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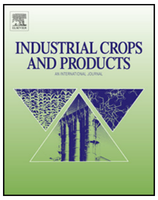

Aroma profile and essential oil composition of *Rhus coriaria* fruits from four Sicilian sites of collection

Silvia Giovanelli[a], Giulia Giusti[a], Pier Luigi Cioni[a], Pietro Minissale[b], Daniela Ciccarelli[c], Luisa Pistelli[a,d,*]

[a] *Dipartimento di Farmacia, Università di Pisa, via Bonanno 6 656126 Pisa, Italy*
[b] *Dipartimento di Scienze Biologiche Geologiche e Ambientali, Università di Catania, Via A. Longo 19, Catania 95125, Italy*
[c] *Dipartimento di Biologia, Università di Pisa, Via Luca Ghini 5, 56126 Pisa, Italy*
[d] *Centro Interdipartimentale di Ricerca "Nutraceutica e Alimentazione per la Salute University of Pisa, Via del Borghetto 80, 56124 Pisa, Italy*

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ABSTRACT

The volatile fractions and essential oils from *Rhus coriaria* fruits collected in four locations in Sicily (Italy) were characterized by GC–FID and GC–MS analysis. Monoterpenes were identified as the main class of constituents in volatiles spontaneously emitted by sumac fruits collected in two of the four sites (42.1–59.9% in 'CNS' and 'CIN' respectively), while non terpenic compounds predominated in the other two (46.1–52.8% in 'MR' and 'CG', respectively). The EO composition were characterized by high amount of non terpenic compounds (from 27.5 to 55.1%), followed by sesquiterpenes and diterpenes. *p*-anisaldehyde was the main constituent both in volatiles emitted by 'CG' sample and in its essential oil (28.4 and 20.8%, respectively). The comparison between the EOs obtained from the Sicilian samples differed from the EO obtained from sumac fruits purchased on the Jordanian market, even though a similar composition were evidenced with Turkish samples reported in the literature.

1. Introduction

Rhus is a genus included in Anacardiaceae family and consists of about 200 species spread in the temperate and subtropical areas of the world. (http://www.theplantlist.org/browse/A/Anacardiaceae/Rhus/).

Four species are present in Italy (Pignatti, 1982): *R. tripartita* (Ucria) Grande, *R. pentaphylla* (Jacq.) Desf. (South-East of Sicily), *R. typhina* L. and *R. coriaria* L. Three of them are typical of Sicily island, while *R. typhina* is growing in Alpi mountains and in the North-East regions of Italy. *Rhus coriaria* was one of the most important cultivation of Sicily during the Nineteenth century for the extraction of tannin (Inzenga 1874). In the island it is a taxon of probable ancient introduction, as supposed by Inzenga (1874). Recently Conti et al. (2005) treats this species as alien naturalized taxon among the flora of Italy, but its story would require further investigations. This species is commonly known as Sumac, because the name is originated from 'sumaga', meaning red in Syriac language (Shabbir, 2012). In Italy it is known as "Sommacco siciliano". It is a shrub or small tree 1–3 m high, with leaves imparipinnate (with 9–15 leaflets). Inflorescence is a compact and erect panicle. The flowers are small and greenish white coloured; the fruit is 1-seeded drupe hirsute, reddish and dark red when ripe (Shabbir, 2012). *Rhus coriaria* is used for its economical importance in the leather (for its high tannin content), pharmacy and food industries. It is also cultivated as an ornamental tree.

