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Comparative phytochemical characterization of three *Rhodiola* species

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Abstract

In comparison to the well-recognized adaptogenic herb *Rhodiola rosea*, phytochemical constituents of two other *Rhodiola* species (*R. heterodonta* and *R. semenovii*) were elucidated and characterized. Two major phytochemical groups; phenolic and/or cyanogenic glycosides and proanthocyanidins, were isolated and identified in the three species. Chemical similarities among the three species were observed; however, each species displayed differences in phytochemical constituents. *R. heterodonta* contained a newly detected phenylethanoid glycoside, heterodontoside, in addition to the known compounds tyrosol, viridoside, salidroside, and rhodiocyanoside A. Both *R. heterodonta* and *R. rosea* contained phenylethanoid/propanoid compounds that were not detected in *R. semenovii*. For *R. semenovii*, the cyanogenic glucosides rhodiocyanoside A and lotaustralin were detected. Although the three species have proanthocyanidins composed of (−)-epigallocatechin and its 3-*O*-gallate esters in common, the degree of polymerization greatly differed between them. In contrast to *R. heterodonta* and *R. semenovii*, *R. rosea* has higher molecular weight polymeric proanthocyanidins. This study resulted in the identification and isolation of phytochemical constituents for direct cross-comparison between three *Rhodiola* species of medicinal and pharmacological value.
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Keywords: *Rhodiola heterodonta*; *Rhodiola semenovii*; *Rhodiola rosea*; Crassulaceae; Heterodontoside; Phenylethanoid glycosides; Cyanogenic glucosides; Proanthocyanidins; Prodelphinidins; EGCG; EGC; HPLC-ESI-MS

1. Introduction

Rhodiola rosea L. (golden root), historically used as an adaptogen in Russia, northern Europe, and in China as a traditional herbal medicine, is valued for its ability to enhance human resistance to stress or fatigue, and promote longevity (Spasov et al., 2000; Kurkin and Zapesochnaya, 1986; Tolonen et al., 2003a). Golden root phytochemical extracts are the source of important commercial preparations widely used throughout Europe, Asia, and more recently in the USA, with biological activities including antiallergenic and anti-inflammatory effects, enhanced mental alertness, and a variety of therapeutic applications (Tolonen et al., 2003a). While phenylethanoid derivatives including salidroside (**3**) (rhodioloside) (Fig. 1) were previously used exclusively to standardize medicinal preparations of *R. rosea* extracts, it is now believed that a variety of co-occurring phytochemical constituents in the plant (including the phenylpropanoids [e.g. rosavins] and possibly terpenoids and flavonoids) may be responsible for its unique pharmacological activity (Brown et al., 2002). The phytochemical constituents in *Rhodiola* are species-dependent, and the predominant species screened in efficacy studies has been *R. rosea*, although salidroside (**3**) production in other species including *R. sachalinensis*, *R. kirilowii*, and *R. crenulata* has also been reported (Kurkin and Zapesochnaya, 1986; Wu et al., 2003).

Two central Asian *Rhodiola* genotypes (*R. heterodonta* and *R. semenovii*), Crassulaceae family, have similar rich

