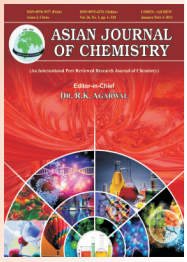
Asian Journal of Chemistry; Vol. 26, No. 8 (2014), 2466-2470

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16425



# Essential Oil Composition of Two *Sideritis* L. Taxa from Turkey: A Chemotaxonomic Approach

OMER KILIC

Technical Science Vocational College, Bingöl University, Bingol, Turkey

Corresponding author: Fax: +90 2151020; Tel: +90 426 2160012; E-mail: omerkilic77@gmail.com

*Received*: 25 September 2013; *Accepted*: 23 October 2013; *Published online*: 15 April 2014; AJC-15050

In this study two *Sideritis* L. taxa from Turkey (*Sideritis montana* L. subsp. *montana* and *Sideritis vulcanica* Hub.-Mor.) have been studied to determine taxonomical classification based on chemical characters. For this purpose hydro distilled essential oil aerial parts of *Sideritis montana* subsp. *montana* and *Sideritis vulcacina* were investigated by GC and GC-MS, forty and forty three compounds were identified representing 90.1 and 92.1 % of the oil, respectively. The yield of oils are about 0.30 and 0.40 mL/100 g, respectively. β-Caryophyllene (30.3 %), α-pinene (12.7 %) and β-pinene (10.6 %) in *S. montana* subsp. *montana*, α-pinene (15.5 %), β-caryophyllene (13.2 %) and 1,8-cineole (9.9 %) were identified as main components in *S. vulcacina.* The chemical distribution of the essential oil compounds in the genus pattern were discussed in means of chemotaxonomy and natural products.

**Keywords: *Sideritis*, Lamiaceae, Essential oil, Chemotaxonomy.**

## INTRODUCTION

The genus *Sideritis* L. represented in the Flora of Turkey by 46 species and altogether 55 taxa, 42 taxa being endemic. *Sideritis* has an important place among the other Lamiaceae genera because of the high percentage of endemism and named 'Dagcayi or Adacayi' are used as herbal tea and folk medicine in Turkey[1]. In Flora of Turkey *Sideritis* is divided into 2 sections according to their habitus, hair, bracts and calyx structures[2].

These sections are *Hesiodia* Bentham. and *Empedoclia* (Rafin.) Bentham. *S. montana* subsp. *montana* is belongs to section *Hesiodia* Bentham. and *S. sipylea, S. erythrantha, S. vulcacina, S. condensata, S. congesta, S. tmolea*, *S. argyrea*, *S. bilgerana, S. syriaca* subsp. *syriaca* and *S. perfoliata* are belongs to *Empedoclia* (Rafin.) Bentham. section. They are annual or perennial herbs or small shrubs, aromatic, pilose or tomentose, with or without glands, rarely glabrous.

*Sideritis* taxa generally grow optimally in full sun and are well suited to drought conditions. They are found on rocky slopes and pastures, from a few meters above the sea level to more than 3000 m and require moderately nutrient-rich soils and slightly alkaline. As many of the endemies in the latter section are centred in areas transitional between two phytogeographical regions, assignment to a particular element is often impossible[2]. The gene center for the section *Empedoclia* is Turkey and all of the 42 endemic taxa are in the *Empedoclia*. *S. montana* has two subspecies (subsp. *montana* and subsp. *remosa*) and *S. vulcacina* is monotypic and endemic in Flora of Turkey[3]. A large scale research program is ongoing in Turkey to investigate the taxonomical, anatomical, morphological, caryological, palinological and genetic aspects of the *Sideritis* taxa[4]. Many *Sideritis* taxa and their constituents have been reported to have analgesic, antiinflammatory, antiulcer[5], antioxidant, antimicrobial[6] effects. Infusion of aerial parts of a number of *Sideritis* taxa are used as tonics, carminatives, antispasmodics, diuretics, digestives and in the treatment of colds[7].

