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ESSENTIAL OILS OF *Sideritis* SPECIES OF TURKEY BELONGING TO THE SECTION *Empedoclia*

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The paper summarizes the work done on the essential oil content and composition of fifty Sideritis *species of Turkey belonging to the section* Empedoclia. *The water-distilled oils were analyzed by GC/MS. The oils were characterized as having mono- and sesquiterpenoids.*

Key words: *Sideritis*, *Lamiaceae*, essential oil, herbal tea.

The genus *Sideritis* numbers more than 150 species occurring mainly in the Mediterranean area [1]. This genus is represented in the Flora of Turkey by 46 species and altogether 55 taxa, 42 taxa being endemic. These species are divided into 2 sections according to their habitus, hair, bracts and calyx structures. These sections are *Hesiodia* and *Empedoclia*. The gene center for the section *Empedoclia* is Turkey. All of the 42 endemic species belong to the section *Empedoclia* [2–4]. A large scale research program is ongoing to investigate the taxonomical, anatomical, morphological, caryological, palinological, and genetic aspects of the *Sideritis* species of Turkey.

Sideritis species are generally known under the names "adacayi, dagcayi" and are widely used as herbal tea and folk medicine in Turkey. In folk medicine, they are used as a nervous system stimulant and as an antiinflammatory, antispasmodic, carminative, analgesic, sedative, antitussive, stomachic, and anticonvulsant, in the treatment of coughs due to colds and for curing gastrointestinal disorders [5]. Recent studies have shown that extracts of some *Sideritis* species have antifeedant [6], anti-stress [7], analgesic [8], antioxidant [9], antibacterial [10–11], and antiinflammatory activity [12].

There are several investigations on the composition of the essential oils and diterpenes of *Sideritis* species [13–28].

In the course of the present study, the main volatile compounds of the members of the Empedoclia section were classified in to three groups as monoterpenes, sesquiterpenes and diterpenes. Oil yields ranged between trace (< 0.01) and 0.85%. A rough correlation may be established according to the oil yield and main groups of constituents in *Sideritis* oils of Turkey as follows (Table 1–7):

The higher the oil yield, the higher the monoterpene hydrocarbon content.

The lower the oil yield, the higher the sesquiterpene content.

Diterpenes may occur at any yield.

There are six groups of peaks in a typical chromatogram of *Sideritis* oils (Fig. 1).

Monoterpene-rich oils (Table 1) were characterized by the main components α- and/or β-pinene. Twenty-one species were rich in these compounds. *S. cilicica* oil contained also β-phellandrene (24%). Three oils contained α- and β-pinene together with epicubebol (Table 2). The oils of three *Sideritis* taxa (Table 3) contained myrcene together with α- and β-pinene as the main constituents; and in those of four taxa, myrcene or sabinene were the main components next to α- and β-pinene (Table 4). Although β-caryophyllene was the main constituent in eleven sesquiterpene-rich oils (Table 5), germacrene D, calamenene, spathulenol, and α-bisabolol were the main constituents in four species (Table 6).

Two species were rich in diterpenes (Table 7). *S. dichotoma* was characterized by the occurrence of geraterpinene (**1,** 9-geranyl-α-terpinene) (9–26%) and geracymene (**2,** 9-geranyl-*p*-cymene) (6–14%), rare diterpenes previously found in *Helichrysum* species [29]. Those were found in *Sideritis* oils for the first time. *S. perfoliata* oil, on the other hand, contained 8α-13-hydroxy-14-en-epilabdane (26–29%), a diterpene, as the main constituent.

