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Composition of the essential oils of two Umbelliferae herbs (*Ferula communis* subsp. *communis* and *Smyrnium cordifolium*) growing wild in Turkey

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Abstract In this study, the essential oil composition of *Ferula communis* L. subsp. *communis* and *Smyrnium cordifolium* collected from Turkey were studied. The qualitative and quantitative essential oil composition were determined and compared with each other. The chemical composition of the essential oils obtained by hydrodistillation from *Ferula communis* subsp. *communis* and *Smyrnium cordifolium* were investigated by GC and GC-MS. The oil yield was determined as 0.2 and 0.3% (v/w) in the both essential oils respectively. Sixty three constituents were comprised the 99.4 % of the total essential oil extracted from the *Ferula communis* subsp. *communis*. The predominant compounds of the oil were determined as α-eudesmol (35.5%), 2-naphtalonemethanol (18%), di-epi-α-cedrene (3.5%) and t-muurolol (2.7%). The furanodiene (28%), bicyclogermacrene (19.5%), β-phellandrene (13.5%), cyclohexadecane (10.0%) and 2-pentadecanone (5.0%) were the main compounds identified in the oil of *Smyrnium cordifolium*, representing 99.2% total oil. The result has been discussed in view of natural products and chemotaxonomical approach in the genera patterns.

Keyword: *Ferula, Smyrnium,* GC-MS, Essential oil, Turkey

1. Introduction

The genus *Ferula* is represented in the Flora of Turkey by 17 species including 6 endemics [1]. The genus includes about 170 species occurring from central Asia westward throughout the Mediterranean region to northern Africa [2]. The Italian Flora comprises of 3 species endemics [3 and in the Flora of Iran by 30 species including 15 [4,5].

Several species of *Ferula* are appreciated in traditional medicine for the treatment of skin infections, stomach disorders, fever, dysentery, hysterias [6,7]. Hormonal effects and, more recently, cytotoxic and cancer preventing properties have been also investigated in plants of this genus [8]. Since the classical period, many species of this genus have been used for culinary or medical purposes. For example, fresh stalks of *F. orientalis* L. are used in Turkey as a flavouring agent in pickles [9]. Herbal products based on *F. hermonis* Boiss. can be found in the USA as a dietary supplement which is reputed to have aphrodisiac activity [10]. Asafoetida, an oleogum resin from the root of *F. assa-fo*etida L. and some other *Ferula* species, is used as a spice in Asia, especially in India, Nepal Iran and Afghanistan [11,12]. In Iranian traditional medicine asafoetida extract was used as an antihelminthic, as well as for teatment of abdominal pain, constipation and diarrhoea [13]. Similarly, oleogum resin obtained from *F. gummosa* Boiss. has been used for treating diarrhea [14]. It is reported that the fatty acids of the Apiaceae genus members is important infrageneric chemotaxonomic relationships [15].

The current interest in *F. communis* focuses on the presence of two chemotypes in the wild; these chemotypes are morphologically indistinguishab le and are endemic in Sardinia, Corsica and Morocco. In Sardinia, the distribution of the two chemotypes is parapatric (adjacent but not overlapping), with one preferring the coastal areas and the other common in mountainous inner lands. These two chemotypes show remarkable differences in secondary metabolites. One chemotype is poisonous to animals (FP) and mainly affects sheep, goats, cattle and horses; the other chemotype is non-poisonous (FNP) and contains mostly daucane derivatives. Today, we know that giant fennel is responsible for a hemorrhagic syndrome known as 'ferulosis', which affects livestock and occasionally even humans. The toxic principles of the plant were identified as a family of prenylated coumarins, which show anti-vitamin K activity in vivo [16].

Genus *Smyrnium* belongs to Umbelliferae family and is used by people as a herbal medicine in treatments for internal organ edema, especially in bladder and kidney problems. The leaves color is light green with colored flowers. The roots, stems and leaves contain strongly odored phenolic esence [17].