In the course of the historical evolution, there have been many attempts to classify the genus *Sideritis*. Degree of polymorphism, the presence of ecotype variation and the frequent hybridization between species already being named making this genus more difficult to classify. The classification of *Sideritis* is based on their morphological, caryological, palinological and genetical aspects. In recent decades a deep researchs on this genus, mainly based on their botanical, phytochemical and pharmacological aspects have taken place. Due to chemical variability, the purpose of this study is to determine essential oil composition of two *Sideritis* taxa, to compare with the genus patterns and to examine potential chemotaxonomic significance infrageneric means. Cluster analysis was performed to the major essential oil compounds from this study and from the literature reviews on the *Sideritis* taxa essential oils all around world. The studies on the Lamiaceae plant groups are continuing in our laboratory[8-11].

## EXPERIMENTAL

The aerial part of samples were collected from their natural habitats. *S. vulcacina* (Kilic 2748) was collected from Elazig-Keban, Pinarlar village, in June 2010 at an altitude of 1150-1250 m. *S. montana* subsp. *montana* (Kilic 4156) was collected from Elazig - 20 km to Keban slopes, in July 2010, at an altitude of 1350 m. The voucher specimens have been deposited at the Herbarium of department of Biology, Firat University.

**Isolation of the essential oils:** Air-dried aerial parts of the plant materials were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h.

**Statistical analysis:** The statistical software Cropstat (IRRI 2005) was used to perform the ANOVA and pattern analysis. Standard analyses of variance (anova) were used to analyze the data obtained.

**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 × 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. 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 Research Laboratory (BUBAL) in Firat University. HP-5 MS column (30 m × 0.25 mm i.d., film tickness (0.25 μm) was used with helium as the carrier gas. Injector temperature was 250 ºC, split flow was 1 mL/min. The GC oven temperature was kept at 70 ºC for 2 min and programmed to 150 ºC at a rate of 10 ºC/min and then kept constant at 150 ºC for 15 min to 240 ºC at a rate of 5 ºC/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). Hierarchical cluster analysis of twenty two *Sideritis* taxa from literature and studied taxa are seen in Fig. 1. The composition of the essential oils of the studied samples are reported in Table-1 and the main constituents of *Sideritis* taxa from literature and studied samples are listed in Table-2.

## RESULTS AND DISCUSSION

GC and GC-MS analyses of the oil resulted, 40 compounds were characterized, representing 90.1 % in *S. montana* subsp. *montana* and 43 components were identified, accounting for 92.1 % in *S. vulcacina* oil. β-Caryophyllene (30.3 %), α-cadinol (16.9 %) and β-pinene (10.6 %) in *S. montana* subsp. *montana*; α-pinene (15.5 %), 1,8-cineole (13.9 %), caryophyllene oxide (9.7 %) and camphor (7.0 %) were identified major components of *S. vulcacina.* The oils were complex mixtures of sesquiterpenes (42-24 %), monoterpenes (44 -58 %) and non-terpenes in *S. montana* subsp. *montana* and *S. vulcacina* respectively.

Many studies have been performed on the chemical composition of essential oil from *Sideritis* taxa. As seen in Table-2, *Sideritis* taxa have some qualitative and quantitative differences. These differences both in the oil content and composition may be due to different reasons such as climatic and genetic factors, agronomical practices, or plant chemotype and plant chemotaxonomy or nutritional status. Baser[12] and Kirimer *et al.*[13] classified *Sideritis* taxa from Turkey into six groups depending on the main essential oil constituent; these groups

TABLE-1
CHEMICAL PROFILES OF *Sideritis* TAXA (%)

