The essential oils composition in two species of the genus *Eriocycla* Lindl. (Apiaceae) from Iran

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Abstract: As a first chemical report in the genus *Eriocycla*, the composition of essential oils of two endemic species from four populations of *E. olivieri* and *E. ghafooriana* were analysed by GC-MS. A total of 118 compounds were identified in these populations. Sesquiterpene hydrocarbons dominate in all populations, followed by phenyl propanoids which surprisingly absent in one population of *E. olivieri* (Tehran). Only ten compounds are common between four populations including α-pinene, β-myrcene, β-bourbonene, β-elemene, α-cedrence, γ-elemene, germacrene D, germacrene B, (+)-spatholenol and α-cadinol. The remarkable major compounds of *E. olivieri* (Tehran) are γ-elemene (25.32%), γ-curcumene (5.51%), germacrene-D (6.12%), δ-cadinene (8.18), and germacrene B (15.31%); those of *E. olivieri* (Shahmirzad) are (-) bornyl acetate (6.13%), trans-caryophyllene (3.04%), γ-curcumene (3.47%), germacrene D (3.29%), bicyclogermacrene (8.56%), myristicine (4.83%), germacrene B (18.49%), apiole (33.46%). In *E. ghafooriana* (Gorgan) α-pinene (4.4%), (-)-bornylacetate (14.8%), γ-elemene (12.73%), germacrene B (7.2%), myristicine (21%), apiole (9.01%) and in *E. ghafooriana* (Golestan) β-elemene (6.42%), germacrene D (4.73%), α-selinene (21.6%), myristicine (8.3%), dillapiole (40.57%) are dominant. As it is evident in the morphological characteristics, the PCA analyses of the oil compounds show variations which by further biosystematic studies their chemotaxonomic value need to be evaluated.

Introduction

The genus *Eriocycla* Lindl. is a small genus of Umbelliferae (Apiaceae) with 7-10 species distributed from SW and Central Asia to SW China (Pimenov & Leonov, 1993). According to Flora Iranica (Rechinger, 1987), only the endemic species *E. olivieri* (Boiss.) Wolff was reported from Iran. Two further species *E. eriocarpa* (Bornm. & Gauba) E. V. Kljuykov & Pimen. and *Eriocycla ghafooriana* Akhani were added to Iran after Flora Iranica (Kljuykov & Pimenov, 1991; Akhani, 1999). In a recent concept of the taxonomic status of the genus, *Eriocycla* is included into *Seseli* (Pimenov & Kljuykov, 2000) which is not followed here. Following our studies on the chemical composition of Iranian Apiaceae (Yassa *et al.*, 2003), we have studied chemical composition of essential oils of *E. ghafooriana* and *E. olivieri*, each represented by two populations.

The habitat and range of both studied species is on vertical or steep cliffs of Central and East Alborz mountains (Fig. 1). *E. olivieri* is endemic in Southern slopes of Central Alborz in altitudes from c. 800-2400m (Fig. 2). It is usually a summer plant mostly occurring with *Parietaria judaica*. The recently discovered *E. ghafooriana* is strongly aromatic and a late flowering plant (flowers and fruits produce during October to December). It grows on vertical cliffs in the Easternmost extension of Alborz mountains from Golestan National Park to Gorgan in association with thermophilous C_4 grasses, mostly occurring with *Cleisteogenes serotina* (Akhani, 1999; Akhani & Ziegler, 2002).

Plant materials

The two studied populations of *E. ghafooriana* include one from type locality NW off the Golestan National Park, near Zav village (voucher No. 12322, designated as Golestan population) and another from 22 km SE of Gorgan in road to Chaharbagh (voucher No. 13702, designated as Gorgan population). One of the populations of *E. olivieri* was originated from mountains N. Tehran, Golabdarreh (voucher No. 13151, designated as Tehran population) and another one from 2 km W Shahmirzad in Semnan Province (voucher No. 15327, designated as Shahmirzad population). All voucher specimens are preserved in the private herbarium of second author (Hb. Akhani).

