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Chemical characterization of the essential oil compositions from Iranian populations of *Hypericum perforatum* L.

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ABSTRACT

Hypericum perforatum L. (St. Johns' wort) is the most commercially important species of the genus *Hypericum* and contains a wide range of components including naphthodianthrones, phloroglucinols, tannins, xanthones, phenolic acids and essential oil. In the present study, for the first time the variation of the essential oil compositions among 10 wild populations of *H. perforatum* growing in Iran was assessed. According to the GC-FID and GC–MS analyses, a total of forty-six components were identified in 10 *H. perforatum* populations with relatively high variation in their composition. Among chemicals, 2,6-dimethyl-heptane (6.25–36.07%), α-pinene (5.56–26.03%), δ-cadinene (0.0–22.58%) and *γ-cadinene* (0.0–16.9%) were found as the most abundant compounds in their essential oils. The higher amounts of this components were identified in the oil of Azadshahr, Kharw, Nor and Mashhad populations, respectively. Cluster analysis grouped the studied populations into four different chemotypes: chemotype I (δ-cadinene/α-humulene), chemotype II (α-pinene), chemotype III (γ-cadinene) and chemotype IV (2,6-dimethyl-heptane/α-pinene). In fact, local abiotic factors such as moisture, temperature, topography, edaphic and/or biotic selective factors (associated fauna and flora) act on loci of the terpene-biosynthesis pathways and contribute to the emergence of different chemical oil profiles. Intraspecific variation in the chemical profile of the Iranian populations provided possibility of selection of those with specific aromas or chemical profiles accompanied with biological document, being of interest at industrial level. Obtained results provided new insight for Iranian *H. perforatum* germplasm to be used in breeding programs and development of effective conservation strategies.

1. Introduction

The genus *Hypericum* is the largest member of the Hypericaceae family including 469 species that have been classified into 36 taxonomic sections. In particular, 19 species have been found in Iran (Crockett, 2010; Robson, 2006; Lebaschi et al., 2003). *Hypericum* species have been used in the traditional medicine for centuries and many of them have great economic importance as natural sources of active compounds (Hosni et al., 2013). Among them, *H. perforatum*, commonly known as St. John's Wort, is traditionally used as a medicinal species for the treatment of mild to moderate depression as well as anxiety and insomnia (Karppinen et al., 2010; Barnes et al., 2001; Greeson et al., 2001; Anonymous, 1997). *H. perforatum* is an herbaceous perennial species and contains different biologically active components including naphthodianthrones, phloroglucinols, tannins, xanthones, flavonoids, phenolic acids and essential oil (Karppinen et al., 2010; Greeson et al., 2001). In particular, the latter were defined by European Pharmacopeia (Council of Europe, 1997) as odorous products, usually of complex composition, obtained from a botanically defined plant raw materials by steam distillation, dry distillation, or a suitable mechanical process without heating.

Nowadays, biological activity of different *Hypericum* species have been investigated and documented in number of studies (Hasanein and Shahidi, 2011; Hernandez et al., 2010; Suntar et al., 2010; Dongre et al., 2008; Wang et al., 2008; Radulovic et al., 2007; Ferraz et al., 2005; Rabanal et al., 2005; Sanchez-Mateo et al., 2002). Most of studies on *H. perforatum* are focused on the hypericin and hyperforin contents. However, some studies have to be performed on its volatile compounds in depth because of their potential appli-

