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Chemical variability in volatile composition between several Italian accessions of *Siler montanum* (*S. montanum* subsp. *montanum* and *S. montanum* subsp. *siculum*)

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ABSTRACT

Laserpitium siler, currently recognized as *Siler montanum*, is a polymorphic species belonging to the Apiaceae family and distributed in mountains of Southern Europe. In the present work we have analysed five accessions from Italy (Piemonte, Valle d'Aosta and Abruzzo) belonging to *S. montanum* subsp. *montanum* and subsp. *siculum* for the essential oil composition with the aim to find correlations between chemical data and taxonomic relationships. Results, obtained by gas chromatography-mass spectrometry (GC-MS), showed a significant variability, with the subsp. *siculum* characterized by one chemotype (sabinene/perilla aldehyde/chamazulene), and the subsp. *montanum* belonging to three different chemotypes (I (*E*)-anethole, II sabinene, III limonene). Principal component analysis (PCA) was used to identify the chemical differences among the five accessions according to geographical origin and subspecies.

1. Introduction

Laserpitium siler L. sensu lato (Apiaceae), also known with the common name of 'Sermontain', encompasses perennial herbs up to 1.8 m tall with stout, glabrous stems, 2–4 pinnate leaves provided with elliptic to lanceolate leaflets, and white to pink flowers gathered in large umbels with 20–40 (50) rays. Fruits are schizocarps 6–12 mm long, brownish, elliptic and aromatic. Root emits a strong odour (Reduron, 2007). The species grows on rocky arid slopes and arid meadows, in a partial shade, and it is distributed in mountains of Southern Europe and Latvia, from Spain to Anatolia and Caucasus (Hand, 2011). *Laserpitium siler* has been used in the traditional medicine, to make liqueurs and as seasoning. Its main secondary metabolites, obtained from all organs, are reported to be flavonoids, phenylpropanoids, essential oil, sesquiterpene lactones and sterols (Reduron, 2007).

Laserpitium siler is reported to be highly variable, especially in Italy, for the following characters: a) plant size; b) hairiness on leaves; c) length-width leaflet ratio; d) shape of schizocarps and width of wings (Reduron, 2007).

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A recent molecular study (Banasiak et al., 2016) reconstructed the phylogeny of all the genera belonging to trib. Scandiceae Spreng. subtrib. Daucinae Dumort., showing that the genus *Laserpitium* L. is polyphyletic. These authors split *Laserpitium* s.l. into 5 genera: *Laserpitium* L., *Ekimia* H.Duman & M.F.Watson, *Laser* Borkh. Ex G.Gaertn., B.Mey. & Scherb., *Siler* Mill., *Silphiodaucus* (Koso-Pol.) Spalik, Wojew., Banasiak, Piwczyński & Reduron, and *Thapsia* L. In this regard, *Laserpitium siler* is transferred by Banasiak et al. (2016) into the genus *Siler* as *S. montanum* Crantz. Recently, Iamonico et al. (2016) proposed two new combinations within *S. montanun* concerning the Italian flora: *S. montanum* Crantz subsp. *siculum* (Spreng.) Iamonico, Bartolucci & F.Conti, endemic to central-southern Italy (Peruzzi et al., 2014, 2015) and *S. montanum* Crantz subsp. *garganicum* (Ten.) Iamonico, Bartolucci & F.Conti, actually confirmed only to Gargano.

Main differences between *S. montanum* subsp. *montanum* and *S. montanum* subsp. *siculum* were reported by Fiori (1925) and currently confirmed by us with slight modifications. *S. montanum* subsp. *montanum* has leaves 30–60 mm long, with entire cartilagineous margin and umbels with 30–60 rays; *S. montanum* subsp. *siculum* has shorter leaves (10–25 mm), with toothed cartilagineous margin and umbels with 10–30 rays.

In order to understand better the variation pattern of the species in Italy we herein reported the chemical analysis of essential oils obtained from five accessions of *S. montanum* belonging to subsp. *siculum* and subsp. *montanum* by gas chromatography coupled with mass spectrometric detection (GC-MS).

2. Material and methods

2.1. Plant material

Flowering aerial parts of *Siler montanum* subsp. *montanum* and *S. montanum* subsp. *siculum* were collected in different localities of Abruzzo, Piemonte and Valle d'Aosta, Italy, in July 2014 (Table 1). Botanical identification was performed according to Santangelo et al. (2002) and the voucher specimens were deposited in APP (acronym according to Thiers, 2016). After collection, the plant material was dried in the shadow at room temperature for one week.

2.2. Isolation of essential oils

The dried aerial parts (35–158 g) were reduced into small pieces, then inserted in 6 L-flasks filled with 2–3 L of deionized water and subjected to hydrodistillation using a Clevenger-type apparatus for 4 h. After distillation the oil samples were dehydrated using anhydrous sodium sulfate and stored at −20 °C in amber-glass vials sealed with teflon-coated septa and aluminium caps before chemical analyses. The oil yields, expressed in percentages, were determined on a dry weight basis (w/w).

2.3. Chemicals

Analytical *n*-nonane, α-pinene, camphene, β-pinene, myrcene, α-phellandrene, *n*-octanal, δ-3-carene, α-terpinene, *p*-cymene, limonene, γ-terpinene, terpinolene, linalool, *cis*-thujone, *trans*-thujone, *trans*-pinocarveol, terpinen-4-ol, α-terpineol, myrtenal, myrtenol, verbenone, *trans*-carveol, carvone, (*E*)-anethole, carvacrol, eugenol, α-copaene, (*E*)-caryophyllene, α-humulene, (*E*)-β-farnesene, (*E*)-β-ionone, caryophyllene oxide, α-bisabolol, *n*-hexadecanoic acid were purchased from Sigma-Aldrich (Milan, Italy) and used for peak identification. For retention index determination, a mix of hydrocarbons ranging from octane (C_8) to triacontane (C_{30}) (Supelco, Bellefonte, CA, USA) was used and analysed at the same conditions reported below. Analytical grade *n*-hexane solvent was purchased from Carlo Erba (Milan, Italy); it was successively distilled by a Vigreux column before use.

Table 1
Main information on *Siler montanum* samples investigated for essential oil composition.

Sample	Subspecies	Date of collection	Site (toponym, province)	Region	Habitat	GPS coordinates	Altitude (m a.s.l.)	Voucher specimen[a]
1	*Siculum*	24.07.2014	Santa Colomba, Teramo	Abruzzo	Rocky slopes	N 42°28′21″ E 13°40′14″	1620	APP 57147
2	*Siculum*	25.07.2014	Vado di Corno, L'Aquila	Abruzzo	Rocky slopes	N 42°27′11.3″ E 13°35′44.3″	1938	APP 57148
3	*Montanum*	12.07.2014	Crissolo, Cuneo	Piemonte	Grassy slopes	N 44°42′08.5″ E 7°08′08.1″	1535–1545	APP 55324
4	*Montanum*	13.07.2014	Valpelline, Bionaz	Valle d'Aosta	Rocky slopes	N 45°53′59.1″ E 7°29′05.2″	2000	APP 57149
5	*Montanum*	13.07.2014	Val di Rhêmes, Aosta	Valle d'Aosta	Rocky slopes	N 45°32′28.2″ E 7°05′58.07″	1900–2000	APP 57150

[a] APP (*Herbarium Apenninicum*), Centro Ricerche Floristiche dell'Appennino, Barisciano, L'Aquila, Italy.