SHORT COMMUNICATION

The chemical composition of the aerial parts essential oils of *Centaurea erycina* (Asteraceae), an endemic species of Sicily (Italy)

Francesco Sgadari[a], Alessandro Vaglica[b*], Antonella Porrello[b], Anna Geraci[b], Rosario Schicchi[a] and Maurizio Bruno[b,c,d]

[a] *Department of Agricultural, Food and Forest Sciences (SAAF), Università degli Studi di Palermo, Viale delle Scienze, ed. 4, 90128 Palermo, Italy.*

[b] *Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, Viale delle Scienze, Palermo, building 17, Italy.*

[c] *NBFC, National Biodiversity Future Center, Palermo 90133, Italy.*

[d] *Centro Interdipartimentale di Ricerca "Riutilizzo bio-based degli scarti da matrici agroalimentari" (RIVIVE), University of Palermo, Viale delle Scienze, Palermo.*

* Corresponding author*:* Alessandro Vaglica

E-mail: alessandro.vaglica@unipa.it

francesco.sgadari@unipa.it
alessandro.vaglica@unipa.it
antonella.porrello@unipa.it
anna.geraci@unipa.it
rosario.schicchi@unipa.it
maurizio.bruno@unipa.it

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In the present study, the chemical composition of the essential oil from aerial parts of a very rare *Centaurea* species, not previously investigated, *Centaurea erycina* Raimondo & Bancheva, collected in Sicily, was evaluated by GC-MS. The new species, classified just twenty years ago, belongs to *Centaurea cineraria* group (sect. *Pannophyllum* Hayek, Asteraceae) and grows in an extremely limited area in the NW part of Sicily. The oil was shown to be rich of aldehydes (41.4%) and sesquiterpenes (33.4%). The main components of the essential oil were *β*-caryophyllene (13.4%), caryophyllene oxide (12.6%), hexanal (11.9%), and *trans*-2-hexenal (10.0%). Furthermore, a complete literature review on the composition of the essential oils of all the other taxa of *Centaurea*, belonging to sections *Pannophyllum*, studied so far, was carried out.

Keywords: Section *Pannophyllum* Hayek; essential oil; *β*-caryophyllene; *β*-caryophyllene oxide; hexanal; *trans*-2-hexenal

1. Introduction

Centaurea is one of the most taxonomically complex genus in the Cardueae tribe of Asteraceae family and includes between 500 and 700 species, depending on the classification used, of annual, biennial, and perennial plants, rarely dwarf shrubs with usually unarmed leaves. The Mediterranean and Irano-Turanian regions are the centers of distribution of the genus (Dostál 1976; Wagenitz 1975; Dittrich 1977; Bancheva and Greilhuber 2006; Susanna and Garcia-Jacas 2007).

Since ancient times many *Centaurea* species have been used in folk medicine of many countries for the treatment of diabetes, diarrhea, hypertension, headache, muscle pains, microbial infections, rheumatism, diabetes, and malaria (Gou et al. 2023). *Centaurea* species have been mostly studied for sesquiterpene lactones (Bruno et al. 2013; Sokovic et al. 2017), flavonoids (Formisano et al. 2012), and alkaloids contents (Xia and Tong 2018).

Centaurea erycina Raimondo & Bancheva belongs to *Centaurea cineraria* group (sect. *Pannophyllum* Hayek), one of the taxonomically most difficult group to define in the Sicilian flora (Sommier 1894; Lacaita 1915; Cela Renzoni and Viegi 1982). It is a mesophylous, calciphylous chamaephyte, with chasmophyte habit, related to rupestrian associations of the *Dianthion rupicolae*

