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Essential Oil Composition of Five *Sideritis* Species Endemic to Turkey

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Abstract: In this study, dried aerial parts of *Sideritis phrygia* Bornm., *Sideritis pisidica* Boiss. & Heldr., *Sideritis brevibracteata* P. H. Davis, *Sideritis bilgerana* P. H. Davis and *Sideritis hispida* P. H. Davis, collected from different regions of Turkey, were investigated the essential oil compositions obtained by hydrodistillation and they were analyzed by using GC-MS/MS. The main compounds in the essential oils of five *Sideritis* species were found as follows*:* caryophyllene oxide (11.4%), limonene (10.6%) and *p*-cymene (10.1%) in *S. phrygia;* β-caryophyllene (32.8%), germacrene D (10.7%) and *(E)*-β-farnesene (10.0%) in *S. pisidica*; β-caryophyllene (43.1%), germacrene D (10.6%) and α-cadinene (10.3%) in *S. brevibracteata*; α-cadinol (28.1%), α-cadinene (11.0%) and undecane (8.5%) in *S. bilgerana*; α-cadinol (41.1%), α-cadinene (13.3%) and β-caryophyllene (5.0%) in *S. hispida*.

Türkiye'ye Endemik Beş *Sideritis* Türünün Uçucu Yağ Bileşimi

Anahtar Kelimeler
Sideritis spp., Uçucu yağ, GC-MS/MS

Özet: Bu çalışmada, Türkiye'nin farklı yerlerinden toplanan *Sideritis phrygia* Bornm., *Sideritis pisidica* Boiss. & Heldr., *Sideritis brevibracteata* P. H. Davis, *Sideritis bilgerana* P. H. Davis and *Sideritis hispida* P. H. Davis bitkilerinin toprak üstü kısımlarından hidrodistilasyon yöntemiyle elde edilen uçucu yağların bileşenleri GC-MS/MS kullanılarak analiz edilmiştir. Çalışılan beş *Sideritis* türünün ana bileşenleri şu şekildedir: *S. phrygia* için karyofilen oksit (%11.4), limonen (%10.6) ve *p*-simen (%10.1)*; S. pisidica* için *β*-karyofilen (%32.8), germakren D (%10.7) ve *(E)*-β-farnesene (%10.0); *S. brevibracteata* için *β*-karyofilen (%43.1), germakren D (%10.6) ve α-kadinen (%10.3); *S. bilgerana* α-kadinol (%28.1), α-kadinen (%11.0) ve andekan (%8.5); *S. hispida* için α-kadinol (%41.1), α-kadinen (%13.3) ve β-caryophyllene (%5.0).

1. Introduction

The genus *Sideritis* L. (Labiatae) comprises of 150 species mainly occurred in Mediterranean area [1-4]. Turkey is the second country with the highest number of species after Spain [5]. *Sideritis* spp. (Lamiaceae) are represented 46 species (52 taxa) in Turkey and endemism rate of this genus is as high as almost 80%. *Sideritis* spp. are generally known under the names ‘‘adacayi or dagcayi” and widely used as herbal tea at folk medicine in Turkey [6,7]. Due to high-rate uses of in the public, the chemical contents of *Sideritis* spp. have been investigated with several studies [4,6-10]. Terpenes, iridoids, coumarins, lignanes and flavonoids were found in the chemical components of the *Sideritis* spp. While, the Lamiaecae are known rich in essential oil, the studies conducted on the *Sideritis* spp. have been showed that *Sideritis* spp. are poor [2,4]. Findings in these studies showed that, the oil of Turkish, Spain and Greece, *Sideritis* spp. mainly covered monoterpene (α-pinene, β-pinene, sabinene and myrcene) and sesquiterpene (β-caryophyllene, α-bisabolol, β-phellandrene, caryophyllene oxide and germacrene D) compounds [6,8,9]. The extracts of *Sideritis* spp. have anti-inflammatory, antirheumatic, antistress, analgesic, antioxidant, antibacterial, digestive, and antimicrobial activites [2,4,8-12].

Although there are some studies on the essential oil composition of the five species [6], locality, climatic and seasonal conditions are affect the chemical

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constituents of the plants. For these reasons, in this study, we decided to re-examine the essential oil contents of *Sideritis phrygia* Bornm. (SP), *Sideritis pisidica* Boiss. & Heldr. (SPi), *Sideritis brevibracteata* P. H. Davis (SB), *Sideritis bilgerana* P. H. Davis (SBi) and *Sideritis hispida* P. H. Davis (SH) which were collected in July 2014.