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TABLE 1. Monoterpene Hydrocarbon-Rich Oils-I: β and α-Pinene-Rich Oils

Sideritis species	Oil yield, %	β-Pinene	α-Pinene	Others (> 10%)	Ref.
S. amasiaca Bornm. (E)	0.02-0.15	9-28	4-11		17
S. armeniaca Bornm. (E)	0.16-0.5	39-45	17-24		18
S. bilgerana P. H. Davis (E)	0.26	34	17		
	0.26	51	30		15
S. cilicica Boiss. & ball. (E)	0.55	30	19	β-phellandrene, 24	
S. gulendamiae H. Duman & Karaveliogullari (E)	Tr. -0.14	9-41	4-18		
S. hispida P. H. Davis (E)	0.45	26	17	limonene, 14; myrcene, 12	
S. hololeuca Boiss. & Heldr. apud Bentham (E)	0.02	20-26	8-16		18
S. huber-morathii Greuter & Burdet (E)	0.08	29	20		
S. libanotica Labil. subsp. linearis (Bentham) Bornm.	Tr.-0.02	17	-	hexadecanoic acid, 20 β-caryophyllene, 15	
S. libanotica Labill. subsp. libanotica	0.25-0.36	22-23	14-15		
S. libanotica Labill. subsp. *kurdica* (Bornm.) Hub.-Mor. (E)	Tr.-0.09	13-19	6-42		
S. lycia Boiss. & Heldr. apud Bentham (E)	0.3-0.7	27-34	16-23	valeranone, 11	19
	0.25	25	16		16
S. ozturkii Aytac & Aksoy (E)	0.15-0.2	7-20	6-31		20
S. phrygia Bornm. (E)	0.02-0.05	20-32	18-20		
S. rubriflora Hub.-Mor. (E)	0.18-0.32	13-15	9-10	germacrene D, 14	21
S. scardica Griseb. subsp. *scardica*	0.02-0.04	14-24	5-7	β-caryophyllene, 6-13; carvacrol, 13	22
S. stricta Boiss & Heldr. (E)	0.14-0.63	21-48	7-24	β-caryophyllene, 10; epicubebol, 10	
S. syriaca L. subsp. *nusairiensis* (Post) Hub.-Mor. (E)	0.07-0.15	11-20	21-35		
S. trojana Bornm. (E)	0.01-0.04	12-17	8-14		
S. vulcanica Hub.-Mor. (E)	Tr.	14	10	germacrene D, 12	
S. vuralii H. Duman & Baser (E)	0.08-0.12	35-38	15-26	β-phellandrene, 12-15	23
S. species nova (E)	0.05	16	9	β-bisabolol	

E: Endemic.

TABLE 2. Monoterpene Hydrocarbon-Rich Oils-II: Pinene + Epicubebol-Rich Oils

Sideritis species	Oil yield, %	β-Pinene, %	α-Pinene, %	Epicubebol, %	Others (> 10%)	Ref.
S. argyrea P. H. Davis (E)	0.1-0.45	7-20	3-14	10-16		18
	0.8	24	17	-	limonene, 18	16
S. brevidens P. H. Davis (E)	0.5-0.7	14-22	8-16	12-13		21
S. congesta P. H. Davis & Hub.-Mor. (E)	0.4-0.85	23-36	12-30	4-7		24
	0.5	29	20	-		16
	0.83	-	-	-	α-cadinol, 22	15

TABLE 3. Monoterpene Hydrocarbon-Rich Oils-III: Myrcene + Pinene-Rich Oils

Sideritis species	Oil yield, %	Myrcene, %	β-Pinene, %	α-Pinene, %	Others (> 10%)	Ref.
S. athoa Papanikolau & Kokkini	0.16-0.25	19-39	7-12	4-7	ar-curcumene, 7-12	25
S. germanicopolitana Bornm. subsp. *germanicopolitana*	0.2-0.33	26-39	4-33	3-24	sabinene, 21	26
S. germanicopolitana Bornm. subsp. *viridis* Hausskn. Ex Bornm. (E)	0.2-0.33	43-49	4-18	3-13		26
S. sipylea Boiss. (E)	0.05-0.15	2-18	9-14	9-18		

TABLE 4. Monoterpene Hydrocarbon-Rich Oils-III: Myrcene or Sabinene + Pinene-Rich Oils