GC/MS Analysis

The aerial parts of examined plants were dried in shadow at room temperature. The amount of plants and oils obtained from each population are for *E. ghafooriana*, Golestan population, 50gr, yielding 0.29 ml oil (0.58%), for Gorgan population 217 gr yielding 0.83 ml oil (0.39%). In case of *E. olivieri*, Tehran population, 183gr. dried plants yielded 0.43ml (0.23%) oil and that of Shahmirzad population from 120gr. dried plant 0.25 ml (0.21%) oil was obtained. The extracted oils were hydrodistillated with a clevenger type apparatus for 4-5 h. The yellowish oil was collected and dehydrated by anhydrous sodium sulfate. The oil was analysed by GC/MS on a HEWLETT-PACKARD 6890 gas

chromatograph coupled a mass detector (HEWLETT-PACKARD model 6973 HP). The column for oil separation use a fused silica HP-5 column, 30 m length, 250μ i.d., and 0.32 mm film thickness. The mass spectra were obtained by electron ionization at 70eV. The oven temperature program was 60°C (30 min) isotherm, then to 250°C at 5°C/min. The injector temperature was 250°C. The carrier gas (helium) flow rate was 1ml/min. The sample (1μl) was injected with a split ratio of 1/90. The compounds were identified using a Wiley 275 library, retention indices and MS fragmentation with published data (Adams, 1995).

Results and Discussion

A total of 118 compounds have been detected in the oils of two Iranian species of *Eriocycla* each from two origins (Table I). Identification of 39 further compounds were not possible by using available libraries and indexes. The data presented in Table 1 evidently show that the distribution of various compounds from four origins are very heterogeneous which even two different origin of the same species resulted different results. In *E. olivieri* a total of 85 and in *E. ghafooriana* a total of 78 compounds are found.

The GC-MS analysis of the oils of *E.olivieri* (origin Tehran) resulted 52 known and 24 unknown (not shown in Table) compounds with highest percentage of sesequiterpen hydrocarbons (83.26%), followed by 4.94% oxygenated sesquiterpenes, 4.02% monoterpene hydrocarbones, 0.72% oxygenated monoterpenes and only 0.47% nonterpenoids which composed a total of 93.41% of the oils. The major compounds of this population are γ-elemene with 25.32%, germacrene B (15.31%), δ-cadinene (8.18%), germacrene D (6.12%), γ-curcumene (5.51%), α-cedrene (2.88%), zingiberene (2.53%), α-gurjunene (2.5%), α-gurjunene and β-elemene. The oils of *E. olivieri* (origin Shahmirzad) resulted 49 compounds with 46.88% sesquiterpene hydrocarbons, 39.68% phenyl propanoids, 7.14% oxygenated monoterpenes, 2.97% oxygenetaed sesquiterpenes, 1.09% monoterpene hydrocarbones and 0.29% nonterpenoides which constitute 98.05% of the known compounds. The highest percentage of oil is apiole with 33.46% of the total oil which follow by germacrene B (18.49%), bicyclogermacrene (8.56%), (-)-bornyl acetate (6.13%), myristicine (4.83%), γ-curcumene (3.47%), germacrene D (3.39%), trans-caryophyllene (3.04%), (-)-β-acoradiene (2.42%) and γ-elemene (2.35%). Among 23 common compounds between two populations, germacrene B, γ-elemene, germacrene D, γ-curcumene and bicyclogermacrene are more dominated.

The oils of *E. ghafooriana* (origin Golestan, type locality) composed of 53 known and 10 unknown (not shown in Table I) compounds. The known compounds resulted 98.31% of the total oil which phenyl propanoids with 49.11%, sesquiterpene hydrocarbons with 39.73% are dominated. Other groups including monoterpene hydrocarbons (3.22%), oxygenated sesquiterpenes (2.91%), oxygenated

monoterpenes (1.03%) and nonterpenoides (2.31%) are less represented. The major compounds of this population are dillapiole(40.57%), α-selinene (21.6%), myristicine (8.3%), β-elemene (6.42%), germacrene D (4.73%) and γ-elemene (2.39%). In *E. ghafooriana* (origin Gorgan), a total of 61 known compounds (98.48% of the total oil) and 6 unknown (not shown in table) are detected. The major compounds of this population are myristicine (21%), (-)-bornyl acetate (14.8%), γ-elemene (12.73%), apiole (9.01%), α-pinene (4.4%), germacrene B (7.2%), cis-ocimene (2.02%), bicyclogermacrene (2.6%), (+)-spatholenol (2.2%) and limonene (2%). Among 31 common compounds between two populations, germacrene B, γ-elemene, β-elemene, (+)-spatholenol, myristicine, apiole and dillapiole occur in remarkable quantities.

