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Essential Oil Composition of Four Endemic *Ferulago* Species Growing in Turkey

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The essential oils from aerial parts of *Ferulago pachyloba* (Fenzl) Boiss., *F. platycarpa* Boiss. & Bal., *F. isaurica* Peşmen, and *F. longistylis* Boiss. (Apiaceae) were obtained by hydrodistillation and analyzed by GC and GC-MS. The highest oil yield (1.50%) was obtained from *F. pachyloba* followed by *F. longistylis* (0.16%), *F. isaurica* (0.08%) and *F. platycarpa* (0.07%). Fifty-three compounds were identified in the oil of *F. pachyloba* with (*Z*)-β-ocimene (25.7%) and α-pinene (9.8%) as main constituents; sixty-seven in the oil of *F. platycarpa* with 2,3,6-trimethylbenzaldehyde (29.8%) and *cis*-chrysanthenyl acetate (24.2%) as main components; seventy-eight in the oil of *F. isaurica* with nonacosane (25.5%) and hexadecanoic acid (14.8%) as main constituents; and fifty-nine in the oil of *F. longistylis* with 2,3,6-trimethylbenzaldehyde (32.7%) and bornyl acetate (12.6%) as main components. Quantitative and qualitative differences in the oil compositions of these four species were observed.

Keywords: *Ferulago pachyloba*, *F. platycarpa*, *F. isaurica*, *F. longistylis*, Apiaceae, essential oil composition, GC analysis, GC-MS analysis.

Ferulago W. Koch. is a perennial genus of the Apiaceae family represented by nearly forty species, thirty-two of which exist in the flora of Turkey, seventeen being endemic. This suggests that the gene centre for this genus is Anatolia [1-7]. The species of this genus are known as kuzukemirdi, kuzukişnişi, kuzubaşı, çakşırotu, cağşır, asaotu and kişniş in different regions of Turkey.

Ferulago species have been used since antiquity for the treatment of intestinal worms, hemorrhoids and as a sedative, tonic and digestive. Moreover, they are used against ulcers, snake bites, spleen diseases and headache [8]. It has also been reported that gums obtained from the incision of the roots of some species are used as seasoning and as a carminative [9]. However, the plants are mainly known as aphrodisiacs and as a preferred fodder to increase animal productivity [10].

Ferulago species have been reported to contain flavonoids, quinones, coumarin esters, sesquiterpenes, coumarins, furanocoumarins and aromatic compounds [11-17]. The genus is rich in essential oil and several species have been studied; *F. angulata* (Schlecht.) Boiss., *F. asparagifolia* Boiss., *F. galbanifera* (Mill.) W. D. J. Koch, *F. humilis* Boiss., *F. sandrasica* Pesmen et Quézel, *F. aucheri* Boiss., *F. confusa* Velen, *F. idaea* Özhatay et E. Akalın, *F. macrosciadia* Boiss. et Bal., *F. mughlae* Pesmen, *F. silaifolia* (Boiss.) Boiss, *F. bernardii* L. Tomkovich & M. Pimenov. *F. carduchorum* Boiss. et Hausskn., *F. contracta* Boiss. et Hausskn, *F. isaurica* Pesmen, *F. syriaca* Boiss., *F. nodosa* (L.) Boiss., *F. thyrsiflora* (Sm.) W. D. J. Koch, *F. phialocarpa* Rech. f. et Riedl, *F. sylvatica* (Besser) Reichb., *F. thirkeana* (Boiss.) Boiss., *F. trachycarpa* Boiss., *F. longistylis* Boiss. The major constituents of the oils of these foregoing species were β-ocimene, α-pinene, α- and β-phellandrene, limonene, myrcene and *p*-cymene [18]. The aim of this paper is to present and compare the chemical composition of the essential oils of four endemic *Ferulago* species; *F. pachyloba*, *F. platycarpa*, *F. isaurica* and *F. longistylis* growing in Turkey. Gas chromatographic (GC) and gas chromatographic-mass spectroscopic (GC-MS) analysis helped us to establish the composition and the relationship of the essential oil constituents. To the best of our knowledge, this is the first report on the chemical analysis of *F. pachyloba* and *F. platycarpa.* The identified constituents are presented in Table 2.

