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THE ESSENTIAL OILS OF SOME EASTERN SPAIN *SIDERITIS**

CARMEN MATEO, JESÚS SANZ and JOSÉ CALDERÓN

Instituto de Química Orgánica General (C.S.I.C.) Juan de la Cierva, 3, Madrid-6, Spain

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Key Word Index—*Sideritis*; Labiatae; essential oil; terpenes.

Abstract—The quantitative composition of the essential oils from 6 different *Sideritis* species collected in the Mediterranean coast of Spain is reported. Sixty-five components have been identified.

INTRODUCTION

The genus *Sideritis* is represented in Spain by more than 30 species. In this work, we wish to report the composition of 12 samples of essential oil from six species of *Sideritis*, collected in the Mediterranean coast of Spain. Table 1 shows the place of collection of these plants. All samples were collected at flowering, and under botanic surveillance.

We have tried to collect samples of the same species in different places, in order to study the differences in composition. However, some *Sideritis* species are rare or sparsely distributed, and it is very difficult to collect them in a sufficient amount to allow the study of their oils. We have collected samples of two species (*S. leucantha* and *S. flavovirens*) at the same place but in different years. We have also analysed two different oils from *S. foetens*: while S7/2 was extracted from the whole plant, S7/1 was obtained by using only the flower heads.

The genus *Sideritis* is difficult to classify because several species have a strong tendency to hybridize. Samples S2/1 and S3/1 were considered by our taxonomist to be true representatives of *S. tragoriganum* and *S. angustifolia*, but the rest of the samples of these species that we were able to collect appeared, from morphological examination, to be hybrids.

*Part 3 in the series "Analytical Study of Essential Oils from Spanish Plants". For Part 2 see ref. [1].

RESULTS AND DISCUSSION

The composition of the essential oils obtained from the plant samples listed in Table 1 is given in Table 2. The component concentrations were calculated from GC peak areas, using an internal standard. Components are arranged in order of GC elution: the missing numbers correspond to compounds characterized by us in other *Sideritis* species. In some cases, the analytical information was insufficient to identify these compounds, but enough to allow their classification. Table 2 includes the concentrations of the components that we were unable to identify only when their values are higher than 1% in at least one of the oils.

Several unidentified components (36, 44, 60, 66, 67, 70, 76, 80, 84, 87 and 96) were also present in *S. hirsuta* [1]. Component 37 is a monoterpene alcohol ($C_{10}H_{18}O$). Components 77 and 99 are sesquiterpene alcohols ($C_{15}H_{26}O$). The molecular formula of component 75 is $C_{15}H_{24}O$. Components 97 and 98 are $C_{15}H_{24}O$ sesquiterpene alcohols. Component 40 is probably *trans*-achillenol [3].

We plan to report soon a study on the correlations existing between the compositions of all the *Sideritis* essential oil samples that we have analysed. From the data in Table 2, it appears that some chemically related compounds seem to be present in one species in higher concentrations than in the rest. This happens with *p*-cymene, thymol and carvacrol for *S. foetens*, caryophyllene and caryophyllene oxide for *S. chamaedryfolia*, and fenchone and fenchyl acetate for *S. flavovirens*.

Table 1. *Sideritis* samples collected in the Mediterranean coast of Spain

Sample	Species	Place of collection
S2/1	*S. tragoriganum* Lag.	Torreblanca (Castellón)
S2/2	*S. tragoriganum* x *S. leucantha* (hybrid)	Villajoyosa (Alicante)
S2/3	*S. tragoriganum* Lag. (atypical)	La Eliana (Valencia)
S3/1	*S. angustifolia* Lag.	Albaida (Valencia)
S3/2	*S. angustifolia* Lag. (hybrid)	Canal de Navarrés (Valencia)
S4/1	*S. leucantha* Cav.	El Altet (Alicante)
S4/2	*S. leucantha* Cav.	" "
S5/1	*S. chamaedryfolia* Cav.	Villena (Alicante)
S6/1	*S. flavovirens* (Rouy) Riv. God. et Gómez	Mazarrón (Murcia)
S6/2	*S. flavovirens* (Rouy) Riv. God. et Gómez	" "
S7/1	*S. foetens* Clem. ex Lag. (flower heads)	Aguilas (Murcia)
S7/2	*S. foetens* Clem. ex Lag.	" "