| Compounds | RRI* | *S. montana* subsp. *montana* | *S. vulcacina* |
|---|---|---|---|
| α-Thujene | 1016 | 0.5 | 0.3 |
| α-Pinene | 1023 | 12.7 | 15.5 |
| Sabinene | 1052 | 0.1 | 0.1 |
| β-Pinene | 1056 | 10.6 | 8.9 |
| Mrycene | 1063 | 1.2 | - |
| Benzene | 1068 | - | 0.6 |
| β-Phellandrene | 1077 | 0.1 | 1.2 |
| *p*-Cymene | 1093 | - | 0.9 |
| Limonene | 1097 | 1.9 | 4.8 |
| 1,8-Cineole | 1095 | 8.1 | 9.9 |
| *cis*-Ocimene | 1100 | - | 0.2 |
| γ-Terpinene | 1115 | 0.5 | 0.3 |
| α-Terpinolene | 1138 | 0.3 | - |
| Linalool | 1145 | 0.1 | 0.4 |
| *trans*-Pinocarveol | 1178 | - | 0.1 |
| Camphor | 1184 | 2.9 | 7.0 |
| Cyclohexanone | 1190 | 0.6 | 0.4 |
| Pinocarvone | 1192 | 0.4 | 1.2 |
| Borneol | 1200 | 0.8 | 0.5 |
| 3-Cyclohexan-1-ol | 1208 | - | 0.1 |
| α-Terpineol | 1215 | 0.3 | - |
| Mrytenol | 1217 | - | 0.7 |
| *trans*-Carveol | 1231 | 0.2 | - |
| Thymol-methyl-ether | 1237 | 1.1 | 0.9 |
| Camphene | 1252 | 0.8 | 5.1 |
| 2-Cyclohexen-1-one | 1254 | - | 0.1 |
| Methyl acetate | 1257 | 0.3 | 4.03 |
| 2-Decanal | 1263 | 0.3 | - |
| Bornyl acetate | 1282 | 1.0 | 0.6 |
| α-Cubebene | 1286 | - | 2.5 |
| Thymol | 1297 | 1.8 | 0.5 |
| β-Bourbenene | 1365 | 0.3 | - |
| β-Cubebene | 1369 | 2.1 | 1.1 |
| Cyclohexane | 1371 | - | 0.4 |
| β-Caryophyllene | 1393 | 30.3 | 13.2 |
| *trans*-β-Farnesene | 1415 | 0.4 | 0.3 |
| α-Humulene | 1418 | 0.6 | - |
| Aromadendrene | 1421 | 0.7 | 0.6 |
| Dodecanal | 1425 | - | 0.1 |
| Germacrene D | 1432 | 0.8 | 0.6 |
| β-Selinene | 1441 | - | 0.5 |
| Bicyclogermacrene | 1443 | 0.2 | - |
| Naphtalene | 1456 | 0.4 | - |
| α-Cadinol | 1458 | 1.9 | 3.5 |
| Nerolidol | 1485 | 0.1 | 0.3 |
| Spathulenol | 1495 | 1.3 | 1.4 |
| Caryophyllene oxide | 1498 | 3.1 | 1.7 |
| Salvial-1-one | 1504 | 0.8 | 0.1 |
| Muurolene | 1523 | 0.2 | - |
| Copaene | 1534 | - | 0.7 |
| α-Cadinol | 1539 | 0.1 | - |
| Valerenol | 1595 | 0.2 | 0.4 |
| Hexadecanoic acid | 1653 | - | 0.1 |
| | Total | 90.1 | 92.1 |

*RRI = Relative retention index

TABLE-2
MAIN CONSTITUENTS OF *Sideritis* TAXA FROM LITERATURE AND STUDIED SAMPLES (%)

