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ESSENTIAL OIL OF *SIDERITIS HIRSUTA**

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Key Word Index—*Sideritis hirsuta*, Labiatae, essential oil, terpenes

Abstract—Fifty-six components have been identified in the essential oils from 12 samples of *Sideritis hirsuta* The correlations among their concentrations in the oils are also discussed

INTRODUCTION

Sideritis hirsuta L is an odorous plant belonging to the Labiatae, widely distributed in the Iberian Peninsula However, its essential oil has not yet been investigated As a part of our study on the essential oils of Spanish plants [1, 2] we wish to report the composition of the essential oils from 12 samples of *S hirsuta*, collected in different parts of Spain

RESULTS AND DISCUSSION

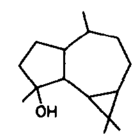
All samples of *S hirsuta* were collected at flowering, and under botanic surveillance The area of collection was spread over the central and western regions of Spain

The methods of distillation of the oils are detailed elsewhere [1, 2] Identification of the oil components, isolated as reasonably pure compounds, was carried out by NMR, IR, GC and GC/MS, when isolation was not possible we used GC R_t and GC/MS Mass spectra and R_ts were compared with data from standards or from the literature

The concentrations of the oil components were calculated from GC peak areas, using an internal standard Table 1 shows these concentrations, components are arranged in order of GC elution The missing numbers correspond to compounds characterized by us in other *Sideritis* species The analytical information was in some cases insufficient to identify the compounds, but enough to allow their classification, and even their tentative identification

Components 36 and 44 are sesquiterpene hydrocarbons ($C_{15}H_{24}$) The molecular formula of components 60, 67, 70, 84, 87 and 96 is $C_{15}H_{24}O$ Component 60 is an ether, and 84, 87 and 96 are alcohols Components 66, 76, 80 and 94 are $C_{15}H_{26}O$ alcohols These components are not shown in Table 1 because their concentration is always quite low

Component 81 is also present, in higher concentration, in the oil of *S foetens*, and was isolated from this oil by prep GC It was tentatively identified as decahydro-1, 1,4,7-tetramethyl 1H-cycloprop(e)azulen-7-ol (**1**) MS 70 eV m/z (rel int) 222 $[M]^+$ (1 4), 204 (26), 109 (85), 81 (74),



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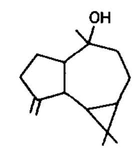

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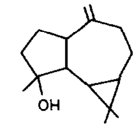

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69 (96), 43 (100) and 41 (100) ^{1}H NMR ($CDCl_3$, 100 MHz, TMS as internal standard) δ 0 06–0 60 (2H, *m*), 0 95 (3H, *d*, $J = 6$ Hz), 1 00 (3H, *s*), 1 03 (3H, *s*) and 1 15 (3H, *s*)

Component 83 was also isolated by prep GC On the basis of its IR ν_{max}^{film} cm^{-1} 3380 (OH) and 1635 (C = C), MS 70 eV, m/z (rel int) 220 $[M]^+$ (6 5), 205 (42), 202 (26), 119 (55), 93 (55), 91 (61), 43 (100) and 41 (74), and ^{1}H NMR ($CDCl_3$, 90 MHz, TMS as internal standard) δ 0 44 (2H, *m*), 1 03 (3H, *s*), 1 04 (3H, *s*), 1 26 (3H, *s*) and 4 66 (2H, *br s*), it was tentatively identified as decahydro-1,1,4-trimethyl-7-methylene 1H-cycloprop(e)azulen-4-ol (**2**), although structure **3** is also possible

The mass spectra of components 92 and 95 are similar to the spectrum given in ref [4] for α-cadinol Their ^{1}H NMR data also confirm a cadinol structure, but they are insufficient to distinguish between the possible isomers

The concentrations in Table 1 are highly correlated, seven components being representative of 99 % and four components of 94 % of the total variance in the data [3] As all the samples belong to the same species, this result was expected

The date of collection seems to be an important factor in the composition of these oils Two oils from samples collected at the same location at different dates in the same year (S1/7 and S1/12) have a quite different composition, although the plant was in both cases at the flowering stage Place of collection seems to be less important Samples S1/1 and S1/3, collected in neighbouring places, are similar in composition, but sample S1/9, collected between these two locations, has a different composition

As *S hirsuta* often crosses with *S arborescens*, we have also tried to relate our results with the degree of hybridization, but without success We have attempted to group the components according to their relative concentration in the oils, supposing that components having high