Rhus coriaria L. is a very important ingredient in Middle Eastern cuisine from Jordan to Egypt where it is used as spice, to give sour lemon taste to grilled meats and stews, but in rice and vegetable dishes too. This plant is used in traditional medicine of Jordan for sweating and cholesterol reduction and in the treatment of diarrhoea. Other reports indicated that Sumac showed antibacterial (Fazeli et al., 2007; Adwan et al., 2009; Iauk et al., 1998; Nasar-Abbas and Halkman, 2004) and hypoglycemic activities (Shabbir, 2012), even though the antioxidant property has been investigated more recently (Kosar et al., 2007; Aliakbarlu et al., 2013; Nasar-Abbas and Halkman, 2004) due to the presence of tannin fractions, both in leaves and fruits. According to its health promoting prop-

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Abbreviations: HPLC-DAD/QTOF-MS, high performance liquid chromatography coupled with electrospray ionization quadrupole time-of-flight tandem mass spectrometry; HS-SPME, headspace–solid phase microextraction; GC–EIMS, gas chromatography with electron impact mass spectrometry.

[*] Corresponding author at: Dipartimento di Farmacia, Università di Pisa, via Bonanno 6, 56126 Pisa, Italy.

E-mail addresses: silvia.giovanelli84@gmail.com (S. Giovanelli), giuliako88@hotmail.it (G. Giusti), pierluigi.cioni@libero.it (P.L. Cioni), p.minissale@unict.it (P. Minissale), daniela.ciccarelli@unipi.it (D. Ciccarelli), luisa.pistelli@unipi.it (L. Pistelli).

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erties, Sumac extracts of fruit epicarp have been studied to identify bioactive constituents by HPLC–DAD/QTOF–MS analysis. More than 200 compounds were identified as organic acids, phenolic acids and derivate flavonoids and hydrolysable tannins together with anthocianins, terpenoid derivates and others (Abu-Reidah et al., 2015). Ripe fruits of *R. coriaria* are rich in vitamins, aminoacids, minerals, and malic acid (25%) responsible for the acidity of fruits (Kossah et al., 2009; Mavlyanov et al., 1997).

R. coriaria is not an aromatic plant, even though cut stems give a characteristic flavour in the closed environment for a few days. A few reports are present in the literature about the aroma profile of this plant collected in different regions of Turkey (Kurucu et al., 1993; Bahar and Altug, 2009) and obtained by hydrodistillation. These authors cited that the great variability observed in the essential oil composition of these samples were due to the analytical conditions, climatic effects, geographical area and harvesting time. However the monoterpene hydrocarbons (MH) were present as main constituents in both samples (limonene (9.4%), nonanal (10.7–13.1%) and (*Z*)-2-decenal (9.9–42.3%), together with cembrene (6.3%)).

The aim of this investigation was to analyse the composition of volatile oils of fruits of *R. coriaria* wild plants collected in four different sites of Sicily, the typical region of Italy where this plant was cultivated in the ancient time (Lojacono Pojero, 1891) (for this reason it is called 'Sommacco siciliano'), even though widespread in almost all Italian regions with the exception of North-West. To the best of our knowledge no other study is present in the literature covering the HS- SPME analysis of the spontaneous emission profile of these fruits

2. Material and methods

2.1. Plant material

Fruits of *R. coriaria* L. were collected in the phase of the whole ripening in four different localities in Sicily: Monterosso Almo 'MR' and Chiaramonte Gulfi 'CG' in Ragusa district, Castronovo di Sicilia 'CNS' and Cinisi 'CIN' near Palermo. 'MR', 'CG' and 'CNS' were collected in November–December 2013, while 'CIN' in autumn 2014 All the samples were collected and identified by one of us (P. Minissale) and the localities of collection are reported in Table 1.

2.2. HS-SPME and essential oil analyses

Fruits of all samples were separated from the other plant material and used for HS-SPME and essential oil (EO) analyses.

Twenty fruits (1 g) of each sample were introduced into a 25-mL glass vial closed with aluminium foil and allowed to equilibrate for 30 min. After the equilibration time, a Supelco SPME device, coated with polydimethylsiloxane (PDMS, 100 μm), was inserted through the septum, and then the fibre was exposed to the headspace of the vial for 30 min at room temperature. Once sampling was finished, the fibre was withdrawn into the neddle and transferred to the injection port of the GC and GC–MS system. All the SPME sampling and desorption condition were identical for all the samples.

The EOs were obtained by hydrodistillation in a Clevenger apparatus for 2-h. Essential oil yields were very low (<0.01%) in all samples, so hexane was added to recover each of them.

