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Essential Oil Composition of *Tanacetum vulgare* subsp. *siculum* (Guss.) Raimondo et Spadaro (Asteraceae) from Sicily

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Ninety-four components of the essential oils from aerial parts and capitula of *Tanacetum vulgare* subsp. *siculum* (Guss.) Raimondo et Spadaro were detected. α-Thujone, β-thujone and 1,8-cineole were the main constituents of the oils. The analysis allows the assignment of this *Tanacetum* species to the thujone chemotype.

Keywords: *Tanacetum vulgare* subsp. *siculum* (Guss.) Raimondo et Spadaro, Asteraceae, essential oil, α-thujone, β-thujone, 1,8-cineole.

Several species of *Tanacetum* L., family Asteraceae, have been investigated for the biological properties of their metabolites, such as anti-inflammatory [1,2], anti-migraine [2], anti-ulcerogenic [3], cytotoxic [4], antifeedant [5] and antibacterial [6]. The genus contains about 200 species, which are widespread, mainly in Europe and western Asia [7]. Some are very popular, such as tansy (*T. vulgare*), Dalmatian insect flower (*T. cinariifolium*), and feverfew (*T. parthenium*).

The roots, leaves and flowers of the two most studied species, *T. vulgare* L. and *T. parthenium* (L.) Sch. Bip. ex Oliv., are rich in sesquiterpene lactones (parthenolide, tanacetin and tanacetols), tannins and flavonoids [8].

Studies on the chemical composition of the essential oil from various *Tanacetum* species revealed considerable variations [9-12]. In these studies, camphor, α- and β-thujone, carvone, pinocarvone, borneol, bornyl acetate and 1,8-cineole were reported as the major constituents of the essential oils. Papers on the composition of the oils of *T. vulgare*, published up to 1996, have been reviewed by Lawrence [13], who classified the oils of tansy plants into twenty-three chemotypes, according to the main components. Furthermore, it was reported that the commercial tansy oils are mostly of the thujone type. It is noteworthy that thujone is a bioactive compound with medicinal properties, but exhibits toxicity at high concentrations. The essential oils of forty samples of *T. vulgare* from Lithuania were analyzed and classified into four groups in which the chemotypes of 1,8-cineole and camphor were predominant [14].

T. vulgare is distributed in some European countries including Italy [7]. In Sicily, apart from the typical form (*T. vulgare* subsp. *vulgare*) [15], subspecies *siculum* (Guss.) Raimondo et Spadaro (syn. *T. siculum* Guss.) is endemic, growing on the eastern side of the Madonie Mountains and on Nebrodi Mountains, in a very restricted area.

As a continuation of our research on the volatile constituents of Sicilian species of Asteraceae [16-19], we have investigated the volatile constituents of the

Table 1: Essential oil composition of *Tanacetum vulgare* subsp. *siculum* .

