

# The Composition of Essential Oils From Two Varieties of *Sideritis erythrantha* var. *erythrantha* and var. *cedretorum*\*

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Water distilled essential oils from two varieties of *Sideritis erythrantha*: var. *erythrantha* and var. *cedretorum*, both endemic in Turkey, were analysed by GC/MS. The main components were characterized as  $\alpha$ -pinene (16.3-19.5%) and sabinene (6.1- 10.4%) for var. *erythrantha*; myrcene (21.9-24.3%) and  $\alpha$ -pinene (11.4- 12.4%) for var. *cedretorum*.

## Introduction

*Sideritis* (Labiatae) is represented by 46 species and 53 taxa in Turkey, 39 taxa being endemic (1-3). *Sideritis* species are widely used as herbal tea in Turkey. They are known by different local names and traditional uses in various regions of Turkey. Infusions of *Sideritis* species are used as stomachic, antispasmodic, carminative and taken for cough (4-9). Antispasmodic and antiinflammatory effects of some *Sideritis* species (10-12) have been reported. The aqueous extracts of five *Sideritis* species of Turkey have been found to have antidepressant and antistress activities in mice (13). Essential oil of *S. congesta* exhibited no significant analgesic action (14).

*Sideritis erythrantha* Boiss. & Heldr. apud Bentham var. *erythrantha* is locally known as “Boz ot” in Isparta while, *Sideritis erythrantha* Boiss. & Heldr. apud Bentham var. *cedretorum* P.H. Davis is locally known as “Yayla çayı” and is used as herbal tea in Antalya: Alanya. In the present work, the essential oils of the varieties of *Sideritis erythrantha* were investigated for the first time.

## Experimental

### Materials

Aerial parts of the plants were collected from the following localities. Voucher specimens are kept the Herbarium of Faculty of Pharmacy Anadolu University in Eskişehir, Turkey (Acronym: ESSE)

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*Sideritis erythrantha* var. *erythrantha*

**A:** Isparta: Sütçüler, Çandır-Söğüt high plate, 1700-1800 m, in August 1993 (ESSE 10979)

**B:** Isparta: Sütçüler, Çandır-Akçal (fire tower road) 1675 m, in July 1995 (ESSE 114887)

*Sideritis erythrantha* var. *cedretorum*

**C:** Antalya: Alanya, Çökele-Gökbel road, 1350 m, in August 1994 (ESSE 10701)

**D:** Antalya: Alanya, Çökele-Gökbel road, 32 km from Alanya, 1275 m, in July 1995 (ESSE 11489)

## Distillation

Air-dried aerial parts were subjected to water distillation for 3 h using a Clevenger apparatus. The percentage yields of the oils based on moisture free basis are shown in Table 1.

## GC/MS

The essential oils were analysed by GC/MS using a Hewlett-Packard GC/MSD system. Innovax FSC column (60 m × 0.25 mm  $\phi$  with 0.25  $\mu$ m film thickness) was used with helium as carrier gas. GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C /min and then kept constant at 220°C for 10 min to 240°C at rate of 1°C /min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). Split ratio was adjusted at 50 mL/min. The injector and detector temperatures were at 250°C. MS were taken at 70 eV. Mass range was from  $m/z$  35 to 425. Library search was carried out using Wiley GC/MS Library and TBAM Library of Essential Oil Constituents. Relative percentage amounts of the separated compounds were calculated from Total Ion Chromatogrammes by the computerized integrator.

## Results and Discussion

Essential oils were obtained from dried herbal plants by water distillation. The physicochemical characteristics of the oils and yields are given in Table 1. The results from GC/MS analyses are presented in Table 2. In the oils of *Sideritis erythrantha* var. *erythrantha* 67 and 68 compounds representing 87.8% and 92.5% of the total oils were characterized with  $\alpha$ -pinene (16.3 and 19.5%) and sabinene (6.1 and 10.4%) as main constituents, respectively. In the oils of *Sideritis erythrantha* var. *cedretorum* 60 and 76 compounds were characterized making up 90 and 87.2 % of the oils with myrcene (24.3 and 21.9%) and  $\alpha$ -pinene (12.4 and 11.4%) as main constituents, respectively. Six components making up 12.3-15.4% of the oils of var. *erythrantha* and three components making up 7.3-8.3% of the oils of var. *cedretorum* were not identified. Their MS values are given in Table 2.

