0.015±0.001	0.07±0.04
Fruiting (27 July; achenes 3-5 cm long, 2-2.5 mm wide)	Root leaf	8.51±0.43	0.30±0.02	0.63±0.03
	Root leaf petiole	3.02±0.15	Tr.	0.18±0.01
	Lower stem leaf	2.54±0.13	0.13±0.01	0.09±0.01
	Middle stem leaf	4.16±0.21	0.11±0.01	0.19±0.01
	Upper stem leaf	2.73±0.14	0.12±0.01	0.14±0.01
	Young root leaf	8.38±0.42	Tr.	0.49±0.02
	Stem (lower part)	0.29±0.01	-	-
	Stem (middle part)	0.46±0.02	0.029±0.001	Tr.
	Stem (upper part)	0.52±0.03	Tr.	-
	Pappus	0.54±0.03	Tr.	Tr.
	Sheath	0.65±0.03	-	0.13±0.01
	Achene	1.71±0.09	Tr.	0.09±0.005
	Rhizomes	2.63±0.13	Tr.	0.26±0.01
	Root leaf	5.13±0.26	0.024±0.001	0.37±0.02
	Root leaf petiole	1.39±0.07	-	0.10±0.005
Aerial part dying (24 August; upper part of generative runner and upper leaf stems dry)	Lower stem leaf	1.92±0.10	-	0.16±0.01
	Middle stem leaf	1.61±0.08	0.026±0.001	Tr.
	Upper stem leaf	0.23±0.01	-	-
	Stem (lower part)	0.41±0.02	Tr.	-
	Stem (middle part)	0.34±0.02	Tr.	-
	Stem (upper part)	0.32±0.02	0.018±0.001	-
	Pappus	0.39±0.02	-	-
	Sheath	0.27±0.01	-	-
	Achene	5.68±0.28	0.036±0.002	0.59±0.03
	Thalamus	3.32±0.17	0.030±0.002	0.11±0.01

*Tr. = trace ($\leq 0.01\mu\text{g/mg}$). Dashes mean that the compound was not observed.

Standards were 20-hydroxyecdysone obtained as before [2], 2-deoxy-20-hydroxyecdysone, α -ecdysone (Sigma, USA), and integristerone A [supplied by Dr. U. A. Baltaev, Institute of Petroleum Chemistry and Catalysis, Academy of Sciences, RB, and USC RAS (IPC), Ufa].

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