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

Table 1 Components of Spanish *S hirsuta* essential oils

	Components	S1/1	S1/2	S1/3	S1/4	S1/5	S1/6	S1/7	S1/8	S1/9	S1/10	S1/11	S1/12
1	α-Pinene*	18 6	42 4	14 5	42 9	31 7	7 5	30 8	43 3	49 0	28 7	29 5	35 6
2	Camphene*	0 2	0 3	0 4	0 3	0 2	0 3	—	—	t	t	—	—
3	β-Pinene*	1 8	2 2	1 9	2 1	2 0	0 8	4 6	4 2	4 0	1 8	3 5	2 1
4	Sabinene*	0 2	4 6	3 5	4 7	4 4	1 3	7 8	8 5	6 3	4 1	5 2	5 8
5	Δ^3-Carene*	0 1	t	1 6	0 4	t	t	—	0 2	2 0	t	t	—
6	Myrcene*	0 2	0 3	1 0	0 3	0 6	0 9	0 7	1 2	—	0 4	0 3	0 4
7	α-Phellandrene*	0 3	5 5	3 5	1 0	6 3	1 1	5 6	4 4	4 0	11 2	1 5	0 5
8	α-Terpinene*	0 7	0 2	0 4	0 4	0 2	0 8	0 3	0 8	0 4	0 3	—	0 5
9	Limonene*	2 5	2 5	4 6	2 3	3 2	0 7	5 4	3 3	4 0	3 7	3 1	2 3
10	β-Phellandrene*	—	0 8	6 2	2 3	—	0 7	10 9	6 0	5 8	25 6	3 6	1 5
11	1,8-Cineol*	8 9	7 1	6 1	5 4	20 6	3 5	5 0	5 6	4 0	1 0	3 7	5 3
12	Pentylfuran	—	0 4	—	—	—	0 2	—	—	—	—	—	—
13	γ-Terpinene*	2 4	0 5	1 4	0 7	0 5	0 4	1 0	2 3	1 0	0 5	1 4	1 0
14	*p*-Cymene*	6 0	0 9	3 4	2 1	2 4	0 6	1 1	2 7	1 5	1 0	4 1	2 1
15	Terpinolene	0 6	0 1	0 1	t	0 1	t	0 3	0 2	0 3	0 1	0 3	—
16	1-Hexanol	—	0 1	0 1	—	—	0 2	—	—	—	—	0 3	—
17	Hexenol	—	—	—	—	—	0 1	—	—	—	—	—	—
18	Fenchone*	0 2	0 1	2 8	0 1	1 5	2 4	1 5	0 2	0 3	t	1 3	1 3
19	1-Octen-3-ol	—	t	t	—	—	1 4	—	—	0 3	0 2	—	—
20	*trans*-Thujanol	—	t	t	—	—	—	—	—	—	—	—	—
21	Fenchyl acetate*	—	0 3	6 5	0 1	—	—	1 1	0 3	0 5	0 3	4 3	3 4
22	α-Copaene*	2 6	1 1	1 5	1 1	1 1	1 4	1 0	0 7	1 2	0 4	1 5	1 5
23	Camphor*	0 5	0 5	1 4	t	0 3	t	0 2	—	0 5	—	—	—
24	β-Bourbonene*	6 4	1 4	4 5	3 1	2 2	1 6	2 1	0 8	1 8	0 9	3 2	3 1
25	Linalool*	0 5	0 4	0 9	0 5	0 7	—	—	—	—	—	—	—
26	*cis*-Thujanol	—	—	—	0 4	—	—	—	—	—	—	—	—
27	Pinocarvone	—	—	—	—	—	—	—	—	0 1	—	—	—
28	1-Octanol	—	—	0 7	—	—	0 9	—	—	0 5	—	—	—
29	*iso*-Octanol	—	—	—	—	—	0 3	—	—	—	—	—	—
30	*endo*-Fenchol*	0 7	0 4	1 6	1 3	—	—	0 5	0 1	0 4	0 2	1 4	0 5
32	Bornyl acetate	—	0 1	0 8	—	—	—	—	—	—	—	—	—
33	4-Terpineol*	6 4	1 4	3 5	2 0	1 6	0 7	2 0	1 5	1 1	0 9	6 2	0 6
34	Caryophyllene*	0 4	0 4	0 8	0 4	0 6	3 2	0 4	0 3	0 4	0 3	0 4	1 5
35	*allo*-Aromadendrene	0 5	0 2	0 3	0 5	—	0 5	—	—	—	—	—	—
41	3(4)-Caren-3-ol	—	—	—	—	0 6	0 1	—	—	—	—	—	—
45	α-Terpineol*	1 3	0 4	1 3	1 2	0 5	1 2	0 4	—	0 3	0 2	—	—
47	Terpinyl acetate*	1 0	0 3	0 8	0 5	—	2 4	0 4	—	0 4	—	—	—
49	Germacrene D*	—	3 0	8 7	2 9	9 3	7 6	4 5	2 6	4 6	3 5	4 4	1 7
51	Borneol	0 7	0 1	—	—	—	—	—	—	—	—	—	—
52	α-Muurolene*	0 9	0 2	0 8	0 3	0 5	0 5	0 2	0 2	0 6	0 1	—	0 2
53	α-Cadinene*	—	0 9	1 2	0 3	0 7	1 7	0 9	0 2	1 0	0 3	—	0 3
55	δ-Cadinene*	7 2	4 7	6 2	3 7	3 4	7 9	3 8	3 3	5 0	1 0	2 7	3 2
56	α-Curcumene*	1 3	—	1 8	0 9	—	2 1	—	—	—	—	—	—
62	Calamenene	0 8	—	0 1	—	—	0 7	—	—	—	—	—	—
65	Calacorene	0 2	—	0 1	—	—	1 8	—	—	—	—	—	—
69	β-Ionone	—	—	—	—	—	1 7	—	—	—	0 1	—	1 6
71	Caryophyllene oxide*	1 0	0 3	0 6	—	—	5 3	—	—	—	—	—	2 1
73	Dodecanenol	—	0 3	—	—	—	—	—	—	—	—	—	—
81	See text	1 5	0 4	0 6	0 7	—	—	—	—	—	—	—	—
83	See text	1 4	0 6	0 6	1 1	—	3 5	—	—	—	0 2	—	—
86	Eugenol*	0 6	0 3	1 6	0 4	—	—	—	—	—	—	—	—
90	Thymol*	2 6	1 2	0 5	1 3	—	—	—	—	—	—	—	—
91	6,10,14-Trimethylpentadecanone	—	—	—	—	—	3 5	—	—	—	—	—	—
92	Cadinol (I) (see text)*	1 4	0 5	0 8	0 5	—	3 2	—	—	—	—	—	1 6
93	Carvacrol*	0 6	0 2	0 4	1 6	—	—	—	—	—	—	—	—
95	Cadinol (II) (see text)*	0 7	—	1 4	1 5	—	3 0	—	—	—	1 4	—	2 4

