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Composition of the essential oil of *Daucus gingidium* L. ssp. *gingidium* ☆

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Abstract

The essential oils obtained from leaves and fruits of *Daucus gingidium* ssp. *gingidium* have been studied. The main constituents of the essential oil from the leaves were sabinene (26.8%), α-pinene (10.8%), germacrene D (6.9%) and limonene (5.7%). Sabinene (60.6%) was the main compound identified in the essential oil of the fruits, followed by α-pinene (12.2%) and 4-terpineol (5.4%). Furthermore, qualitative and quantitative considerations about differences with literature data on *Daucus carota* have been made in order to confirm the species status of *D. gingidium*.

Keywords: *Daucus gingidium* L. ssp. *gingidium*; Apiaceae; Essential oil; Leaves; Fruits; Sabinene

1. Introduction

Carrot is a plant belonging to the Apiaceae family and is grown throughout the temperate regions for its roots that are consumed raw and cooked. Carrot is reported to be endowed with medicinal properties, i.e. hypotensive, diuretic, carminative, stomachic and antilipemic (Gilani et al., 2000; Kumarasamy, Nahar, Byres, Delazar, & Sarker, 2005; Nicolle et al., 2004). In the Italian folk medicine, the leaves are used raw or in an infusion as depurative and diuretic agents (Pieroni, 2000).

In Italy, the *Daucus* genus is represented by some species living in dry and uncultivated areas and, among them, *Daucus carota* is widespread together with its many subspecies. In this group *Daucus gingidium* is quite different from all the other species. Also, *D. gingidium* is characterized by the presence of many subspecies that colonize maritime sands and cliffs (Pignatti, 1997); this author reports for this species *D. gingidium* L. ssp. *gingidium* (without authors) = *D. gingidium* ssp. *gummifer* (All.) Onno.

According to other authors (Tutin et al., 1964–1980), they should not considered as two different species, but they represent a single group showing a considerable morphological variability [*D. carota* ssp. *hispanicus* (Gouan) Thell = *D. gingidium* ssp. *gummifer* (All.) Onno].

Because of the differences observed in the fruits and leaves of the collected samples, in this study the taxonomical scheme outlined by Pignatti (1997) has been followed. Furthermore, this scheme permits to discriminate the more synanthropic continental species from the certainly wild and littoral ones.

D. gingidium ssp. *gingidium* grows along the Central-Western Mediterranean coasts; in Italy it can be found along the Western coasts from Liguria to Naples, in Sicily and in the small Tyrrhenian isles (Pignatti, 1997). It is a small herbaceous plant that grows on maritime sands and cliffs, which can also have a suffruticose habitus. No uses in the folk medicine are known for this species (Benigni, Capra, & Cattorini, 1964; Gastaldo, 1997; Negri, 1979).

Previous studies refer mainly to the different subspecies and varieties of *D. carota*. In this species, a considerable qualitative and quantitative variability has been observed. In the fruits of *D. carota* ssp. *sativus* (Benecke, Reichold, Kessel, & Schmidt, 1987) and *D. carota* (subspecies non

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reported) (Ashraf, Sandra, Saeed, & Bhatty, 1979; Hilal, ElShamy, & Haggag, 1977; Meshcheryuk, Timchuk, & Chelovskaya, 1983; Nigam & Radhakrishnan, 1963; Perineau, Ganou, & Gaset, 1991; Stahl, 1964; Talwar, Nigam, & Harida, 1963; Toulemonde, Paul, & Beauverd, 1987) the main constituents were carotol, daucol, geranyl acetate and terpinyl acetate. For *D. carota* ssp. *gummifer* high percentages of geranyl acetate have been reported (Pinilla, Alonso, & Negueruela, 1995). In the essential oil obtained from fruits, leaves and stems of *D. carota* ssp. *maximus* (Saad, ElSharkawy, & Halim, 1995), *trans*-methylisoeugenol, methyleugenol, β-asarone, shyobunone and preisocalamendiol were identified among the main constituents; in disagreement with other varieties, carotol, daucol and geranyl acetate were completely absent. Sabinene, linalool, linalyl acetate, carvone and carotol were the main compounds identified in the volatile oil of the leaves of *D. carota* ssp. *sativa* (Khanna, Sharma, & Singh, 1989). Kameoka, Sagara, and Miyazawa (1989) identified *cis*- and *trans*-asarone, β-bisabolene, asarone aldehyde, eugenol, 2-hydroxy-4-methoxyacetophenone, 3-carene and methyleugenol among the volatiles of the fruits of *D. carota* (subspecies not reported). The main components contained in the essential oil of the flowers and fruits of *D. carota* ssp. *carota* collected in Poland (Staniszewska & Kula, 2001) were α-pinene, sabinene, myrcene and limonene. Recently, Mockute and Nivinskiene (2004) reported that the essential oil of the fruits of different samples of *D. carota* ssp. *carota* collected in Lithuania contained sabinene, α-pinene and 4-terpineol as main components. They defined this species as a sabinene chemotype.