Table 1: Collection data for the investigated *Ferulago* species.

Code	*Ferulago* species	Specimen Herbarium Number	Collection place, and altitude	Collection date	Oil Yield[¥] (%)
A	*F. pachyloba*	GAZI[Φ]	Niğde, Aladağlar, around Demirkazık, rocky slopes, 2600 m	August 2007	1.5
B	*F. platycarpa*	AEF* 23173	Nevşehir, Üçhisar, Gemil Mount, northern slopes, 1450 m	July 2004	0.07
C	*F. isaurica*	AEF 22957	Alanya – Antalya road, 6 km after Derince turn, rocky slopes, 1110 m	September 2002	0.08
D	*F. longistylis*	AEF 23795	Erzincan, Sakaltutan Pass, roadsides, 2000 m	July 2006	0.16

[Φ] Herbarium of Gazi University Faculty of Arts and Sciences
* Herbarium of Ankara University Faculty of Pharmacy
[¥] Yields are given on moisture free basis

A total of fifty-three compounds representing 96.6% of the oil were identified in the essential oil of *F. pachyloba*. (*Z*)-β-ocimene, α-pinene, sabinene and δ-cadinene were the major components, amounting to 25.7%, 9.8%, 6.3% and 5.6%, respectively. The analysis of *F. platycarpa* resulted in the identification of sixty-seven volatile compounds representing 94.1% of the oil. 2,3,6-Trimethylbenzaldehyde at 29.8% was the most abundant compound in the volatile oil, followed by *cis*-chrysanthenyl acetate (24.2%), nonacosane (7.7%) and α-pinene (4.2%). Seventy-eight compounds were characterized in the oil of *F. isaurica* representing 86.3% of the oil. The major constituents were nonacosane (25.5%), hexadecanoic acid (14.8%), bornyl acetate (5.3%) and terpinen-4-ol (4.6%). Fifty-nine compounds, representing 92.5% of the oil, were identified in the oil of *F. longistylis* with 2,3,6-trimethylbenzaldehyde (32.7%), bornyl acetate (12.6%), *p*-cymene (11.9%) and *cis*-chrysanthenyl acetate (4.2%), as main components.

Considering the different groups of compounds, monoterpene hydrocarbons contributed most to the oils obtained from *F. pachyloba* (57.7%) and *F. longistylis* (22.4%), whereas oxygenated monoterpenes formed the main portion of the oils of *F. platycarpa* (33.1%) and *F. isaurica* (18.0%). Comparison of the main constituents of these four species (Table 2) shows that each species has a different set of dominant compounds. However, previous studies of the oils of *Ferulago* species [18] revealed that the three compounds detected in high percentages in this study, namely (*Z*)-β-ocimene, α-pinene and *p*-cymene have also been detected as major components in many other species. Erdurak *et al*. reported the essential oil contents of the fruit and root of *F. isaurica* [19] in 2006. The oils obtained from the different parts of this species did not show much qualitative resemblance. The major constituents detected, namely α-pinene, limonene, and myrcene in the fruit, and terpinolene and myrcene in the root were not identified in the oil from the aerial parts of *F. isaurica*. Analysis of the fruit oil of *F. longistylis* conducted in 2008 showed 2,3,6-trimethylbenzaldehyde and bornyl acetate as the major compounds, in accordance with the results obtained for the aerial parts of the same species in this study [18].

Chemical profiling of the volatiles may be useful in taxonomical classification. The results presented in this study confirm some specific features of the oil composition of *Ferulago* species in Turkey and contribute to a better knowledge of this genus.

