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Components from the Essential oil of *Centaurea aeolica* Guss. and *C. diluta* Aiton from Sicily, Italy

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Abstract: Volatile components from florets, leaves and stems and branches of *Centaurea aeolica* Guss. harvested in Lipari, Sicily, Italy, were analysed by gas phase chomatography (GC) and gas chomatography mass spectrometry (GC-MS). The main constituents were β-eudesmol, caryophyllene oxide, (*E*)-12-norcaryophyll-5-en-2-one and hexahydrofarnesylacetone in flowers, hexahydrofarnesylacetone, 2-methyloctadecane and tricosane in the leaves and hexadecanoic acid, caryophyllene oxide and β-eudesmol in the stems and branches. The analysis of the essential oil of the aerial parts of *Centaurea diluta* Aiton gave mainly fatty acids and derivatives, the main ones being hexadecanoic acid and (*Z,Z*)-9,12-octadecadienoic acid methyl ester.

Keywords: *Centaurea aeolica*; *Centaurea diluta*; GC-MS; volatile components; β-eudesmol; caryophyllene oxide; hexahydrofarnesylacetone; hexadecanoic acid.

1. Plant Source

Centaurea aeolica Guss. ex DC. (common name: Fiordaliso of the Aeolian islands), belonging to section Alolepidae (J. Arones) Dostal, is a perennial plant, with white-tomentose stems at the youth state, after glabrescent and more or less green, up to 30-40 cm height. Lower leaves are lanceolate and deeply divided, higher cauline ones are linear. Florets (June-July) are violet and united in head inflorescences (capitula), 10-13 mm in diameter, ovoid; the bracts are without appendage. Fruits are small achenes equipped with soft and plumy appendix (pappus), wind disseminated. Usually, it grows on dry slopes and cliffs up to 400 a. s. l. The plant is an Aeolian endemic that can be considered symbol of the flora of the Aeolian Islands. In the island is spread more or less evenly along the coast, especially along the provincial road between Malfa and Pollara (Salina Island) and White Sand Beach (Lipari Island). It is included as rare in the list of species "at risk" in the vascular flora native of Sicily

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[1] and is listed among the species at lower risk of extinction in the regional Red List of Plants in Italy. This taxon was described by the Neapolitan botanist Giovanni Gussone in 1837 [2].

Centaurea diluta Aiton. (North African Knapweed) belongs to section Solstitiaria (Hill) Dobrocz and it is an annual or perennial plant, native to southwestern Europe and northern Africa. The stems are up to 200 cm, erect and branched, glabrous or hairy. The lower leaves are incise-dentate, the lowermost ones – lyrate, while the upper - entire, semiamplexicaul. Capitula are solitary, pedunculate with ovoid nvolucre, 8-12 mm in diameter, while the bracts are brown and appressed. Appendages are shortly decurrent, orbicular-ovate, with membranous margin, irregularly fimbriate-lacerate, the apex is emarginate with a rigid, filiform spine in the notch. Florets are purple, the marginal distinctly patent. Inner achenes are with pappus, as long as achene; outer with very short pappus [3].

In continuation of our studies on *Centaurea* species of the Mediterranean area [4-5] the aerial parts of *C. aeolica* were collected in June, 2011, in White Sand Beach (Lipari Island), Sicily, Italy and the aerial parts of *C. diluta* were collected in June, 2011, near Alimena, Sicily, Italy. Typical specimens were identified by Prof. S. Bancheva, Sofia, Bulgaria and have been deposited in the Department STeBiCEF of the University of Palermo, Palermo, Italy (PAL 11/7MB and PAL 11/8MB, respectivelly).

2. Previous Studies

The presence of polyacetylene compounds has been previously reported in *C. diluta* [6-9], whereas neither studies on its volatile components, nor any paper on *C. aeolica* have been published.