Brullo & Marcenò 1979 alliance. The plant is perennial and densely white tomentose. The stems (20-140 cm high) are sulcate, ascending, or erect, with few branches above, densely leafy up to the apex. The capitula are in clusters of 2-21 or rarely solitary with peduncles 3-5 mm wide, and 3-5 leaves below the capitula. The involucre is ovoid-globose 16-22 mm x 14-16 mm. The bracts are oblong-lanceolate, white tomentose to white arachnoideous, with 5-7 nerves on the back, 1-3 of them extending on the appendages. Appendages are dark to light brown, shortly decurent at the base, fimbriate. Flowers are pink-liliac with grey achenes grey, 4-5 mm long, 2 mm wide. The roots are strongly lignose. It is flowering in June and fruiting in June-July. This endemic chasmophyte grows on the calcareous rocks in San Giuliano Mt. (NW-Sicily), around and below the Venus' Castle (Erice village) at about 550-750 m a.s.l., as well on the walls of the Castle, made by the same rocks. This area is characterized by mesomediterranean climate with 16° annual mean temperature and about 800 mm annual mean rainfall. The air humidity is very high, as there is almost always fog (Raimondo and Bancheva 2004).

As stated before, *Centaurea erycina* belongs to section *Pannophyllum* of the *Centaurea* genus and as all the other species belonging to the same section, comprising taxa found exclusively in the W. Mediterranean area, are totally devoid of guaiane sesquiterpenoids (Bruno et al. 2013). As regards to the sesquiterpene occurrence, the species of this section showed the presence of only of germacrane derivatives such as in *Centaurea affinis* Friv. (Janaćković et al. 2004), *Centaurea cineraria* L. (Nowak et al. 1984; Gousiadou and Skaltsa 2003) and *Centaurea cineraria* subsp. *circae* (Sommier) Cela Renz. & Viegi (Nowak et al. 1984, Gousiadou and Skaltsa 2003) and, of germacranes and elemanes as in *Centaurea busambarensis* Guss. (syn. *Centaurea cineraria* subsp. *busambarensis* (Guss.) Dostál) (Bruno et al. 1998) and *Centaurea panormitana* subsp. *umbrosa* (Fiori) Greuter (syn *Centaurea cineraria* subsp. *umbrosa* (Fiori) Pignatti) (Bruno and Herz 1988; Gousiadou and Skaltsa 2003). From some taxa of this section several flavonoids were also identified such in *C. affinis* (Janaćković et al. 2004), *C. cineraria* (El-Emary et al. 1983) and *C. panormitana* subsp. *umbrosa* (Bruno and Herz 1988).

As for the chemical composition of the essential oils (EOs), few papers have been published on *Centaurea* taxa belonging to sect. *Pannophyllum*. All the data concerning the composition of these oils are resumed in Table S1 and they will be discussed later on.

As part of ongoing research on *Centaurea* species (Bruno et al. 2019; Bancheva et al. 2022; 2023), we decided to investigate, for the first time, the chemical composition of the EO of *C. erycina*.

No investigation has ever been published on the essential oil from this species.

2. Results and discussion

Hydrodistillation of *C. erycina* (**CE**) flowering aerial parts gave a pale-yellow EO. Overall, forty-six compounds were identified, representing 90.0% of total components, listed in Table S2 according to their linear retention indices on a DB-5 MS column and classified into six classes based on their chemical structures. Aldehydes (41.4%) was the principal class with hexanal (11.9%), *trans*-2-hexenal (10.0%), nonanal (5.4%) and decanal (5.1%), as the main constituents. Principal metabolites of the oil were *β*-caryophyllene (13.4%), the only sesquiterpene hydrocarbon (14.8%) present in significant amount, and caryophyllene oxide (12.6%) that together with alloaromadendrene oxide (5.0%) were the main representatives of oxygenated sesquiterpenes (18.6%). Monoterpene hydrocarbons (5.5%) and oxygenated monoterpenes (3.3%) were present in similar and limited amounts.

