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VOLATILE CONSTITUENTS OF SPANISH ORIGANUM (*CORIDOTHYMUS CAPITATUS*) ESSENTIAL OIL

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Abstract—Analysis of the neutral fraction of *Coridothymus capitatus* essential oil (Spanish origanum oil) revealed 61 components. Of the new components reported there were 25 monoterpenes, 9 sesquiterpenes, 5 aliphatic, 1 phenol and 1 phenyl ether.

INTRODUCTION

Spanish origanum oil is distilled from the flowering herb *Coridothymus capitatus* Rchb. (syn. *Thymus capitatus* Hoffmag. et Link) [1]. It is the most important and expensive of all commercial origanum oils. However, its chemical composition is not well known and only 10 compounds have been identified [1–4], carvacrol (2-methyl-5-isopropylphenol) being the main component (>60% of oil).

In the present paper we report the composition of the neutral fraction of Spanish origanum essential oil and record the presence of a substantial number of additional components.

RESULTS AND DISCUSSION

Fractionation of the oil was carried out by aqueous NaOH extraction, column chromatography, vacuum distillation and preparative GLC to yield five major fractions: phenols, mono- and sesquiterpene hydrocarbons, and light and heavy oxygenated compounds (see Experimental). Each of these fractions was analysed by GC–MS. The neutral components identified are listed in Table 1, where they are arranged in order of elution.

Monoterpene hydrocarbons

The components of this fraction were separated on column A at 120°. Of the 13 components identified, seven are reported for the first time in this essential oil. *p*-Cymene was the most abundant, followed by γ-terpinene.

Light oxygenated compounds

This fraction was subfractionated by column chromatography and the subfractions were analysed by GC–MS using column A at 150°. Sixteen of the 21 components identified are reported for the first time in this essential oil. Linalool was the main component, followed by 1-terpinen-4-ol.

Peak 4b was tentatively identified as *p*-menth-3-en-9-al (**1**) on the basis of its MS, *m/e* (rel. int.): $M^{+\cdot}$ 152(2), 123(100), 109(4), 95(19), 81(83), 67(25), 57(21) and 43(44), which was very similar to the MS of *p*-menth-3-en-9-ol [5].

Peak 11b was tentatively identified as isogeranial (**2**). Its MS showed important peaks at *m/e* (rel. int.): M^{+} 152(3), 137(10), 123(100), 109(26), 95(40), 81(80), 67(66), 55(39) and 41(55), in accordance with the expected peaks for this structure.

Peak 14b was tentatively identified as *cis*-3-hexenyl pentanoate (**3**). Its MS (*m/e* (rel. int.): 103(3), 85(53), 82(96), 67(100), 57(64) and 41(52)) showed the characteristic fragmentation pattern of aliphatic *cis*-3-hexenyl esters and may be well correlated with the MS of the propionate and butyrate esters of *cis*-3-hexen-1-ol [6].

Peak 20b gave a MS similar to that of α-terpineol but the relative intensity of the ion at *m/e* 121 was 9% in the sample and 45% in α-terpineol. On the basis of its MS (*m/e* (rel. int): 136(25), 121(9), 107(7), 93(59), 81(47), 67(24), 59(100), 55(16) and 43(32)) peak 20b was tentatively indentified as δ-terpineol (**4**).

Sesquiterpene hydrocarbons

This fraction was subfractionated by column chromatography and the subfractions analysed by GC–MS using column B at 150°. All the components were identified for the first time in Spanish origanum essential oil and β-caryophyllene was the most abundant component (80%).

Heavy oxygenated compounds

This fraction was subfractionated by column chromatography and the subfractions analysed by GC–MS using column C at 160°. Components 3d, 9d, 11d and 13d were isolated pure by preparative GLC. All the components of this fraction were identified for the first time in this essential oil.

Peak 7d was tentatively identified as *cis*-3-hexenyl-*trans*-4-hexenoate (**5**). Its MS showed, as did that of peak 14b, the characteristic fragmentation pattern of aliphatic *cis*-3-hexenyl esters: *m/e* (rel. int.): 114(3.5),