2. Material and Method

2.1. Plant material

The aerial parts of five *Sideritis* species were collected during the full-flowering season in July 2014 from different location in Turkey (Table 1). The species were identified by Prof. Dr. Tuncay Dirmenci from Balıkesir University. The voucher specimens were deposited at the Herbarium of Faculty of Education, Balıkesir University, Balıkesir, Turkey.

2.2. Isolation of essential oil

The air-dried aerial parts of the plants were chopped into small pieces and subjected to hydrodistillation with water for 4 h, using a Clevenger-type apparatus to produce the essential oil. The obtained essential oils were stored in amber vials at 4°C further analyses. The oil yields of species were given in the Table 1.

2.3. GC-MS conditions

GC-MS was conducted on Thermo Electron Trace 2000 GC model gas chromatography and Thermo Scientific TSQ GC-MS/MS. A Phenomenex DB5 fused silica column (30 m x 0.32 mm, with 0.25 µm film thickness) was used with helium as a carrier gas at 1mL/minute flow rate (138 kPa). Detailed procedures of GC-MS conditions and indentification of compounds were reported previously in the literature [13].

3. Results

The chemical content of essential oils of the studied species were given in Table 2. The essential oil contents of five *Sideritis* species were classified into seven groups as hydrocarbons and derivatives, monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes, diterpene alcohols and phenolic compounds (Table 2).

In the essential oil of SP, thirty four compounds were identified representing the 93.5% of the total oil. Monoterpene hydrocarbons were the dominant group (39.5%) in the essential oil of SP. Limonene (10.6%) and *p*-cymene (10.1%) were main monoterpen compounds. Oxygenated sesquiterpenes were represented with 20.5% and caryophyllene oxide (11.4%) was determined as dominant compound. While diterpenes were not detected, sesquiterpene hydrocarbons were detected in scarce amounts (6.2%).

The oils of SB and SPi have similar results and they were characterized by the huge amount of sesquiterpene hydrocarbons (74.4% and 72.0%, respectively) and β-caryophyllene was the major component (43.1% and 32.8%, respectively), followed by germacrene D (10.6% and 10.7%, respectively). Essential oil obtained from SB yielded 28 compounds, representing 99.0% and SPi yielded 30 compounds, representing 99.5% of the oil. Oxygenated sesquiterpenes of essential oil of SB and SPi were detected with the ratio of 5.0% and 17.3% caryophyllene oxide represented as the main constituent of this class (2.9% and 7.6% respectively).

Essential oil of SBi was characterized by 26 compounds constituting 99.0% of the oil. Oxygenated sesquiterpenes and sesquiterpene hydrocarbons were detected almost in equal amount (32.0% and 31.5%, respectively) in SBi essential oil. α-cadinol (28.1%) and α-cadinene (11.0%) were determined as main components. Oxygenated monoterpenes (14.3%) were composed of primarily bornyl acetate (7.7%). Monoterpene hydrocarbons were detected in scarce amounts (3.9%).

Similarly SBi, the essential oil of SH was composed of high amount of oxygenated sesquiterpenes (46.8%), being α-cadinol (41.1%) as the major compound. Sesquiterpene hydrocarbons were presented in 34.1%, and α-cadinene (13.3%) as the main compound of this class. Monoterpenes and diterpenes were detected in small amounts (10.8% and 0.4%, respectively).

Table 1. List of the *Sideritis* species with locality, collection time and oil yields (%)

Code	Species	Herbarium number	Collection Period	Location	Altitude (m)	Oil yield (%w/w)
SP	*S. phrygia* Bornm.	TD 4202	July 2014	Afyon: Akşehir, Sultandağı, Cankurtaran village, Turkey.	1100-1500	0.25
SPi	*S. pisidica* Boiss. & Heldr.	TD 4213	July 2014	Burdur, Ağlasun, Taşocakları, Turkey.	0-2100	0.13
SB	*S. brevibracteata* P. H. Davis	EA 5623	July 2014	Antalya: Alanya-Türbelinaz road, Turkey.	30-80	0.1
SBi	*S. bilgerana* P. H. Davis	TD 4212	July 2014	Between Karaman and Mut, 6th km	650-1400	0.24
SH	*S. hispida* P. H. Davis	TD 4204	July 2014	Between Karaman and Mut, 16th km	1350-1400	0.22

