



Essential Oil Composition of *Chrysophthalmum schultz Bip.* Genus from Turkey: A Study of the Chemotaxonomy

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Abstract The Genus *Chrysophthalmum* is represented with three species in Flora of Turkey. In this study, The essential oils obtained from the aerial parts of *Chrysophthalmum gueneri* Aytac and Anderb, *C. dichotomum* Boiss. & Heldr. and *C. montanum* (DC.) Boiss. were analyzed by using GC and GC/MS. Forty eight, sixty and forty five compounds representing 87.4% , 94.0% and 90.0% of the oil were identified respectively. The main components of the *C. gueneri* oil were β -pinene (18.7%), 2 methyl butanoic anhydride (14.6%), butanol (12.3%), α -pinene (7.4%) and β -caryophyllene (3.3%). The main compounds of *C. dichotomum* were butanol (20.2%), cyclohexadecane (13.5%), nerolidol (13.4%), tributyrin (11.2%) τ -muurolol (10.9%) and also the major compounds in *C. montanum* oil were caryophyllene oxide (20.0%), spathulenol (18.2%), acetic acid (10.3%), τ -muurolol (9.7%) and α -cadinol (4.9%). This study is the first report on the composition of three species. The chemotaxonomic relationships within the genus *Chrysophthalmum* have been discussed in detail.

Keywords *Chrysophthalmum*, Asteraceae, essential oil, GC-MS, chemotaxonomy

Introduction

Turkey has a rich flora with about 12000 plant taxa and the number of the endemic taxa is 3649 [1-4]. Asteraceae is represented by 1209 species in the Flora of Turkey. 447 of these species are endemic for Turkey with endemism ratio as 37 %. With a total number of 134 genera, this family constitutes the second largest family of Turkish flora [1-2, 5-6]. The genus *Chrysophthalmum* Schulz Bip. (Asteraceae) is represented by five species in the world. Three species of this genus are naturally grown in Turkey. The species growing in Turkey are *C. montanum* (DC.) Boiss., *C. dichotomum* Boiss. and Heldr. and *C. gueneri* Aytac and Anderb. *C. dichotomum* and *C. gueneri* are endemic for Turkey [7].

Taxonomy is the theory and practice of classification, and chemotaxonomy incorporates the principles and procedures involved in the use of chemical evidence for classificatory purposes. Chemical Systematics is the study of the chemical variation in a diversity of organisms, and of their relationships [8]. Essential oils are mostly natural mixtures of terpenes/terpenoids, most of which are obtained from aromatic and pharmaceutical plants. The chemical composition of essential oil differs in each species or subspecies and is characteristic for the species in question. Identification of individual components of complex mixtures such as terpenes/terpenoids in essential oils requires the use of several techniques. One of the most popular methods of studying essential oil composition is gas chromatography–mass spectrometry (GC–MS), which allows the identification of the specific natural compounds found in an essential oil by comparing their relative retention times/indices and their mass spectra [9-16].

Chrysophthalmum is commonly used as a folk medicine [17]. *Chrysophthalmum* species have been shown to have antimicrobial activity. antifungal, anticonvulsant, antioxidant, and estrogenic activity [18].



Selvi et al [19]. studied the micromorphological and anatomical characteristics of genus *Chrysophthalmum*. In the this study, cypsela appears to be an important accessory character for identification of species. Moreover, pappus is also an important character for distinguishing the taxa as it is present in *C. montanum* while absent in *C. dichotomum* and *C. gueneri*.

The chemical study of genus *Chrysophthalmum* have not been studied so far. The present study aims to give a detailed account of essential oil components of these species.

Materials and Methods

Plant materials

The specimens of *C. dichotomum* was collected in Malatya-2012 (FUH 9875), the specimen of *C. montanum* was collected in Antalya-2012 (FUH 9876) and the specimen of *C. gueneri* was collected in Antalya-2012 (FUH 9877). Voucher specimens are kept at the Firat University Herbarium (FUH), Elazığ, Turkey.

Isolation 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 to yield.

