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Composition of the essential oils of the subgenus *Grammosciadium* from Turkey; *G. confertum*, *G. cornutum*, *G. macrodon* subsp. *macrodon*, *G. macrodon* subsp. *nezaketae* and *G. daucoides*

Nurgün Küçükboyacı[*1], Betül Demirci [2], Fatma Ayaz [1], Barış Bani [3] and Nezaket Adıgüzel [4]

[1]*Gazi University, Faculty of Pharmacy, Department of Pharmacognosy, 06330 Ankara, Türkiye*
[2]*Anadolu University, Faculty of Pharmacy, Department of Pharmacognosy, 26470 Eskişehir, Türkiye*
[3]*Kastamonu University, Faculty of Arts and Science, Department of Biology, 37200, Kastamonu, Türkiye*
[4] *Gazi University, Faculty of Science, Department of Biology, 06500 Ankara, Türkiye*

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Abstract: Essential oils obtained by hydrodistillation from the aerial parts and fruits of five taxa of genus *Grammosciadium* DC., belonging to subgenus *Grammosciadium* (*G. confertum* Hub.-Mor. & Lamond, *G. cornutum* (Nábělek) C.C.Towns., *G. macrodon* Boiss. subsp. *macrodon*, *G. macrodon* Boiss. subsp. *nezaketae* B.Bani and *G. daucoides* DC.), collected from different locations in Turkey, were simultaneously analyzed by GC and GC/MS systems. 124 components representing 71.1-99.8% of the total contents were identified in the oils. Oil samples from fruits and aerial parts of the plants showed different chemical profiles with regard to species. We have herein demonstrated that the chemical composition of essential oil samples from *G. cornutum*, *G. macrodon* subsp. *macrodon, G. macrodon* subsp. *nezaketae* (an endemic subspecies), and *G. confertum* (an endemic species) growing in Turkey was determined for the first time. Hexadecanoic acid (13.3-21.2% and 48.1-59.8%) was the main component of the samples of *G. cornutum* and *G. confertum*, respectively, while caryophyllene oxide (13.1-29.2%) was the major constituent in the samples of *G. macrodon* subsp. *nezaketae* and *G. macrodon* subsp. *macrodon* as well as *γ*-terpinene (61.9%) and carvacrol (68.9%) in *G. daucoides* samples. In addition, pentacosane can be considered a chemotaxonomic marker for the essential oil of *G. macrodon* subsp. *macrodon.*

Keywords: *Grammosciadium*; Apiaceae; essential oil composition; caryophyllene oxide; hexadecanoic acid.

1. Introduction

The genus *Grammosciadium* DC. from family Apiaceae is mainly characterized by biennial or perennial life span, glabrous habit, 3-4-pinnatisect and filiform segmented leaves, polygamous

[*] Corresponding author: E-Mail: nurgun@gazi.edu.tr; Phone:+90-312-2023177

flowers, white petals and longer fruits (3 x longer than broad) [1]. The genus is represented by 10 taxa worldwide [1-5]. These are recognized under 2 subgenera and within 6 sections. Subgenus *Grammosciadium* differs from subgenus *Caropodium* (Stapf & Wettst.) Tamamsch. & V. M. Vinogr. by its longer sepals and unwinged fruits. The first subgenus *Grammosciadium* contains *G. daucoides* DC., *G. scabridum* Boiss. (not distributed in Turkey), *G. macrodon* Boiss., *G. cornutum* (Nábělek) C. C. Towns. and *G. confertum* Hub.-Mor. & Lamond, while subgenus *Caropodium* is represented remaining 4 species; *G. platycarpum* Boiss. & Hausskn. ex Boiss., *G. pterocarpum* Boiss., *G. schischkinii* (V. M. Vinogr. & Tamamsch.) V. M. Vinogr. and *G. haussknechtii* Boiss [2].

The genus *Grammosciadium* comprises 9 taxa in Turkey, namely *G. confertum*, *G. cornutum*, *G. macrodon* subsp. *macrodon*, *G. macrodon* subsp. *nezaketae*, *G. daucoides*, *G. pterocarpum*, *G. platycarpum*, *G. schischkinii* and *G. haussknechtii* [1,3,5]. Among the species, *G. schischkinii*, *G. haussknechtii*, *G. confertum* and *G. macrodon* subsp. *nezaketae* are endemic to Turkey [3,5]. All the species of the genus are Irano-Turanian element, except for *G. confertum* [1].

