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Composition of the essential oils from leafy parts of the shoots, flowers and fruits of *Eryngium amethystinum* from Amiata Mount (Tuscany, Italy) ☆

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Abstract

The essential oils obtained from the leafy parts of the shoots, inflorescences and fruits of *Eryngium amethystinum* (Apiaceae) from Italy have been studied. The essential oil from the inflorescences was characterised by methyl-derivatives of benzaldehyde (26.4%) and by some phenylpropanoids (3.0%) such as eugenol and (*E*)-methyl isoeugenol. The essential oil of leafy parts of the shoots showed a higher percentage of sesquiterpenes (31.3%) than monoterpenes (20.2%). The main differences between the two essential oils can be referred to α-pinene and germacrene D: the essential oil of the inflorescences contained much more α-pinene than the other one (25.6% vs. 11.8%), while the contrary is true for germacrene D (14.5% vs. 31.3%).

Keywords: *Eryngium amethystinum* L.; Apiaceae; Essential oil; Flowering aerial parts; Benzaldehyde methyl-derivatives; α-Pinene; Germacrene D

1. Introduction

Eryngium amethystinum L. (Apiaceae), commonly known as "calcatreppola ametistina", is widespread in Italy except for Piedmont and Sardinia, on calcareous and arid soil, from 0 to 1600 m above the sea level. Here the genus includes 12 species and three of them are common also to Corsica (Pignatti, 1982).

In folk medicine the roots are used for their diuretic and laxative properties. It is indicated for treatment of urinary ailments, edemas and acidosis; it is also useful as an aid to digestion (Valnet, 1977). In the traditional medicine of Amiata Mount the roots are employed as a diaphoretic and used against cellulite (Mazza, 2000).

Species from this genus, mainly *Eryngium foetidum*, are employed as a substitute or alternative for coriander (*Coriandrum sativum*) because of the similar aroma, as its common name (long coriander) suggests. Although widely used in dishes throughout the Caribbean, Latin America and the Far East, this spice is relatively unknown in the United States, European Union and many other parts of the world. Even if used in small quantities, its pungent unique aroma gives the characteristic flavour to the dishes in which it is incorporated. In Asia, culantro, as the plant is commonly known, is most popular in Thailand, Malaysia, and Singapore where it is regularly used with or in lieu of coriander and topped over soups, noodle dishes and curries. In Latin America, culantro is mostly associated with the cooking style of Puerto Rico, where recipes common to all Latin countries are enhanced with culantro. Equally popular is *sofrito* or *recaito*, the name given to the mixture of seasonings containing culantro and widely used in rice, stews and soups. Culantro is increasingly becoming a crop of international trade mainly to meet the demands of ethnic populations in the developed countries of the West. Large immigrant communities in London, New York and Toronto, represents a vast potential market for the herb. It is also widely used in herbal medicines and reportedly benefi-

☆ In memory of Antonio Lombardi.

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cial in the treatment of a number of ailments (Chanwitheesuk, Teerawutgulrag, & Rakariyatham, 2005; Wong, 1976). Other species of the same genus find applications both as food and officinal plants, i.e., *Eryngium billardieri* (Turan, Kordali, Zengin, Dursun, & Sezen, 2003), *Eryngium campestre* (The Local Food-Nutraceuticals Consortium, 2005) and *Eryngium maritimum* (Facciola, 1990).

Volatiles are mainly responsible for the taste of foods, so in the present paper the composition of the essential oils obtained separately from inflorescences, leafy parts of the shoots and fruits has been analysed. To the best of our knowledge, no previous studies on volatiles from *E. amethystinum* are present in the literature.

2. Materials and methods

The flowering aerial parts of *E. amethystinum* L. were collected at the end of July 2004 in locality Pergole (Amiata Mount, Tuscany, Italy), at the edges of a chestnut at 600 m above the sea level (42°53′46″N, 11°30′57″E). The leafy parts of the shoots and the inflorescences were separately hydrodistilled, the next day, in a Clevenger-like apparatus for 2 h. The fruits were gathered from the same population at the beginning of October 2004 and hydrodistilled as above described. Five replicates have been performed using plants randomly collected from the population.

The GC analyses were accomplished with a HP-5890 Series II instrument, equipped with HP-WAX and HP-5 capillary columns (30 m × 0.25 mm, 0.25 μm film thickness), working with the following temperature program: 60 °C for 10 min, ramp of 5 °C/min up to 220 °C; injector and detector temperatures 250 °C; carrier gas nitrogen (2 ml/min); detector dual FID; split ratio 1:30; injection of 0.5 μl. The identification of the components was performed, for both the columns, by comparison of their retention times with those of pure authentic samples and by mean of their linear retention indices (L.R.I.) relative to the series of *n*-hydrocarbons.

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 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 ionising gas.

3. Results and discussion

The essential oils yields were 0.18%, 0.29% and 0.20% (w/w) for the inflorescences, the leafy parts of the shoots and the fruits, respectively, and their compositions are reported in Table 1.

Seventy-four compounds were identified in the essential oils, accounting for 95.1%, 93.6% and 90.6% of the total compositions, respectively.