The only other study on taxa of section *Pannophyllum* (Table S1) that can be compared with **CE** concerns the chemical composition of the EOs from the aerial parts of *C. panormitana* subsp. *umbrosa*, collected in Sicily (Senatore et al. 2003), of *C. affinis*, collected in Greece (Djeddi et al. 2011), and of *Centaurea gloriosa* Radić (syn. *Centaurea cuspidata* subsp. *multiflora* Radić) endemic of Croatia (Cavar et al. 2011) (Table S1). The first one was shown to be rich of germacrene D (22.0%) and palmitic acid (20.8%), although, as in **CE**, a good quantity of *β*-caryophyllene (8.6%) and moderate amount of caryophyllene oxide (3.2%) were detected. The aldehydic compounds occurred in quite poor quantity (2.6%). The oil of *C. affinis* was quite rich of hydrocarbons (26.9%), followed by oxygenated sesquiterpenes (15.5%). The oil was totally devoid of *β*-caryophyllene, and caryophyllene oxide occurred in limited quantity (2.7%). On the other hands, caryophyllene oxide (16.9%) was the main constituent of *C. gloriosa* followed by torilenol (12.4%). Other caryophyllene derivatives accounted for 10.0%. In this case the oil was totally devoid of aldehydes.

The EOs of several other taxa, collected in Sicily and in some islands of Tyrrhenian Sea, were studied by Viegi et al. (2014), although the authors investigated separately leaves and flowers (Table S1). In almost all this species, among the main constituents, *β*-caryophyllene, germacrene D and phenylacetaldehyde were reported, the last two not present in **CE**. Some of these species showed, as in **CE**, a remarkable amount of aldehydes, up to 24.5%, especially in the flowers.

3. Experimental See Supplementary Material

4. Conclusion

In conclusion, it is the first time that semi-quantitative characterization has been carried out on the essential oil sample obtained from the aerial parts of the rare species *Centaurea erycina* (sect.

Pannophyllum, Asteraceae), endemic of Sicily. The chromatographic analysis highlighted how the **CE** was rich in aldehydes and sesquiterpenes. *C. panormitana* subsp. *umbrosa and C. affinis* showed the most similar composition regards its main constituents. The study of this essential oil has allowed a careful review of what the scientific literature reports on all the other *Centaurea* species belonging to the same section, confirming, once again, how the comparison of the chemical compositions of essential oils is fundamental as a chemotaxonomic marker to support taxonomic decisions regarding the creation of separate and new taxa.

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Disclosure statement

The authors declare no conflict of interest in this article.

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SUPPLEMENTARY MATERIAL

The chemical composition of the aerial parts essential oils of *Centaurea erycina* (Asteraceae), an endemic species of Sicily (Italy)

In the present study, the chemical composition of the essential oil from aerial parts of a very rare *Centaurea* species, not previously investigated, *Centaurea erycina* Raimondo & Bancheva, collected in Sicily, was evaluated by GC-MS. The new species, classified just twenty years ago, belongs to *Centaurea cineraria* group (sect. *Pannophyllum* Hayek, Asteraceae) and grows in an extremely limited area in the NW part of Sicily. The oil was shown to be rich of aldehydes (41.4%) and sesquiterpenes (33.4%). The main components of the essential oil were *β*-caryophyllene (13.4%), caryophyllene oxide (12.6%), hexanal (11.9%), and *trans*-2-hexenal (10.0%). Furthermore, a complete literature review on the composition of the essential oils of all the other taxa of *Centaurea*, belonging to sections *Pannophyllum*, studied so far, was carried out.

Keywords: Section *Pannophyllum* Hayek; essential oil; *β*-caryophyllene; *β*- caryophyllene oxide; hexanal; *trans*-2-hexenal

3. Experimental

3.1. Plant material

Aerial parts (flowers, leaves, and stems) in full bloom of *Centaurea erycina* were collected in Erice, near the Norman castle of Venus, in the province of Trapani, Sicily, Italy (38°2'8'' N 12°35'23'' E), on calcareous rocks at about 740 m a.s.l, in June 2023. One of the samples, identified by Prof. Rosario Schicchi, has been stored in the Herbarium Mediterraneum Panormitanum (PAL), (Voucher N. 109747), of the Botanical Garden of the University of Palermo, Italy.

3.2. Isolation of volatile components

Fresh samples (aerial parts, leaves, and flowers) were ground in a Waring blender and then subjected to hydro-distillation for 3 h, according to the standard procedure described in European Pharmacopoeia (2020). The EOs were dried over anhydrous sodium sulphate and stored in sealed vial under N_2, at -20 °C, ready for the GC and GC-MS analyses. The sample yielded 0.07% oils (*w*/*w*).