In traditionally, leaves of *G. platycarpum* known as “Jafari kohi”, are used for hyperlipidemia and cooked as edible foods in Iran [6]. *G. daucoides* is known as "süpürge otu" in Turkey and it is used as broom in cleaning [7]. According to the biological studies, essential oils from aerial parts of *G. platycarpum* and *G. scabridum* have antibacterial activities [8,9]. In addition, the essential oil obtained from aerial parts of *G. scabridum* [9] and fruits of *G. platycarpum* [10] as well as methanol extracts prepared from aerial parts of *G. platycarpum* [10,11] are known to possess antioxidant and free radical scavenging activity.

Until now, the essential oil composition obtained from different species of the genus *Grammosciadium* have only been reported in several studies [8-10, 12-17]. In a review of the literature, no other phytochemical data on *Grammosciadium* species was found. As a part of our ongoing research on Turkish *Grammosciadium* species, we aimed to evaluate the compositions of hydrodistilled samples of subgenus *Grammosciadium*, namely *G. confertum*, *G. cornutum*, *G. macrodon* subsp. *macrodon*, *G. macrodon* subsp. *nezaketae* and *G. daucoides* by the use of gas chromatography (GC) and gas chromatograpy/mass spectrometry (GC/MS). To the best of our knowledge, the essential oils of *G. cornutum*, *G. confertum*, *G. macrodon* subsp. *macrodon* and *G. macrodon* subsp. *nezaketae* have not been previously investigated, except for *G. daucoides* [12-16].

2. Materials and Methods

2.1. Plant material

Plant materials of aerial parts and fruits of five taxa of genus *Grammosciadium*, *G. macrodon* subsp. *macrodon*, *G. macrodon* subsp. *nezaketae*, *G. cornutum*, *G. confertum* and *G. daucoides*, belonging to subgenus *Grammosciadium*, were collected from various locations in Turkey as shown in Table 1. The plants were identified by Assistant Professor Barış Bani, from the Department of Biology, Faculty of Arts and Science, Kastamonu University. Authenticated voucher specimens were kept in the Herbarium of GAZI.

2.2. Isolation of the Essential Oils

The essential oils from air-dried plant materials were isolated by hydrodistillation for 3 h, using a Clevenger-type apparatus. The essential oil yields are presented in Table 2. The obtained oils were dried over anhydrous sodium sulphate and stored at +4°C in the dark until analyzed and tested.

2.3. Gas Chromatography/Mass Spectrometry (GC/MS)

The GC/MS analysis was carried out with an Agilent 5975 GC-MSD system. 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).

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. Split ratio was adjusted at 40:1. The injector temperature was set at 250°C. Mass spectra were recorded at 70 eV. Mass range was from *m/z* 35 to 450.

Table 1. List of the *Grammosciadium* taxa investigated with locality, collection periods and voucher specimens

Species (Voucher specimen)	Abbreviation	Parts of plants (Sample no)	Locality	Collection period
G. macrodon Boiss. subsp. *nezaketae* B.Bani * (GAZI 6844)	mcn A mcn F	Aerial parts (1) Fruits (2)	B9 Bitlis: Bitlis-Diyarbakır, above Karınca village, clearings of oak woodlands, 1350 m, 13.06.2012	Fruiting
G. macrodon Boiss. subsp. *macrodon* (GAZI 6887)	mac F	Fruits (3)	B7 Elazığ: Maden-Elazığ, around of Pinhan village, oak woodlands, 1400 m, 08.07.2012	Fruiting
G. macrodon Boiss. subsp. *nezaketae* B.Bani * (GAZI 6866)	mcn A mcn F	Aerial parts (4) Fruits (5)	C9 Van: Gürpınar-Çatak, around of Görentaş village, steppe, 2000 m, 25.06.2012	Fruiting
G. macrodon Boiss. subsp. *nezaketae* B.Bani * (GAZI 6832)	mcn A mcn F	Aerial parts (6) Fruits (7)	C9 Van: Çatak, around of Dalbastı village, clearings of oak woodlands, 1450 m, 10.06.2012	Flowering and fruiting
G. cornutum (Nábělek) C.C.Towns. (GAZI 6863)	cor F	Fruits (8)	B10 Hakkari: Yüksekova-Şemdinli 10. km, steppe, 1900 m, 20.06.2012	Fruiting
G. cornutum (Nábělek) C.C.Towns. (GAZI 6857)	cor A cor F	Aerial parts (9) Fruits (10)	C10 Hakkari: Yüksekova-Esendere, Dilezi pass, steppe, 2200 m, 20.06.2012	Fruiting
G. confertum Hub.-Mor. & Lamond * (GAZI 6890)	cnf F cnf A	Fruits (11) Aerial parts (12)	B6 Adana: Tufanbeyli, around of Güzelim village, clearings of blackpine forests, 1450 m, 15.07.2012	Fruiting
G. confertum Hub.-Mor. & Lamond * (GAZI 6204)	cnf A	Aerial parts (13)	B6 Adana: Tufanbeyli, around of Güzelim village, clearings of blackpine forests, 1450 m, 22.06.2008	Fruiting
G. daucoides DC. (GAZI 6877)	dau A	Aerial parts (14)	A8 Gümüşhane: Gümüşhane-Bayburt, Güvercinlik village, Vavuk pass, steppe, 1870 m, 05.07.2012	Flowering and fruiting
G. daucoides DC. (GAZI 6924)	dau A	Aerial parts (15)	C6 Osmaniye: Bahçe-Radar station, steppe, 1500 m, 09.05.2013	Fruiting