| *Sideritis* taxa | α-Pinene | β-Pinene | Limonene | 1,8-Cineole | Camphene | α-Cadinol | β-Caryophyllene | Germacren D | Thymol | Caryophyllene oxide |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 12.7 | 10.6 | 1.9 | 8.1 | 0.8 | 1.9 | 30.3 | 0.8 | 1.8 | 3.1 |
| **2** | 15.5 | 8.9 | 4.8 | 9.9 | 5.1 | 3.5 | 13.2 | 0.6 | 0.5 | 1.7 |
| **3** | 30.2 | 51.2 | 1.47 | - | 0.36 | 0.62 | - | - | - | - |
| **4** | 5.1 | 0.89 | 0.21 | **-** | **-** | 21.94 | 10.63 | 1.31 | - | 3.31 |
| **5** | 2.16 | 0.36 | 0.11 | **-** | **-** | 6.63 | 0.77 | - | - | 1.9 |
| **6** | 27.9 | 6.8 | 5.6 | - | - | - | 1.5 | 2.6 | 0.1 | - |
| **7** | 28.5 | 13.3 | 5.6 | - | **-** | - | 13.3 | 0.4 | 0.2 | - |
| **8** | 20.11 | 7.31 | 1.6 | - | **-** | - | 3.45 | 6.13 | - | 0.91 |
| **9** | 3.63 | 9.06 | - | 0.56 | - | - | 4.17 | - | - | 2.57 |
| **10** | 24.85 | 17.99 | - | 0.31 | - | - | 4.56 | - | - | 0.58 |
| **11** | 35.21 | 8.75 | - | 8.43 | 0.49 | - | 3.17 | - | 0.67 | 0.66 |
| **12** | 3.14 | 1.97 | - | - | - | 0.21 | 8.47 | - | 1.0 | 2.04 |
| **13** | 19.8 | 2.0 | 2.9 | 12.8 | - | 0.1 | 1.3 | 1.6 | 0.2 | 3.1 |
| **14** | 17.6 | 0.1 | 0.9 | - | - | - | 6.5 | 2.0 | - | 0.6 |
| **15** | 10.7 | 0.4 | 1.3 | 13.2 | - | 4.5 | 3.2 | - | 0.6 | 1.5 |
| **16** | 14.9 | 1.8 | 4.7 | 8.6 | - | 2.4 | 3.3 | 2.3 | 0.5 | 6.1 |
| **17** | 33.1 | 2.2 | 2.6 | 10.1 | **-** | 1.0 | - | - | 0.4 | 3.6 |
| **18** | 32.7 | 2.2 | 4.9 | 10.1 | - | 0.1 | 1.7 | 0.5 | 0.1 | 2.4 |
| **19** | 19.5 | 28.8 | 4.0 | - | 1.0 | 0.2 | 0.3 | 1.2 | - | 0.2 |
| **20** | 7.1 | 12.1 | 6.1 | - | 0.1 | 0.5 | 15.9 | 5.4 | - | 6.2 |
| **21** | 16.5 | 23.9 | 18.1 | - | 0.5 | 0.5 | 2.1 | 0.3 | - | 1.8 |
| **22** | 12.1 | 8.7 | 22.4 | - | 0.3 | - | 2.6 | - | 0.1 | 1.3 |

***Sideritis* taxa: 1-** *S. montana* subsp. *montana* and **2-** *S. vulcacina* (Studied samples), **3-** *S. bilgerana,* **4-** *S. tmolea* and **5-** *S. congesta*[19], **6-** *S. erythrantha* var. *cedretorum* and **7-** *S. erythrantha* var. *erythrantha*[14], **8-** *S.clandestina* subsp. *clandestina,* **9-** *S. raeseri* subsp. *raeseri,* **10-** *S. raeseri* subsp. *attica,* **11-** *S. sipylea* and **12-** *S. syriaca* subsp. *syriaca*[17], **13-** *S. spinulosa,* **14-** *S. linearifolia,* **15-** *S. mugronesis,* **16-** *S. serrata,* **17-** *S. leucantha* subsp. *bourgeana,* **18-** *S. pusilla*[20], **19-** *S. congesta,* **20-** *S. condensata,* **21-** *S. argyrea,* **22-** *S. perfoliata*[21].

were named monoterpene hydrocarbon-rich, oxygenated monoterpene-rich, sesquiterpene hydrocarbon-rich, oxygenated sesquiterpene-rich, diterpene-rich and others. 57 % of Turkish *Sideritis* taxa contain monoterpene hydrocarbons as major constituents, among these α-pinene, β-pinene, β-phellandrene, sabinene and myrcene were found in high amounts. In addition, Kirimer *et al.*[13] established a correlation between the oil yield and the main groups of constituents in *Sideritis* essential oil from Turkey. The higher the oil yield, the higher the monoterpene hydrocarbon content; the lower the oil yield, the higher the sesquiterpene content is. Diterpenes may occur at any yield.

The major monoterpenes of *S. vulcacina* were α-pinene (15.5 %), 1,8-cineole (13.9 %) and camphor (7.0 %). The major monoterpenes of *S. montana* subsp. *montana* oil was β-pinene (10.6 %). Other monoterpenes were detected in lower amounts. However, sesquiterpene contents [β-caryophylene (30.3 %), germacrene-D (0.8 %), spathulenol (1.3 %), α-humulene (0.6 %)] of *S. montana* subsp. *montana* oil were found at higher levels than in *S. vulcacina* [β-caryophylene (5.2 %), germacrene-D (0.6 %), spathulenol (1.4 %)] oil. Also, all of the oils of two taxa contained less oxygenated monoterpenes such as linalool, γ-terpinene, *trans*-pinocarveol and α-terpinolene. β-Caryophyllene (30.3 %), α-cadinol (16.9 %) and β-pinene (10.6 %) were the major constituents of *S. montana* subsp. *montana*, while α-pinene (15.5 %), 1,8-cineole (13.9 %), caryophylene oxide (9.7 %) and camphor (7.0 %) in *S. vulcacina*. It is noteworthy that high percentages of β-caryophyllene (30.3 %), α-cadinol (16.9 %) and β-pinene (10.6 %) in *S. montana* subsp. *montana* was distinctive from *S. vulcacina* (Table-1).