Table 1. Components of Spanish origanum essential oil

Peak	Components	Approximate concentration*	Evidence	Reference
	Monoterpene hydrocarbons			
1a	α-Thujene	L	R_t, MS[5]	N.C.
2a	α-Pinene	M	R_t, MS	[1]
3a	Camphene	T	R_t, MS	[3]
4a	β-Pinene	T	R_t, MS	N.C.
5a	Myrcene	M	R_t, MS	N.C.
6a	Δ^3-Carene	T	R_t, MS[7]	N.C.
7a	α-Phellandrene	T	R_t, MS	N.C.
8a	α-Terpinene	M	R_t, MS	[3]
9a	Limonene	T	R_t, MS	[1]
10a	β-Phellandrene	T	R_t, MS[5]	N.C.
11a	*p*-Cymene	H	R_t, MS	[1]
12a	γ-Terpinene	H	R_t, MS	[3]
13a	Terpinolene	T	R_t, MS	N.C.
	Light oxygenated compounds			
1b	1,8-Cineol	L	R_t, MS	[3]
2b	3-Octanol	T	R_t, MS	N.C.
3b	1-Octen-3-ol	L	R_t, MS	N.C.
4b	*p*-Menth-3-en-9-al†	T	MS	N.C.
5b	Octenyl acetate	T	MS[6]	N.C.
6b	Fenchone	T	R_t, MS	N.C.
7b	Sabinene hydrate	L	R_t, MS	N.C.
9b	Thujone	T	R_t, MS	N.C.
10b	Linalool	H	R_t, MS	[3]
11b	Isogeranial†	T	MS	N.C.
12b	Camphor	T	R_t, MS	N.C.
14b	*cis*-3-Hexenyl pentanoate†	T	MS	N.C.
15b	1-Terpinen-4-ol	M	R_t, MS	N.C.
16b	*cis*-Dihydrocarvone	T	R_t, MS	N.C.
17b	*trans*-Dihydrocarvone	T	R_t, MS	N.C.
18b	o-Terpineol†	T	MS	N.C.
20b	α-Terpineol	L	R_t, MS	[3]
21b	Bornyl acetate	T	R_t, MS	[1]
22b	Borneol	L	R_t, MS	[3]
23b	2-Undecanone	T	MS[8]	N.C.
25b	1-Terpinen-4-yl acetate	T	R_t, MS	N.C.
	Sesquiterpene hydrocarbons			
1c	Isocaryophyllene	T	R_t, MS[9]	N.C.
2c	β-Caryophyllene	H	R_t, MS	N.C.
3c	*trans*-α-Bergamotene	T	R_t, MS[10]	N.C.
4c	Aromadendrene	T	MS[9]	N.C.
6c	α-Humulene	T	R_t, MS[11]	N.C.
7c	Allo-aromadendrene	T	R_t, MS[5]	N.C.
8c	γ-Muurolene	T	R_t, MS[5]	N.C.
10c	β-Bisabolene	T	R_t, MS[5]	N.C.
	Heavy oxygenated compounds			
1d	Neral	T	R_t, MS	N.C.
2d	Carvone	T	R_t, MS	N.C.
3d	Carvenone	T	MS[5], IR, ^{1}H NMR	N.C.
4d	Geranial	T	R_t, MS	N.C.
5d	β-Terpinyl acetate	T	R_t, MS	N.C.
7d	*cis*-3-Hexenyl *trans*-4-Hexenoate†	T	MS	N.C.
8d	Carvacryl acetate	T	R_t, MS	N.C.
9d	3-Methyl-2,6-diisopropyl phenol†	T	UV, IR, ^{1}H NMR, MS	N.C.
11d	Caryophyllene oxide	L	R_t, IR, ^{1}H NMR, MS	N.C.

Table 1.—*Continued*

Peak	Components	Approximate concentration*	Evidence	Reference
13d	1-Methyl-4-isopropyl-4-(2-methyl-5-isopropylphenoxy)cyclohexene†	L	UV, IR, ^{1}H NMR, MS	N.C.

* H = high (10–20%), M = medium (5–10%), L = low (1–5%), T = trace (<1%), referred to neutral fraction; carvacrol represents more than 60% of the oil.

† Tentatively identified.

N.C. = New component.

97(11.5), 82(100), 69(62.5), 67(92.5), 55(65) and 41(87). R— was clearly C_5H_9— but there is some doubt about the exact site of the double bond in the acid moiety, although C-4, C-5 is the most likely on the basis of the MS.

Peak 9d was tentatively identified as 3-methyl-2,6-diisopropylphenol (**6**) on the basis of its UV, IR, ^{1}H NMR and MS. Although this compound is a phenol, it is included here because it could not be extracted with 20% cool aqueous solution. It has been obtained for the first time from a natural source. MS (probe, 70 eV) *m/e* (rel. int.): M^+ 192(24), 177(100), 131(14), 105(7) and 91(7). ^{1}H NMR (CCl_4, 90 MHz, TMS as internal standard): δ 1.23 (6H, *d*, $J = 7$ Hz), 1.35 (6H, *d*, $J = 7$ Hz), 2.25 (3H, *s*), 3.00 (1H, *sept*, $J = 7$ Hz), 3.30 (1H, *sept*, $J = 7$ Hz), 4.52 (1H, *s*), 6.57 (1H, *d*, $J = 8$ Hz) and 6.79 (1H, *d*, $J = 8$ Hz).