Experimental

Plant materials: Aerial parts of 4 *Ferulago* species were collected by the authors from their natural habitats in different localities of Turkey by random sampling from a single established population, as shown in Table 1; the plants were identified by Prof. Dr. Hayri Duman and voucher specimens were deposited in GAZI and in AEF.

Essential oil isolation: Air dried aerial parts of plants (50 g) were subjected hydrodistillation for 3 h using a Clevenger-type apparatus according to the method recommended in the European Pharmacopoeia [20]. The obtained oils were dried over anhydrous sodium sulfate and stored in sealed vials at +4°C in the dark until analyzed and tested. All oils were pleasant smelling, transparent with a faint yellow color.

GC/MS analysis: GC-MS analysis was carried out with an Agilent 5975 GC-MSD system. An Innowax FSC column (60 m x 0.25 mm, 0.25 μm film thickness) was used with helium as carrier gas (0.8 mL/min). The GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, and kept constant at 220°C for 10 min and then programmed to 240°C at a rate of 1°C/min. The split ratio was adjusted at 40:1. The injector temperature was set at 250°C. Mass spectra were recorded at 70 eV. The mass range was from *m/z* 35 to 450.

GC analysis: The GC analysis was carried out using an Agilent 6890N GC system. The FID detector temperature was 300°C. To obtain the same elution order with GC/MS, simultaneous autoinjection was used on a duplicate column applying the same operational conditions. Relative percentage amounts of the separated compounds were calculated from FID chromatograms.

Table 2: Composition of the essential oils of A: *Ferulago pachyloba*, B: *F. platycarpa*, C: *F. isaurica*, and D: *F. longistylis*.