Sideritis species	Oil yield, %	Myrcene, %	α-Pinene, %	Others (> 10%)	Ref.
S. erytrantha var. Boiss & Heldr. apud Bentham cedretorum P. H. Davis (E)	0.15-0.7	4-24 sabinene	5-30 α-pinene	α-bisabolol, 5-20	27
S. erytrantha var. Boiss. & Heldr. apud Bentham erytrantha (E)	0.3-0.5	2-18	16-30	β-phellansrene, 10	27
S. pisidica Boiss & Heldr. apud Bentham subsp. Termessi (E)	0.28-0.48	7-10 β-pinene	12-30 α-pinene	β-caryophyllene, 7-8 naphthalene, 29	
S. pisidica Boiss & Heldr. apud Bentham subsp. Pisidica (E)	0.08-0.17	13-15	5-10	β-caryophyllene, 14	

TABLE 5. Sesquiterpene-Rich Oils-I: β-Caryophyllene-Rich Oils-1

Sideritis species	Oil yield, %	β-Caryophyllene, %	Others (> 10%)	Ref.
S. albiflora Hub.-Mor. (E)	0.02	35		
S. arguta Boiss & Heldr. (E)	0.07-0.1	10-20	β-phellandrene, 23 germacrene D, 14	19
S. brevibracteata P. H. Davis (E)	0.06	20	naphtalene, 18	
S. caesarea H. Duman, Aytac & Baser (E)	Tr.-0.09	8-21	α-pinene, 2-21 β-pinene, 4-17 (E)-β-damascenone, 0.1-2.0	23
S. condensata Boiss. & Heldr. apud Bentham (E)	Tr.-0.65 0.1	9-19 16	germacrene D, 5-14; caryophyllene oxide, 6-11; hexahydrofarnesylacetone, 6-15; β-pinene, 12	28 16
S. leptoclada O. Schwarz & P. H. Davis (E)	0.04	14	germacrene D, 10	
S. libanotica Labill. subsp. *microchlamys* (Hand.-Mazz.) Hub.-Mor.	0.02	12	-	
S. libanotica Labill. subsp. *violascens* (P. H. Davis) (E)	0.1	20	-	
S. niveotomentosa Hub.-Mor. (E)	0.04	10	-	
S. phlomoides Boiss. & Bal. (E)	0.2	24	caryphyllene oxide 8 α-bisabolol 7 limonene 6	
S. tmolea P. H. Davis (E)	0.04	21	-	

TABLE 6. Sesquiterpene-Rich Oils-II

Sideritis species	Oil yield, %	Main components, %	Ref.
S. taurica Stephan ex Willd.	0.05 0.08	germacrene D, 12 α-bisabolol, 10	
S. galatica Bornm. (E)	Tr.	germacrene D, 10	
S. serratifolia Hub.-Mor. (E)	Tr.	calamenene, 8	
S. akmanii Aytac, Ekici & Donmez (E)	0.06-0.1	spathulenol, 16-17 ar-curcumene, 8-18	 16

TABLE 7. Diterpene-Rich Oils

Sideritis species	Oil yield, %	Main components, %	Others (> 10%)	Ref.
S. dichotoma Huter (E)	0.2-0.5	geraterpinene, 9-26	geracymene, 6-14; valeranone, 6; hexahydrofarnesylacetone, 3-9	
S. perfoliata L.	0.12-0.36	8α-13-hydroxy-14-en-epilabdane, 26-29	limonene, 19-24; viridiflorol, 14; sabinene, 11; β-caryopyllene, 10	
	0.3	Limonene, 22; α-pinene, 12; β-pinene, 9		16