According to Köse *et al.*[14], β-caryophyllene (17.30 %), β-pinene (13.29 %), sabinene (12.17 %) and limonene (5.65 %) were the main components of *S. erythrantha* Boiss. & Heldr. var. *erythrantha* and the main components of the essential oil of *S. erythrantha* Boiss. & Heldr. var. *cedretorum* were α-bisabolol (7.80 %), β-pinene (6.78 %), limonene (5.60 %) and α-terpinene (5.53 %)[14]. The essential oil of *S. montana* subsp. *montana* was characterized by a high content of β-caryophyllene (30.3 %) and β-pinene (10.6 %) whereas these constituents were found in low amount *S. vulcacina*'s oil (Table-1). Furthermore, α-pinene (15.5 %), 1,8-cineole (13.9 %), caryophyllene oxide (9.7 %) and camphor (7.0 %) were the main components of the *S. vulcacina* but these compounds were detected in few amount in the oil of *S. montana* subsp. *montana* (Table-1). Tabanca *et al.*[15] reported that the main components two varietes of the *S. erythrantha* (var. *erythrantha* and var. *cedretorum*) were α-pinene (16.3-19.5 %), sabinene (6.1-10.4 %) and myrcene (24.3-21.9 %), respectively. According to Chalchat and Ozcan[16], *S. erythrantha* var. *erythrantha* essential oil contained α-pinene (25.13 %), eucalyptol (8.83 %), linalool (7.88 %), α-bisabolol (7.32 %), germacrene-D (5.87 %) and carvacrol (4.90 %) as the main components. In our study, linalool, α-bisabolol, germacrene-D and carvacrol were absent or present only in low percentages (Table-1).

Koedam[26] reported that, germacrene D, α-bisabolol, β-copaene, δ-cadinene, calacorene and α-cadinol were high percentages volatile oil of *S. clandestina* subsp. *clandestina*[26]. Whereas β-copaene, δ-cadinene, calacorene and α-cadinol were not identified at all in the present study (Table-1). According to Kirimer *et al.*[13] α-pinene (10 %) and β-pinene (14 %) showed the highest percentage in the *S. vulcacina* sample,

which was also characterized by the presence of α-pinene (15.5 %) in *S. vulcacina* (Table-1). Aligiannis *et al.*[17] reported that α-pinene (20.11 %), (3.63 %), (24.85 %), (35.21 %), (3.14 %) and β-pinene (7.31 %), (9.06 %), (17.99 %), (8.75 %), (1.97 %) showed the highest percentage in the *S. clandestina* subsp. *clandestina, S. raeseri* subsp. *raeseri, S. raeseri* subsp. *attica, S. sipylea, S. syriaca* L. subsp. *syriaca* respectively. Similarly α-pinene (15.5-2.7 %) and β-pinene (4.9-10.6 %) were the main components of *S. vulcacina* and *S. montana* subsp. *montana* respectively. Also, Kirimer *et al.*[18] established the presence of β-pinene and α-pinene as major constituents in the essential oil of *S. dichotoma* Huth.

