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Essential oil of *Stachys aleurites* from Turkey

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Abstract

The essential oil obtained from the aerial parts of the Turkish endemism *Stachys aleurites* (Lamiaceae) has been studied. The main constituents were sesquiterpene hydrocarbons: β-caryophyllene (33.7%), bicyclogermacrene (14.5%) and germacrene D (9.6%). The main monoterpene was α-pinene (8.4%). Some chemotaxonomical considerations have been provided.

Keywords: *Stachys aleurites*; Lamiaceae; Essential oil composition; Turkey; β-Caryophyllene; Bicyclogermacrene; Germacrene D; α-Pinene

1. Introduction

Since the revision of the 72 Turkish species of *Stachys* (Lamiaceae) by Bhattacharjee (1982), nine new species have been described: *Stachys choruhensis* Kit Tan and Sorger, *Stachys antalyensis* Y. Ayasligil and P.H. Davis, *Stachys chasmosericea* Y. Ayasligil and P.H. Davis, *Stachys tundjeliensis* Kit Tan and Sorger (Davis et al., 1988), *Stachys*

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anamurensis Sumbul (1990), *Stachys sivasica* Kit Tan and Yildiz, *Stachys baytopiorum* Kit Tan and Yildiz, *Stachys willemsei* Kit Tan and Hedge (Yildiz and Tan, 1988), and *Stachys cydni* Kotschy ex Gemici and Leblebici (Gemici and Leblebici, 1998).

Stachys aleurites is a 80 cm perennial suffrutescent erect species with purple flowers. It is endemic to Anatolia, where it grows in Antalya province only. This plant may be described as a termophilous species; it prefers calcareous rocks near the coast.

2. Materials and methods

The flowering aerial parts of *S. aleurites* Boiss. and Heldr. were collected in Turkey, C3 Antalya, Konyaalti, Varyant (36° 53′ 068″ N, 30° 40′ 697″ E), on calcareous rocks near the coast, about 10 m above the sea level at the end of May 2003. A voucher specimen is deposited at AKDU (Herbarium of the Biology Department of Akdeniz University) as Gokturk 5100. The plant material, deprived of the woody parts, was dried in the shade and hydrodistilled in a Clevenger-like apparatus for 2 h.

The GC analyses were accomplished with a HP-5890 Series II instrument equipped with HP-WAX and HP-5 capillary columns (both 30 m × 0.25 mm, 0.25 μm film thickness), working with the following temperature program: 60 °C for 10 min, ramp of 5 °C/min up to 220 °C; injector and detector temperatures 250 °C; carrier gas nitrogen (2 ml/min); detector dual FID; split ratio 1:30; injection of 0.5 μl). The identification of the components was performed, for both columns, by comparison of their retention times with those of pure authentic samples and by means of their linear retention indices (l.r.i.) relative to a series of *n*-hydrocarbons.

The relative proportions of the essential oil constituents were percentages obtained by FID peak-area normalization, without using response factors.

GC/EIMS analyses were performed with a Varian CP-3800 gas-chromatograph equipped with a DB-5 capillary column (30 m × 0.25 mm; coating thickness 0.25 μm) and a Varian Saturn 2000 ion trap mass detector. Analytical conditions: injector and transfer line temperatures 220 and 240 °C, respectively; oven temperature programmed from 60 °C to 240 °C at 3 °C/min; carrier gas helium at 1 ml/min; injection of 0.2 μl (10% hexane solution); split ratio 1:30. Identification of the constituents was based on comparison of the retention times with those of authentic samples, comparing their linear retention indices relative to the series of *n*-hydrocarbons, and on computer matching against commercial (NIST 98 and ADAMS) and home-made library mass spectra built up from pure substances and components of known oils and MS literature data (Stenhagen et al., 1974; Massada, 1976; Jennings and Shibamoto, 1980; Swigar and Silverstein, 1981; Davies, 1990; Adams, 1995). Moreover, the molecular weights of all the identified substances were confirmed by GC/CIMS, using MeOH as CI ionizing gas.

3. Results and discussion

The composition of the essential oil of *S. aleurites* is reported in Table 1. In total 51 compounds were identified, amounting to 92.2% of the whole oil.