Gas chromatographic (GC) analysis

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

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 °C, split flow was 1 ml / min. The GC oven temperature was kept at 70 °C for 2 min. and programmed to 150 °C at a rate of 10 °C / min and then kept constant at 150 °C for 15 min to 240 °C at a rate of 5 °C / min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). MS were taken at 70 eV and a mass range of 35-425. Component identification was carried out using spectrometric electronic libraries (WILEY, NIST).

Results and discussion

The hydrodistillation of the aerial parts of three *Chrysophthalmum* species, *i.e.* *C. montanum*, *C. dichotomum* and *C. gueneri*, gave oils in 0.2, 0.1 and 0.5% (w/w) yields, based on the dry weight of the plants. The components of the essential oils and their percentages of the studied species are presented in Table I.

Table 1: Chemical composition of the essential oils of three *Chrysophthalmum* species

No	Components	RRI	<i>C.dichotomum</i>	<i>C. montanum</i>	<i>C. gueneri</i>
1	4-hexen-1-ol	964	-	0.1	-
2	α -pinene	1021	-	0.5	7.4
3	Camphene	1033	-	-	0.2
4	β -pinene	1054	-	0.2	18.7
5	β -myrcene	1063	-	-	0.6
6	3-carene	1078	-	-	0.7
7	β -cymene	1090	-	0.1	-
8	Limonene	1093	-	0.1	0.5
9	Sabinene	1095	-	-	0.4
10	Benzeneacetaldehyde	1099	-	0.1	-
11	1,3,7- octatriene	1107	-	-	0.1
12	γ -terpinene	1115	-	-	0.1
13	α -terpinolene	1146	0.2	0.8	0.4
14	Sabinyl acetate	1176	-	0.1	-
15	Verbenone	1180	-	0.1	-
16	Propenylbicyclo(3.1.0)hexan-2-one	1183	-	0.1	-
17	p-mentha -1,5-dien-8-ol	1198	-	0.3	-
18	4-terpineol	1204	-	0.1	0.1
19	α -p-dimethylstyrene	1208	-	0.1	-



20	Myrtenol	1214	0.1	0.4	0.7
21	I-verbenone	1222	-	0.3	-
22	Trans-carveol	1230	-	0.1	-
23	Cyclohexene, 1-methyl-4(1methylethylidene)	1237	-	0.2	-
24	+carvone	1247	-	0.1	-
25	2-cyclohexen-1-on	1250	-	-	0.2
26	Neryl acetate	1251	-	0.1	-
27	Acetic acid	1280	-	-	0.1
28	Copaene	1358	-	-	0.1
29	β -damascenone	1360	-	0.2	-
30	Benzene, 1-4, methoxy-2 methyl-5-isopropyl	1385	-	-	0.4
31	β -caryophyllene	1390	0.4	1.6	3.3
32	Trans- β -farnesene	1416	-	-	0.3
33	Alloaromadendrene	1419	0.2	0.7	-
34	α -amorphene	1429	0.5	-	0.5
35	Germacrene D	1433	0.1	0.4	1.4
36	α -longipinene	1434	0.1	-	-
37	Eudesma-4(14),11-diene	1439	-	0.8	0.2
38	Bicyclogermacrene	1443	-	0.6	-
39	α -muurolene	1444	0.5	-	-
40	Naphthelene	1454	0.6	0.3	0.1
41	β -cadinene	1456	0.1	0.5	-
42	Cis- α -bisabolene	1470	-	-	0.1
43	δ -cadinene	1478	0.5	-	-
44	Nerolidol	1483	13.4	-	0.1
45	3-hexen-1-ol	1489	-	1.0	-
46	Spathulenol	1493	-	18.2	-
47	Caryophyllene oxide	1496	0.4	20.0	0.8
48	γ -gurjunene	1503	-	2.2	-
49	1H-benzocycloheptene	1512	-	2.4	0.2
50	Decahydrocyclopenta (dec) phenanthrene	1514	0.1	-	-
51	5-methyl tetralin	1516	-	-	0.1
52	Isospathulenol	1525	-	1.8	0.1
53	3-methyl-bicyclo (3-2-1)oct-6-en-8-ol	1527	-	-	0.2
54	τ -muurolol	1530	10.9	9.7	0.5
55	α -copaene	1532	-	-	0.1
56	α -cadinol	□ □ □ □	3.4	□ □ □	□ □ □
57	β -selinene	1539	0.3	-	0.2
58	Phenol, 3(1,1-dimethylethyl)-4-metoxi	1543	0.1	-	0.3
59	β -humulene	1545	-	1.5	0.2
60	Acetic acid	1555	-	10.3	-
61	Aristol-9-en-3-ol	1556	-	-	0.1
62	Tributylin	1565	11.2	-	1.5
63	2 acetyl-5,8-dimethoxy-1,4-epoxy, 1,2,3,4-tetrahydronapthalene	1567	-	1.5	-
64	Cedren-13-ol	1580	-	-	0.3
65	Cyclonanosiloxane	1584	0.3	-	-
66	Tetradecenoic acid	1588	0.7	-	0.5
67	Hexane, 3,3-dimethyl	1590	0.2	-	-
68	Tridecyl iodide	1591	0.1	-	-
69	2,6-dimethyl-3-(methoxymethyl)-p-	1601	-	0.8	-