All the *Sideritis* species of Turkey have been collected by our group and their oils have been analysed. They can be classified into six groups, namely “monoterpene hydrocarbon-rich”, “oxygenated monoterpene-rich”, “sesquiterpene hydrocarbon -rich”, “oxygenated sesquiterpene-rich”, “diterpene-rich” and “others”. 57% of the *Sideritis* species existing in Turkey belong to the “monoterpene hydrocarbon-rich” group as shown in Table 3. (15-31). Two varieties of *Sideritis erythrantha* are also included in this group.

Table 4. illustrates the status of *Sideritis* species growing outside Turkey according to main components in their oils. Ambiguous conclusions have been indicated. The results show a clear correlation with those of the Turkish species in that 60% of the oils have been classified as “monoterpene hydrocarbon-rich”.

**Table 1.** Physical characteristics of the essential oils of *Sideritis erythrantha* varieties

| Plant material | Yield % | Physicochemical properties |                 |            |
|----------------|---------|----------------------------|-----------------|------------|
|                |         | $d^{20}$                   | $[\alpha]^{20}$ | $[n]^{20}$ |
| A              | 0.39    | 0.9500                     | -8.42           | 1.4820     |
| B              | 0.49    | 0.9000                     | -7.70           | 1.4800     |
| C              | 0.70    | 0.9591                     | -12.51          | 1.4840     |
| D              | 0.56    | 0.9444                     | -14.82          | 1.4842     |

**Table 2.** Percentage composition of components identified in the oils of *Sideritis erythrantha* var. *erythrantha* and var. *cedretorum*

| Compound                            | RRI  | A    | B    | C    | D    |
|-------------------------------------|------|------|------|------|------|
| $\alpha$ -pinene                    | 1032 | 16.3 | 19.5 | 12.4 | 11.4 |
| $\alpha$ -thujene                   | 1035 | 0.7  | 1.3  | -    | 0.1  |
| 1,3,5 cycloheptatriene              | 1056 | 1.0  | -    | -    | -    |
| camphene                            | 1076 | -    | 0.1  | -    | <0.1 |
| $\beta$ -pinene                     | 1118 | 3.2  | 4.0  | 3.7  | 3.9  |
| sabinene                            | 1132 | 6.1  | 10.4 | 0.2  | 0.2  |
| myrcene                             | 1174 | 0.7  | 0.3  | 24.4 | 21.9 |
| $\alpha$ -phellandrene              | 1176 | 0.6  | 0.3  | -    | -    |
| $\alpha$ -terpinene                 | 1188 | 0.2  | 0.3  | -    | 0.2  |
| limonene                            | 1203 | 1.8  | 1.8  | 0.8  | 0.8  |
| 1,8-cineole                         | 1213 | 2.1  | 2.0  | -    | <0.1 |
| $\beta$ -phellandrene               | 1218 | 10.0 | 6.5  | 0.1  | 0.1  |
| ( <i>E</i> )-2-hexenal              | 1232 | 0.1  | 0.1  | 0.2  | <0.1 |
| ( <i>Z</i> )- $\beta$ -ocimene      | 1246 | -    | -    | <0.1 | 0.1  |
| $\gamma$ -terpinene                 | 1255 | 0.5  | 0.6  | -    | 0.1  |
| ( <i>E</i> )- $\beta$ -ocimene      | 1266 | -    | <0.1 | 0.1  | 0.3  |
| <i>p</i> -cymene                    | 1280 | 0.4  | 0.1  | -    | <0.1 |
| terpinolene                         | 1290 | 0.1  | 0.1  | 0.2  | 0.3  |
| 1-hexanol                           | 1360 | -    | <0.1 | 0.1  | 0.1  |
| 3-octanol                           | 1393 | 0.1  | 0.1  | 0.2  | 0.1  |
| nonanal                             | 1400 | -    | <0.1 | -    | -    |
| perillen                            | 1429 | -    | -    | <0.1 | <0.1 |
| 1-octen-3-ol                        | 1452 | 0.3  | 0.1  | 0.4  | 0.2  |
| $\alpha$ -cubebene                  | 1474 | -    | -    | 0.4  | 0.6  |
| <i>trans</i> -sabinene hydrate      | 1474 | 0.6  | 0.6  | -    | -    |
| $\alpha$ -copaene                   | 1497 | 0.1  | 0.1  | 0.9  | 0.9  |
| $\beta$ -bourbonene                 | 1535 | 0.5  | 0.3  | 0.2  | 0.1  |
| benzaldehyde                        | 1541 | 0.1  | <0.1 | 0.1  | <0.1 |
| $\alpha$ -gurjunene                 | 1544 | -    | -    | 0.2  | 0.2  |
| $\beta$ -cubebene                   | 1547 | -    | -    | 0.2  | 0.2  |
| linalool                            | 1553 | 2.7  | 1.8  | 1.2  | 1.3  |
| <i>cis</i> -sabinene hydrate        | 1556 | 0.2  | 0.2  | -    | -    |
| octanol                             | 1562 | 0.1  | 0.1  | -    | 0.1  |
| <i>trans-p</i> -menth-2-en-1-ol     | 1571 | 0.1  | 0.1  | -    | -    |
| methyl citronellate                 | 1571 | -    | 0.1  | -    | -    |
| bornyl acetate                      | 1591 | 0.1  | 0.1  | <0.1 | 0.1  |
| <i>trans</i> - $\beta$ -bergamotene | 1594 | -    | -    | -    | <0.1 |
| $\beta$ -elemene                    | 1600 | -    | 0.2  | -    | -    |
| terpinen-4-ol                       | 1607 | 1.6  | 2.8  | 0.1  | -    |