mcn A: aerial parts of *G. macrodon* subsp. *nezaketae*; mcn F: fruits of *G. macrodon* subsp. *nezaketae*; mac F: fruits of *G. macrodon* subsp. *macrodon*; cor A: aerial parts of *G. cornutum*; cor F: fruits of *G. cornutum*; cnf A: aerial parts of *G. confertum*; cnf F: fruits of *G. confertum*; dau A: aerial parts of *G. daucoides*; *: endemic

2.4. Gas Chromatography (GC)

The GC analysis was carried out using an Agilent 6890N GC system. FID detector temperature was 300°C. To obtain the same elution order with GC/MS, simultaneous auto-injection was done on a duplicate of the same column applying the same operational conditions. Relative percentage amounts of the separated compounds were calculated from FID chromatograms. The analysis results are given in Table 2.

2.5. Identification of the Essential Oil Components

Identification of the essential oil components were carried out by comparison of their relative retention times with those of authentic samples or by comparison of their relative retention index

(RRI) to series of *n*-alkanes. Computer matching against commercial (Wiley GC/MS Library, MassFinder 3 Library) [18,19] and in-house "Başer Library of Essential Oil Constituents" built up by genuine compounds and components of known oils, as well as MS literature data [20,21], was used for the identification.

3. Results and Discussion

The chemical composition of the essential oils from five taxa of genus *Grammosciadium*, *G. macrodon* subsp. *macrodon*, *G. macrodon* subsp. *nezaketae*, *G. cornutum*, *G. confertum* and *G. daucoides*, belonging to subgenus *Grammosciadium*, were listed in Table 2, according to their relative retention indices and percentages. The essential oils were obtained using a Clevenger apparatus by hydrodistillation from the plant materials which were separately investigated as fruits and aerial parts, collected from different localities and in various collection periods in Turkey. The composition of the essential oil samples was determined by GC and GC/MS analysis. The essential oil yields obtained by hydrodistillation were almost found to be in trace amounts for all samples, with the exception of *G. daucoides*. Since some of the plant parts weren't in enough amounts for obtaining their essential oils, we couldn't analyze the essential oils of these parts. A hundred and twenty-four compounds, accounting between 71.1 and 99.8% of the oils, were identified by GC and GC/MS analysis. We defined main components as caryophyllene oxide (13.1-29.2%), caryophylla-2(12),6-dien-5*β*-ol (=caryophyllenol II) (2.8-6.8%), spathulenol (2.4-12.3%) and eudesma-4(15), 7-dien-4*β*-ol (3.1-8.7%) in six oil samples of *G. macrodon* subsp. *nezaketae*. The fruit oil of *G. macrodon* subsp. *macrodon* mainly contained caryophyllene oxide (16.4%), caryophyllenol II (13.0%), pentacosane (5.9%) and hexadecanoic acid (5.4%). In three oil samples of *G. cornutum*, hexadecanoic acid (13.3-21.2%), caryophyllene oxide (6.8-11.7%) and eudesma-4(15),7-dien-4*β*-ol (3.9-6.4%) were found as major compounds. In addition, we detected that main constituents of three oil samples from *G. confertum* were hexadecanoic acid (48.1-59.8%), tetradecanoic acid (5.7-10.6%), eudesma-4(15),7-dien-4*β*-ol (1.7-6.4%) and salvial-4(14)-en-1-one (3.4-4.6%). Finally, in two samples of *G. daucoides*, *γ*-terpinene (18.7-61.9%), *p*-cymene (8.9-19.5%) and carvacrol (13.5-68.9%) were found as major compounds.