Table 2. Essential oil composition (%) of the studied *Sideritis* species

Compounds[c]	KI*	KI[b]	SP	SPi	SB	SBi	SH
Hydrocarbons and derivatives							
3-methyl nonane	971	968-973[a]	-	0.4	3.4	7.2	2.5
1-octen-3-ol	979	975-979[g,h]	-	2.4	-	1.4	0.8
3-octanol	991	997[h]	-	0.1	-	0.2	0.1
2-methyl decane	1063	1100[a]	-	-	-	-	0.2
nonanal	1098	1100[g]	-	0.1	-	-	0.1
undecane	1100	1100[a]	-	2.0	0.3	**8.5**	2.1
tricosane	2300	2300[b]	1.1	-	-	-	-
		% identified	**1.1**	**5.0**	**3.7**	**17.3**	**5.8**
Monoterpene hydrocarbons							
α-pinene	939	935-939[a-c]	5.8	-	1.6	1.3	0.4
camphene	954	948-954[c,d]	1.0	-	-	-	-
β-pinene	979	974-982[a-c]	7.1	0.1	4.6	0.1	0.1
α-phellandrene	1003	1002[c]	0.9	-	0.4	-	-
carene-3-Δ	1006	1006[a]	-	-	1.0	-	-
p-cymene	1025	1017-1026[a,b]	**10.1**	t	0.9	0.1	0.1
limonene	1029	1024-1032[a,b]	**10.6**	0.4	1.6	2.1	2.4
(Z)-β-ocimene	1037	1037-1040[a]	3.3	0.1	0.3	-	0.1
τ-terpinene	1060	1060[a]	0.2	t	0.1	-	0.1
terpinolene	1089	1085,1086,1088[b,g,h]	-	0.1	-	0.2	0.1
(E)-β-ocimene	1050	1050[c]	0.3	-	-	-	-
γ-terpinene	1059	1057-1062[c,h]	0.2	-	-	-	-
		% identified	**39.5**	**0.7**	**10.5**	**3.9**	**3.3**
Oxygenated monoterpenes							
1,8-cineole	1031	1031[b]	6.9	-	-	-	-
4-terpineol	1177	1177-1184[a]	3.6	0.6	0.4	1.9	2.4
α-terpineol	1189	1186-1188[a]	-	1.1	0.6	4.7	2.5
carvone	1243	1242[c]	-	-	-	-	0.3
sabinene hydrate	1070	1098[b]	1.7	-	-	-	-
limonene oxide	1137	1138[d]	0.5	-	-	-	-
trans-pinocarveol	1139	1139-1147[b,c]	1.0	-	-	-	-
linalyl acetate	1257	1252[a]	0.6	-	-	-	-
bornyl acetate	1289	1285[b]	1.1	1.5	-	7.7	2.3
terpinyl acetate	1301	1352[e]	0.9	-	-	-	-
isopulegyl acetate	1335	1273[c]	0.4	-	-	-	-
carvacryl acetate	1367	1371[c]	0.6	-	-	-	-
geranyl butyrate	1564	1562[c]	0.5	-	-	-	-
		% identified	**17.8**	**3.2**	**1.0**	**14.3**	**7.5**
Sesquiterpene hydrocarbons							
α-copaene	1377	1374-1377[a]	-	1.4	3.7	2.2	2.4
β-bourbonene	1388	1383-1387[a,c]	-	3.2	0.8	2.2	0.7
β-elemene	1391	1389[a]	-	1.4	1.0	-	-
α-gurjunene	1410	1412[b]	-	2.4	-	1.1	1.7
β-caryophyllene	1411	1411-1419[a,b]	1.4	**32.8**	**43.1**	6.6	**5.0**
α-humulene	1455	1452-1456[a]	-	-	1.5	3.4	1.1
(E)-β-farnesene	1457	1454[g]	-	**10.0**	-	1.3	0.4
aromadendrene	1464	1475[b]	0.9	-	-	2.8	-
τ-muurolene							
α-curcumene	1487	1481[a]		-	1.4	-	-
γ-cadinene	1514	1512,1522[a,b]	-	-	0.1	0.9	5.5
α-cadinene	1539	1529-1537[a]	-	4.3	**10.3**	**11.0**	**13.3**
β-gurjunene	1434	1432[c]	0.7	-	-	-	-
germacrene D	1485	1473-1485[a,b]	-	**10.7**	**10.6**	-	1.4
β-bisabolone	1506	1494-1507[b,h]	2.3	-	-	-	-
α- bisabolone	1506	1538[f]	0.9	-	-	-	-
		% identified	**6.2**	**72.0**	**74.4**	**31.5**	**34.1**
Oxygenated sesquiterpenes							
spathulenol	1572	1577-1578[a]	6.1	4.2	0.5	-	-
caryophyllene oxide	1583	1572-1583[a]	**11.4**	7.6	2.9	1.9	1.1
viridiflorol	1593	1590[h]	-	1.2	-	-	0.9
ledol	1590	1565c	-	1.4	-	-	0.1
δ-cadinol	1636	1640-1652[g-i]	-	2.2	-	1.5	1.6
α-cadinol	1660	1640-1652[a]	0.9	-	1.4	**28.1**	**41.1**
valeranone	1675	1674[a]	-	-	0.1	-	0.5
α-bisabolol	1686	1685-1688[a]	-	0.7	0.1	0.5	1.5
globulol	1585	1576[c]	0.9	-	-	-	-
β-eudesmol	1651	1654[b]	1.2	-	-	-	-
		% identified	**20.5**	**17.3**	**5.0**	**32.0**	**46.8**
Diterpene alcohols							
phytol	1943	1943[b]	-	1.3	-	0.9	0.4
		% identified	**-**	**1.3**	**-**	**0.9**	**0.4**
Phenolic compounds							
thymol	1290	1290[b]	7.3	-	-	-	-
carvacrol	1299	1298-1299[a,c,b]	1.1	-	5.3	-	-
		% identified	**8.4**	**-**	**5.3**	**-**	**-**
Total (%)			**93.5**	**99.5**	**99.0**	**99.0**	**97.9**