2.3. Gas chromatography–Mass spectrometry

The essential oils were analysed with a Varian CP-3800 gas chromatograph equipped with a DB-5 capillary column (30 m × 0.25 mm; coating thickness 0.25 μm) and a Varian Saturn 2000 ion trap mass detector. Analytical conditions were set as follows: injector and transfer line temperatures, 220 °C and 240 °C, respectively; oven temperature was programmed from 60 °C to 240 °C at 3 °C/min; carrier gas was helium at 1 ml/min; injection, 0.2 μl (10% hexane solution); split ratio, 1:30. Identification of the constituents was based on both comparison of the retention times with those of authentic samples, comparing their linear retention indices relative to the series of *n*-hydrocarbons, and on computer matching against commercial (NIST 98 and ADAMS) and home-made mass spectra library built up from pure substances and components of known essential oils as well as MS literature data (Davies 1990; Adams 1995).

2.4. Statystical analysis

Two matrices–one for essential oils and another for HS-SPME–of taxa x chemical compounds (values under 1.5% were excluded) were analysed. Both matrices were square-root transformed and then subjected to the Cluster analysis (CA) using average-linkage clustering and Bray-Curtis similarity index. The same resemblance matrices were used to perform Non-metric Multidimensional scaling (NMDS), which is a technique that represents samples in a low-dimensional space by optimising the correspondence between original dissimilarities and distances in the ordination (Økland, 1996). The Spearman product-moment correlation coefficient was calculated in order to point out which variable was more correlated to the NMDS axes. All statistical analyses were performed using R 2.14.0 software (vegan package, Oksanen et al., 2012; http://www.r-project.org/).

3. Results and discussion

3.1. HS-SPME analysis

The compositions of the aroma profile of *Rhus coriaria* fruits obtained by HS-SPME from the different Sicilian populations are reported in Table 2. A total of 76.3–97.9% of compounds were identified (N 57 for 'CNS', 51 For 'CG', 61 for 'MR' and 51 for 'CIN').

The *not terpenic* compounds were abundant in the aroma of all the Sicilian samples (32.9%–52.8%), even though 'CIN' and 'CNS' showed monoterpenes as main constituents (59.9 and 42.1%, respectively). In particular 'CNS' evidenced a 36.1% of monoterpene hydrocarbons while the oxygenated monoterpenes were very low (only 6%); on the contrary 'CIN' showed the major percentage of oxygenated monoterpenes (51.7%) in comparison with monoterpene hydrocarbons (8.2%). The main constituent present in 'CNS' was α-pinene (26.0%), while fenchone (20.7%) and camphor (12.5%) were the most abundant in 'CIN'. 'MR' sample presents the lowest percentage of mononerpenes.

Aldehydic compounds and *n*-nonanal in particular were the most representative constituents with a percentage ranging from 9.8% in 'CIN' and 25.1% in 'MR'. However 'CG' sample was very rich in *p*-anisaldehyde (28.4%) and 'CIN' evidenced high percentage of decanal (11.9%).

The sesquiterpene hydrocarbon content was particularly abundant in 'MR' and 'CNS' samples, (35.0% and 13.0%, respectively), with the highest percentage of β-caryophyllene (6.8%) in 'MR' followed by δ-cadinene (4.2%) and γ-muurolene (4.1%) respectively). This class of compounds was no present in 'CIN'. The SPME profile of all the samples related to the environmental conditions of the four Sicilian sites, evidenced the highest monoterpenes percentages in 'CIN' and 'CNS', probably due to the 'Thermomediterranean subhumid' climate, in comparison with 'MR' and 'CG'. However 'CIN' and 'CNS' differed each other for the soil composition and altitude that might influence the monoterpene hydrocarbons (MH) and oxygenated monoterpene (OM) amounts in the two samples (36.1% MH in 'CNS' and 51.7% of OM in 'CIN'). The aroma profile of 'CG' and 'MR'