Topcu *et al.*[22] reported that *S. albiflora* Hub.-Mor. contained *trans*-caryophyllene (17.4 %), α-pinene (15.4 %), β-pinene (13.5 %), cadinene (12.1 %), pulegone (9.7 %), myrcene (6.5 %) and copaene (4.4 %). In the essential oil of *S. hirsuta* from Spain, β-phellandrene (23.8 %), α-phellandrene (9.2 %) and α-pinene (8.2 %) were found to be the major components[23]. α-Pinene (31.1 %, 16.0 %, 6.2 %) and β-pinene (20.2 %, 14.2 %, 7.3 %) have been reported to be basic components of *S. ozturkii* which was collected from two localities at different times in three samples[24]. The essential oils of *S. cilicica* and *S. bilgerana* contained β-pinene (39 and 48 %) and α-pinene (28 and 32 %) as the first and second major components, respectively[25]. Ozcan *et al.*[19] found that contents of essential oils of *S. bilgerana*, *S. tmolea* and *S. congesta* showed more differentiation. Köse *et al.*[14] reported that β-caryophyllene was the second major component in the *S. erythrantha* var. *erythrantha*, but this component was found to exist in much lower amounts in the previously conducted study[15]. In our study, β-caryophyllene (30.3 %) was one of the major component in *S. montana* subsp. *montana* and α-pinene (15.5 %) was one of the major component in *S. vulcacina* (Table-1). Hierarchical cluster analysis of twenty two *Ideritis* taxa is seen in Fig. 1. Results of cluster analysis (Fig. 1) based on the distribution of essential oil show two main groups. One of them *S. leucantha* subsp. *bourgeana* - 17, *S. pusilla* - 18, *S. sipylea* - 11, *S. erythrantha* var. *erythrantha* - 7, *S. raeseri* subsp. *attica* - 10, *S. clandestina* subsp. *clandestina* - 8, *S. erythrantha* var. *cedretorum* - 6, *S. spinulosa* - 13, *S. serrata* - 16, *S. mugronesis* - 15, *S. vulcacina* - 2, *S. raeseri* subsp. *raeseri* - 9, *S. syriaca* subsp. *syriaca* - 12, *S. congesta* - 5, *S. condensata* - 20, *S. congesta* - 19, *S. argyrea* - 21, *S. perfoliata* - 22, *S. montana* subsp. *montana* - 1 and *S. tmolea* - 4 samples. The other group is *S. bilgerana* - 3 sample. In fact, in the dendrogram *S. bilgerana* was very far apart from all the other taxa. Furthermore we can seperate first main group (17, 18, 11, 7, 10, 8, 6, 13, 16, 15, 2, 9, 12, 5, 20, 19, 21, 22, 1, 4) in two groups. First 17, 18, 11, 7, 10, 8, 6, 13, 16, 15, 2, 9, 12, 5, 20, 19, 21, 22 and second 1, 4 samples. Also we can seperate first main group (17, 18, 11, 7, 10, 8, 6, 13, 16, 15, 2, 9, 12, 5, 20, 19, 21, 22) in two groups (17, 18, 11, 7, 10, 8, 6, 13, 16, 15, 2, 9, 12, 5, 20 and second 19, 21, 22 samples). In the first main group, infrageneric variation of the essential oil patterns between 17, 18, 11, 7, 10, 8, 6, 13, 16, 15, 2, 9, 12, 5, 20 taxa are relatively small but, comparing with the 19, 21, 22 patterns the variation is considerable higher particularly in 1,4 samples. In the second main group, *S. bilgerana* was very far apart from all the other *Sideritis* taxa (Fig. 1).