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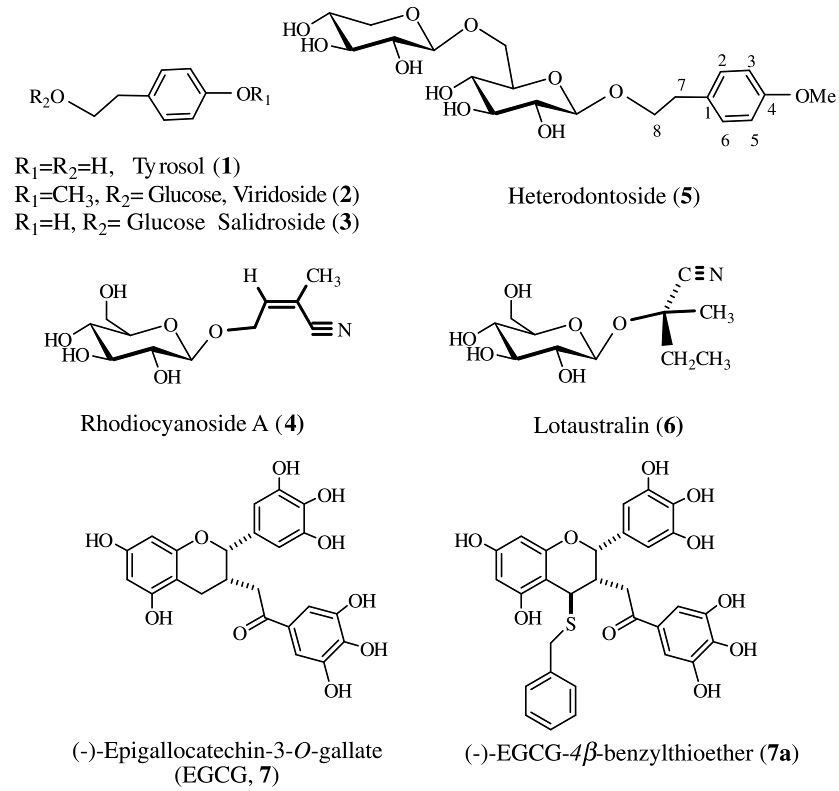

Fig. 1. Isolated and characterized phenolic and cyanogenic glycosides **1**–**6** and proanthocyanidin basic unit **7** and its benzylthioether adduct (**7a**) from the three *Rhodiola* species; *R. heterodonta*, *R. semenovii*, and *R. rosea*.

ethnobotanical histories and are locally valued as adaptogens, but have not been well investigated outside of the former Soviet Union. *R. heterodonta*, indigenous to Uzbekistan, has been found to contain salidroside (**3**) (rhodioloside) in common with golden root, and its extract is included, along with extracts of other *Rhodiola* species, in a medicinal preparation (carpediol) used to treat depression (Krasnov et al., 1976; Wikman and Panossian, 2003). *R. semenovii*, indigenous to Kyrgyzstan and locally valued for endurance-enhancing and anti-hypoxic properties, contains dimeric and oligomeric proanthocyanidins (Kuliev et al., 2004; Matamarova et al., 1999) which have been linked to the hypolipidemic, hypocholesteremic, and anti-inflammatory properties of extracts from this plant. *R. semenovii* was reclassified by some Russian authors as a separate genus (*Clementsia semenovii*), because it did not contain detectable levels of tyrosol (**1**), salidroside (**2**), and herbacetin characteristic of other members of *Rhodiola* (Kurkin et al., 1986).

In previous studies, complete phytochemical characterization of, and cross-comparison between, various species has been complicated by the intermittent use of dried, powdered and/or pulverized plant preparations for analysis. Although the natural isomeric forms, functional groups, and bioactivity of many phytochemical components may be altered during extraction and processing, in many cases the methods used to prepare herbal extracts/dried preparations are unknown or vary widely between processors. The objectives of this study were to compare the phytochemical constituents of the two central Asian *Rhodiola* species (*R. heterodonta* and *R. semenovii*) to the well-characterized golden root (*R. rosea*), using freshly harvested live rhizomes and standardized reproducible extraction and separation methods, in order to examine the inherent constituents potentially responsible for the above mentioned metabolic-enhancing properties. All three species were characterized in terms of phenylethanoid and/or cyanogenic glycosides as well as proanthocyanidin content.

2. Results and discussion

2.1. Identification of phytochemicals in Rhodiola species

Two distinct groups of compounds, which have recognized pharmacological activities were isolated and identified from the three *Rhodiola* species. The first group included phenolic and/or cyanogenic glycosides with anti-allergy, anti-inflammatory, anti-anoxia, anti-fatigue, hepatoprotective, and cognitive-enhancing properties (Brown et al., 2002; Darbinyan et al., 2000; Diaz-Lanza et al., 2001). The second group was proanthocyanidins, which were noted for significant bioactivities including anti-oxidant, anti-cancer, anti-inflammatory, anti-allergic, anti-mutation, anti-aging and improving liver function

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