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ACCUMULATION DYNAMICS OF TANNING AGENTS AND RHODIOLOSIDE IN *Rhodiola semenovii* RHIZOMES AND ROOTS

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Rhodiola semenovii (Rgl et Herd.) Boriss (Grassulaceae) is a valuable medicinal raw material with therapeutic properties nearly as strong as those of *Rhodiola rosea* L. [1, 2]. It is a perennial plant with woody, thick, branching rhizomes. It grows in moist rocky soils of alpine glades in Tashkent and Kashkadarin Oblasts of Uzbekistan [3]. A comparison of the chemistry and pharmacology of rhizomes and roots of this plant growing in Uzbekistan with the official species *R. rosea* showed that they are identical [4]. We used raw material collected separately during each vegetative phase near the Pskent River of Tashkent Oblast. Dried rhizomes and roots of *R. semenovii* were collected according to the VFS [5] and ground and analyzed for authenticity. Tanning agents and rhodioloside were determined quantitatively (Table 1).

Table 1 shows that the accumulation of tanning agents in rhizomes with roots of *R. semenovii* was greatest (14.91%) during senescence whereas the rhodioloside content was greatest (0.858%) at the end of flowering. The maximum amount of rhodioloside in rhizomes of *R. rosea*, the official species that does not grow in Uzbekistan, was 0.933%. Thus, *R. semenovii* growing in Uzbekistan can be recommended as an official substitute for *R. rosea*.

Grinding of Raw Material. Absolute dry raw material (roots and rhizomes of *R. semenovii*) was ground in a mill (LT-101) and sieved through a 7-mm sieve. Raw material that did not pass through a 2-mm sieve was used for the analysis.

Quantitative determination of rhodioloside was performed by the method in the SP XIth Ed. [6].

Tanning agents were determined according to the SP XIth Ed. [7]. Then, the extract of tanning agents was worked up with EtOAc. The EtOAc fraction (30 g) was chromatographed over a column of Sephadex LH-20 (d 5 cm, h 160 cm) with elution by aqueous EtOH (80%). This isolated the known dimeric proanthocyanidine (–)-epicatechin-(4β-8)-(–)-epogallocatechin-3-*O*-gallate [8] and three dimeric proanthocyanidines [9] that were identified using PMR spectra:

(+)-Catechin-(4α-8)-(+)-catechin, amorphous powder (0.150 g), $C_{30}H_{26}O_{12}$, $[M]^+$ 578, $[\alpha]_D^{25}$ +32° (*c* 0.43, acetone).

PMR spectrum (100 MHz, acetone-d_6 + D_2O, δ, ppm, J/Hz): 1.53 (s, Ac), 1.63 (Ac), 2.7 (m, H-4′), 4.84 (d, $J_{2,3}$ = 10, H-2), 4.85 (dd, $J_{4,3}$ = 10.0, $J_{4,5}$ = 1.5, H-4), 4.93 (d, $J_{2,3}$ = 10, H-2′), 4.97 (m, H-3′), 6.10 (t, H-3), 6.36 (d, $J_{6,8}$ = 2.5, H-8), 6.46 (s, H-6′), 6.47 (dd, $J_{6,5}$ = 8.5, $J_{6,8}$ = 2.5, H-6);

(–)-Epicatechingallate-(4β-8)-(–)-epicatechingallate, amorphous powder (0.210 g), $C_{44}H_{36}O_{20}$, $[M]^+$ 884, $[\alpha]_D^{25}$ +25.1° (*c* 0.95, acetone).

PMR spectrum (100 MHz, acetone-d_6 + D_2O, ppm, J/Hz): 2.55 (dd, $J_{4,3}$ = 8.0, $J_{4,4}$ = 16.0, βH-4′), 2.89 (dd, $J_{4,3}$ = 6.0, $J_{4,4}$ = 16.0, αH-4′), 4.04 (m, H-3′), 4.43 (d, $J_{2,3}$ = 6.0, H-2′), 4.60 (d, $J_{4,3}$ = 2.0, H-4), 5.08 (s, H-6′, H-8′), 5.31 (m, H-3), 5.46 (br.s, H-2), 5.80 (d, $J_{6,8}$ = 2.0, H-6), 5.93 (d, $J_{8,6}$ = 2.0, H-8), 6.95 (s, OGal);

(–)-Epicatechin-(4β-8)-(–)-epicatechingallate, amorphous powder (0.250 g), $C_{37}H_{31}O_{16}$, $[M]^+$ 731, $[\alpha]_D^{25}$ +31.5° (*c* 0.78, acetone).

PMR spectrum (100 MHz, acetone-d_6 + D_2O, ppm, J/Hz): 3.0 (m, H-4′), 4.79 (d, $J_{4,3}$ = 3, αH-4), 4.98 (br.s, H-2′), 5.55 (m, H-3), 5.55 (m, H-3′), 5.65 (s, H-2), 5.93 (s, H-5), 5.93 (s, H-6), 6.13 (s, H-5′, H-6′), 6.99 (s, OGal), 7.07 (s, OGal).

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TABLE 1. Content of Tanning Agents and Rhodioloside in *Rhodiola Semenovii* Rhizomes and Roots

Content of compound During vegetative period, % of abs. Dry raw matl.	Budding (May-early June)	Flowering (June-July)	Fruiting (August)	Start of senescence (September)	Senescence (October)	Senescence (November)
Tanning agents	13.14	12.43	11.52	12.82	13.74	14.91
Rhodioloside	0.67	0.858	0.77	0.63	0.59	0.57

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