Comparison of two species show that 12 compounds are known to occur in all four populations and a further 15 compounds occur in three populations with different combinations. The clustering analysis of essential oils compounds based on UPGMA method and Euclidean coefficient cluster four populations into two main branches (Fig. 3, right). This separation is weakly supported by PCA (Principle Component Analyses) which indicates rather long distance between each populations of both species. The PCA pattern is better corresponding with the geographical distribution of four populations. Accordingly the two populations Gorgan (*E. ghafooriana*), and Shahmirzad (*E. olivieri*) - which are geographically rather close - are plotted nearby, but either populations of two species with long distance show also long distance in the PCA plot. These basic data are of value for considering this small genus as a model for future studies on the influence of climatic conditions on production of essential oils.

As no other chemical report on this genus is available, we can only compare our data with other possible related genera in Apiaceae. The nearest affinity seems to be the genus *Seseli* that include the species of *Eriocycla* in wide sense (Pimenov & Kljuykov 2000). The chemical constituents of essential oils of *S. tortuosum* L. subsp. *kiabii* Akhani from Iran have been studied by Habibi et al (2003) and that of *S. tortuosum* from Italy and Turkey by Bader et al. (2003) and Kaya et al. (2003). The major compounds reported by these authors from Iran/Italy/Turkey are: α-pinene (21.2%/18.6%/35.9%), sabinene (13.4%/2.4%/8.8%), β-pinene (14.2%/13.2%/7%), camphene (2.7%/1.1%/3.9%), and myrcene (6%/29.2%/2.2%). Limonene was reported only from Italy and Turkey with 10.6 and 4 percentages, respectively. These compounds or their affinities are known in all or some populations of *Eriocycla*, but mostly as minor or trace compounds.

Table I: Chemical constituents of the essential oils of *Eriocycla olivieri* and *E. ghafooriana* from Iran.

			E. olivieri		*E. ghafooriana*	
No.	Compounds Name	RRI[a]	Tehran %	Shahmirzad %	Gorgan%	Golestan%
1	tricyclene	925	-	-	0.04	-
2	α-pinene	940	0.14	0.63	4.4	0.11
3	camphene	952	-	0.03	1.84	0.04

4	sabinene	976	-	-	0.1	0.02
5	β-thujene	978	-	-	-	0.01
6	β-pinene	981	0.01	0.01	0.3	-
7	β-myrcene	990	0.08	0.04	0.72	1.62
8	mesitylene	996	0.03	-	-	-
9	α-phellandrene	1004	-	-	0.04	-
10	δ-3-carene	1010	-	-	0.01	-
11	α-terpinene	1017	-	-	0.01	-
12	p-cymene	1025	-	-	0.2	0.08
13	benzene,2-ethyl-1,3-dimethyl	1029	-	0.06	-	-
14	limonene	1030	0.12	0.07	2	0.9
15	1,8-cineol	1032	0.19	-	-	-
16	cis-ocimene	1038	1.93	0.2	2.02	-
17	trans-β-ocimene	1051	-	0.02	0.5	-
18	γ-terpinene	1064	-	0.09	0.8	0.3
19	α-terpinolene	1090	1.43	-	1.5	0.14
20	l-linalool	1096	0.43	0.46	0.13	-
21	allo-ocimene	1130	0.31	-	0.5	-
22	(-)-camphor	1145	-	-	0.21	-
23	mintfuranone	1160	0.06	-	-	-
24	l-borneol	1166	-	0.1	1.14	0.04
25	4-terpineol	1175	-	-	0.05	0.01
26	α-terpineol	1186	0.02	-	-	0.11
27	myrtenol	1196	-	0.04	0.2	-
28	α-fenchyl acetate	1218	-	-	-	0.66
29	trans-geraniol	1254	0.02	-	-	-
30	thymol	1279	-	-	-	0.05
31	(-)-bornyl acetate	1282	-	6.13	14.8	-
32	trans-pinocarvyl acetate	1295	-	-	0.05	-
33	bicycloelemene	1328	0.26	-	0.74	-
34	α-cubeben	1350	0.09	-	-	-
35	α-longipinene	1351	1.79	0.02	-	-
36	citronellyl acetate	1355	-	-	-	0.16
37	cis-carvyl acetate	1360	-	0.3	0.93	-
38	2,4,5-trimethylbenzaldehyde	1364	-	-	-	0.43
39	γ-terpineol	1367	-	0.11	-	-
40	α-copaen	1374	2.13	0.05	0.2	0.15
41	δ-selinene	1381	-	-	-	0.36
42	β-bourbonene	1385	1.87	0.76	0.44	0.63
43	β-elemene	1392	2.35	0.59	1.13	6.42
44	italicene	1400	0.24	0.05	-	-
45	α-cedrene	1408	2.88	1.81	0.1	0.13
46	α-gurjunene	1410	2.5	-	-	-
47	α-amorphene	1413	-	-	0.37	0.55
48	trans-caryophyllene	1420	-	3.04	-	-
49	γ-elemene	1431	25.32	2.26	12.73	2.39
50	trans-β-farnesen	1432	0.41	-	-	0.85
51	α-curcumene dihydro(+)	1445	-	0.24	-	-
52	α-humulen	1453	0.58	-	0.21	-
53	(-)-β-acoradiene	1468	-	2.42	-	-
54	γ-gurjunene	1473	0.15	-	-	-
55	γ-muurolene	1477	-	0.25	-	0.3
56	γ-curcumene	1479	5.51	3.47	0.2	-
57	germacrene D	1481	6.12	3.29	1.7	4.73
58	β-selinene	1485	0.22	-	0.35	-

