

Volatile aroma compounds of flowering stems and rosette leaves of *Sideritis raeseri*, Headspace GC/FID/MS profile

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Introduction

Sideritis raeseri Boiss. & Heldr. is endemic to the Balkan Peninsula and is reported to grow in Greece, R.N. Macedonia and Albania (Obon de Castro and Rivera - Núñez, 1994). Mountain tea is a traditional beverage in the Balkan countries, prepared as a refreshing herbal tea. Aerial parts of this plant are widely utilized in folk medicine in the form of a decoction or infusion (Karapandzova et al., 2013; Romanucci et al., 2017). The specific and particular aroma is maybe the most important reason for the wide use of the flowering stems of *S. raeseri* by the Balkan peoples. Rosette leaves traditionally is not used (Qazimi et al., 2014). There are not data about the volatile aroma compounds in the dried rosette leaves of *S. raeseri*. To analyze these compounds a refined method of headspace sampling hyphenated with GC/FID/MS analysis can be utilized (Watson, 2005).

The aim of this work was the determination of the volatile aroma compounds in the dried flowering stems and rosette leaves of spontaneous *S. raeseri* using a headspace (HS) method with GC/FID/MS.

Materials and methods

Plant material: The flowering stems (S-f) and rosette leaves (S-r) of *Sideritis raeseri* were collected in 3 different localities from National Park Galichica in R. N. Macedonia (Kazani, Krstec and Vojtino). The plant material was air dried, packed in paper bags and kept in a dark and cold place until analysis.

Analyses of aroma compounds:

GC and GC-MS analyses: 0.3 g of dried flowering stems ((homogenized samples from flower, leaf and stem) (S-f) and rosette leaves (S-r) was put in sealed vials, warmed for 5 minutes and the gas phase (highly volatile compounds) was investigated on Agilent 7890A Gas Chromatography system equipped with flame ionization detector (FID) and Agilent 5975C Mass Quadrupole detector as well as capillary flow technology which enable simultaneous analysis of the sample on both detectors. HP-5ms (30 m x 0.25 mm, film thickness 0.25 µm) capillary column was used. Operating

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conditions were as follows: oven temperature 60°C, 20°C/min to 280°C; helium as carrier gas at a flow rate of 1 mL/min; injector temperature 260°C and FID temperature 270°C. 1000 µL of gas phase was injected at split ratio 1:1. The mass spectrometry conditions were: ionization voltage 70 eV, ion source temperature 230°C, transfer line temperature 280°C and mass range from 50-500 Da. The MS was operated in scan mode.

Headspace method: Incubation temperature 80°C; incubation time 5 min; syringe temperature 85°C; agitator speed 500 rpm.

Identification of components: Identification of the components was made by comparing the mass spectra of components with those from NIST, Wiley and Adams mass libraries, by AMDIS (Automated Mass Spectral Deconvolution and Identification System) and by comparing literature and estimated Kovat's (retention) indices that were determined using a mixture of a homologous series of normal alkanes from C₉ to C₂₅ in *n*-hexane, under the same conditions. The percentage ratio of the components was computed by the normalization method of the GC/FID peak areas and average values were taken.

Results and discussion

Total of 16 individual volatile aroma compounds were identified in dried flowering stems (S-f) of *S. raeseri*, representing 91.93-92.17% of the total content. Data analysis of the chemical composition revealed three different classes of components: monoterpene hydrocarbons (MH) (6) 83.08-88.96%, oxygen containing monoterpenes (OM) (4) 2.21-4.57% and sesquiterpene hydrocarbons (SH) (6) 0.87-3.7%. The most abundant components in S-f samples were MH: β-pinene (44.35-47.32%), α-pinene (37.51-38.96%) and limonene (1.38-1.72%), followed by OM: pinocarvone (1.03-1.72%) and myrtenal (1.18-1.82%) as and sesquiterpene hydrocarbon α-copaene (0.35-1.76%).

Total of 16 individual volatile aroma compounds were identified in dried rosette leaves (S-r) of *S. raeseri*, representing 94.49-97.42% of the total content. Data analysis of the chemical

composition revealed three different classes of components: MH (5) 91.58-93.15%, OM (3) 0.03-1.04% and SH (8) 1.31-3.93%. The prevailing components in all S-r samples were MH: β-pinene (48.96-56.17%), α-pinene (33.06-38.82%) and limonene (2.45-3.93%), followed by SH: α-copaene (0.68-1.75%) and trans-caryophyllene (0.52-1.23%).

Conclusion

Rosette leaves of *S. raeseri* exhibit very similar volatile aroma compounds profile with the flowering stems, comprising β-pinene, α-pinene, limonene and α-copaene as predominate components and accordingly can be consider as an additional plant material source of this aromatic plant. For complete assessment additional phytochemical analysis are require.

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