SHORT REPORT

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Volatile Constituents of *Ferula communis* L. subsp. *communis* Growing Spontaneously in Greece

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Abstract: The essential oils of Greek *Ferula communis* subsp. *communis* from different plant parts were obtained by hydrodistillation and analyzed by means of GC and GC-MS. Ninety three compounds were identified in the total essential oils. Sesquiterpenes were the most dominant class of compounds in the leaves and inflorescences oils, while infructescences oils were rich in monoterpenes with α-pinene (35.2-40.6%) being the dominant component.

Keywords: *Ferula communis* subsp. *communis*; essential oil composition; δ-cadinene; α-eudesmol; α-pinene.

1. Plant Source

Ferula L. is the third largest genus in the Umbelliferae family and is comprised of 172 species, 8 of which are represented in Europe. The genus is widespread from the Mediterranean region to central Asia. *Ferula communis* L. ("giant fennel") is a perennial plant growing wild from southern Europe to Syria [1] and includes two subspecies; *F. communis* subsp. *communis* and *F. communis* subsp. *glauca* [2]. In ancient Greece, *F. communis* was known as *Narthex* and according to the Greek mythology, its stem had been used by Prometheus in order to bring fire to Earth hidden in it [3]. Although several *Ferula* species have been used in folk medicine, *F. communis* was reported to be highly toxic to animals and humans [4]. It has been used in traditional Arabic medicine for the treatment of skin infections, fever and dysentery [5]. *Ferula* species have also a long story of their hormonal effects and especially *F. communis* has been reported as a possible source of phytoestrogens [6]. In the course of phytochemical studies of medicinal plants from Greece, we analyzed the volatile constituents from different parts of *F. communis* subsp. *communis*.

The plant was collected from three different regions in Chania (Crete) at the flowering stage (May 2007) [samples le_1, $infl_1$: 3 km SW Chania] and at the fruiting stage (April 2008) [samples le_2, $infr_2$: along the road between airport and Ag. Triada, samples le_3, $infr_3$: 5 km SW Chania]. Voucher

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specimens (le_1, $infl_1$-OT81a; le_2, $infr_2$-OT81b; le_3, $infr_3$-OT81c) have been kept at the Herbarium of the University of Athens (ATHU).

2. Previous Studies

Coumarins, sesquiterpenoid esters such as daucane derivatives are often isolated as characteristic constituents of *F. communis* [6,7]. Concerning *F. communis* volatiles constituents only a few studies have been reported the chemical composition of essential oils [8-11].

3. Present Study

Leaves [samples le_1, le_2, le_3], inflorescences [sample $infl_1$] and infructescences [samples $infr_2$, $infr_3$] were subjected separately to hydrodistillation for 3 hours using a modified Clevenger-type apparatus with a water-cooled oil receiver to obtain the essential oils. The essential oils were dried over anhydrous sodium sulfate and kept at -4^{o}C until analysis.

GC/MS: Analysis of the essential oils was performed using a Hewlett Packard (Hewlett Packard GmbH, Waldbronn, Germany) model 5973-6890 GC-MS system operating in the EI mode at 70eV, equipped with a split/splitless injector (200^{o}C). The transfer line temperature was 250^{o}C. Helium was used as carrier gas (1 mL/min) and the capillary column used was HP 5MS (30 m × 0.25 mm; film thickness 0.25 μm; Agilent, Palo Alto, CA, USA). The temperature program was the same with that used for the GC analysis; split ratio 1:10. The obtained oils were dissolved in n-hexane (100 μL/mL). The injected volume was 1μL. Total scan time 83.33 min. Acquisition mass range 40-400 amu. The identification of the compounds was based on comparison of their retention indices (RI), their retention times (RT) and mass spectra with those obtained from authentic samples (purchased from the Sigma-Aldrich, Buchs SG, Switzerland) and/or the NIST 02, Wiley 6th libraries (available through Hewlett Packard) and the literature [12].

GC/FID: GC analysis of the essential oils was carried out using a SRI (Brooks, Hatfield, PA, USA) 8610C GC-FID system, equipped with DB-5 capillary column (30 m x 0.32 mm; film thickness 0.25 μm; J & W, CA, USA) and connected to a FID detector. The injector and detector temperature was 280^{o}C. The carrier gas was He, at flow rate of 1.2 mL/min. The thermal program was 60^{o}C - 280^{o}C at a rate of 3^{o}C/min; split ratio 1:20. Two replicates of each oil were processed in the same way. The injected volume was 1μL (10% hexane soln. of each oil).