3.3. GC and GC-MS analysis

Analysis of EOs were performed according to the procedure reported by Porrello et al. (2023). GC-MS analyses were performed using a Shimadzu QP 2010 plus equipped with an AOC-20i autoinjector (Shimadzu, Kyoto, Japan) gas chromatograph equipped with a FID, a non-polar capillary column (DB-5 MS) 30 m × 0.25 mm i.d., film thickness 0.25 μm and a data processor. The oven program was as follows: temperature increase at 40 °C for 5 min, at a rate of 2 °C/min up to 260 °C, then isothermal for 20 min. Helium was used as carrier gas (1 mL min^{-1}). The injector and detector temperatures were set at 250 °C and 290 °C, respectively. 1 µL of EO solution (3% EO/hexane *v/v*) was injected with split mode 1.0; MS range 40-600. The percentage in Table S2 are calculated with the TIC from MS peaks. The settings were as follows: ionization voltage, 70 eV; electron multiplier energy, 2000 V; transfer line

temperature, 295 °C; solvent delay, 3 min. Kovats indices (KI) were determined by using retention times of *n*-alkanes (C_8-C_{40}) and the peaks were identified by comparison with mass spectra and by comparison of their relative retention indices with WILEY275, NIST 17, ADAMS, and FFNSC2 libraries.

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Table S1. Chemical compositions of the Eos of all the taxa of *Centaurea* sect. *Pannophyllum*, studied so far.

Taxa	Origin	P.	Compounds	Ref.
C. affinis Friv.	Mt Parnassos, Greece	ap	tetracosane (7.8), thymol (6.7), *n*-dodecanol (6.7), *n*-eicosane (5.4), hexacosane (4.3), (*E*)-*β*-ionone (3.5), ledol (3.5), tricosane (3.0), caryophyllene oxide (2.7), (*E*)-*β*-damascenone (2.5), *t*-muurolol (2.5), neophytadiene (2.4), carvacrol (2.0), pentadecanal (2.0), docosane (2.0)	Djeddi et al. 2011
C. busambarensis Guss.	Mt Busambra, Sicily, Italy	l	germacrene D (31.6), *β*-caryophyllene (5.2), *cis*-3-hexen-1-ol (6.2), phenylacetaldehyde (3.3), benzyl alcohol (2.9), *trans*-2-hexenal (2.3)	Viegi et al. 2014
	Mt Busambra, Sicily, Italy	fl	*β*-caryophyllene (17.8), germacrene D (17.6), caryophyllene oxide (4.3), phenylacetaldehyde (3.8), dodecanol (3.0), tricocane (3.0), *α*-humulene (2.60), hexanal (2.5), tetradecanol (2.4), (*E*)-*β*-farnesene (2.3),	Viegi et al. 2014
C. gloriosa var. *multiflora* Radić	Mt Biokovo, Croatia	ap	caryophyllene oxide (16.9), torilenol (12.4), dihydroactinidiolide (5.8), *n*-hexacosane (5.6), *n*-heptacosane (5.0), caryophylla-3(15),7(14)-dien-6*β*-ol (8.2), *β*-eudesmol (3.5), *n*-pentacosane (3.5), bisabola-1,3,5,11-tetraene (3.4), *n*-octacosane (3.0), isogermacrene D (2.9), *n*-tetracosane (2.8), *n*-nonacosane (2.4), *n*-tricosane (2.3)	Cavar et al. 2011
C. gymnocarpa Moris & De Not.	Capraia Island, Italy	l	germacrene D (13.8), 1-pentadecene (7.6), germacra-4(15),5,10(14)trien-1-ol (6.8), *β*-caryophyllene (4.9), decanal (3.6), *α*-zingiberene (3.2), phenylacetaldehyde (3.1)	Viegi et al. 2014
	Capraia Island,	fl	germacrene D (20.5), 1-pentadecene (6.9), (*E*)-*α* -	Viegi et al.