RRI	Compound	A (%)	B (%)	C (%)	D (%)
1032	α-Pinene	9.8	4.2	-	3.5
1035	α-Thujene	0.3	0.1	-	0.1
1076	Camphene	0.8	0.2	-	0.2
1118	β-Pinene	0.6	0.3	-	0.2
1132	Sabinene	6.3	1.6	-	0.4
1159	δ-3-Carene	3.0	-	-	-
1174	Myrcene	1.9	1.7	-	1.4
1176	α-Phellandrene	0.5	-	-	-
1195	Dehydro-1,8-cineole	0.1	-	tr	-
1203	Limonene	2.2	0.6	0.9	0.5
1218	β-Phellandrene	0.2	0.1	-	0.1
1246	(*Z*)-β-Ocimene	25.7	0.2	-	2.3
1255	γ-Terpinene	3.1	0.3	0.3	1.4
1266	(*E*)-β-Ocimene	1.9	0.4	-	0.4
1280	*p*-Cymene	1.2	1.5	0.2	11.9
1286	Isoterpinolene	0.2	-	-	-
1290	Terpinolene	1.2	-	0.2	-
1294	1,2,4-Trimethyl benzene	-	0.8	-	1.8
1355	1,2,3-Trimethyl benzene	-	0.3	-	0.7
1382	*cis*-Alloocimene	0.2	-	-	-
1429	Perillen	-	0.1	-	-
1439	γ-Campholene aldehyde	-	0.1	-	0.1
1441	(*E*)-2-Octenal	-	0.1	-	-
1446	2,6-Dimethyl-1,3(*E*),5(*Z*),7-octatetraene	0.1	-	-	-
1452	α,*p*-Dimethylstyrene	-	0.1	0.2	0.2
1476	(*Z*)-β-Ocimene epoxide	-	tr	-	0.1
1479	δ–Elemene	-	0.1	-	-
1492	Cyclosativene	-	0.1	tr	-
1497	α-Copaene	0.2	0.2	0.3	tr
1499	α-Campholene aldehyde	-	0.6	0.1	0.7
1528	α-Bourbonene	-	-	0.1	-
1535	β-Bourbonene	0.1	0.1	0.5	0.2
1553	Linalool	-		0.7	-
1562	Octanol	-	0.1	tr	-
1571	*trans*-*p*-Menth-2-en-1-ol	-	0.1	0.3	tr
1582	*cis*-Chrysanthenyl acetate	-	24.2	-	4.2
1586	Pinocarvone	0.1	-	-	-
1589	β-Ylangene	-	-	0.1	-
1591	Bornyl acetate	0.9	2.1	5.3	12.6
1597	β-Copaene	tr	-	0.1	-
1600	β–Elemene	0.6	0.2	1.2	-
1611	Terpinen-4-ol	-	1.3	4.6	0.4
1612	β-Caryophyllene	4.4	-	-	0.3
1639	*trans*-*p*-Mentha-2,8-dien-1-ol	-	-	0.3	-
1639	Cadina-3,5-diene	0.1	-	-	-
1645	*cis*-Verbenyl acetate	-	-	-	0.3
1648	Myrtenal	-	0.3	0.1	0.2
1650	γ–Elemene	-	-	-	-
1661	*trans*-Pinocarvyl acetate	0.3	0.9	-	1.0
1670	*trans*-Pinocarveol	-	0.7	0.4	0.4
1678	*cis*-*p*-Mentha-2,8-dien-1-ol	-	-	0.1	-
1683	*trans*-Verbenol	-	0.7	0.2	-
1687	α-Humulene	0.6	-	0.2	-
1700	*p*-Mentha-1,8-dien-4-ol (=Limonen-4-ol)	-	-	0.8	-
1704	Myrtenyl acetate	0.1	-	-	-
1704	γ-Muurolene	0.2	-	-	-
1706	α-Terpineol	-	-	0.5	-
1719	Borneol	-	0.1	0.3	0.3
1725	Verbenone	-	0.1	tr	0.1
1726	Germacrene D	1.9	-	1.7	-
1738	*p*-Mentha-1,5-dien-8-ol	-	-	-	0.7
1740	α–Muurolene	0.8	-	-	-
1741	β–Bisabolene	-	-	-	-
1742	β–Selinene	-	0.3	-	-
1744	α-Selinene	-	tr	0.2	-
1751	Carvone	-	0.1	0.7	-
1755	Bicyclogermacrene	1.2	-	-	-
1758	*cis*-Piperitol	-	tr	0.2	-
1763	Naphthalene	-	-	0.2	0.3
1764	*cis*-Chrysanthenol	-	0.7	-	-
1773	δ-Cadinene	5.6	-	0.3	-
1776	γ-Cadinene	1.2	-	0.2	-
1785	7-*epi*-α-Selinene	0.2	-	-	-
1786	*ar*-Curcumene	-	0.1	-	0.4
1797	*p*-Methyl acetophenone	-	-	0.1	-
1799	Cadina-1,4-diene (=Cubenene)	0.1	-	-	-
1804	Myrtenol	-	0.2	0.1	-
1811	*trans*-*p*-Mentha-1(7),8-dien-2-ol	-	-	0.3	-
1827	(*E,E*)-2,4-Decadienal	-	0.1	0.1	0.1
1838	(*E*)-β-Damascenone	-	-	0.1	-
1845	*trans*-Carveol	-	0.4	0.9	0.3
1857	Geraniol	-	-	0.3	-
1864	*p*-Cymen-8-ol	-	0.3	0.8	0.4
1868	(*E*)-Geranyl acetone	-	0.1	0.4	0.1