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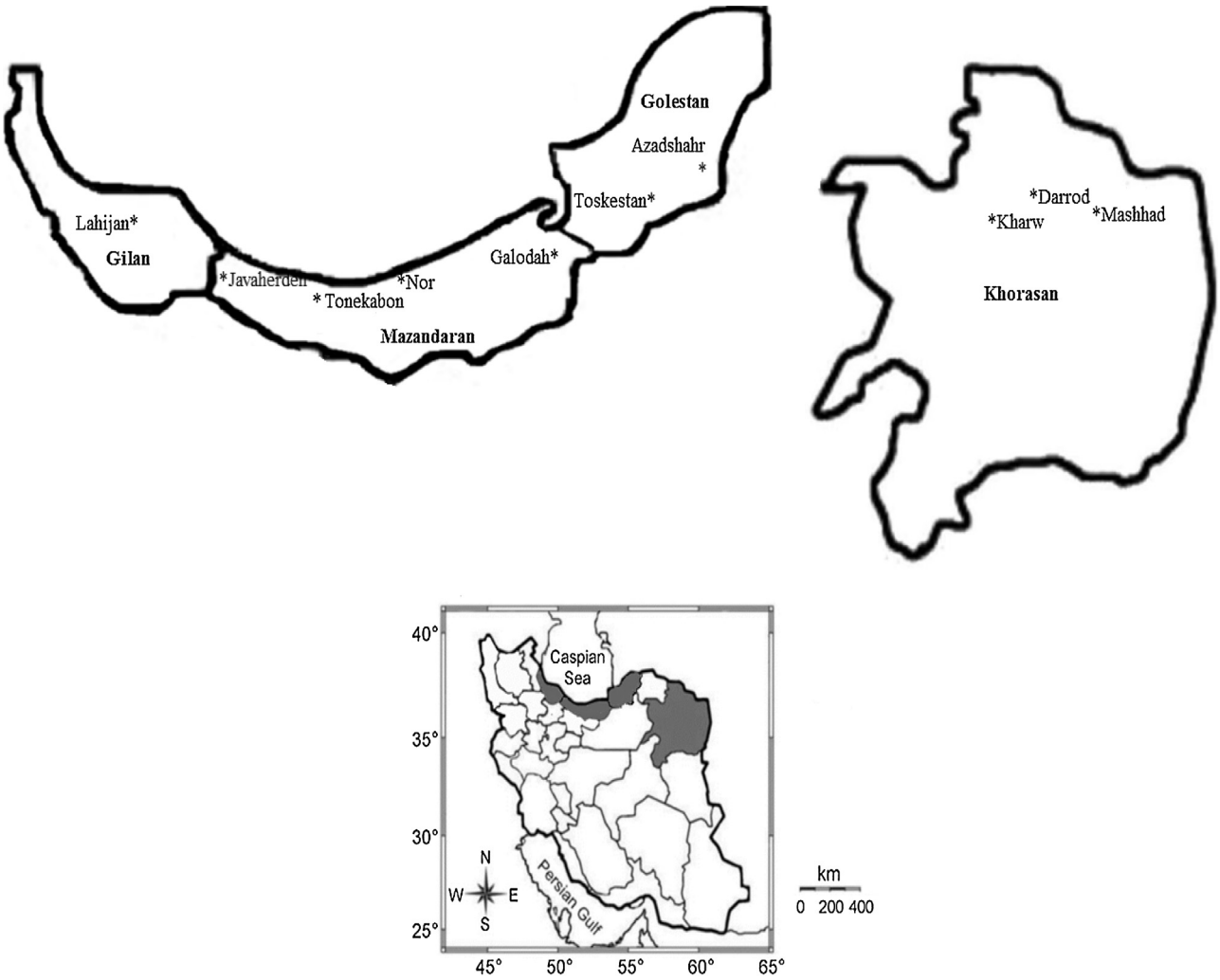

Fig. 1. Collection sites of the investigated *Hypericum perforatum* populations.

cations in cosmetology and pharmacology (Schwob et al., 2002). So far, biological activities of essential oils isolated from *H. perforatum* have been considered in some studies and their antioxidant, larvicidal, antibacterial and antifungal effects revealed (Rouis et al., 2013; Akhbari et al., 2012; Saroglou et al., 2007; Rancic et al., 2005).

Morphologically, this species is characterized by the presence of different types of secretory structures including translucent glands, black nodules and secretory canals. Essential oils are synthesized either in translucent glands or in secretory canals that may be localized in leaves, petals, sepals and pistil (Ciccarelli et al., 2001). *H. perforatum* has great versatility in medicine and its diversity in plant morphology, chemotype and essential oil composition make this plant as a continuous subject of interest (Chauhan et al., 2011).

According to the extensive phytochemical studies on *H. perforatum*, it has been reported that the essential oil constituents belong to different chemical classes with a considerable qualitative and quantitative variation in composition (Akhbari et al., 2012; Chauhan et al., 2011; Helmja et al., 2011; Pavlovic et al., 2006; Baser et al., 2002; Erken et al., 2001; Cakir et al., 1997). This variability could be related to the effect of variables such as genetic factors, developmental stages, types of plant materials, methods of extraction, environmental conditions, etc.

Although, there are many comparative studies on the volatile constituents of *H. perforatum* from different Countries (Bertoli et al., 2011; Crockett, 2010; Radusiene et al., 2005; Schwob et al., 2002) to the best of our knowledge this is the first comprehensive work on Iranian populations. Therefore, the present study was conducted to characterize the essential oil compositions of ten St. Johns' wort populations collected from different bioclimatic and geographical zones of Iran. Cluster analysis (CA) was used to characterize the samples according to the geographical origin. The presented work is part of our ongoing research programs on *H. perforatum*, aimed at detecting interesting genotypes for industrial use and conservation management (Morshedloo et al., 2015).

2. Materials and methods

2.1. Plant material

In this study, ten wild populations of St. John's wort were considered and their aerial parts collected at the flowering stage in August 2011 from different parts of Iran according to the published data (Rechinger, 1987) and our knowledge on distribution of the species. The botanist of the University of Tehran (Dr. Vahideh Nazeri) performed the botanical identification. Origins and geographical characteristics of studied populations are presented in Fig 1. and Table 1. Voucher specimens were deposited at the Herbarium of Department of Horticulture, Faculty of Agricultural Sciences and Engineering, University of Tehran, under the voucher codes reported in Table 1.