	Italy		bergamotene (6.0), *β*-caryophyllene (4.5), tricocane (3.4), phenylacetaldehyde (2.8), (*E*)-*β*-farnesene (2.7)	2014
C. panormitana subsp. *seguenzae* (Lacaita) Greuter	Capo Tindari, Sicily, Italy	l	germacrene D (33.0), *β*-caryophyllene (4.5), *cis*-3-hexen-1-ol (3.0), benzyl alcohol (2.7), nonanal (2.3), phenylacetaldehyde (2.3), eugenol (2.0)	Viegi et al. 2014
	Capo Tindari, Sicily, Italy	fl	germacrene D (15.2), *β*-caryophyllene (10.0), heptacosane (5.1), phenylacetaldehyde (5.0), tricocane (4.7), 2-methylbutanal (4.6), hexanal (4.5), hexadecanoic acid (4.4), 3-methylbutanal (4.3), 1-pentadecene (4.0), nonacosane (3.3)	Viegi et al. 2014
C. panormitana subsp. *todaroi* (Lacaita) Greuter	Bagheria, Sicily, Italy	l	germacrene D (20.6), *cis*-3-hexen-1-ol (9.1), 4,5-di-methyl-4-hexen-3-one (7.1), benzyl alcohol (5,5), *β*-caryophyllene (5.0), 4-methyl-4-hepten-3-one (3.0), 2-phenylethanol (2.9), heptacosane (2.8), nonacosane (2.8), phenylacetaldehyde (2.0)	Viegi et al. 2014
	Bagheria, Sicily, Italy	fl	germacrene D (23.7), *β*-caryophyllene (11.3), phenylacetaldehyde (8.1), 1-pentadecene (3.9), caryophyllene oxide (2.9)	Viegi et al. 2014
C. panormitana subsp. *ucriae* (Lacaita) Greuter	Sferracavallo Sicily, Italy	l	germacrene D (11.1), nonacosane (9.0), 4,5-di-methyl-4-hexen-3-one (8.9), eugenol (7.17%), heptacosane (4.8), nonanal (4.1), benzyl alchol (3.9), phenylacetaldehyde (2.8), *trans*-2-decenal (2.3), 2-methylbutanal (2.2),	Viegi et al. 2014
	Sferracavallo Sicily, Italy	fl	germacrene D (27.9), *β*-caryophyllene (8.1), phenylacetaldehyde (7.9), 2-methylbutanal (5.8), tricocane (2.7), 1-pentadecene (2.2), heptacosane (2.0)	Viegi et al. 2014
C. panormitana subsp. *umbrosa* (Fiori) Greuter	Mt. Gallo, Sicily, Italy	l	germacrene D (16.3), *cis*-3-hexen-1-ol (5.6), 4,5-dimethyl-4-hexen-3-one (4.0), nonanocosane (3.2), decanal (2.8), *β*-caryophyllene (2.7), phenylacetaldehyde (2.2), nonanal (2.1), *cis*-3-hexenyl acetate (2.1)	Viegi et al. 2014
	Mt. Gallo, Sicily, Italy	fl	germacrene D (21.0), phenylacetaldehyde (12.7), *β*-caryophyllene (7.6), tricocane (4.0), hexanal (3.9), *β*-elemene (2.4), nonanocosane (2.4), hexadecanoic acid (2.1)	Viegi et al. 2014
	Mt Pellegrino,	l	germacrene D (38.5), *β*-caryophyllene (4.9),	Viegi et al.