Smyrnium olusatrum L. is known by many names. For example, in Italian as "Macerone", "Corinoli" or "Sedano selvatico", in English as "Alexanders" and "wild Celery", and in French as "Maceron". The plant grows in hedgerows, hedged banks, sea cliffs and quarries. It is usually associated with old dwellings or ruins, especially monasteries or castles, where it is probably a relic of kitchen gardens. Indeed, many sites where Alexanders can be found growing wild today used to be monastery sites. Since ancient times (e.g. Roman age), this plant has been used as an edible vegetable because of the aromatic flavour of its parts [18].

Smyrnium cordifolium Boiss, is a native of Iran and eaten as a green by some people in West part of Iran. *S. cordifolium* Boiss., which is a biennial herb and widely distributed in the Zagroose Mountains at an altitude of 1400-2000 m in Iran. A number of medicinal facilities, e.g. diuretic, regenerative and counteracting renal calculus, have been described for all parts of the plant. It is often used internally for bladder and kidney swelling [19]. Additionally, the fleshy stems of the plant are used as vegetables [17].

Only a few reports on the analysis of essential oils of *Smyrnium* species have been published [20]. Essential oils obtained from stem leaves, roots and fruit of *Smyrnium cordifolium* have antibacterial effects, which they claim are due to the large amounts of sesquiterpene hydrocarbons such as curzerene, curzerenone and germacrone [21]. It is reported that the essential oils of *Smyrnium olusatrum* possess a good potential as chemopreventive agents, mainly on colon and breast cancer cells. The main furanosesquiterpenes, namely isofuranodiene, 1β-acetoxyfuranoeudesm-4(15)-ene and furanoeremophil-1-one, might partly contribute to the cytotoxic effects of essential oils although a synergistic effect, resulting from the complex composition, has to be taken into consideration [22].

2. Materials and Methods

2.1. Plant material

The plant specimens were collected from the natural habitats. *Ferula communis* L. subsp. *communis* was collected from Aydin and *Smyrnium cordifolium* from Tunceli/Turkey (Bagci, 4501 and 4720). Two voucher specimens (FUH-9252 and 9293) are kept at the Fırat University Herbarium (FUH), Elazig, Turkey.

2.2. Extraction of the essential oils

Air-dried aerial parts of the plant materials (100 g) were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h.

2.3. Gas chromatographic (GC) analysis

The essential oil was analyzed using HP 6890 GC equipped with FID detector and HP- 5 MS (30 m x 0.25 mm *i.d.*, film tickness 0.25 µm) capillary column was used. The column and analysis conditions were the same as in GC-MS expressed as below. The percentage composition of the essential oils was computed from GC-FID peak areas without correction factors.

2.4. Gas chromatography / mass spectrometry (GC-MS) analysis

The oils were analyzed by GC-MS, using a Hewlett Packard system. HP- Agilent 5973 N GC-MS system with 6890 GC in Plant Products and Biotechnology Res. Lab. (BUBAL) in Firat University. HP-5 MS column (30 m x 0.25 mm *i.d.,* film thickness 0.25 µm) was used with helium as the carrier gas. Injector temperature was 250 ^{o}C, split flow was 1 ml / min. The GC oven temperature was kept at 70 ^{o}C for 2 min. and programmed to 150 ^{o}C at a rate of 10 ^{o}C / min and then kept constant at 150 ^{o}C for 15 min to 240 ^{o}C at a rate of 5 ^{o}C / min. Alkanes were used as reference points in the calculation of Retention Indices (RI). MS were taken at 70 eV and a mass range of 35-425. Component identification was carried out using spectrometric electronic libraries WILEY, NIST.

3. Results and Discussion

The chemical composition of essential oils obtained by hydrodistillation of *Ferula communis* L. subsp. *communis* and *Smyrnium cordifolium* were investigated by GC and GC-MS. The composition of both oils are listed in Table 1, in which the percentage and Retention Indices of components are given.