Recently, a literature reported that morphological variation of *G. macrodon* was scored and analysed using multivariate analysis using Principal Component Analysis. In the literature, *G. cornutum* is found to be morphologically the most similar species compared with *G. macrodon*. Moreover, it was reported that *G. macrodon* subsp. *nezaketae* differs remarkably from the *G. macrodon* subsp. *macrodon* based on fruit characters. In addition to the diagnostic fruit characters, other significant morphological and anatomical differences between these two taxa were presented as well in the literature [5]. As for our present study, the essential oil samples of *G. cornutum* and two subspecies of *G. macrodon*, mentioned above, have generally similar constituents, while the essential oils obtained from *G. daucoides* and *G. confertum* showed a unique composition for each species. The chemical profiles of the essential oils from *G. macrodon* subsp. *nezaketae* and *G. macrodon* subsp. *macrodon* were not found significant difference between each other. However, in the essential oil of *G. macrodon* subsp. *macrodon* (sample 3), pentacosane was determined in the highest amount (5.9 %) among all of the studied samples from subgenus *Grammosciadium*. Pentacosane can be considered a chemotaxonomic marker for the essential oil of *G. macrodon* subsp. *macrodon.* The chemical composition of the essential oils from *G. macrodon* subsp. *nezaketae* (samples 1-2 and 4-7) showed various patterns due to variations of collection localities and periods.

As shown in generally in Table 2, caryophyllene oxide and spathulenol were almost found in all investigated samples, except for both essential oils from the aerial parts of *G. confertum* and *G. daucoides* (samples 12 and 15), respectively. Eudesma-4(15),7-dien-4*β*-ol was also detected in all samples with the exception of essential oils from aerial parts of *G. daucoides* (samples 14 and 15). In addition, hexadecanoic acid, which was prominent constituent of the oil samples of *G. confertum* and *G. cornutum*, was found in various amounts in all samples, except for the fruit oil of *G. macrodon* subsp. *nezaketae* (sample 2).

Table 2. Chemical composition of the essential oils from subgenus *Grammosciadium* (%).

RRI	**Compound**	**1 mcn A***	**2 mcn F***	**3 mac F**	**4 mcn A***	**5 mcn F***	**6 mcn A***	**7 mcn F***	**8 cor F**	**9 cor A**	**10 cor F**	**11 cnf F***	**12 cnf A***	**13 cnf A***	**14 dau A**	**15 dau A**
1032	*α*-Pinene	-	-	-	0.2	-	-	-	-	-	-	-	-	-	tr	0.1
1118	*β*-Pinene	-	-	-	2.1	-	-	-	-	-	-	-	-	-	0.2	-
1132	Sabinene	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3	-
1174	Myrcene	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.1
1188	*α*-Terpinene	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.1
1203	Limonene	-	-	-	tr	-	-	-	-	-	0.9	-	-	-	0.1	-
1213	1,8-Cineole	-	-	-	0.5	-	-	-	-	-	-	-	-	-	-	0.2
1218	*β*-Phellandrene	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.1
1255	*γ*-Terpinene	-	-	-	1.5	tr	-	-	-	-	-	-	-	-	61.9	18.7
1280	*p*-Cymene	-	-	-	1.5	-	-	-	-	-	-	-	-	-	19.5	8.9
1296	Octanal	-	-	2.9	1.2	-	-	-	-	-	0.3	0.6	-	-	-	-
1398	2-Nonanone	-	-	0.5	-	-	-	-	-	-	-	0.3	-	-	-	-
1399	Methyl octanoate	-	-	-	-	-	-	-	-	0.1	0.1	-	-	-	-	-
1466	*α*-Cubebene	-	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-
1474	*trans*-Sabinene hydrate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2
1495	Bicycloelemene	0.5	-	-	-	-	0.3	-	-	0.1	-	-	-	-	-	-
1497	*α*-Copaene	0.4	-	0.1	-	0.2	0.2	-	0.1	0.1	0.2	-	-	-	-	-
1535	*β*-Bourbonene	0.5	-	0.5	-	0.1	0.3	-	0.2	0.2	-	0.3	-	-	-	-
1548	(*E*)-2-Nonenal	-	-	-	-	-	-	-	0.2	-	-	1.1	-	-	-	-
1549	*β*-Cubebene	-	-	-	-	0.1	-	-	-	-	-	-	-	-	-	-
1553	Linalool	-	-	-	-	-	-	-	-	0.1	0.3	0.1	-	-	0.1	-
1556	*cis*-Sabinene hydrate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2
1562	Octanol	-	-	0.7	-	-	-	-	-	0.1	-	0.1	-	1.0	-	-
1589	*β*-Ylangene	0.7	0.2	-	0.4	0.2	0.4	0.3	-	0.5	0.4	-	-	-	-	-
1597	*β*-Copaene	-	-	-	0.3	0.1	0.4	-	-	-	-	-	-	-	-	-
1600	*β*-Elemene	0.4	-	-	-	0.1	0.1	0.1	1.1	1.5	2.1	0.6	0.2	-	-	-
1606	*iso*-Isopulegol	-	-	-	1.1	-	-	-	-	0.4	-	-	-	-	-	-
1611	Terpinen-4-ol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2
1612	*β* -Caryophyllene	4.3	1.1	1.1	1.9	3.1	2.6	2.9	0.7	2.2	2.3	-	-	-	-	-
1614	Carvacrol methyl ether (=*Methyl carvacrol*)	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-
1648	Myrtenal	-	-	-	-	-	-	-	-	-	-	-	-	-	-	tr
1650	*γ*-Elemene	0.3	0.3	-	-	-	3.1	2.9	-	0.3	0.1	-	-	-	-	-
1655	(*E*)-2-Decenal	0.2	0.2	0.8	0.2	0.5	0.2	0.5	1.4	0.5	0.5	1.8	tr	1.4	-	-
1659	*γ*-Gurjunene	0.6	-	-	0.1	-	0.1	-	-	-	0.2	-	-	-	-	-
1662	Pulegone	-	-	-	0.7	-	-	-	-	0.1	-	-	-	-	-	-