**Table 2.** Continue

|  |      |     |      |      |      |
|--|------|-----|------|------|------|
| $\beta$ -caryophyllene                 | 1612 | 2.2 | 4.2  | 8.0  | 5.5  |
| 2-methyl-6-methylene-3,7-octadien-2-ol | 1628 | -   | -    | 0.2  | 0.1  |
| <i>cis-p</i> -menth-2-en-1-ol          | 1638 | 0.1 | -    | -    | -    |
| citronellyl acetate                    | 1668 | 0.4 | 0.2  | -    | 0.1  |
| ( <i>E</i> )- $\beta$ -farnesene       | 1671 | 0.2 | 0.3  | 0.1  | -    |
| $\alpha$ -humulene                     | 1684 | 0.1 | 0.2  | 0.4  | 0.4  |
| $\delta$ -terpineol                    | 1684 | 0.2 | 0.2  | -    | -    |
| <i>trans</i> -verbenol                 | 1684 | 0.5 | -    | 0.1  | -    |
| cryptone                               | 1687 | -   | 0.1  | -    | -    |
| <i>p</i> -mentha-1,8-dien-4-ol         | 1700 | -   | -    | -    | <0.1 |
| $\alpha$ -terpineol                    | 1707 | 1.7 | 1.2  | 0.2  | 0.1  |
| ledene                                 | 1707 | -   | -    | <0.1 | 0.1  |
| germacrene D                           | 1726 | 4.0 | 6.0  | 3.2  | 4.2  |
| $\beta$ -bisabolene                    | 1740 | 0.2 | 0.6  | 0.3  | 0.3  |
| bicylogermacrene                       | 1751 | 1.9 | 1.1  | 3.4  | 3.7  |
| $\alpha$ -farnesene                    | 1755 | -   | -    | 0.4  | 0.3  |
| geranyl acetate                        | 1765 | 0.1 | -    | -    | -    |
| $\delta$ -cadinene                     | 1772 | -   | 0.1  | 1.9  | 1.4  |
| citronellol                            | 1772 | 0.5 | 0.3  | 0.1  | 0.2  |
| $\gamma$ -cadinene                     | 1776 | -   | <0.1 | -    | <0.1 |
| $\beta$ -sesquiphellandrene            | 1783 | -   | 0.3  | 0.1  | 0.2  |
| cadina-1,4-diene                       | 1797 | -   | -    | 0.4  | 0.3  |
| <i>p</i> -methyl acetophenone          | 1797 | 0.2 | -    | -    | -    |
| methyl salicylate                      | 1800 | 0.1 | -    | -    | -    |
| isobutyl benzoate                      | 1808 | 0.8 | 0.1  | 0.1  | <0.1 |
| $\beta$ -damascenone                   | 1838 | 0.1 | -    | -    | <0.1 |
| calamenene                             | 1849 | -   | -    | 0.1  | 0.1  |
| geraniol                               | 1857 | -   | <0.1 | -    | -    |
| butyl benzoate                         | 1882 | 0.3 | -    | -    | -    |
| epicubebol                             | 1900 | -   | -    | 6.3  | 6.3  |
| isoamyl benzoate                       | 1937 | 0.3 | -    | 0.1  | <0.1 |
| cubebol                                | 1957 | -   | -    | 2.1  | 1.9  |
| isocaryophyllene oxide                 | 2000 | -   | -    | 0.1  | 0.1  |
| caryophyllene oxide                    | 2008 | 1.6 | 0.6  | 0.8  | 0.4  |
| pentadecanal                           | 2041 | 0.1 | -    | -    | <0.1 |
| gleenol                                | 2049 | -   | -    | -    | 0.1  |
| ( <i>E</i> )-nerolidol                 | 2053 | 0.1 | 0.1  | 0.1  | 0.1  |
| germacrene D-4-ol                      | 2069 | -   | -    | -    | 0.1  |
| humulene epoxide-II                    | 2069 | -   | 0.1  | <0.1 | -    |
| 1-epicubenol                           | 2088 | -   | -    | 1.0  | 0.7  |
| globulol                               | 2096 | -   | -    | -    | 0.1  |
| hexyl benzoate                         | 2096 | 0.1 | -    | -    | -    |
| viridiflorol                           | 2100 | -   | -    | 0.1  | 0.1  |
| hexahydrofarnesyl acetone              | 2131 | 0.5 | 0.9  | -    | -    |
| spathulenol                            | 2144 | 0.9 | 0.1  | 0.1  | -    |
| valeranone                             | 2144 | -   | -    | 0.1  | 0.7  |
| ( <i>Z</i> )-3-hexen-yl-benzoate       | 2148 | 0.3 | 0.1  | 0.1  | 0.1  |
| $\alpha$ -bisabolol oxide B            | 2157 | -   | 0.1  | -    | -    |
| eugenol                                | 2162 | 0.4 | 0.1  | -    | 0.1  |
| thymol                                 | 2205 | 0.2 | -    | -    | 0.1  |

