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Sumac (*Rhus coriaria* L.) fruit: Essential oil variability in Iranian populations

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ABSTRACT

Sumac (*Rhus coriaria* L.), recognized in Iran and other areas of the Middle East as a very popular flavoring spice, contains a wide range of medicinally active components including organic acids, phenolic acids, flavonoids, anthocyanins, hydrolyzable tannins and terpenoids. In the present study, for the first time the variation of the essential oil compositions in *R. coriaria* fruits, collected from fourteen different locations in Iran, was assessed. A significant variability in the essential oil content was observed among the investigated populations (ranging from 0.04 to 0.19% (v/w)). GC-FID and GC–MS analyses of the essential oils identified a total of fifty-seven components. (*E*)-Caryophyllene (5.9–50.3%), *n*-nonanal (1.8–23.3%), cembrene (1.9–21.7%), α-pinene (0.0–19.7%), (2*E*,4*E*)-decadienal (2.4–16.5%) and nonanoic acid (0.0–15.8%) were identified as the main constituents of the essential oils, depending on the populations. The highest amounts of the mentioned components were identified in the essential oil of Tovrivar, Torbat jam, Qom, Kashmar, Torbat jam and Yazd populations, respectively. According to principal component (PCA) and cluster analyses (CA) the studied populations grouped into five different chemotypes: *i.e.*, chemotype I ((*E*)-caryophyllene), chemotype II ((*E*)-caryophyllene/α-pinene), chemotype III ((*E*)-caryophyllene/cembrene), chemotype IV (nonanoic acid/cembrene), chemotype V (*n*-nonanal/(2E,4E)-decadienal). Such variability in essential oil compositions of Iranian sumac provides possibility to select populations with specific aroma profiles for domestication, breeding and industrial applications and suggests the effective *in situ* and *ex situ* conservation strategies for all populations and chemotypes of *R. coriaria*.

1. Introduction

The genus *Rhus* L. belongs to the Anacardiaceae family and comprises over 200 species throughout the world (Giovanelli et al., 2017; Mozaffarian, 2013; Peter, 2012). Commonly known as sumac, *Rhus coriaria* L. is widely used throughout the Middle Eastern countries such as Iran as a very popular spice in food production, to give sour lemon taste to various foods such as rice, vegetable, meat dishes and stews (Peter, 2012). *R. coriaria*, the only species of the *Rhus* genus occurring in Iran, is a large shrub or small tree (1–3 m high), with pinnately compound leaves, greenish-white flowers in dense panicles and brown to red fruits, from which the spice is derived (Mozaffarian, 2013; Peter, 2012; Shabbir, 2012). The plant has been used for centuries in Middle East and Iranian traditional medicine to treat various ailments such as dysentery, diarrhea, hemorrhoids and gout and also frequently used for wound healing and reduction of blood sugar, cholesterol and uric acid levels (Candan, 2003; Mozaffarian, 2013; Rayne and Mazza, 2007; Shabbir, 2012). Previous studies have demonstrated that *R. coriaria* has important biological effects, including antimicrobial, antifungal, antiviral (Rayne and Mazza, 2007), antioxidant (Bozan et al., 2003), anti-inflammatory (Panico et al., 2009), hepatoprotective (Pourahmad et al., 2010), xanthine oxidase inhibition (Candan, 2003), hypoglycemic (Peter, 2012; Pourahmad et al., 2010) and cardiovascular protective activities (Beretta et al., 2009). Sumac fruits have a great economic importance as a natural source of bioactive compounds and its consumption has been increasing around the world (Abu-Reidah et al., 2014; Kizil and Turk, 2010; Shabbir, 2012).

Previous works have reported *R. coriaria* to contain a wide range of biologically active components including hydrolysable tannins, anthocyanins, various organic acids such as malic and citric acids (Kossah et al., 2010; Shabbir, 2012), fatty acids, vitamins, flavonoids and terpenoid derivates (Abu-Reidah et al., 2014). Among the latter, volatile

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terpenes constituting the essential oils are often extracted by hydrodistillation or a suitable mechanical process resulting in the so-called essential oil that is rich in monoterpenes, and/or sesquiterpenes (Morshedloo et al., 2017a; Morshedloo et al., 2015). According to the previous phytochemical studies on the essential oil composition of sumac, different chemotypes with a considerable qualitative and quantitative variation in constituents have been reported from different geographic regions (Bahar and Altug, 2009; Brunke et al., 1993; Gharaei et al., 2013; Giovanelli et al., 2017; Kossah et al., 2009; Kurucu et al., 1993). Previous works reported that the variability in essential oil composition could be due to the geographical distribution, analytical conditions, genetic factors, harvesting time, environmental conditions, etc. (Giovanelli et al., 2017; Morshedloo et al., 2015). Over 169 terpenic and non terpenic compounds have been reported in the essential oil profiles of Sicilian (Italy) sumac plants (Giovanelli et al., 2017). The marker compounds reported are the non terpenic compounds such as nonanal and *p*-anisaldehyde (Giovanelli et al., 2017; Kurucu et al., 1993), the sesquiterpene hydrocarbon (*E*)-caryophyllene (Brunke et al., 1993; Gharaei et al., 2013), and the diterpene cembrene (Gharaei et al., 2013; Giovanelli et al., 2017).