1687	*α*-Humulene	0.7	0.2	-	0.1	0.5	0.4	0.5	0.2	0.5	0.4	-	-	-	-	-
1693	*β*-Acoradiene	-	-	-	-	-	-	-	-	-	-	0.7	-	-	-	-
1695	(*E*)-*β*-Farnesene	-	-	-	-	-	-	-	-	-	-	-	-	-	1.5	-
1700	Heptadecane	-	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-
1704	*γ*-Muurolene	-	-	-	-	0.2	-	0.1	-	0.1	-	-	-	-	-	-
1706	*α*-Terpineol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
1726	Germacrene D	4.7	1.1	-	2.3	1.4	2.8	2.3	0.2	4.2	3.9	-	-	-	-	-
1740	*α* -Muurolene	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1742	*β* -Selinene	-	-	-	-	-	-	-	0.5	0.4	0.3	-	0.1	-	-	-
1744	*α*-Selinene	-	-	-	-	-	-	-	-	0.4	-	-	-	-	-	-
1751	Carvone	-	-	-	0.1	-	-	-	-	-	0.1	-	-	-	-	-
1755	Bicyclogermacrene	1.0	-	-	-	-	0.5	-	-	-	-	-	-	-	-	-
1758	(*E*,*E*)-*α*-Farnesene	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-
1765	(*E*)-2-Undecanal	-	-	-	-	-	-	-	-	-	0.3	-	-	-	-	-
1766	Decanol	-	-	0.4	0.2	-	-	-	0.2	0.4	-	-	-	-	-	-
1773	*δ*-Cadinene	0.5	0.4	-	0.1	0.5	0.2	0.2	0.2	0.2	0.2	-	-	-	-	-
1776	*γ*-Cadinene	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-	-
1779	(*E*,*Z*)-2,4-Decadienal	-	-	-	-	-	-	-	-	0.2	-	-	-	-	-	-
1800	Octadecane	-	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-
1802	Cumin aldehyde	-	-	-	-	-	-	-	-	-	-	-	-	-	tr	0.2
1827	(*E*,*E*)-2,4-Decadienal	-	-	-	-	-	-	-	-	0.2	-	-	-	-	-	-
1849	Calamenene	-	-	-	-	-	-	-	0.1	0.1	-	-	-	-	-	-
1854	Germacrene-B	-	-	-	-	-	0.5	-	-	-	-	-	-	-	-	-
1864	*p*-Cymen-8-ol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2
1868	(*E*)-Geranyl acetone	0.4	-	tr	0.6	0.1	-	-	0.4	0.4	0.1	-	-	-	-	-
1900	Nonadecane	-	-	-	-	-	-	-	-	-	0.2	-	-	-	-	-
1941	*α*-Calacorene	-	-	-	-	0.2	-	-	-	0.1	-	-	-	-	-	-
1945	1,5-Epoxy-salvial(4)14-ene	1.4	2.0	-	1.0	0.7	1.3	0.8	0.5	1.1	1.3	-	-	1.6	-	-
1949	(Z)-3-Hexenyl nonanoate	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-
1958	(*E*)-*β*-Ionone	0.8	-	-	-	-	-	-	-	0.7	-	-	-	-	-	-
1973	Dodecanol	-	-	-	-	-	-	-	-	0.3	-	-	-	-	-	-
2001	Isocaryophyllene oxide	0.9	0.5	-	0.9	1.0	1.4	1.3	0.5	0.6	0.5	-	-	-	-	-
2008	Caryophyllene oxide	15.7	13.1	16.4	17.3	29.2	21.8	24.0	11.7	6.8	11.4	1.9	-	0.9	0.3	-
2022	Methyl tetradecanoate	-	-	-	-	-	-	-	-	0.8	1.0	-	-	-	-	-
2037	Salvial-4(14)-en-1-one	4.0	5.6	4.5	2.7	3.0	2.3	2.9	3.7	2.4	3.1	4.6	3.4	4.6	-	-
2046	Norbourbonone	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-
2050	(*E*)-Nerolidol	-	-	-	-	-	-	-	0.2	-	-	-	-	-	-	-
2071	Humulene epoxide-II	1.6	-	1.0	1.6	-	1.6	1.9	1.5	0.8	0.5	-	-	-	-	-
2074	Caryophylla-2(12),6(13)-dien-5-one	-	-	1.1	-	2.6	-	-	-	-	-	-	-	-	-	-
2077	Tridecanol	-	-	-	-	-	-	-	-	-	-	-	-	0.9	-	-

