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Analysis of the Essential Oil Composition of *Sideritis albiflora* Using Direct Thermal Desorption and Headspace GC-MS Techniques

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The main constituents of *Sideritis albiflora* were found to be *trans*-caryophyllene, α-pinene, β-pinene, γ-cadinene, pulegone, and caryophyllene oxide by both thermal desorption GC/MS and headspace GC/MS techniques.

Key Words: Thermal desorption, headspace, GC/MS, essential oil, *Sideritis albiflora* Hub.-Mor.

Introduction

In Turkey, there are more than 11,000 wild flowering plant species, one-third of which are aromatic. Herbal tea consumption in Turkey is quite common, especially in rural areas. One of the most commonly used plants for herbal tea is the genus *Sideritis*, which is widespread particularly in Aegean and Mediterranian areas, and represented by 46 species with high endemism ($\cong$80%) in Turkey.[1] *Sideritis* species are used in folk medicine due to their antimicrobial, anti-inflammatory, antirheumatic, antispasmodic, digestive and diuretic activities[2,3]. To date over 15 *Sideritis* species have been investigated for their non-volatile constituents and mainly ent-kaurane diterpenes[4–8] have been isolated while 50 *Sideritis* species have been investigated for their essential oil composition, most of them contain α or β-pinene or both as the main constituents[9–18]. Başer[9,17] and Kırımer[18] classified *Sideritis* essential oils based on their main components, and *S. albiflora* was included in the sesquiterpene-rich ones, however, its whole essential composition was not presented previously; only the major component was given β-caryophyllene[18]. In fact, *Sideritis* species are not rich in essential oil, but their smell and aroma are pleasant. In the present study, thermal desorber GC-MS and headspace GC-MS techniques were used for the analysis of essential oil from *S. albiflora*.

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Experimental

Plant Material and Determination of Essential Oil

The aerial parts of *Sideritis albiflora* Hub.-Mor. were collected from Fethiye-Muğla in July 2004 by Dr. T. Kılıç. The plant was identified by one of the authors, Prof. Dr. G.Tümen, and a voucher specimen was deposited in the Herbarium of the Faculty of Pharmacy, Anadolu University (ESSE 10467).

Analysis of Essential Oil Composition by Thermal Desorption GC/MS

A Perkin-Elmer Turbomatrix ATD was used for thermal desorption analysis. The temperature program was as follows: tube 100 °C, transfer line 150 °C, valve 150 °C, trap low –30 °C (Tenax-TA was used for trapping), and trap high 280 °C. The pneumatic program was inlet split 50 mL/min, outlet split 20 mL/min, and desorb 10 mL/min. The time program was tube desorb 10 min, and trap hold 5 min. For the capillary GC-MS analysis, a Fisons model 8000 series gas chromatograph connected to a Fisons model MD800 mass spectrometer was used. The temperature programs were 60 to 260 °C at a rate of 3 °C/min,and held isothermally for 20 min. High purity helium was used as carrier gas (20 psi) and an HP5-MS capillary column (30 m, 0.25 mm, 0.5 μm) was employed. The ion source and transfer line temperatures were maintained at 200 and 250 °C, respectively. Electron ionization MS in the range 50-400 Da was recorded at 70 eV energy with an ionization current of 200 μA. The scan time was 0.5 ms, and the multiplier potential was 300 V. Dried and powdered *S. albiflora* (35 μg) was put in a sample tube, and the analysis was started using the above conditions.

Analysis of Essential Oil Composition by Headspace GC/MS

A Thermo HS2000 was used for Headspace analysis. The analysis program and conditions were as follows: the vial oven temperatures were 140 °C, and needle temperatures were 25 °C and then 165 °C, respectively. Oven time with the shaker was 20 min, and injection volume was 1 mL.

Identification of Components

The components were identified by comparision of their mass spectra with the Wiley and NIST GC-MS libraries and TÜBİTAK UME library of essential oil constituents and with authentic samples. The authentic samples were obtained from ULTRAkit®WRK-105 Terpenes (ULTRA Scientific, North Kingstown, RI, USA) and 1,8-cineole (98%), linalool oxide (97%) and caryophyllene oxide (99%) purchased from Fluka, and thymol (97%) purchased from Merck. Percentage amounts of separated compounds were calculated automatically from peak areas of total ion chromatograms (TIC). *n*-Alkanes were used as reference points in the calculation of relative retention indices (RRI). The volatile compounds identified in the leaves of *S. albiflora* are seen in Table 1.