The essential oils yield is 0.2 (v/w) of *Ferula communis* subsp. *communis*. Sixty three constituents were comprised the 99.4 % of the total essential oil extracted from this plant. The predominant compounds of the oil was determined as α–eudesmol (35.5%), 2-Naphtalonemethanol (18%), Di-epi-α–cedrene (3.5%), t-muurolol (2.7%).

Ferula glauca was formerly considered to the range of subspecies of *F. communis* (i.e. *F. communis* subsp. *glauca*), but actually is considered a different species, distinguishable by several differences in terms of morphology, anotomy, phenology and ecology. As concerning volatile fraction, that can be often a helpful tool to discriminate between different taxa, no report have been found to date on *F. glauca*, while few studies were recently conducted on *F. communis.* The following compounds were reported as major volatiles; myrcene and aristolene in the leaf oil from Corsica; α-and β-gurjunene in flowerheads oil from Sardinia; aristolene and farnesol in the poisonous chemotype, and allohedycaryol in the nonpoisonous chemotype, respectively, from aerial parts of Sardinian populations [3,23-24.

The essential oil of *Ferula communis* L., collected at Djebel El Ouahch- Constantine (North Eastern Algerian), is mainly characterized by the presence of myrcene, α- pinene and β-phellandrene. α- Pinene, reported as the main components of most studied *Ferula* species, could be considered as a chemotype of *Ferula* genus, but β-phellandrene (7.7%), seems to be exclusive to the present essential oil as a major component [25].

Mortazaienezhad and Sadeghian, reported only the identification of the major components of *Ferula gummasa*, namely α-and β-pinene, followed by α-thujene, δ-3-carene, β-phellandrene and sabinene, which accounted for 82% of the oil composition [26]. Ghannadi and Amree reported the volatile composition *F. gummosa* oleoresin essential oil collected in Kahsan (Center of Iran). The essential oil yield was 10.6% and the major components of the plant were β-pinene (58.8%), δ-3-carene (12.1%), α-pinene (5.7%) and β-myrcene (4.6%) [27].

The analysis of the essential oil from rhizome and roots of *Ferula hermonis* Boiss. (Apiaceae) by GC-FID, GC-MS and ^{13}C NMR allowed the identification of 79 constituents, more than 90% of the oil, the major one being α–pinene (43.3%), α-bisabolol (11.1%) and the unusual acetylenic compound 3,5-nonadiyne (4.4%) [28]. Several species of *Ferula* are reported as major components in the volatile oil from subterranean parts were oxygenated monoterpenes methyl thymol (41.2%) in *F. oopoda* [29], sesquiterpene hydrocarbons such as E-β-farnesene (8.4%) and α-zingiberene (6.9%) in *F. glauca* [18], sulphur-containing compounds (25.8%) in *F. persica* [30]. α-pinene has also been reported as major constituent in the essential oils from aerial parts of several species of *Ferula*, particularly from tops and seeds of *F. hermonis* [31].

In the study of Pavlovic et al. showed that, the sixty seven constituents that were identified account for 94.4% of the total oil. The essential oil was characterised by a high content of phenylpropanoids (56.0%). The most prominent compounds were phenylpropanoids elemicin (35.4%) and myristicin (20.6%), foolowed by cedrol (5.1%) and α-pinene (4.0%) [32]. Elemicin and myristicin were also among the main constituents of essential oil from roots of *F. glauca* [18]. On the other hand, essential oil obteined from oleogum resin of *F. gummosa* was rich in monoterpene hydrocarbons such as sabinene, α-pinene and β-pinene [33].