2080	Cubenol	-	-	-	-	-	-	-	0.8	-	-	-	-	-	-	-
2080	Junenol (=Eudesm-4(15)-en-6-ol)	-	-	-	1.1	-	-	-	-	0.5	-	-	-	-	-	-
2118	Methyl pentadecanoate	-	-	-	-	-	-	-	-	-	0.6	-	-	-	-	-
2130	Salviadienol	1.5	2.8	2.1	2.4	1.5	0.5	1.8	1.5	1.3	2.3	1.2	1.1	2.5	-	-
2131	Hexahydrofarnesyl acetone	1.5	0.4	1.5	1.0	-	1.5	-	0.5	1.1	-	1.9	3.5	1.4	-	-
2144	Spathulenol	12.3	5.8	2.2	2.4	2.5	9.8	4.3	1.4	2.6	5.7	1.0	-	1.3	0.3	-
2161	Muurola-4,10(14)-dien-1-ol	-	-	1.0	-	0.5	-	-	-	-	-	-	-	-	-	-
2179	Nor-Copaonone	-	-	-	-	-	0.7	1.1	0.9	-	-	1.5	0.8	1.4	-	-
2179	Tetradecanol	-	-	-	-	-	-	-	-	0.5	-	-	-	-	-	-
2181	Isothymol (=*2-Isopropyl-4-methyl phenol*)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3
2187	T-Cadinol	-	-	-	-	-	-	-	0.9	-	-	2.1	-	-	-	-
2198	Thymol	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.2
2211	Clovenol	-	-	1.5	-	0.7	-	-	0.6	-	-	-	-	-	-	-
2221	Isocarvacrol (=*4-Isopropyl-2-methyl phenol*)	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.3
2226	Methyl hexadecanoate	-	2.1	-	-	0.5	-	-	0.6	2.6	4.2	-	0.5	-	-	-
2239	Carvacrol	-	-	-	-	-	-	-	-	-	-	-	-	-	13.5	68.9
2247	*trans-α*-Bergamotol	0.5	-	-	-	-	0.4	-	-	-	-	-	-	-	-	-
2255	*α* -Cadinol	0.4	-	-	-	-	-	-	1.3	0.2	-	-	-	0.5	-	-
2269	Guaia-6,10(14)-dien-4β-ol	-	-	-	-	-	1.1	1.3	-	0.8	-	-	-	-	-	-
2273	Selin-11-en-4*α*-ol	-	-	-	-	-	-	-	1.0	-	-	-	-	-	-	-
2278	Torilenol	1.8	5.3	2.0	3.5	3.2	1.9	3.0	2.9	1.0	1.5	0.9	1.8	5.0	-	-
2289	Oxo-*α*-Ylangene	-	-	-	-	-	-	-	0.5	-	-	-	-	-	-	-
2300	Tricosane	-	-	0.5	-	-	-	-	-	1.6	-	-	-	-	-	-
2316	Caryophylla-2(12),6(13)-dien-5*β*-ol (=*Caryophylladienol I*)	-	-	-	-	1.4	-	-	-	-	-	-	-	-	-	-
2324	Caryophylla-2(12),6(13)-dien-5*α*-ol (=*Caryophylladienol II*)	1.8	2.1	4.5	2.5	4.0	1.7	2.0	2.1	0.9	1.6	-	-	-	-	-
2369	Eudesma-4(15),7-dien-4*β*-ol	3.3	8.7	1.3	4.6	4.8	3.1	5.0	3.9	3.9	6.4	2.2	1.7	6.4	-	-
2373	14-oxo-α-Muurolene	-	-	-	-	-	-	0.4	0.7	-	-	1.0	-	-	-	-
2389	Caryophylla-2(12),6-dien-5*α* -ol (=*Caryophyllenol I*)	1.3	1.7	4.9	-	2.2	1.0	1.6	1.2	0.5	-	-	-	-	-	-
2384	Hexadecanol	-	-	-	-	-	-	-	-	-	-	-	0.6	-	-	-
2384	Farnesyl acetone	-	-	-	-	-	-	-	0.6	1.0	-	-	-	-	-	-
2392	Caryophylla-2(12),6-dien-5*β*-ol (=*Caryophyllenol II*)	2.8	4.2	13.0	4.6	6.8	3.4	4.9	-	2.0	-	-	-	-	-	-