3. Present Study

The volatile components from air-dried and ground florets (AF), leaves (AL) and stems and branches (AS) of *C. aeolica* and from the aerial parts of *C. diluta* (DAP) were isolated by hydrodistillation for 3 h, using a Clevenger-type apparatus according to the method recommended in the European Pharmacopoeia [10]. The oil was dried over anhydrous sodium sulphate and stored under N_2 at +4°C in the dark until tested and analysed. The samples yielded 1.93% (AF), 0.02% (AL), 0.02% (AS) and 0.13% (DAP) of yellow oils (w/w). The yields are moisture free basis.

GC analysis: Analytical gas chromatography was carried out on a Perkin-Elmer Sigma 115 gas chromatograph fitted with a HP-5 MS capillary column (30 m x 0.25 mm i.d.; 0.25 μm film thickness). Helium was the carrier gas (1 mL min^{-1}). Column temperature was initially kept at 40°C for 5 min, then gradually increased to 250°C at 2°C min^{-1}, held for 15 min and finally raised to 270°C at 10°C min^{-1}. Diluted samples (1/100 v/v, in *n*-hexane) of 1 μL were injected manually at 250°C, and in the splitless mode. Flame ionization detection (FID) was performed at 280°C. Analysis was also run by using a fused silica HP Innowax polyethylenglycol capillary column (50 m x 0.20 mm i.d.; 0.20 μm film thickness).

GC-MS analysis: GC-MS analysis was performed on an Agilent 6850 Ser. II apparatus, fitted with a fused silica HP-1 capillary column (30 m x 0.25 mm i.d.; 0.25 μm film thickness), coupled to an Agilent Mass Selective Detector MSD 5973; ionization voltage 70 eV; electron multiplier energy 2000 V. Gas chromatographic conditions were as reported above; transfer line temperature, 295°C. Analysis was also run by using a fused silica HP Innowax polyethylenglycol capillary column (60 m x 0.25 mm i.d.; 0.25 μm film thickness) [11].

Qualitative and quantitative analyses: Most constituents were identified by gas chromatography by comparison of their retention indices (Ri) with either those of the literature [12, 13] or with those of authentic compounds available in our laboratories. The retention indices were determined in relation to a homologous series of *n*-alkanes (C_8-C_{32}) under the same operating conditions. Further identification was made by comparison of their mass spectra on both columns with either those stored in NIST 02 and Wiley 275 libraries or with mass spectra from the literature [12, 14] and our home made library. Component relative concentrations were calculated based on GC peak areas without using correction factors.

Hydrodistillation of *C. aeolica* florets (**AF**), leaves (**AL**) and stems and branches (**AS**) gave overall 49 compounds were identified: 17 in (**AF**), 17 in (**AL**) and 37 in (**AS**), respectively. The components are listed in Table 1 according to their retention indices on a HP 5MS column and are classified on the basis of their chemical structures into 8 classes. The three oils presented a different composition and the identity of the most dominant components differed notably. Furthermore, the composition of *C. aeolica* is different from that studied so far [15, 16], in fact, it is to highlight the content in oxygenated sesquiterpenes that varies between 18.8% (**AL**) and 64.0% (**AF**), higher than that described for other *Centaurea* species. The most abundant component of this class in **AL** is β-eudesmol (26.3%), followed by caryophyllene oxide (12.6%) and (*E*)-12-norcaryophyll-5-en-2-one (10.8%).

A high content of β-eudesmol and caryophyllene oxide has been also reported for *C. mucronifera* (Sect. Psephelloides, 17.4% and 5.2%, respectively) [17], *C. aladaghensis* (Sect. Cynaroides, 11.8% and 7.5%, respectively) [18], *C. gracilenta* (Sect. Arenariae, 12.8% and 6.7%, respectively) [19] and *Centaurea ensiformis* (Sect. Cheirolepis, 29.8% and 7.6%, respectively) [20]. The last two, similarly to *C. aeolica*, are devoid of germacrene D that, instead, is the main compound of *C. mucronifera* and *C. aladaghensis*. Furthermore, caryophyllene oxide (18.2%) was detected as the main product in *C. helenoides* [21] and one of the main component (5.4%) in *C. pulcherrima* var. *pulcherrima* [22], and β-eudesmol was the principal metabolite of *C. sessilis* (11.1%) and *C. armena* (11.2%) [23]. On the other hand, it is worthy to point out that (*E*)-12-norcaryophyll-5-en-2-one has never been detected in other *Centaurea* species although it was identified in species belonging to other Families [24-27].