59	β-guaine	1492	-	-	0.1	-
60	bicyclogermacrene	1494	2.08	8.56	2.6	-
61	α-selinene	1494	-	-	-	21.6
62	zingiberene	1495	2.53	0.1	-	-
63	β-himachalene	1500	0.32	0.38	-	-
64	germacrene A	1503	-	0.25	-	-
65	allo aromadendrene	1508	-	-	0.22	-
66	γ-cadinene	1515	0.58	-	0.1	0.16
67	myristicine	1519	-	4.83	21	8.3
68	δ-cadinene	1522	8.18	-	-	-
69	β-sesquiphellandrene	1526	-	-	0.7	-
70	α-cadinene	1532	-	-	0.32	-
71	trans-γ-bisabolene	1535	0.29	0.65	-	-
72	naphthalene,1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methyl)	1539	-	-	-	0.06
73	selina,3,7-(11)-dien	1543	1.53	-	-	-
74	α-calacorene	1545	-	-	-	0.2
75	elemicin	1552	-	1.39	-	-
76	germacrene B	1557	15.31	18.49	7.2	1.06
77	δ-gurjunene	1571	-	-	0.2	-
78	(+)-spatholenol	1575	0.33	1.52	2.2	0.22
79	(-)-globulol	1580	0.27	-	0.4	-
80	(-)-caryophyllene oxide	1581	-	0.23	-	-
81	epiglobulol	1585	0.45	-	-	-
82	eremophyllene	1586	-	-	0.25	-
83	viridiflorol	1589	-	0.13	-	-
84	(+)-carotol	1593	-	0.12	0.3	0.37
85	α-cedrol	1596	0.19	-	-	-
86	fonenol	1617	0.21	-	-	-
87	dillapiole	1620	-	-	1.3	40.57
88	junipene	1624	-	-	0.13	-
89	torreyol(α-muurolol)	1631	0.76	-	-	-
90	T-cadinol	1636	-	-	0.2	0.59
91	β-eudesmol	1650	-	0.06	-	-
92	isospathulenol	1652	-	0.3	0.37	-
93	α-cadinol	1653	1.05	0.28	0.43	0.5
94	5-isocedranol	1665	-	0.33	-	-
95	bulnesol	1669	-	-	-	0.68
96	1,4-dimethyl-7-(1-methyl) azulene (azulon)	1677	-	-	-	0.2
97	apiole	1682	-	33.46	9.01	0.24
98	juniper camphor	1695	1.02	-	0.3	0.13
99	1-hydroxy-(1-methoxy)-7-(methylethyl)[1,2,3,3α,4,5,6,7] octahydroazulen	1735	0.6	-	-	-
100	mintsulfide	1750	0.04	-	-	0.08
101	zierone(elleryone)	1754	-	-	-	0.2
102	benzylbenzoate	1760	0.13	-	-	0.43
103	hexahydrofarnesyl acetone	1777	0.03	-	-	0.16
104	2-pentadecanone,6,10,14-trimethyl	1783	-	-	-	0.25
105	neo-phytadiene	1790	-	-	0.03	-
106	octadecane	1800	-	-	-	0.03
107	benzylsalicylate	1863	0.06	-	0.11	-
108	isobutylphthalate	1877	-	-	-	0.1