1882	*cis*-Carveol	-	-	0.2	-
1896	*cis*-*p*-Mentha-1(7),8-diene-2-ol	-	-	0.1	-
1900	*epi*-Cubebol	0.5	-	-	-
1925	2,3,4-Trimethyl benzaldehyde	-	1.5	-	3.1
1941	α-Calacorene	0.1	-	0.1	-
1945	1,5-Epoxy-salvial(4)14-ene	-	-	-	0.1
1957	Cubebol	0.6	-	-	-
1958	(*E*)-β-Ionone	-	-	0.1	-
1973	Dodecanol	-	0.1	-	-
2008	Caryophyllene oxide	0.5	-	1.7	0.2
2019	2,3,6-Trimethylbenzaldehyde	-	29.8	0.7	32.7
2037	Salvial-4(14)-en-1-one	-	-	0.3	0.1
2050	(*E*)-Nerolidol	-	-	0.5	-
2069	Germacrene D-4β-ol	5.3	-	-	-
2071	Humulene epoxide-II	-	0.1	0.2	0.1
2073	*p*-Mentha-1,4-dien-7-ol	-	-	0.1	-
2080	Cubenol	0.2	-	-	-
2088	1-*epi*-Cubenol	0.2	-	-	-
2100	Heneicosane	-	0.1	-	-
2103	Guaiol	0.6	-	-	-
2122	Hedycaryol	1.9	-	-	-
2130	Salviadienol	-	-	0.3	0.2
2131	Hexahydrofarnesyl acetone	-	0.3	0.8	-
2144	Spathulenol	1.1	0.7	0.9	-
2148	(*Z*)-3-Hexen-1-yl benzoate	-	-	-	0.9
2179	Tetradecanol	-	0.2	0.3	-
2187	T-Cadinol	1.8	-	-	-
2200	Docosane	-	0.1	-	-
2209	T-Muurolol	1.5	-	-	-
2219	Dimyrcene II-a	-	0.1	0.7	-
2226	Methyl hexadecanoate	-	tr	0.3	-
2250	α-Eudesmol	0.2	-	-	-
2255	α-Cadinol	4.2	-	tr	-
2269	Guaia-6,10(14)-dien-4β-ol	-	12	0.3	-
2269	Dimyrcene II-b	-	-	0.4	-
2278	Torilenol	-	tr	0.4	-
2296	Myristicine	-	-	3.4	-
2300	Tricosane	-	0.2	0.6	0.1
2324	Caryophylla-2(12),6(13)-dien-5α-ol (=Caryophylladienol II)	-	-	0.5	0.3
2369	Eudesma-4(15),7-dien-1β-ol	-	-	1.1	0.3
2384	Hexadecanol	-	-	-	0.2
2384	Farnesyl acetone	-	-	1.0	-
2392	Caryophylla-2(12),6-dien-5β-ol (=Caryophyllenol II)	-	-	-	0.4
2500	Pentacosane	-	0.7	0.7	0.2
2622	Phytol	tr	0.4	3.9	0.2
2655	Benzyl benzoate	-	-	0.6	0.7
2670	Tetradecanoic acid	-	0.1	0.6	tr
2700	Heptacosane	-	-	0.6	tr
2822	Pentadecanoic acid	-	tr	tr	tr
2900	Nonacosane	-	7.7	25.5	2.7
2931	Hexadecanoic acid	-	3.9	14.8	1.7
	Monoterpene Hydrocarbons	**57.7**	**11.2**	**1.4**	**22.4**
	Oxygenated Monoterpenes	**2.9**	**33.1**	**18**	**21.9**
	Sesquiterpene Hydrocarbones	**17.3**	**1.1**	**5.0**	**0.9**
	Oxygenated Sesquiterpenes	**18.6**	**2.0**	**7.2**	**1.7**
	Diterpenes	**-**	**0.5**	**5. 0**	**0.2**
	Fatty acid	**-**	**4.0**	**15.4**	**1.7**
	Others	**0.1**	**42.2**	**34.3**	**43.7**
	Identified compounds	**53. 0**	**67. 0**	**78. 0**	**59. 0**
	Total	**96.6**	**94.1**	**86.3**	**92.5**

Identification of components: Identification of the essential oil components was carried out either by comparison of their relative retention times with those of authentic samples or by comparison of their relative retention index (RRI) with a series of *n*-alkanes. Computer matching against commercial (Wiley GC/MS Library, Adams Library, MassFinder 2.1 Library) [21,22], and in-house "Başer Library of Essential Oil Constituents" built up from genuine compounds and components of known oils, as well as MS literature data [23-25], was used for the identification.

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