In the **AL** oil the main fractions were represented by hydrocarbons (35.1%) and carbonylic compounds (34.5%), the last one including just hexahydrofarnesylacetone while in **AS** oil fatty acids and derivatives (31.3%) was the main fraction with hexadecanoic acid (24.7%) as principal compound.

Thirty-five compounds were determined in the essential oil of the aerial parts of *C. diluta* (**DAP**), representing 90.5% of total oil content. By far the main class is fatty acids and derivatives with hexadecanoic acid (21.3%) and (*Z,Z*)-9,12-octadecadienoic acid methyl ester (12.2%) as most abundant compounds. Hydrocarbons accounted for the 15.3% being pentacosane the most abundant one (7.1%). Terpenoids were present in low amount (2.8%) and among the carbonylic compounds (8.7%) only (*E*)-β-damascenone (3.5%) was present in good quantity. The chemical profile of *C. diluta* is quite similar to those of *C. nicaensis* (sect. Solstitiaria) and *C. solstitialis* ssp. *shouwii* (sect. Solstitiaria) [28], in fact, in both cases the main compounds were hexadecanoic acid (33.5%-29.4%) and (*Z,Z*)-9,12-octadecadienoic acid (28.8%-4.9%) and this fact confirm that *C. diluta* has been placed in the same section Solstitiaria.

Table 1. Composition of essential oils from of *Centaurea aeolica* and *C. diluta*.

Compounds	K_i [a]	K_i [b]	AF [c]	AL [d]	AS [e]	DAP [f]	Ident. [g]
Hydrocarbons			**9.4**	**35.1**	**7.2**	**15.3**	
1-Pentadecene	1492	1544			0.2		1, 2
Cadalene	1677	2256			1.0		1, 2
Octadecane	1800	1800			0.4		1,2,3
1-Nonadecene	1893	1942	0.8				1, 2
2-Methyloctadecane	1945	1854		15.5			1, 2
Eicosane	2000	2000	2.8	3.4			1,2,3
Heneicosane	2100	2100	3.7	1.3			1,2,3
Docosane	2200	2200	0.4	t	0.9		1, 2, 3
Tricosane	2300	2300	1.2	13.0	3.9	0.3	1, 2, 3
Tetracosane	2400	2400		1.9	0.8	0.7	1, 2, 3
Pentacosane	2500	2500	0.5			7.1	1, 2, 3
Hexacosane	2600	2600				0.6	1, 2, 3
Heptacosane	2700	2700				3.0	1, 2, 3
Octacosane	2800	2800				0.4	1, 2, 3
Nonacosane	2900	2900				2.8	1, 2, 3
Hentriacontane	3100	3100				0.1	1, 2, 3