	benzoquinone				
70	Butanol	1610	20.2	-	12.3
71	Neoisolongifolene	1615	-	-	1.1
72	2-pentadecanone, 6,10,14-trimethyl	1630	-	2.9	-
73	2,3-epoxycarane	1632	-	-	0.4
74	ar-curcumene	1642	1.1	-	-
75	Cyclohexadecane	1649	13.5	-	-
76	Cyclotetradecane	1650	6.1	-	-
77	2methylbutanoic anhydride	1651	-	-	14.6
78	Linoleic acid	1654	-	0.3	-
79	Nonadecane	1661	-	0.3	-
80	n-hexadecanoic acid	1690	-	0.8	-
81	Nonanedioic acid	1694	3.7	-	4.0
82	2-methylbutenoic acid anhydride	1695	3.8	-	-
83	2H-pyran	1696	-	-	11.4
84	2-butoxyoxane	1698	1.2	-	-
85	3,4-dimethyl-1H-indazole	1724	-	-	0.2
86	2,3-bis(acetyloxy)propyl ester	1887	-	2.8	-
87	Cholesta-3,5-diene	1907	-	-	1.1
88	Nonacosane	1942	-	1.6	-
	Total		94.0	90.0	87.4

60 compounds representing 94.0% of *C. dichotomum* oil were identified: butanol (20.2%), cyclohexadecane (13.5%), nerolidol (13.4%), tributyrin (11.2%) and τ -muurolol (10.9%) were the main components. The volatile components of the aerial parts of *C. montanum*, among the 45 compounds identified of 90.0%, major components were caryophyllene oxide (20.0%), spathulenol (18.2%), acetic acid (10.3%), τ -muurolol (9.7%) and α -cadinol (4.9%). The investigation led to the identification of 48 constituents, representing 87.4% of the total oil of *C. gueneri*. The main components of the oil were β -pinene (18.7%), 2 methyl butanoic anhydride (14.6%), butanol (12.3%), α -pinene (7.4%) and β -caryophyllene (3.3%).

The essential oils of three species were not found the common major components. Butanol characterises the essential oils of *C. dichotomum* and *C. gueneri*, whereas it was not found the essential oil of *C. montanum*. Caryophyllene oxide, the first major components of the *C. montanum* oil, was not determined in other two species. The first major compound β -pinene (18.7 %) was determined in the *C. gueneri*, it is not reported in the *C. dichotomum*. Moreover, it was found as minor component of essential oil of *C. montanum*. Spathulenol was the main component of *C. montanum* oil, in contrast to the other species, it was not found.

Essential oil analysis relating to *Chrysophthalmum* genus are not study. Therefore, in the same subtribus near strains it was compared to other species.

The chemical composition of the volatile oil constituent from *Pulicaria odora* L. roots has been analyzed by GC/MS. Twenty-seven components were identified, being thymol (47.83%) and its derivative isobutyrate (30.05%) the main constituents in the oil.

In conclusion, this study demonstrates the occurrence of caryophyllene oxide/ spathulenol chemotype of *C. dichotomum*, β -pinene/methyl butanoic anhydride chemotype of *C. montanum* and β -pinene/2 methyl butanoic anhydride chemotype of *C. gueneri* in Turkey.

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