Results and Discussion

Over the last decade, for the analysis of essential oils, head-space GC-MS has become a common technique, while analyses by thermal desorber coupled with GC-MS have been exemplified by a limited number of studies[19−21].

Table 1. Chemical composition of essential oil of *Sideritis albiflora* obtained by direct thermal desorber and headspace GC-MS techniques.

RI[a]	RI	Thermal Desorption[b]	Headspace[b]	Identification
$\alpha-$ pinene	937	15.4	16.3	MS, Co-GC
camphene	953	0.2	0.2	MS, Co-GC
$\beta-$ pinene	986	13.5	15.4	MS, Co-GC
myrcene	995	6.4	8.7	MS, Co-GC
$\alpha-$ phellandrene	1003	0.6	t	MS, Co-GC
$\alpha-$ terpinene	1007	t	-	MS, Co-GC
p-cymene	1024	0.5	0.2	MS
limonene	1030	1.0	0.8	MS, Co-GC
1-8-cineol	1032	t	t	MS, Co-GC
(Z)-β-ocimen	1037	0.7	t	MS
(E)- β-ocimen	1048	0.1	t	MS
$\gamma-$ terpinene	1055	0.1	t	MS, Co-GC
cis-sabinol	1082	0.6	0.1	MS
linalool	1100	1.1	0.8	MS, Co-GC
borneol	1168	0.8	2.4	MS, Co-GC
terpinen-4-ol	1177	0.3	t	MS, Co-GC
$\alpha-$ terpineol	1188	2.1	3.8	MS, Co-GC
pulegone	1245	9.7	9.1	MS, Co-GC
thymol	1295	0.9	0.2	MS, Co-GC
copaene	1375	4.4	5.6	MS, Co-GC
$\alpha-$ cubebene	1391	0.7	1.4	MS
unidentified	1391	0.5	0.4	MS
$\beta-$ elemene	1393	0.9	0.3	MS
$\beta-$ bourbonene	1398	1.3	1.8	MS
unidentified	1405	0.2	t	MS
trans-caryophyllene	1420	17.4	14.8	MS, Co-GC
aromadendrene	1460	t	t	MS
$\gamma-$ gurjunene	1472	t	t	MS
germacrene D	1480	0.1	t	MS
selinene	1487	0.4	0.3	MS
$\alpha-$ muurolene	1500	0.6	0.5	MS
$\gamma-$ cadinene	1512	12.1	12.8	MS
$\delta-$ cadinene	1518	0.8	0.5	MS
nerolidol	1569	0.3	t	MS
spathulenol	1579	0.8	0.4	MS
caryophyllene oxide	1590	2.8	2.1	MS, Co-GC
Total 36		**97.3**	**98.9**	

[a]RI =retention indices relative to C_9-C_{24} n-alkanes on the HP5-MS column.

[b]Percentages were calculated from TIC.

t < 0.1

Essential oil analysis of *S. albiflora* by a thermal desorber coupled with a GC-MS spectrometer afforded 36 constituents (Table 1). The main constituents of *S. albiflora* were *trans*-caryophyllene (17.4%), α-pinene (15.4%), β-pinene (13.5%), γ-cadinene (12.1%) pulegone (9.7%), myrcene (6.5%), copaene (4.4%) and caryophyllene oxide (2.8%). The other constituents and percentages are given in Table 1.

Secondly, we analyzed the essential oil of the plant by headspace GC-MS, which yielded results similar to those of thermal desorption (Tables 1 and 2). There were small differences in the percentages of *trans*-caryophyllene (14.8%), α-pinene (16.3%), β-pinene (15.4%), γ-cadinene (12.8%), pulegone (9.1%), myrcene (8.7%), copaene (5.6%) and caryophyllene oxide (2.1%) (Table 1).

Table 2. Essential oil composition of *Sideritis albiflora* classified as mono- and sesqui-terpenes.