The chemical composition of the essential oils from different plant parts of *F. communis* subsp. *communis* is reported in Table 1. The essential oils from the leaves (samples le_1, le_2, le_3) were characterized by the abundance of sesquiterpenes (85.7-88.7%). Specifically, in sample le_1 the main constituents were α- and β- eudesmol (12.6%, 9.7%), in sample le_2 δ-cadinene (10.8%) and germacrene B (10.1%) and in the sample le_3 α-eudesmol (16.1%), δ- and γ- cadinene (13.6%, 12.5%). The inflorescences oil (sample inf_1) was also abundant in sesquiterpenes with γ- and ar- curcumene (14.0%, 8.5%) being the main ones, while γ-terpinene (10.8%) was the major component in monoterpenes fraction. In contrary the infructescences oils [samples $infr_2$, $infr_3$] possessed high levels of monoterpenes, with α-pinene (35.2% and 13.6%, respectively) and β-pinene (40.6%, 10.2%) being the major compounds. In the literature, composition of *F. communis* volatiles from the Mediterranean area have been reported: leaves oil from Corsica was characterized by the presence of myrcene (53.5%) and aristolene (8.5%) [8]; in the inflorescences oil from Sardinia the main metabolites were the sesquiterpenes α- and β-gurjunene (40.7 and 7.1%, respectively) [9]; the oils from the aerial parts of Sardinian populations had as major volatiles in the poisonous chemotype the sesquiterpenes aristolene (47.1%) and (*E*,*E*)-farnesol (21.2%), while in the non poisonous chemotype, the main component was the sesquiterpene *allo*-hedycaryol (53.7%) [10]. The essential oil composition of *F. glauca* (formely considered as a subspecies of *F. communis*) from central Italy appear to be different having as major volatiles in leaves (*E*)-caryophyllene and caryophyllene oxide, in flowers α-pinene, myrcene and germacrene D and in fruits α- and β-pinene [11]. It seems that going East in the Mediterranean basin leaves and inflorescences oils from populations of *F. communis* are richer in sesquiterpenes, while the infructescences oils are rich in monoterpenes.

Table 1. Chemical composition of the essential oils from different parts of *F. communis* subsp. *communis*

RI	Constituents	le_1	le_2	le_3	$infl_1$	$infr_2$	$infr_3$
927	α-Thujene	-	-	-	-	t	t
936	α-Pinene	t	t	7.2	5.0	35.2	40.6
951	Camphene	-	-	-	-	t	t
972	Sabinene	-	-	-	-	t	t
976	β-Pinene	t	-	1.4	1.4	13.6	10.2
987	Myrcene	2.4	-	-	2.8	t	4.4
988	1,8-Dehydro-cineole	-	t	-	-	-	-
995	n-Octanal	-	t	-	-	t	-
998	δ-2-Carene	t	-	-	-	-	-
999	α-Phellandrene	-	-	-	-	-	t
1020	*p*-Cymene	5.0	t	-	5.8	t	-
1024	Limonene	-	t	-	-	-	-
1026	δ-3-Carene	-	-	-	-	1.8	2.8
1031	(*Z*)-β-Ocimene	-	-	-	-	-	t
1045	(*E*)-β-Ocimene	-	-	-	-	-	t
1055	γ-Terpinene	t	t	-	10.8	t	t
1082	Fenchone	t	-	-	-	-	-
1085	Terpinolene	-	t	-	-	t	t
1092	Linalool	t	-	-	-	-	t
1100	n-Undecane	-	-	-	-	t	-
1101	n-Nonanal	-	t	-	-	t	t
1105	1,3,8-*p*-Menthatriene	-	-	-	-	-	t
1143	(*Z*)-2-Nonen-1-al	-	t	-	-	t	t
1343	α-Cubebene	t	t	-	-	t	-
1345	α-Longipinene	t	-	-	t	-	t
1367	α-Ylangene	1.4	1.7	t	t	t	t
1367	α-Copaene	1.4	1.4	1.4	0.9	t	t
1368	Isoledene	-	t	-	t	-	-
1372	Daucene	t	1.5	2.1	1.6	t	0.5
1377	β-Cubebene	-	t	-	t	t	t
1378	β-Bourbonene	t	t	t	t	t	t
1381	β-Elemene	t	-	-	0.6	-	-
1392	β-Longipinene	-	-	2.8	-	-	t
1393	*iso*-Italicene	-	-	-	-	t	t
1394	Italicene	t	-	-	1.2	t	t
1395	β-Isocomene	-	-	-	t	-	-
1397	Dodecanal	-	-	-	-	2.2	t
1401	α-Cedrene	t	t	-	2.0	-	-
1407	β-Caryophyllene	3.8	-	-	-	-	-
1409	β-Cedrene	-	t	-	4.3	1.6	t
1410	β-Ylangene	-	2.4	-	-	t	t
1419	*cis*-Thujopsene	-	t	-	-	t	t
1420	β-Copaene	t	2.3	1.1	t	t	t
1424	α-*trans*-Bergamotene	t	t	-	t	t	t
1425	γ-Elemene	t	5.5		0.2	t	t
1429	Aromadendrene	1.0	1.5	-	t	t	t
1443	α-Humulene	t	1.3	-	t	-	-
1444	(*E*)-β-Farnesene	2.9	3.8	-	1.1	2.2	t
1447	*allo*-Aromadendrene	-	t	-	0.7	-	-
1454	α-Acoradiene	2.3	t	-	7.5	1.1	1.2
1456	*cis*-Muurola-4(14),5-diene	-	t	-	1.9	1.4	2.1
1459	β-Acoradiene	t	-	-	2.0	t	t
1462	*trans*-Cadina-1,(6),4-diene	-	t	4.5	-	1.4	-
1463	γ-Gurjunene	-	t	-	-	t	t
1465	γ-Muurolene	3.8	6.9	1.5	0.8	2.7	t
1466	*ar*-Curcumene	3.7	-	-	8.5	1.5	1.5
1468	γ-Curcumene	t	-	-	14.0	t	-