**Table 2.** Contumie

|  |      |     |      |     |      |
|--|------|-----|------|-----|------|
| $\delta$ -cadinol  | 2219 | -   | -    | -   | 0.1  |
| $\alpha$ -bisabolol  | 2232 | 1.1 | 7.2  | 5.0 | 4.8  |
| carvacrol  | 2246 | 1.0 | 1.8  | 0.3 | 0.9  |
| diterpene (M <sup>+</sup> 272)                                   | 2251 | 2.0 | 4.2  | 2.6 | 4.5  |
| $\alpha$ -cadinol  | 2255 | -   | 0.1  | 0.7 | 0.8  |
| dimyrcene-II-b   | 2269 | 0.5 | -    | 0.7 | 0.6  |
| sesquiterpene (M <sup>+</sup> 262)                               | 2308 | 2.1 | 1.5  | -   | -    |
| diterpene (M <sup>+</sup> 270)                                   | 2312 | 2.3 | 1.3  | 1.5 | 1.2  |
| caryophylladienol*   | 2320 | -   | <0.1 | -   | -    |
| $\alpha$ , -13 oxy-14-en-epilabdane                              | 2396 | 0.2 | 0.1  | 0.1 | 0.2  |
| sesquiterpene (M <sup>+</sup> 262)                               | 2411 | 6.0 | 1.8  | -   | -    |
| kaur-16-ene  | 2426 | -   | -    | -   | 0.3  |
| sesquiterpene (M <sup>+</sup> 220)                               | 2459 | 0.6 | 2.2  | 3.2 | 2.6  |
| sesquiterpene (M <sup>+</sup> 220)                               | 2577 | 2.4 | 1.3  | -   | -    |
| heptacosane  | 2700 | 0.6 | 0.1  | -   | <0.1 |
| hexadecanoic acid  | 2931 | 0.5 | -    | -   | -    |
| RRI= Relative retention indices                                  |      |     |      |     |      |
| *Tentative identification by GC/MS data alone                    |      |     |      |     |      |
| <b>A,B:</b> <i>Sideritis erythrantha</i> var. <i>erythrantha</i> |      |     |      |     |      |
| <b>C,D:</b> <i>Sideritis erythrantha</i> var. <i>cedretorum</i>  |      |     |      |     |      |

