

ESSENTIAL OILS OF SOME *SIDERITIS* SPECIES FROM CENTRAL AND SOUTHERN SPAIN

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Key Word Index—*Sideritis* species; Labiatae; essential oils; terpenes

Abstract—The quantitative composition of the essential oils from eight different *Sideritis* species collected in central and southern Spain is reported. Sixty-seven components have been identified.

INTRODUCTION

In this paper, we report the composition of 10 samples of essential oils from eight species of *Sideritis* from central and southern Spain. The place of collection of the plants is given in Table 1. All samples were collected at flowering; *S. pusilla* and *S. leucantha* were collected at two adjacent locations.

RESULTS AND DISCUSSION

Table 2 shows the composition of the essential oils obtained from the plants listed in Table 1. The components are arranged in order of GC elution: the missing numbers correspond to compounds characterized by us in other *Sideritis* species [1, 2]. The component concentrations were calculated from GC peak areas. The Table also includes concentrations of unidentified components when their values are higher than 1% in at least one of the oils.

Some unidentified components (36, 60, 66 and 76) were

also present in other *Sideritis* essential oils [1, 2]. Component 68 ($C_{10}H_{18}O$) is a monoterpene alcohol, and components 72 ($C_{15}H_{26}O$), and 100 ($C_{15}H_{24}O$) are sesquiterpene alcohols.

The data of Table 2 completes our study of essential oils from Spanish *Sideritis* [1, 2]. We have now analysed 34 samples from 15 different species. Most of these plants are sparsely distributed and their oil yield is small (ca. 0.1%). We have been able to collect only one or two samples for most of the species, and as a consequence we were unable to correlate statistically the composition of each oil with the botanic classification of the samples.

However, as in ref. [2], we have calculated, using the ARTHUR package [3], the correlation coefficients between the relative concentration values of the components marked '*' in Table 2 for the 34 oil samples analysed. We have found the highest correlation coefficients in pairs or groups of compounds chemically related, e.g. caryophyllene and caryophyllene oxide, thymol, *p*-cymene and carvacrol, α - and β -phellandrene, α - and β -pinene and fenchone and fenchyl acetate.

Table 1. *Sideritis* samples studied in this work

Sample code		Location
S8	<i>S. spinulosa</i> Barn. ex Asso.	Teruel
S9	<i>S. linearifolia</i> Lamk.	Arcos de Jalón (Soria)
S10	<i>S. mugronensis</i> Borja.	El Mugrón (Albacete)
S11	<i>S. serrata</i> Lag.	Tobarra (Albacete)
S12/1	<i>S. leucantha</i> Cav. subsp. <i>bourgeana</i> Boiss. Reut.	Tobarra-Hellín (Albacete)
S12/2	<i>S. leucantha</i> Cav. subsp. <i>bourgeana</i> Boiss. Reut.	Tobarra (Albacete)
S13/1	<i>S. pusilla</i> (Lge) Pau.	Níjar (Almería)
S13/2	<i>S. pusilla</i> (Lge) Pau.	Adra (Almería)
S14	<i>S. arborescens</i> Salzm.	Carratraca (Almería)
S15	<i>S. ilicifolia</i> Willd.	Bujaraloz (Zaragoza)