109	n-nonadecane	1902	-	0.02	-	0.1
110	dibutylphthalate	1907	-	0.11	-	-
111	phytol	1950	0.14	0.02	-	-
112	hexadecanoic acid	1978	0.08	-	-	-
113	n-eicosane	2002	-	-	-	0.07
114	heneicosane	2112	-	-	-	0.3
115	phytolisomer	2168	-	-	0.12	0.4
116	docosane	2205	-	-	0.15	0.1
117	tetracosane	2401	-	-	0.03	-
118	suberosine	2414	-	0.08	0.05	-
	monoterpene hydrocarbons		4.02	1.09	14.94	3.22
	oxygenated monoterpenes		0.72	7.14	17.54	1.03
	sesquiterpene hydrocarbons		83.26	46.88	29.99	39.73
	oxygenated sesquiterpenes		4.94	2.97	4.2	2.91
	phenyl propanoids		-	39.68	31.31	49.11
	nonterpenoids		0.47	0.29	0.53	2.31
	Known		93.41	98.05	98.48	98.31

[a] Relative Retention Indices

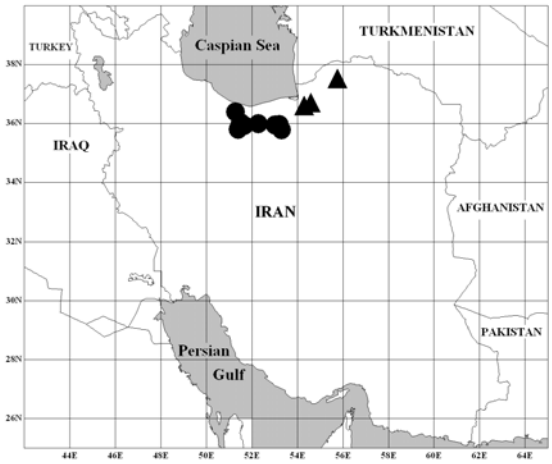
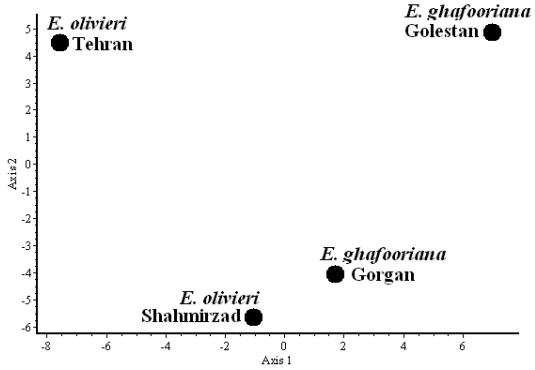


Fig. 1. Distribution map of *Eriocycla olivieri* (dot) and *E. ghafooriana* (triangle) in Iran

Fig. 2. *Eriocycla olivieri*, near Shahmirzad



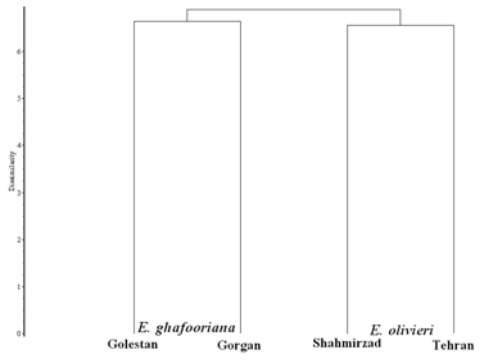


Fig. 3. PCA ordination (left) and clustering analysis using UPGMA method based on Euclidean coefficient (right) of essential oil composition of four populations of *Eriocycla* from Iran

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Erratum

Regretly in the abstract of our paper titled "Essential oils from two endemic species of *Apiaceae* from Iran. Z. Naturforschung 58c: 459-463. the specific epithet of *Zeravschania pastinacifolia* (Boiss. & Hausskn.) Salimian & Akhani was deleted during final publication process.