	Sicily, Italy		nonacosane (3.7), heptacosane (3.3), *cis*-3-hexenyl acetate (2.4)	2014
	Mt Pellegrino, Sicily, Italy	fl	germacrene D (16.8), *β*-caryophyllene (14.4), 1-pentadecene (9.2)	Viegi et al. 2014
	Capo Zafferano, Sicily, Italy	ap	germacrene D (22.0), palmitic acid (20.8), *β*-caryophyllene (8.6), heptacosane (3.5), α-terpinyl propionate (3.4), caryophyllene oxide (3.2), pentacosane (2.2), tricosane (2.1)	Senatore et al. 2003
C. veneris (Sommier) Bég.	Palmaria Island, Italy	l	germacrene D (42.6), *β*-caryophyllene (5.7), phenylacetaldehyde (4.5), bicyclogermacrene (3.3), germacra-4(15),5,10(14)trien-1-ol (2.4), 4,5-dimethyl-4-hexen-3-one (2.3), nonacosane (2.3), 1-pentadecene (2.1)	Viegi et al. 2014
	Palmaria Island, Italy	fl	germacrene D (30.3), *β*-caryophyllene (5.8), tricocane (4.4), *α*-ylangene (4.3), phenylacetaldehyde (3.2), bicyclogermacrene (2.7), guaiol (2.4), germacrene B (2.3)	Viegi et al. 2014

Table S2. Composition (%) of *Centaurea erycina* essential oil, collected in Sicily, Italy.

No.	Compounds[a]	KI[b]	KI[c]	Area (%)
1	Hexanal	798	798	11.9
2	*trans*-2-Hexenal	842	845	10.0
3	1-Hexanol	863	863	0.8
4	Nonane	899	900	2.0
5	*α*-Pinene	928	930	0.8
6	*β*-Pinene	969	970	0.4
7	2-Pentylfuran	989	990	2.0
8	Octanal	999	999	1.4
9	*α*-Terpinene	1012	1015	0.8
10	*p*-Cymene	1020	1020	0.9
11	*β*-Phellandrene	1023	1026	0.9
12	Phenylethanal	1034	1032	1.1
13	*γ*-Terpinene	1055	1054	1.4
14	1-Octanol	1069	1069	0.2
15	Nonanal	1101	1101	5.4
16	2,6-Dimethyl-1,3,5,7-octatetraene	1134	1137	0.3
17	1,4-Dimethyl-3-cyclohexenyl methyl Ketone	1142	1145	0.2
18	Nonadienol	1147	1153	0.1
19	*trans*-2-Nonenal	1155	1157	0.3

20	4-Terpineol	1170	1171	1.4
21	Betula	1185	1187	0.1
22	Isopinocampheol	1190	1190	0.1
23	Dodecane	1200	1200	0.2
24	Decanal	1202	1202	5.1
25	2,4-Nonadienal	1207	1203	0.1
26	*trans*-2-Decenal	1251	1254	1.6
27	Dihydroedulan I	1287	1289	0.4
28	Isomenthyl acetate	1291	1291	0.1
29	Tridecane	1300	1300	0.1
30	Undecanal	1303	1305	0.8
31	2,4-Decadienal	1310	1317	0.6
32	2-Undecenal	1359	1359	0.7
33	*trans*-β-Damascenone	1378	1380	1.1
34	Tetradecane	1400	1400	0.5
35	Dodecanal	1405	1407	0.4
36	β-Caryophyllene	1414	1417	13.4
37	α-Ionone	1421	1421	0.2
38	*trans*-α-Bergamotene	1432	1432	0.5
39	Humulene	1447	1450	0.6
40	Geranyl acetone	1449	1452	0.1
41	*trans*-β-Farnesene	1455	1455	0.3
42	Tridecanal	1507	1510	1.4
43	Caryophyllene oxide	1575	1579	12.6
44	*trans*-Longipinocarveol	1618	1618	1.0
45	Alloaromadendrene oxide	1628	1636	5.0
46	Pentadecanal	1711	1711	0.6
	Monoterpene Hydrocarbons			**5.5**
	Oxygenated Monoterpenes			**3.3**
	Sesquiterpene Hydrocarbons			**14.8**
	Oxygenated Sesquiterpenes			**18.6**
	Aldehydes			**41.4**
	Other			**6.4**
	Total			**90.0**

[a] Components listed in order of elution on an DB-5MS column; [b] Kovats indices on a DB-5MS apolar column; [c] Kovats indices based on literature (https://webbook.nist.gov/).