Table 2. Components of Spanish *Sideritis* essential oils

Components	S2/1	S2/2	S2/3	S3/1	S3/2	S4/1	S4/2	S5/1	S6/1	S6/2	S7/1	S7/2
1 α-Pinene	17.7	50.1	7.8	10.8	20.6	23.6	25.8	0.4	18.7	8.2	11.6	5.5
2 Camphene	0.4	*t*	0.3	*t*	*t*	0.4	0.4	*t*	1.1	0.7	0.1	*t*
3 β-Pinene	0.8	1.8	0.6	0.5	1.6	1.2	1.0	0.3	1.5	0.4	0.9	0.7
4 Sabinene	5.0	10.6	2.3	3.0	4.3	10.4	7.2	0.4	6.3	2.0	13.4	8.6
5 Δ^3-Carene	0.9	*t*	0.1	*t*	0.5	*t*	*t*	*t*	*t*	—	*t*	*t*
6 Myrcene	—	0.7	0.9	0.5	1.3	0.9	0.8	1.7	0.7	0.7	0.3	0.4
7 α-Phellandrene	1.0	0.1	1.1	0.9	0.2	0.1	0.1	*t*	*t*	0.8	1.6	0.6
8 α-Terpinene	—	0.7	0.4	0.1	0.9	0.2	0.8	—	*t*	0.6	0.9	0.2
9 Limonene	1.5	5.4	2.0	1.7	3.4	5.5	4.7	0.8	3.4	12.7	2.2	2.0
10 β-Phellandrene	1.1	0.7	0.3	0.8	0.8	*t*	*t*	0.7	0.1	0.6	1.9	2.4
11 1,8-Cineol	15.9	7.1	6.8	4.6	16.6	5.8	6.5	1.6	13.4	1.4	2.0	2.7
12 Pentylfuran	—	—	0.3	—	—	—	*t*	0.4	0.1	—	*t*	—
13 γ-Terpinene	2.4	1.3	1.9	0.3	1.0	0.4	1.4	0.3	*t*	1.4	1.6	0.3
14 *p*-Cymene	1.5	0.4	0.8	0.8	3.7	2.7	0.4	0.5	6.5	1.1	12.3	19.8
15 Terpinolene	0.5	0.1	0.2	0.1	0.2	0.3	0.4	0.1	*t*	0.7	0.3	—
16 1-Hexanol	—	*t*	0.1	—	0.2	—	0.2	0.2	0.3	—	—	—
17 Hexenol	—	—	—	—	—	—	*t*	—	—	—	—	—
18 Fenchone	6.1	3.5	7.8	1.9	8.0	6.2	10.2	2.6	11.9	25.3	1.7	0.6
19 1-Octen-3-ol	—	—	—	—	0.2	—	0.4	—	—	—	—	—
20 *trans*-Thujanol	—	—	—	—	0.2	—	—	—	—	—	0.2	—
21 Fenchyl acetate	—	1.4	0.5	0.2	2.7	0.8	0.8	0.4	12.0	27.7	0.5	0.4
22 α-Copaene	—	0.2	0.3	0.1	0.4	0.7	0.4	0.5	—	—	0.3	—
23 Camphor	1.2	*t*	0.5	0.1	—	0.7	0.9	—	1.7	—	—	—
24 β-Bourbonene	0.6	1.0	3.5	0.8	2.5	1.4	0.9	1.7	1.2	1.3	—	—
25 Linalol	—	0.2	0.3	0.1	2.1	0.8	0.4	1.3	0.4	—	1.3	2.7
26 *cis*-Thujanol	—	—	0.3	—	—	—	—	—	—	—	—	—
28 1-Octanol	—	—	0.1	—	0.6	—	—	—	—	—	—	—
30 *endo*-Fenchol	—	1.4	0.3	0.2	0.1	0.7	4.0	0.4	1.2	2.2	—	—
31 β-Farnesene	—	—	0.2	—	—	—	—	—	—	—	—	—
32 Bornyl acetate	—	—	—	—	—	—	—	—	—	0.2	—	—
33 4-Terpineol	4.6	1.1	2.6	1.2	2.9	5.4	1.4	0.6	6.3	3.2	4.5	3.6
34 Caryophyllene	14.6	0.3	0.3	3.5	0.2	4.7	1.3	32.5	0.8	1.2	—	—
35 *allo*-Aromadendrene	—	—	—	—	—	0.5	—	0.4	0.7	0.1	—	—
36 See text	—	—	1.7	0.7	1.1	0.6	0.4	0.4	0.7	—	—	—
39 Cryptone	—	—	—	0.9	—	—	—	0.9	—	—	2.5	2.5
40 Achillenole	—	—	0.3	—	—	—	—	—	—	—	—	—
41 3(4)-Caren-3-ol	—	—	0.2	—	—	—	—	—	—	—	0.9	0.7
42 Limonen-4-ol	—	—	0.1	—	—	—	—	—	0.1	—	—	—
43 Piperitone	—	—	—	—	—	—	—	—	—	—	0.1	—
45 α-Terpineol	1.6	—	1.7	0.4	3.1	1.3	0.4	0.9	1.2	0.5	1.3	1.8