The essential oil from the inflorescences contained about twice as much monoterpenes as sesquiterpenes (41.5% vs. 20.3%). Hydrocarbon derivatives (58.2%) prevailed on oxygenated ones, which were produced in very small amounts (2.8% and 0.8%, respectively). This essential oil was characterised by methyl-derivatives of benzaldehyde (26.4%) and by some phenylpropanoids (3.0%) such as eugenol and (*E*)-methyl isoeugenol.

On the contrary, the essential oil of the leafy parts of the shoots showed a higher percentage of sesquiterpenes (31.3%) than monoterpenes (20.2%). Oxygenated derivatives were not detected among the monoterpenes, while they represented only 2.8% of sesquiterpenes. Furthermore, phenylpropanoids were absent, but high amounts of aromatic aldehydes (31.0%) were identified.

The essential oil of the fruits contained 57.3% of terpene derivatives (33.2% and 24.1% mono- and sesquiterpenes, respectively). Among monoterpenes, hydrocarbons were prevalent on oxygenated constituents (29.8% vs. 3.4%, respectively). The latter were mainly represented by alcohols and aldehydes. Also among sesquiterpenes, hydrocarbons were detected in higher percentages (18.0%) than oxygenated ones (6.1%). The remaining part was mainly constituted by methyl-derivatives of benzaldehyde (20%), non-terpene hydrocarbons (6.6%) and non-terpene oxygenated compounds (6.7%).

Comparing the three essential oils, monoterpenes reached the highest amounts in the inflorescences (41.5%), followed by fruits (33.2%) and the leafy aerial parts (20.2%). The fruits were the main producer of oxygenated monoterpenes (3.4%).

For sesquiterpenes, the highest percentages were detected in leafy branches (31.3%), followed by fruits (24.1%) and inflorescences (20.3%). Again, the highest values of oxygenated derivatives was found in the fruits (6.1%).

The fruits contained the least amounts of methyl-derivatives of benzaldehyde (20%, with respect to leafy branches, 31.0% and inflorescences, 26.4%). Conversely, they produced a higher percentage of aromatic hydrocarbons (6.6% vs. 1.9% and 2.9%, respectively) and non-terpene aldehydes (6.7% vs. 0.3% and 1.0%, respectively).

The principal differences in the three essential oils were related to α-pinene and germacrene D: in the oil from the flowers the former (26.6%) was about twice

Table 1
Composition[a] of the essential oils of inflorescences, leafy parts of the shoots and fruits of *Eryngium amethystinum* from Italy