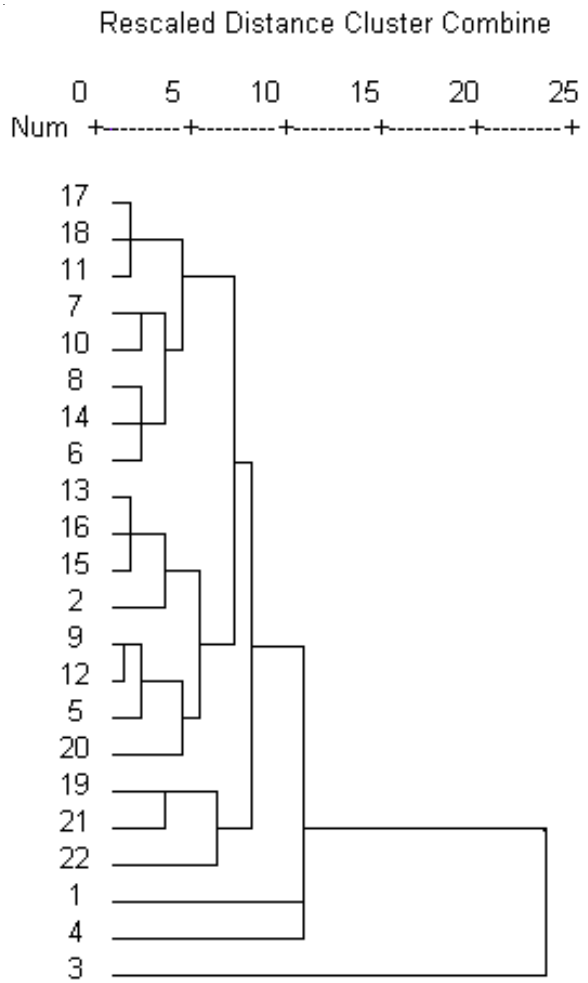



Fig. 1. Hierarchical cluster analysis of twenty two *Sideritis* taxa from literature and studied taxa; **1-** *S. montana* subsp. *montana,* **2-** *S. vulcacina,* **3-** *S. bilgerana,* **4-** *S. tmolea,* **5-** *S. congesta,* **6-** *S. erythrantha* var. *cedretorum,* **7-** *S. erythrantha* var. *erythrantha,* **8-** *S. clandestina* subsp. *clandestina,* **9-** *S. raeseri* subsp. *raeseri,* **10-** *S. raeseri* subsp. *attica,* **11-** *S. sipylea,* **12-** *S. syriaca* subsp. *syriaca,* **13-** *S. spinulosa,* **14-** *S. linearifolia,* **15-** *S. mugronesis,* **16-** *S. serrata,* **17-** *S. leucantha* subsp. *bourgeana,* **18-** *S. pusilla,* **19-** *S. congesta,* **20-** *S. condensata,* **21-** *S. argyrea,* **22-** *S. perfoliata*

Chemical dendrogram obtained by cluster analysis of the percentage composition of essential oils from *Sideritis* taxa showed that *S. leucantha* subsp. *bourgeana, S. pusilla, S. sipylea, S. erythrantha* var. *erythrantha, S. raeseri* subsp. *attica, S. clandestina* subsp. *clandestina, S. linearifolia, S. erythrantha* var. *cedretorum, S. spinulosa, S. serrata, S. mugronesis, S. vulcacina, S. raeseri* subsp. *raeseri, S. syriaca* subsp. *syriaca, S. congesta, S. condensata* samples were closest to *S. congesta, S. argyrea, S. perfoliata.* samples and they were related with the *S. montana* subsp. *montana, S. tmolea*. It is noteworthy that, in the dendrogram *S. bilgerana* was very far apart from all the other *Sideritis* taxa (Fig. 1).

In conclusion, studied taxa synthesized many similar compounds in their essential oils that could be justified by the similar ecological conditions of their habitat (biochemical convergence). However, taking into account the differences referred to some constituents, also the taxonomic distance of these species could be confirmed by our chemical data. The comparison between two taxa evidenced a similarity, at least with reference to the presence of the main constituents: in fact

β-caryophyllene, α-pinene, 1,8-cineole and β-pinene was among the principal one in both taxa. Monoterpene (α-pinene, β-pinene) and sesquiterpene (β-caryophyllene) derivatives are characteristic for *Sideritis* taxa and they represent excellent chemotaxonomical markers. Work described in this paper showed that in respect to the major components of *Sideritis* taxa were chemically similar expect *S. tmolea* and *S. congesta* but the composition of the cultivated oils of *S. raeseri* subsp. *raeseri* differed from that of the other twenty two taxa. On the other hand, the oils of the *S. tmolea*, *S. argyrea* and *S. perfoliata* species were chemically distinct from others in respect to α-cadinol and limonene content. It has been stated that intermediate and mixed chemical types are in common existence within this genus in the natural habitat of eastern Turkey. Moreover, genetic and environmental factors both play a role in determining the composition of essential oils of the *Sideritis* taxa studied. Furthermore findings showed that the genus *Sideritis* had a considerable variation in essential oil composition and this study demonstrates the occurrence of the β-caryophyllene, α-cadinol, β-pinene chemotype of *S. montana* subsp. *montana* and β-pinene, 1,8-cineole, caryophyllene oxide chemotype of *S. vulcacina* in the eastern Anatolian region of Turkey. Some of the *Sideritis* species showed different chemotype of essential oil, like α-pinene, β-pinene chemotype in *S. bilgerana, S. raeseri* subsp. *attica, S. congesta, S. sipylea*, *S. erythrantha, S. argyrea* and *S. perfoliata* taxa. α-Cadinol and β-caryophyllene chemotype in *S. tmolea*. α-Pinene, 1,8-cineole chemotype in *S. spinulosa, S. mugronensis, S. serrata, S. pusilla* and *S. leucantha* subsp *bourgeana.* β-pinene, β-caryophyllene chemotype in *S. condensata.* Chemical analysis has shown that the essential oil of *Sideritis* taxa has chemical variatons and different oil profiles.