Table 2. Components of Spanish *Sideritis* essential oils

Components	S8	S9	S10	S11	S12.1	S12.2	S13.1	S13.2	S14	S15
1 α -Pinene*	19.8	17.6	10.7	14.9	33.1	43.1	32.7	34.2	0.1	1.2
2 Camphene*	0.2	t	0.1	0.1	0.7	t	0.5	0.2		t
3 β -Pinene*	2.0	0.1	0.4	1.8	2.2	4.0	2.2	0.3	t	t
4 Sabinene*	5.8	20.8	3.1	20.6	10.9	8.7	8.8	12.3	0.2	0.3
5 Δ^3 -Carene*	1.3		t	0.1	t		0.2	0.2		
6 Myrcene*	7.0	0.8	0.2	0.5	1.5	2.4	1.9	2.1	0.9	0.3
7 α -Phellandrene*	2.6	2.3	1.3	0.1	0.4	0.8	0.1	t	0.4	t
8 α -Terpinene*	0.8	0.8	0.5	0.4	0.5		1.1	0.9		0.3
9 Limonene*	2.9	0.9	1.3	4.7	2.6	3.4	4.9	5.3	0.9	0.8
10 β -Phellandrene*	1.0		1.2	0.2	0.4	0.9	t	t	0.8	t
11 1,8-Cineol*	12.8	14.0	13.2	8.6	10.1	5.1	10.1	11.7	4.5	1.0
12 Pentylfuran	0.6				t					0.2
13 γ -Terpinene*	2.4	5.1	0.8	0.4	1.1	1.5	1.8	1.5	1.9	1.1
14 p-Cymene*	2.3	4.8	0.7	0.2	1.1	1.9	1.6	2.0	5.2	1.2
15 Terpinolene	0.6	0.7	0.2	0.1	0.2	0.1	0.4	0.5	0.3	0.2
16 1-Hexanol	2.0	0.5			0.2		0.1	t		1.0
17 Hexenol	1.0				t					
18 Fenchone*	0.9	2.3			2.4	2.6	12.4	12.2	3.0	1.1
19 1-Octen-3-ol		0.5		0.8					3.2	
20 <i>trans</i> -Thujanol		0.6				0.2				
21 Fenchyl acetate*	0.4	0.1			2.9	5.1	1.8	1.7	0.8	5.8
22 α -Copaene*		1.8	1.6	0.2	1.0	0.6				2.4
23 Camphor*	1.8	0.9			0.7	0.3	0.2			0.8
24 β -Bourbonene*	0.9	1.7	2.4	0.8	0.3	0.9	1.0	0.8		1.5
25 Linalool*	3.1	2.4	0.9	1.0	0.7	0.3	t			21.9
26 <i>cis</i> -Thujanol		1.6			t	0.3		0.1		
27 Pinocarvone								0.1	1.0	
28 1-Octanol			0.5		0.2				1.3	
30 <i>endo</i> -Fenchol*			0.5	0.5	2.0	4.5	2.2	2.5		0.7
33 4-Terpineol*	2.9		3.4	2.9	1.6	2.1	2.0	3.0	8.4	2.7
34 Caryophyllene*	1.3	6.5	3.2	3.9	3.3	3.9	1.7	0.6	19.7	2.7
35 <i>allo</i> -Aromadendrene	0.7		1.2	0.2				0.3		
36 See text	0.5		1.6	0.3		0.1	0.2	0.1		
38 <i>trans</i> -Pinocarveol								t		
40 Achillenole									2.1	0.4
41 3(4)-Caren-3-ol	0.1					0.4			2.2	
42 Limonen-4-ol								0.1		
43 Piperitone					0.1					
45 α -Terpineol*	2.6	2.7	2.1	1.8	0.7	0.8		0.8	3.9	3.5
46 Isoborneol							0.4	t		
47 α -Terpenyl acetate*	1.2	0.7	3.3	1.6		0.2		0.1	0.7	0.3
48 Phellandren-8-ol									3.0	
49 Germaerene D*	1.6		2.0	2.3		0.1	0.5	0.2		
50 Nerol										1.5
51 Borneol					0.1	0.1				
52 α -Muurolene*		0.3	0.9	0.4		0.1				
53 γ -Cadinene*	0.4	0.3	1.7	0.4		0.1	0.6	0.2		
54 Carvone					t					
55 δ -Cadinene*	1.8	2.5	7.2	3.3	1.3	1.1	2.2	0.9		
56 α -Curcumene*	1.4	0.7	1.7		0.7	0.6	0.4	0.1		
57 Geraniol										1.5
60 See text			9.3				0.1			
62 Calamenene	0.1	t	t		0.2		0.1	0.2		0.1
63 p-Cymen-8-ol					t		0.1	0.1	0.2	
64 <i>t</i> -2- <i>p</i> -Menthen-4-ol									2.2	
65 Calacorene	t		t		0.1		0.1	0.1		1.3
66 See text		0.8	1.4							
68 See text									3.0	
69 β -Ionone			t							
71 Caryophyllene oxide*	3.1	0.6	1.5	6.1	3.6		2.4	0.2	19.6	
72 See text										5.0
73 1-Dodecanol					1.7					

Table 2. *Continued*

Components	S8	S9	S10	S11	S12/1	S12/2	S13/1	S13/2	S14	S15
74 Dodecadenol	—	—	—	—	2.5	—	—	—	—	—
76 See text	—	—	1.1	5.1	—	—	—	—	—	—
78 Nerolidol	—	—	—	—	—	—	—	—	0.3	7.0
79 Cadinenol	—	—	0.1	—	0.1	t	—	—	—	—
83 Spathulenol	0.7	—	2.6	—	0.6	0.3	1.0	0.3	—	—
86 Eugenol*	—	—	0.2	—	—	—	—	—	—	0.2
89 α -Betulenol	—	—	—	—	—	—	—	—	2.1	—
90 Thymol*	0.2	—	0.6	0.5	0.4	—	0.1	t	1.8	1.0
92 Cadinol (I) (see 2)*	0.1	—	4.5	2.4	1.0	0.8	—	0.1	—	23.6
93 Carvacrol*	—	—	—	—	0.1	—	0.1	0.1	—	—
95 Cadinol (II) (see 2)*	—	—	3.7	4.5	—	—	—	—	—	—
100 See text	—	—	—	—	—	—	—	—	1.6	—

t, Trace.

EXPERIMENTAL

Dried and ground samples were steam distd. The oil yield was usually *ca* 0.1–0.2% of the dry wt. Oil was first subjected to CC fractionation. When possible, we used prep. GC for isolation of pure compounds, which were then 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. Concns were calculated by GC of the original oils. Sepn and identification techniques are detailed in ref. [4].

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

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REFERENCES

1. Mateo, C., Sanz, J. and Calderón, J. (1984) *Phytochemistry* **23**, 319.
2. Mateo, C., Sanz, J. and Calderón, J. (1983) *Phytochemistry* **22**, 171.
3. Duewer, D. L., Koskinen, J. R. and Kowalski, B. R. ARTHUR, available from B. R. Kowalski, Laboratory for Chemometrics, Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195.
4. Mateo, C., Morera, M. P., Sanz, J., Calderón, J. and Hernández, A. (1979) *Riv. Ital. Essence, Profumi, Piante Off. Aromi Saponi Cosmet.* **60**, 621.