Constituents	L.R.I.[b]	Flowers	Leafy parts	Fruits
(*E*)-2-Hexenal	856	–[c]	[d]	–
Heptanal	902	0.2 (0.1)	tr	1.0 (0.3)
α-Thujene	933	0.3 (0.1)	0.1 (0.0)	0.2 (0.1)
α-Pinene	941	25.6 (1.9)	11.8 (1.0)	17.0 (1.1)
Camphene	955	0.2 (0.1)	0.1 (0.0)	0.2 (0.1)
Thuja-2,4(10)-diene	959	tr	tr	tr
(*Z*)-2-Heptenal	964	–	–	tr
Benzaldehyde	968	–	–	tr
Heptanol	970	–	–	tr
Sabinene	977	1.4 (0.2)	0.6 (0.1)	0.8 (0.2)
β-Pinene	984	1.5 (0.4)	0.5 (0.2)	1.2 (0.2)
Myrcene	991	4.8 (0.6)	3.7 (0.8)	5.0 (0.7)
Mesitylene	996	2.1 (0.3)	1.3 (0.3)	4.5 (0.8)
Octanal	1003	0.7 (0.1)	0.3 (0.2)	4.9
α-Terpinene	1020	0.1 (0.0)	tr	tr
Pseudocumene	1026	0.8 (0.2)	0.6 (0.2)	2.1 (0.4)
p-Cymene	1028	tr	tr	tr
Limonene	1033	5.0 (0.9)	3.0 (0.5)	4.9 (1.0)
(*Z*)-Ocimene	1041	0.2 (0.1)	0.1 (0.0)	0.2 (0,1)
(*E*)-Ocimene	1052	0.4 (0.1)	0.3 (0.2)	0.3 (0.1)
γ-Terpinene	1063	0.2 (0.2)	tr	–
(*E*)-2-Octenal	1065	–	–	0.2 (0.1)
cis-Sabinene hydrate	1070	0.1 (0.1)	–	–
Terpinolene	1089	tr	tr	–
Linalool	1099	0.3 (0.1)	–	–
Nonanal	1104	0.1 (0.0)	–	0.2 (0.1)
α-Campholenal	1127	0.1 (0.1)	tr	1.0 (0.3)
trans-Pinocarveol	1142	–	–	0.6 (0.2)
cis-Verbenol	1144	–	–	1.0 (0.4)
(*E*)-2-Nonenal	11.65	–	–	0.4 (0.1)
Pinocarvone	1168	–	–	0.2 (0.1)
4-Terpineol	1180	1.0 (0.2)	tr	tr
α-Terpineol	1190	0.3 (0.1)	–	0.2 (0.2)
Decanal	1206	–	–	tr
Verbenone	1208	–	–	tr
trans-Carveol	1220	–	–	0.4 (0.2)
cis-Carveol	1231	–	–	tr
Carvone	1244	–	–	tr
(*E*,*Z*)-2,4-Decadienal	1293	–	–	tr
2,3,4-Trimethylbenzaldehyde	1315	4.4 (0.8)	6.3 (0.8)	3.1 (0.9)
(*E*,*E*)-2,4-Decadienal	1317	–	–	tr
2,3,6-Trimethylbenzaldehyde	1355	22.0 (1.5)	24.7 (1.4)	16.9 (1.7)
α-Copaene	1377	0.4 (0.1)	0.9 (0.3)	0.8 (0.3)
β-Bourbonene	1386	0.4 (0.2)	0.7 (0.2)	0.8 (0.2)
β-Cubebene	1390	0.2 (0.2)	0.4 (0.1)	0.3 (0.2)
b-Elemene	1392	–	–	0.2 (0.1)
Methyl-eugenol	1402	2.3 (0.3)	–	–
a-Cedrene	1411	–	–	0.1 (0.0)
β-Caryophyllene	1420	0.5 (0.1)	0.9 (0.3)	0.5 (0.2)
β-Gurjunene	1432	0.1 (0.0)	0.1 (0.0)	–
trans-α-Bergamotene	1439	–	–	tr
(*E*)-β-Farnesene	1455	0.5 (0.2)	0.1 (0.1)	3.8 (0.9)
α-Humulene	1457	0.1 (0.1)	0.1 (0.1)	–
γ-Muurolene	1479	0.1 (0.0)	0.1 (0.1)	tr
γ-Curcumene	1480	–	–	tr
Germacrene D	1482	14.5 (1.1)	31.3 (1.8)	7.6 (1.2)
Bicyclogermacrene	1494	1.0 (0.2)	1.3 (0.6)	0.5 (0.2)
(*E*)-Methyl-isoeugenol	1496	0.7 (0.2)	–	–
α-Muurolene	1499	–	–	tr
β-Bisabolene	1509	1.1 (0.4)	–	0.9 (0.3)
δ-Cadinene	1524	0.3 (0.1)	0.5 (0.2)	0.2 (0.2)
β-Sesquiphellandrene	1525	0.3 (0.1)	tr	tr
Elemol	1550	–	–	0.4 (0.2)
Germacrene B	1558	–	–	2.3 (0.6)
Spathulenol	1577	0.8 (0.2)	1.1 (0.4)	1.3 (0.4)
Caryophyllene oxide	1582	–	–	0.5 (0.3)
β-Copaen-4-α-ol	1591	–	0.4 (0.2)	–
T-Muurolol	1643	–	0.3 (0.2)	–
α-Muurolol	1647	–	0.2 (0.0)	–
α-Eudesmol	1654	–	–	0.7 (0.4)
β-Bisabolol	1672	–	–	2.6 (0.4)
Occidentalol acetate	1682	–	0.8 (0.3)	–
a-Bisabolol	1684	–	–	0.6 (0.2)
Heptadecane	1700	–	1.0 (0.3)	–
Total identified		*95.1*	*93.6*	*90.6*
Essential oil yields (% w/w)		*0.18*	*0.29*	*0.20*

[a] Percentages (SD in parenthesis) are means of five replicates.
[b] Linear retention indexes (DB-5 column).
[c] Not detected.
[d] tr < 0.1%.

as much those produced by the leafy branches (11.8%), whereas it reached an intermediate value (17.0%). In the case of germacrene D, the highest percentage was found in the leafy branches (31.3%), followed by considerably lower percentages in the inflorescences (14.5%) and in the fruits (7.6%).

Within this genus, the most studied species is *E. foetidum*, which has been investigated for the essential oils obtained from aerial parts, seeds and roots (Cardozo, Rubio, Rojas, & Usubillaga, 2004; Leclercq, Nguyen, Vu, & Nguyen, 1992; Martins et al., 2003; Pino, Rosado, & Fuentes, 1997a, Pino, Rosado, & Fuentes, 1997b; Wong, Feng, Sam, & Tan, 1994).

Other papers report the composition of the essential oils obtained from *Eryngium paniculatum* (Cobos et al., 2002), *E. billardieri* (Sefidkon, Dabiri, & Alamshahi, 2004), *Eryngium expansus*, *Eryngium pandanifolium*, *Eryngium rostratum* (Brophy, Goldsack, Copeland, Lachlan, & Pala-Paul, 2003), *Eryngium vesicolosum* (Pala-Paul et al., 2003) and *Eryngium caeruleum* (Morteza-Semnani, Azadbakht, & Hooshmand, 2003).

All these studies evidenced a great qualitative and quantitative difference in the composition of the respective essential oils, not only among the different species but also within the same species, probably according to the characteristics of the growth place. All these characteristics must be taken into account when the plant could be used as aroma source.

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