Kavoosi and Rowshan reported that, the properties of essential oils obtained from *Ferula assa-foetida* oleo-gum-resins (OGRs) collected in three collections times in 15 June (OGR1), 30 June (OGR2) and 15 July (OGR3) 2011 was investigated. Essential oil from OGR1 has contained the (E)-1-propenyl sec-butyl disulfide (23.9%) and 10-epi-γ-eudesmol (15.1%) in the high levels. Essential oil from OGR2 has also constituted the high levels of (Z)-1-propenyl sec-butyl disulfide (27.7%) and (E)-1-propenyl sec-butyl disulfide (20.3%). Finally, OGR3 has constituted β-pinene (47.1%) and α-pinene (21.3%) in high amounts [34].

The yields of essential oils of *S. cordifolium* was 0.3% (v/w). The composition of the essential oil are listed in Table 1. Thirty eight components representing 97.2% of the oil of *S. cordifolium* were identified with the furanodiene (28%), bicyclogermacrene (19.5%), β-phellandrene (13.5%), cyclohexadecane (10.0%) and 2-pentadecanone (5.0%) were found to be the major constituents.

Table 1: Constituents of the essential oil from *Ferula communis* L. subsp. *communis* and *Smyrnium cordifolium* Boiss.

Compounds	**RI**	**Percent Composition (%)**	
		F.com.* ssp. *com.	***S. cord.***
α-Thujone	1016	-	0.1
α-Pinene	1021	1.2	1.0
Camphne	1048	-	0.1
β-Pinene	1056	0.7	0.7
β- Myrcene	1064	-	2.5
α-Terpinene	1077	-	0.5
Limonene	1094	1.1	-
β-Phellandrene	1096	-	13.1
cis- Ocimene	1107	-	0.2
γ-Terpinene	1118	0.1	-
Linalool-L	1147	-	0.2
α-Terpineol	1215	-	0.3
Myrtenol	1216	0.1	-
Thymol	1296	0.2	-
α-Ylangene	1355	0.6	-
Piperidine	1359	0.4	-
α-Copaene	1360	0.2	0.1
β-Elemene	1370	-	0.5
1H-3a,7-Methanoazulene	1390	0.7	-
β-*C*aryophyllene	1393	1.5	1.7
β-Cubebene	1398	-	0.3
β-Copaene	1400	0.7	-
Cycloundecane	1401	0.4	-
Aromadendrene	1402	-	0.2
Azulene	1408	1.1	-
5,9-Undecadien	1411	0.8	-
α-Humulene	1418	0.5	0.2
Cyclohexene	1429	0.3	-
Napthalene	1431	0.4	-
Di-epi-α-cedrene	1432	3.5	-
Germacrene D	1435	2.5	2.2
Eudesma-4[14],11-diene	1440	0.7	-
Methyl-isoeugenol	1442	0.3	-
Bicyclogermacrene	1445	0.6	19.5
Isoledene	1450	1.3	-
β-Bisobolene	1452	2.1	-

Benzene-1-methyl-4	1453	2.0	-
γ-Cadinene	1455	0.3	-
δ-Cadinene	1458	0.2	-
cis-Calamenene	1462	0.2	0.2
γ-Bisobolene	1463	0.2	-
α-Cadinene	1470	0.5	-
α-Calacorene	1473	0.8	-
β-Sesquiphellandrene	1477	1.6	-
α-Farnesene	1482	0.3	-
Nerolidol	1484	0.6	-
Germacrene B	1486	-	1.7
1,5-Epoxysalvial-4[14]-ene	1490	0.2	-
α-Muurolene	1492	0.3	-
(+) Sphathulenol	1495	0.4	0.4
Caryophyllene oxide	1498	0.7	0.8
Salvial-4[14]en-1-one	1504	0.3	-
γ-Muurolene	1506	1.1	-
Ledol	1057	-	0.4
Jasmone	1510	0.6	-
α-Selinene	1512	-	0.6
Humulene epoxideII	1514	0.2	-
β-Selinene	1516	-	0.1
Isolongifolene	1518	1.1	-
Vulgarol B	1521	2.1	-
Isospathulenol	1526	18.0	-
t-Muurolol	1531	2.7	-
δ-Selinene	1535	1.0	-
Caryophylla-3,8[13]dien-5β-ol	1539	-	0.2
α-Eudesmol	1540	35.5	-
γ-Gurjunene	1544	1.0	-
Cadelene	1548	1.1	-
Ethanone	1555	0.7	-
Thujopsene	1556	0.7	0.3
Cyercene	1558	0.3	-
Valeranone	1560	-	2.6
γ-Curcumene	1567	0.4	-
Isoaromadendrene epoxide	1569	0.4	0.2
Ledene	1575	0.2	-
2- Heptanone	1586	0.2	-
Benzylbenzoate	1595	-	0.2
Ledene oxide	1596	0.2	-
2-Pentadecanone	1631	0.6	5.0
Ethanone	1640	-	1.0