LRI[a]	LRI[b]	COMPONENT	A[c]	C[c]	ID[d]
928		Tricyclene	0.1	t	1, 2
930		α-Thujene	t	t	1, 2
935	1075	α-Pinene	0.3	0.4	1, 2, 3
953		Camphene	t	t	1, 2, 3
959		Benzaldehyde		t	1, 2, 3
973	1132	Sabinene	0.2	0.3	1, 2
979	1283	1,3,5-Trimethylbenzene	0.2	0.8	1, 2, 3
1003	**1292**	**1,2,4-Trimethylbenzene**	**3.6**	**3.7**	**1, 2, 3**
1026	1278	*p*-Cymene	0.6		1, 2, 3
1034	**1213**	**1,8-Cineole**	**11.8**	**11.4**	**1, 2, 3**
1042	1305	1,2-Diethylbenzene		1.6	1, 2, 3
1048		Terpinolene		t	1, 2, 3
1057	1256	γ-Terpinene	0.4	0.2	1, 2, 3
1105	**1430**	**α-Thujone**	**23.8**	**21.1**	**1, 2**
1115	**1451**	**β-Thujone**	**18.0**	**34.5**	**1, 2**
1118	1490	Isophorone		1.0	1, 2
1126	**1521**	**Chrysanthenone**	**1.3**	**1.7**	**1, 2**
1138		*trans*-Pinocarveol		0.4	1, 2
1141	1684	*trans*-Verbenol	0.5	0.6	1, 2
1142	1721	*trans*-Sabinol		0.4	1, 2
1144	1663	*cis*-Verbenol	0.3		1, 2
1148		α-Thujenol		0.3	1, 2
1152		Sabinaketone		0.2	1, 2
1154	1587	Pinocarvone	0.3	0.7	1, 2
1164		(*E*)-Chrysanthemol		0.3	1, 2
1165	1774	*trans*-*p*-Mentha-1(7),8-dien-2-ol	0.3		1, 2
1168	1638	3-Thujanol		0.6	1, 2
1174	1610	Terpinene-4-ol	1.4	1.5	1, 2, 3
1175	1656	Umbellulone	0.2	0.2	1, 2
1187	1706	α-Terpineol	0.7		1, 2, 3
1196		4-Ethylbenzaldehyde	0.1		1, 2, 3
1196	1804	Myrtenol	0.4	0.2	1, 2
1201		Safranal	0.5	0.2	1, 2
1208	1723	*cis*-Verbenone	0.5	0.6	1, 2
1217	1845	*trans*-Carveol	0.3		1, 2
1217	1725	*trans*-Verbenone	0.5	0.4	1, 2
1223		*cis*-Carveol	0.2	0.2	1, 2
1223		Carvotanacetone	0.2	t	1, 2
1227	1813	(*E*)-Ocimenone		0.7	1, 2
1243		Carvone	0.9	0.9	1, 2
1252	1802	Cumin aldehyde	0.3	0.3	1, 2
1257	1582	(*Z*)-Chrysanthenyl acetate	0.6	0.4	1, 2
1268	1856	Isopiperitone	0.7		1, 2
1288	2112	Cumin alcohol	0.5	0.2	1, 2
1292	1659	(*E*)-Sabinyl acetate	1.0	0.3	1, 2
1297	2239	Carvacrol	0.4	0.5	1, 2, 3
1315		1,4-*p*-Menthadien-7-ol	0.2		1, 2
1329	1949	Piperitenone	0.3	0.3	1, 2
1339		(*E*)-Carvyl acetate	0.5		1, 2
1343	1748	Piperitone	0.2		1, 2
1344		α-Terpenyl acetate	0.9	0.6	1, 2, 3
1353	2186	Eugenol	0.2		1, 2, 3
1382	1838	(*E*)-β-Damascenone	0.4		1, 2
1432		Cuminyl acetate	0.1		1, 2
1437		Aromadendrene	0.1		1, 2
1453	1867	(*E*)-Geranyl acetone	0.3		1, 2
1489	1649	(*Z*)-Lyratyl acetate	1.1		1, 2
1526	1773	δ-Cadinene	0.3	0.2	1, 2
1545	1940	Calacorene	0.2		1, 2
1553	2076	*cis*-α-Copaen-8-ol	0.8		1, 2
1577	2150	Spathulenol	1.7	1.1	1, 2
1581	2008	Caryophyllene oxide	0.4		1, 2, 3
1598		α-Cedrol	0.4		1, 2
1599		Curcumol	0.3		1, 2
1600		Widdrol	0.2	0.2	1, 2
1622	2181	*nor*-Coopanone	0.2		1, 2
1630		γ-Eudesmol		0.3	1, 2
1640	2316	Caryophylladienol	0.2		1, 2
1652		9-Aristolen-1-α-ol	0.4	0.5	1, 2
1654	2235	Isospathulenol	0.5		1, 2
1677	2256	Cadalene	0.5		1, 2
1764		Guaiazulene		0.1	1, 2, 3
1769	2713	Tetradecanoic acid	0.5		1, 2, 3
1776	2606	α-Costol	0.2		1, 2
1814		Eudesm-4(14)-en-3α,11-diol	0.2		1, 2
1845	2131	Hexahydrofarnesylacetone	0.8	0.3	1, 2
1892	1946	1-Nonadecene	0.8		1, 2
1921		γ-Tetradecalactone		0.1	1, 2
1925	2208	Hexadecanoic acid methyl ester	0.2		1, 2, 3
1949	2622	(*Z*)-Phytol	0.5		1, 2
1972	**2931**	**Hexadecanoic acid**	**3.3**	**0.5**	1, 2, 3
1993		1-Eicosene	0.3		1, 2
2082		Octadecanol	0.2		1, 2
2100	2100	Heneicosane		0.1	1, 2, 3
2117	3168	(*Z*)-9-Octadecenoic acid		0.1	1, 2, 3
2118	2813	γ-Hexadecalactone		0.1	1, 2
2300	2300	Tricosane	0.6	0.3	1, 2, 3
2400	2400	Tetracosane	0.1	0.1	1, 2, 3
2500	2500	Pentacosane	0.9	1.1	1, 2
2600	2600	Hexacosane	0.1	0.2	1, 2
2700	2700	Heptacosane	0.7	0.6	1, 2
2800	2800	Octacosane	0.1	0.1	1, 2
2822		Squalene	0.2		1, 2
2900	2900	Nonacosane	0.6	0.3	1, 2
		TOTAL	**91.8**	**94.0**	