This study is part of a research project on the chemistry of food and medicinal plants from Caprione Promontory (Flamini, Cioni, Morelli, Maccioni, & Baldini, 2004; Flamini, Cioni, Morelli, Maccioni, & Tomei, 1994; Maccioni, Flamini, Cioni, & Tomei, 1992), within Montemarcello-Magra Natural Regional Park (Cardelli, DiTommaso, & Signorini, 2000) (La Spezia province, Eastern Liguria). Here, *D. gingidium* ssp. *gingidium* grows on the South-Western slope, from the sea level up to about 80 m.

This paper deals with the composition of the essential oil obtained from the leaves and the fruits of *D. gingidium* ssp. *gingidium* growing in this area. This is the first study of the essential oil obtained from this species.

2. Materials and methods

The leaves of *Daucus gingidium* ssp. *gingidium* were collected during February 2004 on a rocky slope facing South-West, on calcareous soil, near the shore, in locality Punta Corvo (La Spezia province, Italy). The fruiting umbrellas were gathered at the end of August 2004 in the same place. All the umbrellas were chosen in full ripening stage. Other species living together with *D. gingidium* ssp. *gingidium* were *Psoralea bituminosa* L., *Helichrysum italicum* (Roth) Don, *Helichrysum stoechas* (L.) Moench, *Dorycnium hirsutum* (L.) Ser. and, near to the sea, *Senecio cineraria* DC. and *Crithmum maritimum* L.

A voucher specimen of *D. gingidium* ssp. *gingidium* from this location is deposited in *Herbarium Horti Botanici Pisani* (Nuove Acquisizioni N. 6142/1).

The fresh plant material, about 150 g (about 40 individuals), was coarsely cut and separately hydrodistilled the next day in a Clevenger-type apparatus for 2 h.

GC/EIMS analyses were performed 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: injector and transfer line temperatures 220 and 240 °C, respectively; oven temperature programmed from 60 °C to 240 °C at 3 °C/min; carrier gas helium at 1 ml/min; injection of 0.2 μl (10% hexane solution); split ratio 1:30. Identification of the constituents was based on 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 library mass spectra built up from pure substances and components of known oils and MS literature data (Adams, 1995; Davies, 1990; Jennings & Shibamoto, 1980; Massada, 1976; Stenhagen, Abrahamsson, & McLafferty, 1974; Swigar & Silverstein, 1981). Moreover, the molecular weights of all the identified substances were confirmed by GC/CIMS, using MeOH as CI ionizing gas. Percentages were calculated by integration of the RIC (Reconstructed Ion Current) of the GC/MS data (scan range 35–350 u.m.a.).

3. Results and discussion

The essential oil yields were 0.04% and 1.21% (w/w) for the leaves and the fruits, respectively. Their compositions are reported in Table 1. Altogether, 100 compounds were identified in the two essential oils, accounting for 97.6% and 98.4% of the whole oils, respectively.

In the essential oil of the leaves, the monoterpene hydrocarbons accounted for 66.2% of the whole composition; in particular, 40.0%, 17.1% and 9.1% was represented by bicyclic, monocyclic and acyclic monoterpenes, in that order. Among monoterpenes, oxygenated derivatives such as alcohols (8.2%), ketones, phenols and ethers were also identified. Sesquiterpene hydrocarbons were represented by many derivatives, but their percentage (18.7%) was considerably lower than for the monoterpenes. Overall, the hydrocarbons accounted for 84.9% of the whole essential oil of the leaves. Furthermore, some non-terpene derivatives were also detected, mainly straight-chain aldehydes and alcohols. The main constituents of the essential oil of the leaves (Table 1) were sabinene (26.8%), α-pinene (10.8%), germacrene D (6.9%), limonene (5.7%) and (*Z*)-ocimene (5.0%).

The essential oil of the fruits was constituted by fewer compounds with respect to the leaves (39 versus 97). Again, monoterpene hydrocarbons (87.8%) were the most important derivatives identified, mainly because of the high per-

Table 1
Composition of the essential oils of the leaves and the fruits of *Daucus gingidium* ssp. *gingidium* from Italy