## REFERENCES


1. Z. Tunalier, M. Kosar, N. Ozturk, K.H.C. Baser, H. Duman and N. Kirimer, *Chem. Nat. Comp*., **40**, 206 (2004).
2. P.H. Davis, Flora of Turkey and East Eagean Island: Edinburgh University Press, vol. 7 (1982).
3. P.H. Davis, R.R. Mill and T. Kit, Flora of Turkey and the East Aegean Islands, Edinburgh University Press, vol. 10 (1988).
4. A. Guner, N. Ozhatay, T. Ekim and K.H.C. Baser, Flora of Turkey and the East Aegean Islands, Edinburgh University Press*,* vol. 11 (2000).
5. E.A. Aboutabl, M.I. Nassar, F.M. Elsakhawy, Y.A. Maklad, A.F. Osman and E.A.M. El-Khrisy, *J. Ethnopharmacol*., **82**, 177 (2002).
6. A. Basile, F. Senatore, R. Gargano, S. Sorbo, M.D. Pezzo, A. Lavitola, A. Ritieni, M. Bruno, D. Spatuzzi, D. Rigano and M.L. Vuotto, *J. Ethnopharmacol*., **107**, 240 (2006).
7. N. Ezer, E. Sezik, K. Erol and M. Ozdemir, 9th Symp. on Plant Drugs, pp. 88-93 (1991).
8. E. Bagci and K.H.C. Baþer, *Flav. Fragr. J.*, **19**, 1 (2004).
9. O. Kilic, S. Hayta and E. Bagci, *Asian J. Chem*., **23**, 2788 (2011).
10. O. Kilic and E. Bagci, *Asian J. Chem*., **25**, 7263 (2013).
11. O. Kilic, L. Behçet and E. Bagci, *Asian J. Chem.*, **25**, 8181 (2013).
12. K.H.C. Baser, *Pure Appl. Chem*., **74**, 527 (2002).
13. N. Kirimer, K.H.C. Baser, B. Demirci and H. Duman, *Chem. Nat. Comp.*, **40**, 19 (2004).
14. E.O. Köse, I.G. Deniz, C. Sarikurkcu, O. Aktas and M. Yavuz, *Food Chem. Tox*., **48**, 2960 (2010).
15. N. Tabanca, N. Kirimer and K.H.C. Baser, *Turk. J. Chem*., **25**, 201 (2001).
16. J.C. Chalchat and M. Ozcan, *Gen. Appl. Plant Physiol.,* **31**, 65 (2005).
17. N. Aligiannis, E. Kalpoutzakis, I.B. Chinou, S. Mitakou, E. Gikas and A. Tsarbopoulos, *J. Agric. Food Chem.*, **49**, 811 (2001).
18. N. Kirimer, K.H.C. Baser, G. Tumen and E. Sezik, *J. Essent. Oil Res.*, **4**, 641 (2001).
19. M. Ozcan, J.C. Chalchat and A. Akgul, *Food Chem.*, **75**, 459 (2001).
20. C. Mateo, J. Calderon and J. Sanz, *Phytochemistry*, **27**, 151 (1988).
21. N. Ezer, R. Vila, S. Canigueral and T. Adzet, *Phytochemistry*, **41**, 203 (1995).
22. G. Topcu, A. Barla, A.C. Goren, G. Bilsel, M. Bilsel and G. Tumen, *Turk. J. Chem*., **29**, 525 (2005).
23. J. Pala-Paul, M.J. Perez-Alonso, A. Velasco-Negueruela, M.T. Ballesteros and J. Sanz, *Flav. Fragr. J.*, **21**, 410 (2006).
24. N. Kirimer, N. Tabanca, B. Demirci, K.H.C. Baser, H. Duman and Z. Aytac, *Chem. Nat. Comp.*, **37**, 234 (2001).
25. G. Iscan, N. Kirimer, M. Kurkcuoglu and K.H.C. Baser, *Chem. Nat. Comp.*, **41**, 679 (2005).
26. A. Koedam, *J. Sci. Food Agric*., **36**, 681 (1986).