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 positive correlation coefficients could be related in a metabolic pathway The 35 components chosen as the most important in the composition of the oils are marked '*' in Table 1

Table 2 lists the highest positive correlation coefficients found for these 35 components In Table 3 we have grouped several components according to the following rules In each group, all pairs of components have a positive correlation coefficient, and at least one pair has a correlation coefficient higher than 0 7 It is worth noting that, for pairs having one component from groups 4 or 5, and other component from groups 1, 6 or 7, the correlation coefficient is always negative As we can see from these tables, in many cases the compounds grouped present chemical similarities

Table 2 Highest positive correlation coefficients for the most important components of *S hirsuta* essential oils

Components	*r*
Caryophyllene–Caryophyllene oxide	0 978
Caryophyllene oxide–Cadinol (I)	0 961
Caryophyllene–Cadinol (I)	0 904
allo-Aromadendrene-α-Curcumene	0 892
α-Copaene-β-Bourbonene	0 891
Camphor–Eugenol	0 888
p-Cymene–4-Terpineol	0 884

Table 3 Correlation groups amongst components of *S hirsuta* essential oils

Group 1
- Camphene
- α-Terpineol
- Terpenyl acetate
- α-Muurolene
- δ-Cadinene
- α-Curcumene
- Caryophyllene
- Caryophyllene oxide
- Cadinol (I)
- Cadinol (II)

Group 2
- γ-Terpinene
- *p*-Cymene
- α-Copaene
- β-Bourbonene
- 4-Terpineol

Group 3
- Fenchyl acetate
- *endo*-Fenchol

Group 4
- α-Pinene
- β-Pinene
- Sabinene

Group 5
- α-Phellandrene
- β-Phellandrene

Group 6
- Fenchone
- Germacrene D

Group 7
- Eugenol
- Camphor

EXPERIMENTAL

IR spectra were run as liquid films ^1H 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 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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