Tritriacontane						0.3	2
Carbonylic compounds			**9.2**	**34.5**	**13.3**	**8.7**	
(*E*,*E*)-2,4-Heptadienal	1015	1507		t			1, 2
Phenylacetaldehyde	1045	1663				0.8	1,2,3
(*E*,*E*)-2,4-Decadienal	1315	1827				t	1, 2
Nonanal	1102	1399				1.4	1,2
Decanal	1206	1510				t	1,2,3
(*E*)-β-Damascenone	1358	1787				3.5	1, 2
Tetradecanal	1611	1934			0.5		1, 2
Pentadecanal	1715	2038			2.7		1, 2
2-Hexadecanone	1805	2203			0.5		1, 2
Hexadecanal	1817	2121			0.9		1, 2
Hexahydrofarnesylacetone	1845	2131	9.2	34.5	6.8	1.9	1, 2
2-Octadecanone	1902	2402			0.1		1, 2
Heptadecanal	1920	2241			0.8		1, 2
Octadecanal	2042	2357			0.3		1, 2
Nonadecanal	2110	2464			0.2		1, 2
(*E*,*E*)-Farnesylacetone	1920	2387				1.1	1, 2
Eicosanal	2221	2571			0.2		1, 2
Heneicosanal	2329	2682			0.3		1, 2
Sesquiterpene hydrocarbons					**3.3**	**1.8**	
Cyclosativene	1363	1492			0.2		1, 2
α-Copaene	1377	1497				1.6	1, 2
β-Elemene	1387	1600				0.2	1, 2
γ-Muurolene	1478	1704			3.1		
Oxygenated monoterpenes						**1.0**	
cis-Pinocamphone	1174	1565			t		1, 2
Pulegone	1236	1662				1.0	1, 2
Oxygenated sesquiterpenes			**64.0**	**18.8**	**24.1**		
Ledol	1565	2057	0.9				1, 2
Spathulenol	1578	2150	1.1				1, 2, 3
Caryophyllene oxide	1579	2208	12.6	4.3	7.4		1, 2, 3
β-Oplopenone	1608	2093			0.4		1, 2
Caryophylla-2(12),6(13)-dien-5β -ol (=*Caryophylladienol I*)	1638	2317	7.1	t			1, 2
Caryophylla-3,8(13)-dien-5β-ol	1639	2371	1.3				1, 2
Caryophylla-2(12),6(13)-dien-5β-ol (=*Caryophylladienol II*)	1649	2396	3.9	1.1			1, 2
β-Eudesmol	1650	2258	26.3	4.4	6.9		1, 2
Selin-11-en-4α-ol	1656	2275		8.4	2.6		1, 2
(*E*)-12-Norcaryophyll-5-en-2-one	1668	1984	10.8	0.6	3.6		1, 2
Valerenal	1716	2238			2.5		1, 2
β-Costol	1780	2607			0.7		1, 2
Fatty acids and derivatives			**11.1**	**3.6**	**42.2**	**51.4**	
Octanoic acid	1180	2053			0.1		1, 2, 3
Nonanoic acid	1278	2159			0.8		1, 2, 3
Decanoic acid	1367	2316			1.9		1, 2, 3
Undecanoic acid	1467	2419			0.5		1, 2, 3
Dodecanoic acid	1566	2503			7.6	2.6	1, 2, 3
Tetradecanoic acid	1758	2723	3.3		2.9	0.9	1, 2, 3
Benzyl benzoate	1760	2655			0.7		1, 2, 3
Pentadecanoic acid	1873	2825		t		0.9	1, 2, 3
Hexadecenoic acid	1909	2962				0.2	1, 2, 3
Hexadecanoic acid methyl ester	1925	2208			0.5		1, 2, 3
Hexadecanoic acid	1957	2932	7.8	3.6	24.7	21.3	1, 2, 3
Heptadecanoic acid	2074	3023				0.5	1, 2, 3
(*Z*,*Z*)-9,12-Octadecadienoic acid ethyl ester	2078	2532				7.3	1, 2, 3
(*Z*,*Z*)-9,12-Octadecadienoic acid methyl ester	2098	2507				12.2	1, 2, 3

(*Z*,*Z*)-9,12-Octadecadienoic acid	2104	3160			2.5	1.0	1, 2, 3
(*Z*,*Z*,*Z*)-9,12,15-Octadecatrienoic acid methyl ester	2107	2583				3.8	1, 2, 3
Octadecanoic acid	2172	3172				0.7	1,2,3
Phenolic compounds						**6.4**	
4-Vinylguaiacol	1312	2180				6.4	1,2
Others						**5.9**	
2-Pentylfuran	1002	1243				t	1, 2
Benzothiazole	1231	1943				0.7	1, 2,3
Hexadecanol	1878	2389				5.2	1, 2, 3
Total amount of compounds			**93.7**	**92.0**	**90.1**	**90.5**	

[a]: HP-5 MS column; [b]: HP Innowax column; [c]: *C. aeolica* florets; [d]: *C. aeolica* leaves; [e]: *C. aeolica* stems and branches; [f]: *C. diluta* aerial parts; [g]: 1: retention index, 2: mass spectrum, 3: co-injection with authentic compound; t: traces, less than 0.05%.

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