2431	Methyl stearate	-	1.2	-	-	-	-	-	0.6	0.9	2.1	-	1.0	-	-	-
2456	Methyl oleate	7.1	4.7	-	4.1	0.2	-	-	3.0	1.3	1.7	1.4	3.2	-	-	-
2458	Methyl elaidate	-	0.2	-	-	-	-	-	-	0.4	0.3	0.2	-	-	-	-
2500	Pentacosane	1.5	-	5.9	0.2	-	1.6	0.5	0.4	-	-	1.9	-	2.5	-	-
2503	Dodecanoic acid	-	-	-	4.2	-	-	-	-	1.1	-	-	-	2.4	-	-
2509	Methyl linoleate	-	2.6	-	-	0.8	-	-	-	2.1	1.8	-	1.4	-	-	-
2568	14-Hydroxy-*α*-muurolene	0.5	0.5	-	-	0.2	0.5	0.6	0.2	0.4	0.1	-	-	-	-	-
2607	14-Hydroxy-*δ*-cadinene	0.5	0.8	-	-	0.5	0.4	0.8	0.4	0.5	0.2	-	-	-	-	-
2622	Phytol	1.2	-	-	0.2	0.1	0.4	0.2	0.7	0.5	-	-	0.8	-	-	-
2638	Methyl arachidate	-	-	-	-	-	-	-	-	-	0.2	-	-	-	-	-
2670	Tetradecanoic acid	-	-	-	3.3	1.1	0.9	-	1.7	3.8	1.9	5.7	6.0	10.6	-	-
2700	Heptacosane	-	1.6	-	-	-	0.5	0.6	-	-	-	-	-	-	-	-
2822	Pentadecanoic acid	-	-	-	-	0.7	0.2	-	0.9	1.4	0.8	2.8	4.1	0.4	-	-
2839	Methyl behenate	-	-	-	-	-	-	-	-	-	tr	-	-	-	-	-
2900	Nonacosane	-	4.8	-	-	-	-	-	-	-	-	-	-	-	-	-
2931	Hexadecanoic acid	1.6	-	5.4	8.3	10.6	8.2	3.2	18.1	21.2	13.3	48.1	59.8	48.4	0.7	0.7
3290	Linoleic acid	-	-	-	-	-	-	2.0	-	-	-	-	-	-	-	-
3300	Linolenic acid	-	-	-	-	-	-	1.0	-	-	-	-	-	-	-	-
Total identification (%)		79.3	74.3	76	81.2	86.1	78.3	75	71.1	81.2	75.4	84	90	93.2	99.8	99.7
Oil yield (%)		tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	0.42	1.33