46	Isoborneol	—	—	—	—	—	—	—	—	0.1	*t*	—	—
47	α-Terpenyl acetate	—	—	—	—	0.5	—	—	0.8	—	1.7	—	—
49	Germacrene D	—	—	2.1	1.7	0.9	—	0.7	0.5	—	—	1.5	1.5
51	Borneol	—	0.3	0.2	—	—	—	—	—	—	—	—	—
52	α-Muurolene	—	—	0.8	0.4	0.7	—	—	—	0.2	0.2	1.2	1.1
53	γ-Cadinene	—	—	0.9	0.6	0.6	—	0.8	0.4	*t*	0.3	0.2	0.3
54	Carvone	—	—	—	—	—	—	—	—	—	—	0.4	0.3
55	δ-Cadinene	0.9	0.6	9.5	2.1	3.2	3.1	2.3	1.3	1.4	1.7	1.6	2.5
56	α-Curcumene	0.9	0.1	1.5	0.3	0.6	1.3	0.7	1.2	0.7	0.3	*t*	*t*
58	Cuminaldehide	—	—	—	—	—	—	—	—	—	—	1.5	1.0
59	1-Decanol	—	—	0.1	—	—	—	—	—	—	—	—	—
60	See text	—	—	10.4	4.7	6.3	3.1	2.7	—	0.7	—	1.2	0.6
61	*trans*-Carveol	—	—	—	—	—	—	—	—	—	—	*t*	*t*
62	Calamenene	—	—	0.9	—	—	—	—	—	0.1	—	*t*	1.3
63	*p*-Cymen-8-ol	—	—	*t*	—	—	—	—	—	0.1	—	0.1	—
65	Calacorene	—	0.7	—	—	0.1	—	—	—	0.1	—	—	—
66	See text	—	—	1.8	—	—	—	—	—	—	0.2	—	—
67	See text	—	—	—	3.5	1.6	—	—	—	—	—	—	—
69	β-Ionone	—	1.5	—	—	0.2	—	—	—	—	—	—	—
71	Caryophyllene oxide	10.2	0.4	—	4.1	—	3.1	1.9	14.3	1.3	—	0.8	2.4
73	1-Dodecanol	—	0.7	1.1	—	—	0.8	—	—	1.4	—	—	—
74	Dodecanenol	—	1.6	2.1	3.9	—	3.9	0.9	—	1.3	—	0.7	—
75	See text	—	—	—	1.7	—	—	—	1.5	—	—	—	—
76	See text	—	0.2	2.3	—	0.8	—	—	0.4	—	—	—	—
78	Nerolidol	—	—	0.2	—	—	—	—	—	—	—	—	—
79	Cadinenol	—	—	0.2	—	—	—	—	—	—	—	—	—
81	See [1]	—	—	1.2	—	1.3	—	—	—	—	—	10.5	5.1
82	Cuminol	—	—	—	—	—	—	—	—	—	—	0.3	—
83	See [1]	—	0.2	—	—	1.0	2.6	—	1.4	1.3	—	1.1	0.9
86	Eugenol	—	—	—	—	—	—	—	1.2	—	—	—	—
88	T-Cadinol	—	—	0.1	—	—	—	—	—	—	—	—	—
90	Thymol	—	0.2	2.4	0.1	0.8	0.9	0.7	0.6	*t*	—	2.3	20.0
92	Cadinol (I) (see [1])	3.8	0.5	2.5	2.0	1.0	2.2	1.5	—	0.7	—	0.9	—
93	Carvacrol	—	—	—	—	—	—	—	—	*t*	—	5.0	2.5
94	β-Bisabolol	—	0.2	0.2	20.2	2.5	2.0	1.4	—	—	—	—	—
95	Cadinol (II) (see [1])	—	0.2	5.3	0.9	1.0	—	—	—	1.9	—	0.9	—
97	See text	—	—	—	—	—	—	—	7.2	—	—	—	—
98	See text	—	—	—	1.5	—	—	—	—	—	—	—	—
99	See text	—	—	—	—	1.0	—	—	—	—	—	—	—

Component 45 was eluted together with 44, but GC/MS data from the original oils shows than α-terpineol is in all cases the main component of the peak.

EXPERIMENTAL

Dried and ground plant samples were steam distilled. The oil yield was usually about 0.1–0.2%. Oil was first subjected to CC fractionation. When possible, we used prep. GC to isolate pure compounds, that were identified by NMR, IR and MS. The rest of the components were identified or characterized from GC or CC fractions by GC/MS and GC retention. Concentrations were calculated from the original oils by GC. Separation and identification techniques are detailed in ref. [2].

IR spectra were run as liquid films. ^{1}H NMR spectra were measured in $CDCl_3$ at 90 or 100 MHz, with TMS as int. standard. MS were determined at 70 eV. Analytical GC was carried out with a WCOT glass column (48 m × 0.2 mm i.d.) coated with Carbowax 20 M, using N_2 as carrier gas. The column was programmed from 80 to 170° at 3°/min after 8 min at 80°. For GC/MS a SCOT glass column (23 m × 0.3 mm i.d.) coated with Carbowax 20 M on Chromosorb W was used with He as a carrier gas. For prep. GC we used a stainless steel column (3.6 m × 9.5 mm i.d.) coated with Carbowax 20 M on Chromosorb G, using a concn gradient (from 7% at the inlet to 4% at the outlet).

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