**RRI** MS of unidentified components are the following

2251 *m/z* 272 (M<sup>+</sup>, 0.5%), 119 (100%), 69 (81%), 93 (68%), 132 (52%), 41 (41%), 91 (32%)

2308 *m/z* 262 (M<sup>+</sup>, 0.3%), 43 (100%), 93 (54%), 91 (39%), 133 (39%), 79 (36%), 105 (30%)

2312 *m/z* 270 (M<sup>+</sup>, 0.3%), 119 (100%), 132 (82%), 145 (52%), 69 (34%), 41 (33%), 105 (31%)

2411 *m/z* 262 (M<sup>+</sup>, 0.23%), 43 (100%), 93 (54%), 79 (33%), 91 (31%), 119 (27%), 41 (26%)

2459 *m/z* 220 (M<sup>+</sup>, 1%), 93 (100%), 91 (79%), 79 (74%), 133 (64%), 41 (62%), 43 (50%), 189 (46%)

2577 *m/z* 220 (M<sup>+</sup>,  $\leq$  0.01%), 93 (100%), 79 (63%), 43 (61%), 41 (55%), 133 (48%), 105 (39%), 107 (37%), 189 (30%)

**Table 3.** Classification of *Sideritis* species according to main components in essential oils (15-31)

|                            |   |
|----------------------------|---|
| Monoterpene Hydrocarbons   | <i>amasiaca, argyrea, armeniaca, athoa, bilgerana, brevidens, congesta, dichotoma, erythrantha</i> var. <i>erythrantha, erythrantha</i> var. <i>cedretorum, galatica, germanicopolitana</i> ssp. <i>germanicopolitana, germanicopolitana</i> ssp. <i>viridis, gulendamii, hispida, huber-morathii, libanotica</i> ssp. <i>libanotica, libanotica</i> ssp. <i>kurdica, lycia, niveotomentosa, phrygia, rubriflora, scardica</i> ssp. <i>scardica, serratifolia, sipylea, stricta, syriaca</i> ssp. <i>nusairiensis, trojana, vuralii</i> |
| Oxygenated Monoterpenes    | <i>arguta, libanotica</i> ssp. <i>microchlamys, romana</i> ssp. <i>romana</i>   |
| Sesquiterpene Hydrocarbons | <i>akmanii, albiflora, brevibracteata, caesarea, cilicica, condensata, curvidens, hololeuca, leptoclada, libanotica</i> ssp. <i>linearis, libanotica</i> ssp. <i>violascens, montana</i> ssp. <i>montana, montana</i> ssp. <i>remota, ozturkii, pisidica, tmolea, vulcanica</i>   |
| Oxygenated Sesquiterpenes  | <i>phlomoides, taurica</i>  |
| Diterpenes                 | <i>perfoliata</i>   |
| Others                     | <i>lanata</i>   |

**Table 4.** Classification of *Sideritis* species according to main components in essential oils growing outside Turkey (32-49)

|                            |  |
|----------------------------|--|
| Monoterpene Hydrocarbons   | <i>angustifolia, clandestina</i> ssp. <i>cyllena, foetens, granatensis, hirsuta, javalambrensis, leucantha</i> ssp. <i>bourbeana, linearifolia, mugronensis, paulii, pusilla, raeseri</i> ssp. <i>raeseri, scardica</i> ssp. <i>scardica</i> |
| Oxygenated Monoterpenes    | <i>flavovirens, mugronensis, reverchonii, romana, scardica</i>   |
| Sesquiterpene Hydrocarbons | <i>arborescens, chamaedryfolia, clandestina</i> ssp. <i>clandestina, hyssophila</i> var. <i>pyrenaica, scordioides, cavanillesii, scardica</i>   |
| Oxygenated Sesquiterpenes  | <i>illicifolia</i>   |
| Others                     | <i>raeseri</i> ssp. <i>raeseri</i>   |
| Others                     | <i>lanata</i>  |

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