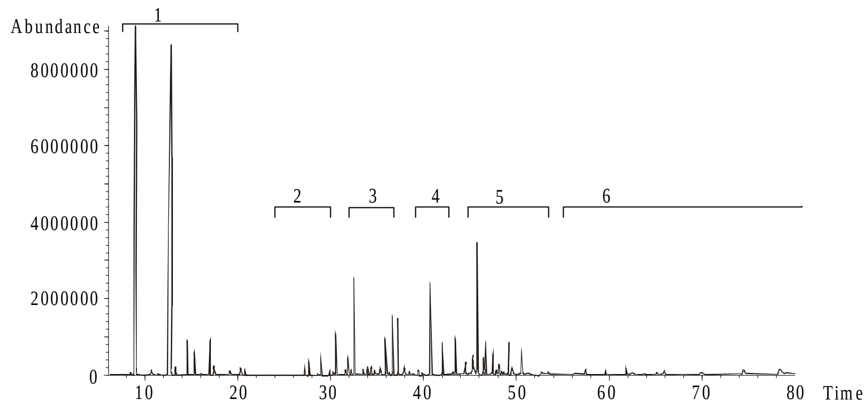
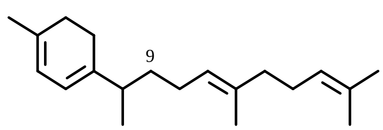


Fig. 1. TIC of *Sideritis lycia*: typical chromatogram of *Sideritis* oils. 1 – α-Pinene, β-pinene, sabinene, δ-3-carene, myrcene, limonene, β-phellandrene; 2 – Nonanal, 1-octen-3-ol, α-copaene, β-bourbonene; 3 – Linalool, β-caryophyllene, (*Z*)-β-farnesene; 4 – Germacrene D, bicyclogermacrene, δ-cadinene, naphthalene; 5 – Caryophyllene oxide, spathulenol; 6 – Diterpenes.



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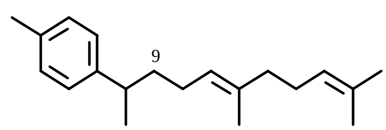

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The results of classification of *Sideritis* taxa according to the main constituents in their oils show that diterpenes were found in *S. dichotoma*, *S. perfoliata*; sesquiterpenes, in *S. akmanii*, *S. albiflora*, *S. arguta*, *S. brevibracteata*, *S. caesarea*, *S. condensata*, *S. galatica*, *S. leptoclada*, *S. libanotica* ssp. *microchlamys*, *S. libanotica* ssp. *violascens*, *S. niveotomentosa*, *S. phlomoides*, *S. serratifolia*, *S. taurica*, *S. tmolea*, *S. vulcanica*; monoterpenes, in the remaining species studied.

EXPERIMENTAL

Plant Material. Plant materials were collected while flowering and were shade dried. Voucher specimens are kept at Prof. Dr. Hayri Duman’s herbarium.

Essential Oil Distillation. Aerial parts of the air-dried plants including inflorescences were subjected to water distillation for 3 h using a Clevenger apparatus to yield oils.

Gas Chromatography/Mass Spectrometry. The essential oils were analyzed by gas chromatography/mass spectrometry using a Hewlett-Packard GC-MS system. Innowax FSC column (60 m × 0.25 mm, 0.25 mm 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 and programmed to 240°C at a rate of 1°C min. Split flow was adjusted at 50 mL/min. The injector temperature was at 250°C. MS were taken at 70 eV. Mass range was from *m/z* 35 to 425. Library search was carried out using the Wiley GC/MS Library and the BASER Library of Essential Oil Constituents.