[a]: HP-5 MS column; [b]: HP Innowax column; [c]:**A**: aerial parts; **C**: capitula; t: trace, <0.05%; [d]: 1D: retention index, 2: mass spectrum, 3: co injection with authentic compound.

flowers of *T. vulgare* subsp. *siculum*.The components detected in the aerial parts (A) and capitula (C) are shown in Table 1, listed in order of elution from a HP 5MS column. Ninety-four components were identified, 77 in A and 60 in C, which represented 91.8% and 94.0% of the oils, respectively. In both oils, α-thujone, β-thujone and 1,8-cineole were the main components: 67.0% (C) and 53.6% (A). The capitula oil contains a greater amount of thujones than the oil from the aerial parts, while the content of 1,8-cineole is the same in both oils. Furthermore, while the oil from the capitula is richest in β-thujone, the oil from the aerial parts contains a greater amount of α-thujone. Among the other terpenoids characteristic of the oils of *Tanacetum* species, the total content of the chrysanthenol derivatives represents 2.1% (C) and 1.9% (A); the absence of camphor in both oils is also noteworthy. The oils show also the presence of sesquiterpenes with a prevalence of oxygen containing sesquiterpenes that amounted to 5.5% for the twelve constituents of the oil from A and to 2.1% for the four components of this fraction of oil C. In both oils, spathulenol is the main sequiterpenoid. In previous works [10,14,20] interesting comparisons between samples of *T. vulgare* collected in different regions were reported. The results showed that within the same species great variability was connected to the habitat [10,20]; this was also highlighted by morphological considerations [10], whereas *T. vulgare* subsp. *siculum* is a very localized species and appears to be morphologically uniform.

Data obtained from the present study allow us to affirm that *T. vulgare* subsp. *siculum* is a thujone chemotype. This high content of thujone could also be ascribed to the plants high exposure to sunshine [20].

Experimental

Plant material: Aerial parts of *Tanacetum vulgare* subsp. *siculum* (Guss.) Raimondo et Spadaro were collected at Caserma Mafauda (1250 m s.l.), Nebrodi Mountians, Sicily, in July 2008. Samples of the studied material, identified by F. M. Raimondo and V. Spadaro, are kept in the Herbarium Mediterraneum of the Palermo University [Raimondo & Spadaro (PAL)].

Isolation of essential oil: The air-dried samples of aerial parts (A) and capitula (C) of *T. vulgare* subsp. *siculum* were ground in a Waring blender and the oils were obtained by hydrodistillation for 3 h, using *n*-hexane as solvent and a Clevenger-type apparatus, according to the European Pharmacopoeia method [21]. The oils were dried over anhydrous sodium sulfate and stored under N_2 at +4°C in the dark until tested and analyzed. The sample yielded 0.19% (A) and 0.31% (C) of yellow oil (w/w), with a pleasant smell.

Gas chromatography-mass spectrometry: 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, 0.25 μm film thickness). Column temperature was initially kept at 40°C for 5 min, then gradually increased to 250°C at 2°C/min, held for 15 min and finally raised to 270°C at 10°C/min. Diluted samples (1/100 v/v, in *n*-pentane) of 1μL were manually injected at 250°C, in the splitless mode. Flame ionization detection (FID) was performed at 280°C. A fused silica HP Innowax polyethylenglycol capillary column (50 m x 0.20 mm, 0.25 μm film thickness) was also used for analysis. In both cases helium was the carrier gas (1 mL/min). GC-MS analysis was performed on an Agilent 6850 Ser. II apparatus, fitted with a fused silica DB-5 capillary column (30 m x 0.25 mm, 0.33 μm film thickness), coupled to an Agilent Mass Selective Detector MSD 5973; ionization voltage 70 eV; electron multiplier energy 2000 V; source temperature 250°C. Mass spectra were scanned in the range 35-450 amu, scan time 5 scans/s. Gas chromatographic conditions were the same as those for GC; transfer line temperature, 295°C.

Identification of components: Most constituents were identified by gas chromatography by comparison of their retention indices (LRI) on apolar and polar columns, determined relative to the retention times of a series of *n*-alkanes (C_8-C_{24}) with linear interpolation with those of the literature [22,23]. Further identification was achieved by comparison of their mass spectra from both columns with either those stored in NIST 02 and Wiley 275 libraries or with mass spectra from the literature [22, 24] and our home made library. Component relative concentrations were calculated based on GC peak areas without applying any correction factors.

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