RRI: Relative retention indices calculated against n-alkanes; % calculated from FID data; tr : Trace (< 0.1%); mcn A: aerial parts of *G. macrodon* subsp. *nezaketae*; mcn F: fruits of *G. macrodon* subsp. *nezaketae*; mac F: fruits of *G. macrodon* subsp. *macrodon*; cor A: aerial parts of *G. cornutum*; cor F: fruits of *G. cornutum*; cnf A: aerial parts of *G. confertum*; cnf F: fruits of *G. confertum*; dau A: aerial parts of *G. daucoides*; *: endemic

Up to date, the chemical characterization of the essential oil from the species of the subgenus *Grammosciadium* from Turkey was only reported on *G. daucoides* gathered from Turkey and Azerbaidzhan. In a previous report by Shikhiev et al. [12], the essential oil of the fruits of *G. daucoides* from Azerbaidzhan mainly contained *o*-cymol (32.7%) and *p*-cymol (25.1%), as well as *β*-pinene (5%), sabinene (2.1%) and *α*-pinene (1.5 %). In another previous study by Göger et al. [16], the volatile oils obtained from herb and fruits of *G. daucoides* from Central Anatolia (Konya) in Turkey were analyzed respectively, as well as *γ*-terpinene (73.8% and 46.2%), *p*-cymene (6.7% and 18.5%) and carvacrol (11.4% and 30.4%) were found to be major components. In the present study, our results showed that *γ*-terpinene (61.9 and 18.7%), *p*-cymene (19.5 and 8.9%) and carvacrol (13.5 and 68.9%) were also found to be main components of the essential oils from *G. daucoides* collected from northern (Gümüşhane) and southern (Osmaniye) parts of Turkey, respectively. Our results were in good agreement with Göger et al.'s study, but not Shikhiev et al.'s report. However, we reported that carvacrol in the essential oil obtained from *G. daucoides* growing in Osmaniye was detected higher than Göger et al.'s study. The differences of the amounts of the major compounds in *G. daucoides* oils have been attributed to the geographical differences, collection periods and investigated parts of the plants.

In other studies on subgenus *Grammosciadium*, *G. scabridum* Boiss., not growing in Turkey, was investigated for their essential oil composition from Iran [9,14]. In these studies, the major compounds were reported to be different from each other. Sonboli et al.'s study [9] revealed that the major compounds in the essential oil of *G. scabridum* were detected as *γ*-terpinene (73.5%), *p*-cymene (14.2%) and (*E*)-*β*-farnesene (5.3%), while Nori-Shargh et al. [14] reported that the major components were *α*-pinene (32.4%), bornyl acetate (13.7%), limonene (11.8%), endo-fenchyl acetate (9.7%) and *trans*-caryophyllene (8.9%).

There are a number of studies on the chemical composition of the essential oils from various parts of some *Grammosciadium* species belonging subgenus *Caropodium* such as *G. platycarpum* [8,10,12,13] and *G. pterocarpum* [15,17] growing in different countries. In our previous study on *G. pterocarpum*, sesquiterpenes such as caryophyllene oxide (55.1%) and *β*-caryophyllene (15.3%) were reported to be the principal compounds of the volatiles [17]. In the present study, our results showed that caryophyllene oxide (6.8-29.2%) was detected mainly in the oils of *G. macrodon* and *G. cornutum*, while *β*-caryophyllene was found in small quantities (0.7-4.3%) in these oils. In another study, the oil of the leaves of *G. pterocarpum* has been reported to contain *γ*-terpinene (24 %) as the major compound [15]. However, in the present study, our results showed that *γ*-terpinene (61.9 and 18.7%) was also predominantly found in *G. daucoides* samples (samples 14 and 15), respectively. In several studies regarding the oils of *G. platycarpum*, some differences were reported in their qualitative composition. In these studies, linalool, limonene and *α*-farnesene were described as the main constituents [8,10,12,13], while these compounds were only detected in small quantities of some investigated samples in the present study.

To the best of our knowledge, it is the first time that the essential oil samples of four taxa of subgenus *Grammosciadium*, *G. cornutum*, *G. macrodon* subsp. *macrodon*, *G. macrodon* subsp. *nezaketae*, an endemic subspecies, and *G. confertum*, an endemic species, growing different locations in Turkey, were analyzed by GC and GC/MS. In addition, the essential oil of *G. daucoides* collected from different locations in Turkey was investigated. We have been investigating the chemical characterization of the essential oils of subgenus *Caropodium* to complete the essential oil composition of the genus *Grammosciadium*.

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