1469	γ-Himachalene	-	3.6	-	-	1.5	1.1
1470	α-Amorphene	2.3	2.8	-	-	t	t
1474	(*E*)-β-Ionone	2.2	t	-	-	-	t
1478	*cis*-β-Guaiene	-	3.9	1.2	-	t	t
1481	γ-Amorphene	1.8	-	-	-	-	-
1485	Bicyclogermacrene	-	t	-	0.9	t	1.1
1486	α-Muurolene	1.8	2.0	-	-	-	-
1490	β-Himachalene	-	-	-	2.3	t	t
1488	*trans*-β-Guaiene	-	-	-	-	t	t
1490	Cuparene	1.5	1.7	1.6	2.4	0.9	0.9
1491	β-Bisabolene	3.6	3.7	-	0.8	5.8	3.5
1497	δ-Amorphene	-	1.9	-	-	t	t
1499	γ-Cadinene	5.4	5.2	12.5	-	-	-
1501	β-Curcumene	-	-	-	3.5	t	t
1508	δ-Cadinene	7.0	10.8	13.6	1.7	4.1	t
1515	Zonarene	t	2.5	-	-	-	-
1520	*trans*-Cadina-1(2),4-diene	t	t	t	1.9	t	t
1524	α-Cadinene	t	t	t	-	t	-
1525	*cis*-Calamenene	-	-	t	-	-	t
1531	α-Calacorene	-	t	t	-	t	t
1532	Selina-3,7,(11)-diene	t	t	-	-	-	-
1534	Elemol	t	-	-	1.0	-	t
1545	Germacrene B	2.0	10.1	2.2	1.6	1.4	t
1550	β-Calacorene	t	t	-	-	-	-
1568	Caryophyllene oxide	8.2	1.8	1.3	t	-	-
1576	β-Copaen-4-α-ol	-	-	-	-	t	4.6
1580	Carotol	t	-	t	2.9	-	2.1
1613	1-*epi*-Cubenol	-	t	t	t	2.2	-
1615	Eremoligenol	3.5	-	3.8	t	1.8	2.2
1615	γ-Eudesmol	6.2	-	7.4	0.9	-	6.7
1622	β-Acorenol	t	-	-	0.9	3.3	1.3
1625	*epi*-α-Cadinol	t	3.2	-	-	1.5	t
1631	α-Muurolol	2.8	4.2	4.3	-	2.0	-
1632	Cubenol	t	t	-	t	-	-
1636	β-Eudesmol	9.7	-	8.6	0.9	-	4.7
1639	α-Eudesmol	12.6	-	16.1	2.4	-	4.1
	Total	**98.3**	**85.7**	**94.6**	**97.2**	**89.2**	**95.6**
	Grouped components						
	Monoterpenes	7.4	t	8.6	25.8	50.6	58.0
	Oxygenated monoterpenes	t	-	-	-	t	t
	Sesquiterpenes	45.7	76.5	44.5	62.4	25.6	11.9
	Oxygenated sesquiterpenes	43.0	9.2	41.5	9.0	10.8	25.7
	Others	2.2	t	-	-	2.2	t

RI= retention indices relative to C_9-C_{23} *n*-alkanes on the HP-5MS column; le=leaves, infl=inflorenscences, infr=infructescences; le_1, $infl_1$: 3 km SW Chania, le_2, $infr_2$: along the road between airport and Ag. Triada, le_3, $infr_3$: 5 km SW Chania; t= trace (<0.1%)

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