1,2-Benzenedicarboxylicacid	1645	0.3	0.3
Cyclohexadecane	1650	-	10.0
Cycloprop[e]azulene	1668	-	0.2
Alexandrofuran	1677	-	2.0
Furanodiene	1707	-	28.0
Hexadecanal	1732	0.1	-
Heneicosane	1793	0.3	-
Tetracosane	1947	-	1.6
Total		**99.4**	**99.2**
Monoterpenes		3.4	18.7
Sesquiterpenes		94.3	32.2
Ketones		1.3	6.5
Alkanes		-	10.2
Fat		0.3	1.6
Furanosesquiterpenes		-	30.0
Aldehydes		0.1	-

Maggi et al. reported that the composition of essential oils from different parts of *S. olusatrum*, as eighty-four components corresponding to 92.1-99.0% of the total oils [18]. The essential oil compositions of Alexanders (*S. olusatrum*) were dominated by furanogermacrane-type sesquiterpenes, notably isofuranodiene (32.3–45.8%) in roots, isofuranodiene (24.6–26.7%) together with 1-bacetoxyfuranoeudesm-4(15)-ene (16.5–31.0%) in fruits, and isofuranodiene (24.6%) together with furanoeremophil-1-one (33.1%) in basal leaves. These molecules are considered to be precursors of sesquiterpene lactones which are in turn regarded as marker compounds of the genus *Smyrnium* [35]. In study of Khanahmadi et al., the antibacterial activity of *S. cordifolium* correlates large amounts of sesquiterpene hydrocarbons such as curzerene, curzerenone and germacrone [19].

Amiri et al. reported that the stem oil consisted of 20 identified compounds representing 92.7% of the oil composition. The main compounds were curzerene (22.7%) and hexadecanoic acid (13.6). In the leaf oil, 13 compunds were identified representing 89.4% of the oil composition. They detected main compounds of which were curzerenone (22.8%), hexadecanoic acid (18.7%), curzerene (45.7%), spathulenol (7.7%) and germacrone (6.1%) were also found in the fruit oil. The leaf and root oils were also characterized by high concentration of these compounds but in reversed order; curzerenone (21.8 % and 56.6%) and curzerene (16.9% and 18.7%). Hexadecanoic acid (13.6% and 18.7%) was reported also prodominant in the stem and leaf oils [17].

The essential oil of leaves and stems of *Smyrnium olusatrum* from Constantine (Algeria) were analyzed by GC/MS. Thirty-three compounds were characterized, representing 94.3% of the essential oil. As the major components; sabinene (27.1%), curzerene (13.7%), methyl-1-benzyl-2oxocyclooctane carboxylate (12.3%), α-pinene (7.2%), cryptone (7.1%) and β-pinene (5.7%). In this study, essential oil of *S. olusatrum* was tested against a wide range of fungal and bacterial strains and this oil showed significant antimicrobial activity [36].

4. Conclusion

In conclusion, this study demonstrates the occurrence of α-eudesmol / 2-naphtalonemethanol chemotype of *Ferula communis* subsp. *communis* and furanodiene / bicyclogermacrene chemotype of *Smyrnium cordifoilum* naturally growing in Turkey.

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