*KI Kovats indices, [b] Kovats indices of literature a) [13] b) [21], c) [22], d) [23], e) [24], f) [19], g [2], h [25], I [26], [c] Compounds listed in order of elution from a DB-5 column.

Table 3. The main compounds of the studied species

Species	Previous study	Present study
SP	α-pinene, β-pinene [6]	caryophyllene oxide, limonene, *p*-cymene
SPi	α-pinene, β-pinene, β-caryophyllene [6]	β-caryophyllene, germacrene D, β-farnesene
SB	β-caryophyllene [6]	β-caryophyllene, germacrene D, α-cadinene
SBi	α-pinene, β-pinene [15, 16]	α-cadinol, α-cadinene, undecane
SH	α-pinene, β-pinene, limonene, myrcene [6]	α-cadinol, α-cadinene, β-caryophyllene

In previous studies, main compounds of essential oil of *Sideritis* species belonging to section of Empedoclia were classified by Kırımer *et al.* [6] in to three groups as monoterpenes rich, sesquiterpenes rich and diterpenes rich [6]. According to the main constituents classified most of them were belong to monoterpene rich group and especially presence of α- and/or β-pinene was observed in particular. Results of the comparison our study and previous study were given in Table 3. According to the previous studies, while SPi and SBi were determined as monoterpene rich (α-pinene and β-pinene were major compound), in our study they were found sesquiterpene rich (β-caryophyllene). Similarly previous studies, we found SP, SB and SH oil as sesquiterpene rich.

4. Discussion and Conclusion

The present work was a study of essential oil of five endemic *Sideritis* species (*Sideritis phrygia* Bornm. (SP), *Sideritis pisidica* Boiss. & Heldr. (SPi), *Sideritis brevibracteata* P. H. Davis (SB), *Sideritis bilgerana* P. H. Davis (SBi) and *Sideritis hispida* P. H. Davis (SH)).

The major compound in the essential oil of SPi and SB was found to be β-caryophyllene (32.8% and 43.1%, respectively) while in the essential oil of SBi and SH was α-cadinol (28.1% and 41.1%, respectively). Additionally caryophyllene oxide (11.4%) was determined as main compound of the essential oil of SP. These results indicate that chemical constituents in the essential oils and the amounts of the major compounds showed difference, according to the geographical location, season, climatological variations, plant variety and experimental conditions investigated parts of the plants [17-20].

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