Table 1
Composition[a] of the essential oil of *Stachys aleurites*

Constituents	LRI[b]	%
(*E*)-2-Hexenal	855	0.3
Heptanal	901	0.1
α-Thujene	933	0.2
α-Pinene	941	8.4
Benzaldehyde	963	tr[c]
Sabinene	978	tr
1-Octen-3-one	980	tr
1-Octen-3-ol	982	1.0
Myrcene	992	0.5
2-Pentylfuran	993	0.8
3-Octanol	995	tr
Octanal	1003	tr
α-Phellandrene	1007	tr
3-Carene	1013	0.2
p-Cymene	1028	tr
Limonene	1032	1.8
(*Z*)-Ocimene	1040	tr
(*E*)-Ocimene	1051	0.5
γ-Terpinene	1064	0.2
Terpinolene	1089	0.2
Linalool	1101	0.8
Nonanal	1104	0.7
(*E*)-2-Nonenal	1165	0.1
Decanal	1206	0.1
β-Cyclocitral	1223	0.1
α-Copaene	1377	0.4
β-Bourbonene	1384	1.0
Sativene	1392	0.2
Isocaryophyllene	1404	0.1
β-Caryophyllene	1420	33.7
β-Gurjunene	1432	0.2
α-Guaiene	1440	1.5
α-Humulene	1455	4.1
(*E*)-β-Farnesene	1460	0.4
Alloaromadendrene	1462	0.3
β-Chamigrene	1475	0.4
Germacrene D	1481	9.6
Bicyclogermacrene	1495	14.5
β-Himachalene	1499	0.1
β-Bisabolene	1509	1.1
cis-γ-cadinene	1511	tr
δ-Cadinene	1524	0.4
β-Sesquiphellandrene	1526	0.1
(*E*)-γ-Bisabolene	1533	1.9
trans-nerolidolo	1564	0.4
Spathulenol	1577	2.1
Caryophyllene oxide	1582	2.5
Cedrol	1598	0.5

(*continued on next page*)

Table 1 (*continued*)

Constituents	LRI[b]	%
T-Cadinol	1642	0.2
T-Muurolol	1643	0.3
n-Tricosane	2300	0.2
Total identified		92.2

[a] Percentages obtained by FID peak-area normalization (HP-5 column).
[b] Linear retention indices (HP-5 column).
[c] tr < 0.1%.

The main constituents of the essential oil were terpene derivatives; only a small percentage (3.6%) was represented by oxygenated straight-chain non-terpenic aldehydes, ketones and alcohols. Furthermore, an aromatic aldehyde (benzaldehyde) and an aliphatic hydrocarbon were present.

Monoterpenes represented 13 of the 51 compounds, corresponding to 12.8% of the whole oil. Linalool was the only monoterpene alcohol present (0.8%). In contrast, sesquiterpenes constituted 76% of the whole oil (25 derivatives) and oxygenated compounds were scarcely represented (6%). The main sesquiterpene hydrocarbons were β-caryophyllene (33.7%), bicyclogermacrene (14.5%), germacrene D (9.6%), followed by the monoterpene hydrocarbon α-pinene (8.4%).

Many other *Stachys* species have been investigated for their essential oil composition. In fact, taking into account the main constituents identified in these species, it is possible to differentiate among four groups of species:

1. Species producing principally monoterpene hydrocarbons such as *Stachys aegyptiaca* (Halim et al., 1991) or sesquiterpene hydrocarbons such as *Stachys officinalis* (Chalchat et al., 2001), *Stachys cretica* ssp. *cretica*, *Stachys menthifolia*, *Stachys germanica* ssp. *heldreichii*, *Stachys euboica*, *Stachys scardica* (Skaltsa et al., 2003) and *Stachys* subsect. Swainsonianeae (Skaltsa et al., 2001) or both the classes such as *Stachys lavandulifolia* (Javidnia et al., 2003; Feizbakhsh et al., 2003) (even if also high oxygenated sesquiterpene percentages have been reported for this species by Ramzani et al. (2002)).
2. Species containing mainly oxygenated monoterpenes (*Stachys iberica* (Kaya et al., 2001), *Stachys acerosa* (Masoudi et al., 2003)) or oxygenated sesquiterpenes (*Stachys candida*, *Stachys chrysantha* (Skaltsa et al., 1999), *Stachys pilifera* (Masoudi et al., 2003)).
3. Species containing similar amounts of mono and sesquiterpene hydrocarbons and oxygenated mono- and sesquiterpenes, such as *S. officinalis*, *Stachys grandiflora*, *S. germanica*, *Stachys sylvatica* (Radnai et al., 2003) *Stachys byzantina* (Khanavi et al., 2003; Radnai et al., 2003), *Stachys balansae* (Cakir et al., 1997), *Stachys alopecuros*, *Stachys spinulosa* (Skaltsa et al., 2003) and *Stachys obliqua* (Harmander et al., 1997).
4. Species producing non-terpenic alcohols and terpene oxides (*Stachys recta* (Cakir et al., 1997; Chalchat et al., 2000)).

S. aleurites, because of its high content of sesquiterpenes (76%), in particular sesquiterpene hydrocarbons (70%), could be inserted in the first proposed group, together with *S. officinalis* and the species of the Swainsonianeae subsection.

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