REFERENCES

1. C. Obon de Castro and D. R. Nunez, *Phanerogamarum monographiae Tomus XXI: A Taxonomic revision of the section Sideritis (Genus Sideritis) (Labiatae)*, J. Cramer, Berlin (1994).
2. P. H. Davis (Ed.), *Flora of Turkey and the East Aegean Islands*, Edinburgh University Press, Edinburgh, **7** (1982).
3. P. H. Davis, R. R. Mill, and Kit Tan (Eds.), *Flora of Turkey and the East Aegean Islands*, Edinburgh University Press, Edinburgh, **10** (1988).
4. A. Guner, N. Ozhatay, T. Ekim, and K. H. C. Baser (Eds.), Flora of Turkey and the East Aegean Islands, Edinburgh University Press, Edinburgh, **11** (2000).
5. N. Kirimer, N. Tabanca, G. Tumen, H. Duman, and K. H. C. Baser, *Flavour Fragr*., **14**, 421 (1999).
6. M. L. Bondi, M. Bruno, F. Piozzi, K. H. C. Baser, and M. S. J. Simmonds, *Biochem. Syst.Ecol.* **28**, 299 (2000).
7. Y. Ozturk, S. Aydin, N. Ozturk, and K. H. C. Baser, *Phytotherapy Res.*, **10**, 70 (1996).
8. S. Aydin, Y. Ozturk, R. Beis, and K. H. C. Baser, *Phytotherapy Res*., **10**, 342 (1996).
9. Z. Tunalier, N. Ozturk, M. Kosar, K. H. C. Baser, H. Duman, and N. Kirimer, 14. BIHAT, 29–31 May 2002, Eskisehir, Turkey.
10. N. Ezer, G. Usluer, I. Gunes, and K. Erol, *Fitoterapia*, **65**, 549 (1994).
11. N. Ezer and U. Abbasoglu, *Fitoterapia*, **67**, 474 (1996).
12. E. Yesilada and N. Ezer, *Int. J. Crude Drug Res*., **27**, 38 (1989).
13. K. H. C. Baser, M. L. Bondi, M. Buruno, N. Kirimer, F. Piozzi, G. Tumen, and N. Vassallo, *Phytochem*., **43**, 1293 (1996).
14. G. Topcu, A. C. Goren, Y. K. Yildiz, and G. Tumen, *Nat. Prod. Letts*., **14**, 123 (1999).
15. M. Ozcan, J. C. Chalchat, and A. Akgul, *Food Chem*., **75**, 459 (2001).
16. N. Ezer, R. Vila, S. Canigueral, and T. Adzet, *Phytochem*., **41**, 203 (1996).
17. K. H. C. Baser, N. Kirimer, and N. Ermin, *J. Essent. Oil Res*., **7**, 699 (1995).
18. N. Kirimer, N. Tabanca, T. Ozek, K. H. C. Baser, G. Tumen, and H. Duman, *J. Essent. Oil Res*., **15**, 221 (2003).
19. K. H. C. Baser, N. Kirimer, T. Ozek, G. Tumen, and F. Karaer, *J. Essent. Oil Res*., **8**, 699 (1996).
20. N. Kirimer, N. Tabanca, B. Demirci, K. H. C. Baser, H. Duman, and Z. Aytac, *Chem. Nat. Comp*., **37**, 234 (2001).
21. N. Kirimer, N. Tabanca, T. Ozek, K. H. C. Baser, and G. Tumen, *Khim. Prirod. Soedin*., 76 (1999).
22. K. H. C. Baser, N. Kirimer, and G. Tumen, *J. Essent. Oil Res*., **9**, 205 (1997).
23. N. Kirimer, N. Tabanca, G. Tumen, H. Duman, and K. H. C. Baser, *Flavour Fragr. J.*, **14**, 421 (1999).
24. N. Kirimer, N. Tabanca, K. H. C. Baser, and G. Tumen, *J. Essent. Oil Res.*, **13**, 132 (2001).
25. T. Ozek, K. H. C. Baser, and G. Tumen, *J. Essent. Oil Res*., **5**, 669 (1993).
26. N. Kirimer, T. Ozek, H. Tanriverdi, F. Koca, A. Kaya, and K. H. C. Baser, *J. Essent. Oil Res*., **4**, 583 (1992).
27. N. Tabanca, N. Kirimer, and K. H. C. Baser, *Turk. J. Chem*., **25**, 201 (2001).
28. N. Kirimer, M. Kurkcuoglu, T. Ozek, and K. H. C. Baser, *Flavour Fragr. J*., **11**, 315 (1996).
29. F. Bohlmann, C. Zdero, E. Hoffmann, P. K. Mahanta, and W. Dorner, *Phytochem.*, **17**, 1917 (1978).