	Thermal Desorption	Headspace
Monoterpene Hydrocarbons	$\alpha-$ pinene, camphene, β-pinene, α-phellandrene, p-cymene, limonene, (Z)- β-ocimen, (E)-β-ocimen, γ-terpinene, linalool	$\alpha-$ pinene, camphene, β-pinene, p-cymene, limonene, linalool
Total	**33.2%**	**33.7%**
Oxygenated Monoterpenes	*cis*-sabinol, borneol, terpinen-4-ol, α-terpineol, pulegone, thymol	*cis*-sabinol, borneol, α-terpineol, pulegone, thymol
Total	**14.4%**	**15.6%**
Sesquiterpene Hydrocarbons	Myrcene, copaene, α-cububene, β-elemene, β-bourbonene, *trans*-caryophyllene, germacrene D, selinene, α-muurolene, γ-cadinene, δ-cadinene	Myrcene, copaene, α-cububene, β-elemene, β-bourbonene-trans- caryophyllene, selinene, α-muurolene, γ-cadinene, δ-cadinene
Total	**45.1%**	**46.7%**
Oxygenated Sesquiterpenes	nerolidol, spathulenol, caryophyllene	spathulenol, caryophyllene
Total	**3.9%**	**2.5%**

In conclusion, in both techniques the essential oil was most rich in sesquiterpene hydrocarbons (namely *trans*-caryophyllene and γ-cadinene), followed by monoterpene hydrocarbons. However, by thermal desorption and headspace techniques, total amounts of monoterpenes (hydrocarbons and oxygenated), were 47.7% and 49.3% and total amounts of sesquiterpenes (hydrocarbons and oxygenated) were 49.0% and 49.2%, respectively, which were almost equal (Table 2).

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References

1. A. Huber-Morath, Sideritis in *Flora of Turkey and East Aegean Islands, Vol 7.,*Ed. P.H. Davis. Edinburgh University Press, Edinburgh, 1982; 178.
2. E. Sezik and N. Ezer, **Turk. J. Chem. 7,** 163-167 (1983).
3. E. Yeşilada and N. Ezer, **Int. J. Crude Drug Res. 27,** 38-40 (1989).
4. K.H.C. Başer, M.L. Bondi, M. Bruno, N. Kırımer, F. Piozzi, G. Tümen and N. Vasallo, **Phytochemistry 43,** 1293-1296 (1996).
5. G. Topcu, A.C. Gören, Y.K. Yıldız and G. Tümen, **Nat. Prod. Lett. 14,** 123-129 (1999).
6. G. Topcu, A.C. Gören, T. Kılıç, Y.K. Yıldız and G. Tümen, **Fitoterapia. 72,** 1-4 (2001).

7. G. Topcu, A.C. Gören, T. Kılıç, Y.K. Yıldız and G. Tümen. **Nat. Prod. Lett. 16,** 33- 37 (2002).
8. G. Topcu, A.C. Gören, T. Kılıç, Y.K. Yıldız and G. Tümen, **Turk. J. Chem. 26,** 189-194 (2002).
9. K.H.C. Başer (Editor). *Proceedings of the 13th International Congress of Flavours, Fragrances and Essential Oils; in Flavours, Fragrances and Essential Oils Congress, İstanbul, Turkey, 15-19 October 1995, AREP Publ., İstanbul, Turkey.*
10. N. Ezer, R. Villa, S. Canigueral and T. Adzet, **Phytochemistry 41:** 203-205 (1996).
11. N. Kırımer, N. Tabanca, G. Tümen, H. Duman and K.H.C. Başer, **Flavour Frag J. 14,** 421-425 (1999)
12. N. Kırımer, N. Tabanca, K.H.C. Başer and G. Tümen, **J. Essent. Oil Res. 13**, 132-133 (2001).
13. N. Kırımer, N. Tabanca, B. Demirci, K.H.C. Başer, H. Duman and Z. Aytaç, **Chem. Nat. Compd. 37,** 234-237 (2001).
14. N. Kırımer, N. Tabanca, T. Özek, K.H.C. Başer, G. Tümen and H. Duman, **J. Essent. Oil Res. 15,** 221-225 (2003).
15. N. Tabanca, N. Kırımer and K.H.C. Başer. **Turk. J. Chem. 25,** 201-208 (2001).
16. M. Özcan, J.C. Chalcat and A. Akgül, **Food Chem. 75**, 459-463 (2001).
17. K.H.C. Başer, **Pure and Appl. Chem. 74**, 527-545 (2002).
18. N. Kırımer, K.H.C. Baser, B. Demirel and H. Duman, **Chem. Nat. Compd.** 40, 19-23 (2004)
19. T.G. Hartman, K. Karmas and N.J. Chen, **Acs. Sym. Ser**. **506,** 60-76 (1992).
20. A. Bianchi and H.A. Cook, **J. Chromatography A**. **449,** 175-181 (1998).
21. A.C. Gören, G. Topçu, G. Bilsel, M. Bilsel, J.M. Wilkinson and H.A. Cavanagh, **Nat. Prod. Res. 18,** 189-195 (2004).