Constituents	l.r.i.[a]	Leaves	Fruits
(*E*,*Z*)-2,4-Hexadienal	841	tr[b]	–[c]
(*E*)-3-Hexen-1-ol	852	0.5[d]	–
(*E*)-2-Hexen-1-ol	862	tr	–
1-Nonene	892	tr	–
3-Nonene	898	0.1	–
Nonane	900	tr	–
Heptanal	902	0.1	–
α-Thujene	933	0.4	0.4
α-Pinene	941	10.8	12.2
Camphene	955	0.4	0.6
Thuja-2,4(10)-diene	959	tr	–
Benzaldehyde	962	tr	–
(*E*)-2-Heptenal	978	tr	–
Sabinene	979	26.8	60.6
β-Pinene	982	1.4	3.4
6-Methyl-5-hepten-2-one	987	tr	–
Myrcene	991	2.3	3.0
2,3-Dehydro-1,8-cineole	993	tr	tr
Mesitylene	996	tr	–
Octanal	1003	0.1	–
α-Phellandrene	1007	0.2	tr
3-Carene	1012	0.2	tr
(*E*,*E*)-2,4-Heptadienal	1017	tr	–
α-Terpinene	1020	1.7	1.5
p-Cymene	1028	0.4	0.2
Limonene	1032	5.7	2.1
β-Phellandrene	1034	1.0	0.3
1,8-Cineole	1035	tr	–
(*Z*)-Ocimene	1041	5.0	0.4
(*E*)-Ocimene	1051	1.8	0.1
γ-Terpinene	1063	3.8	2.4
cis-Sabinene hydrate	1070	0.4	1.2
1-Nonen-3-ol	1084	0.1	–
Terpinolene	1089	4.7	0.6
2-Nonanone	1092	tr	–
3-Nonanol	1099	0.1	–
Linalool	1101	1.2	0.6
trans-Sabinene hydrate	1102	0.4	0.6
Nonanal	1104	0.1	–
α-Thujone	1105	tr	–
1,3,8-*p*-Menthatriene	1113	tr	–
β-Thujone	1116	0.3	–
cis-*p*-Menth-2-en-1-ol	1123	0.3	0.4
Chrysanthenone	1127	0.2	–
trans-*p*-Menth-2-en-1-ol	1141	0.3	0.2
cis-Verbenol	1143	0.1	–
(*E*)-2-Nonenal	1164	0.5	–
Pinocarvone	1166	0.1	–
Borneol	1168	–	tr
Umbellulone	1173	tr	–
4-Terpineol	1179	4.8	5.4
p-Cymen-8-ol	1185	tr	–
α-Terpineol	1191	0.6	0.5
cis-Piperitol	1195	tr	–
trans-Piperitol	1207	0.1	–
β-Cyclocitral	1223	0.1	–
Methyl thymol	1235	0.3	–
Cuminaldehyde	1241	0.1	–
Geraniol	1255	0.2	–
(*E*)-2-Decenal	1263	tr	–
Isobornyl acetate	1286	0.2	0.2
Thymol	1292	0.1	–
Carvacrol	1301	tr	–
δ-Elemene	1339	0.1	–
α-Longipinene	1352	tr	–
Eugenol	1357	tr	–
cis-Carvyl acetate	1362	tr	–
α-Ylangene	1372	tr	–
α-Copaene	1377	0.2	tr
(*E*)-β-Damascenone	1381	tr	–
β-Bourbonene	1384	0.1	–
β-Cubebene	1390	0.3	0.1
β-Elemene	1391	tr	–
β-Caryophyllene	1420	2.9	0.4
Methylthymohydroquinone	1423	tr	–
β-Gurjunene	1432	0.2	tr
trans-α-Bergamotene	1439	0.1	tr
α-Humulene	1456	0.4	tr
(*E*)-β-Farnesene	1458	0.3	0.3
γ-Decalactone	1465	tr	–
Germacrene D	1482	6.9	0.2
(*Z*,*E*)-α-Farnesene	1491	0.6	–
Bicyclogermacrene	1494	0.4	–
Viridiflorene	1496	–	0.1
α-Muurolene	1499	0.1	–
(*E*,*E*)-α-Farnesene	1508	0.8	–
cis-γ-Cadinene	1511	0.1	–
δ-Cadinene	1524	0.4	0.1
β-Sesquiphellandrene	1525	0.3	tr
(*E*)-γ-Bisabolene	1533	0.3	–
Selina-3,7(11)-diene	1542	0.1	–
Elemicin	1554	–	0.1
Germacrene B	1556	4.1	–
Spathulenol	1577	0.1	–
Caryophyllene oxide	1581	0.1	–
Carotol	1596	0.1	–
(*E*)-Asarone	1679	0.2	–
epi-α-Bisabolol	1688	0.5	–
Juniper camphor	1693	tr	0.2
Tricosane	2300	tr	–
Number identified		97	39
Total identified (%)		97.6	98.4
Essential oil yield (% w/w)		0.04	1.21

[a] Linear retention indices (HP-5 column).
[b] tr < 0.1%.
[c] Not detected.
[d] Percentages.

centage of sabinene (60.6%). Monoterpene alcohols accounted for 8.9% of the essential oil, with 4-terpineol (5.4%) as the main one. Sesquiterpenes were less represented, both as number of derivatives (13) and percentage (1.2%). The main compounds identified in the essential oil of the fruits were sabinene (60.6%), α-pinene (12.2%) and 4-terpineol (5.4%).

The composition of the essential oil of the fruits of *D. gingidium* ssp. *gingidium* was very different from all the data reported for *D. carota:* no samples contained such high percentages of sabinene (60.6%); furthermore, in *D. gingidium* ssp. *gingidium,* carotol, daucol, geranyl acetate and terpinyl acetate were not identified.

Further studies on the composition of the essential oil of other populations of *D. gingidium* ssp. *gingidium,* will

permit to evaluate if these differences will be confirmed and to ascertain if it is correct to characterize this species apart from *D. carota* as affirmed by Pignatti (1997), or if it should be considered as a subspecies as reported by Tutin et al. (1964–1980).

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