To the best of our knowledge this is the first comprehensive study on the essential oil composition of Iranian wild populations of *R. coriaria*. The aim of this investigation was to analyse the fruit volatile chemical composition of fourteen Iranian sumac populations collected from different bioclimatic and geographical zones in order to identify those chemotypes for industrial use, domestication and breeding programs and development of effective conservation management.

2. Materials and methods

2.1. Plant material

In the present study, a total of fourteen wild populations of sumac (*R. coriaria*) were investigated across nine provinces of Iran. Identification of samples was performed by Valiollah Mozaffarian (botanist from Research Institute of Forests and Rangelands, Tehran, Iran). For each population the fruits of nine individuals were collected and each three of them were bulked together. The fruits were collected according to nested method (Acquaah, 2009) in the phase of the whole ripening, from various ecological environments, in October 2016. Geographical origin and climatic features of studied populations are presented in Table 1.

2.2. Essential oil isolation

The essential oil of each population (100 g of fruits in three replications) was obtained by hydrodistillation in a Clevenger-type apparatus for 3 h (British Pharmacopoeia, 1993). As the plant is poor in essential oil, in each sample *n*-hexane was used to recover the essential oil. Thereafter, the solvent was removed under a nitrogen flow and the essential oils were dried using Na_2SO_4, then stored in dark vials sealed with teflon-faced septa (Supelco, Bellefonte, CA, USA) and kept at 4 °C until use. The essential oil content was reported as relative percentage (%, v/w).

2.3. GC-FID analysis

The GC analyses was performed with an Agilent technology apparatus (Agilent 7990B, USA), coupled to a flame ionization detector (FID) and a VF-5MS capillary column (30 m length, 0.25 mm i.d., 0.50 µm film thickness). The oven temperature was programmed for 5 min at 60 °C, and rinsing from 60 to 240 °C at 3 °C/min, and then held isothermal for 10 min at 240 °C; injector temperature 230 °C, detector temperature 240 °C, carrier gas, He (flow rate of 1 mL/min); split ratio 1:20; injection volume, 1 µL. Essential oils were diluted to 1: 100 in *n*-hexane.

2.4. GC–MS analysis

GC–MS Analysis was performed on an Agilent 7990 B gas chromatograph coupled to a 5977A mass spectrometer and a HP-5 MS capillary column (30 m, 0.25 mm i.d., 0.1 µm film thickness; J & W Scientific, Folsom). The oven temperature program was the same as described for GC-FID analysis. Injector and transfer line temperatures, 260 °C; carrier gas, He (flow rate of 1 mL/min); split ratio 1:24; acquisition mass range 40–400 *m/z*; ionization voltage, 70 eV.

2.5. Identification and quantification of the essential oil components

A mixture of *n*-alkanes (C_8–C_{40}; Sigma–Aldrich, USA) was injected using the same temperature programmed chromatographic conditions reported above to calculate the Arithmetic Retention Index (AI) of peaks in the chromatogram. The essential oil constituents were analysed using MSD ChemStation software and NIST Mass Spectral Search Program (NIST 08, 2008). Major constituents of the oils were identified

Table 1
Origins and geographical characteristics of studied *Rhus coriaria* populations.

Number	Area of sampling collection	Populations	Longitude (E)	Latitude (N)	Altitude (m)	Mean Annual Temperature (°C)	Mean Annual rainfall (mm)	Habitat
1	Khorasan province – Gonabad	Gonabad	58°33′	34° 08′	1990	137	17.5	Mountain-arid
2	Khorasan province – Torbat jam	Torbat jam	60°26′	35°12′	1304	172	15.8	Mountain- inferior semiarid.
3	Khorasan province – Kashmar	Kashmar	58°2′	35°28′	1639	197	17.8	Mountain-inferior semiarid
4	Khorasan province-Neyshaboor-Kharw	Kharw	59°03′	36°10′	1550	260	13.4	Mountain-inferior semiarid
5	Tehran province-Cann	Tehran	51°15′	35°46′	1376	420	15.7	Mountain-semiarid
6	Qom province-Qom	Qom	50 ° 59′	34°14′	2042	149	18.2	Mountain-arid
7	East Azarbaijan province-Maragheh	Maragheh	46°19′	37°31′	1839	310	13.2	Mountain-semiarid
8	East Azarbaijan province-Arasbaran	Arasbaran	47°02′	38°52′	1078	450	12.4	Mountain- semiarid
9	Kurdestan province-Tovrivar	Tovrivar	46°48′	35°10′	1627	440	13.6	Mountain- semiarid
10	Kurdestan province-Paigelan	Pagelan	43°35′	35°08′	1760	449	13.2	Mountain- semiarid
11	Kermanshah province-Paveh	Paveh	46°15′	35°11′	1450	520	12.8	Mountain-Temperate
12	Kohgiluyeh and Boyer-Ahmad province- Yasuj	Yasuj	51°28′	30°50′	2177	700	13.3	Mountain-Cold temperate
13	Yazd province-Menshad	Yazd	54°25′	31°58′	2295	59	19.2	Mountain-arid
14	Kerman province-Golbaf	Golbaf	57°43′	29°52′	1727	148	15.9	Mountain-arid