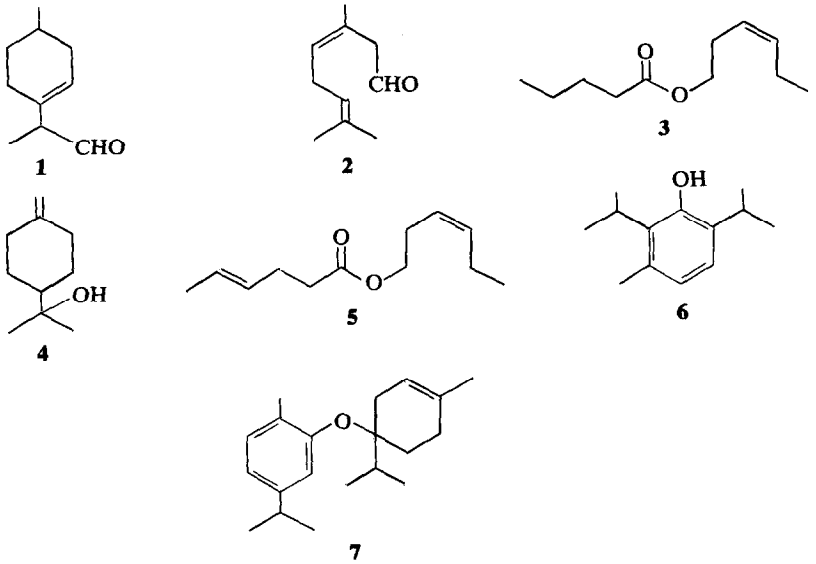
Peak 13d was tentatively identified as 1-methyl-4-isopropyl-4-(2-methyl-5-isopropylphenoxy)cyclohexene (**7**) from its UV, IR, ^{1}H NMR and MS. This product is a new natural compound. MS (probe, 70 eV) *m/e* (rel. int.); 150(32), 136(40), 135(100), 121(48), 107(9.5), 93(80), 91(44), 77(28), 65(9.5), 51(11) and 41(23). ^{1}H NMR (CCl_4, 90 MHz, TMS as internal standard): δ 1.02 (3H, *d*, $J = 7$ Hz), 1.05 (3H, *d*, $J = 7$ Hz), 1.19 (6H, *d*, $J = 7$ Hz), 1.62 (3H, *s br*), 2.09 (3H, *s*), 2.68 (1H, *sept*, $J = 7$ Hz), 5.20 (1H, *m*), 6.60 (1H, *dd*, $J_1 = 8$, $J_2 = 2$ Hz), 6.70 (1H, *d*, $J = 2$ Hz) and 6.90 (1H, *d*, $J = 8$ Hz).

EXPERIMENTAL

IR spectra were run as liquid films. UV spectra were measured in 96% EtOH. ^{1}H NMR spectra were measured in CCl_4 at 90 MHz with TMS as internal standard. MS were determined at 70 eV. Analytical GLC was carried out with three columns: (A) stainless steel capillary column (90 m × 0.5 mm i.d.) coated with UCON-LB-550-X, (B) stainless steel capillary column (100 m × 0.5 mm i.d.) coated with Silicone SF 96(50), (C) Pyrex glass capillary (PLOT) column (14 m × 0.6 mm i.d.) coated with Silicone OV-17 on Chromosorb R-6470-1. For preparative analyses two columns were used: (D) Pyrex glass column (1.5 m × 9 mm i.d.) packed with 3% Silicone OV-17 on 60–80 mesh Chromosorb A, and (E) stainless steel column (3.5 m × 3 mm i.d.) packed with 3% Silicone SE-52 on 80–100 mesh Gas Chrom Q.

An authentic sample of *Coridothymus capitatus* essential oil was purchased from Destilerias Adrian & Klein S.A. (Benicarló, Castellón, Spain).

Fractionation of oil. Acids and most of the phenols were removed by extraction with aq. NaOH soln: samples of oil (50 ml) were dissolved in Et_2O (400 ml) and shaken with 10% cold aq. NaOH soln (10 × 200 ml), the Et_2O layer removed,



washed with HCl soln (5%) until pH was 7, then with saturated NaCl soln, dried overnight over dry Na_2SO_4 and the excess Et_2O evapd *in vacuo*. The non-phenolic fraction was separated into hydrocarbons and oxygenated compounds by CC. Samples (25 ml) were loaded onto a column (50×3 cm) of deactivated 70–230 mesh Si gel and eluted with *n*-hexane (700 ml) to remove hydrocarbons, followed by Et_2O (400 ml) to remove oxygenated compounds. The hydrocarbon fraction was subfractionated into mono- and sesquiterpene hydrocarbons by distillation *in vacuo* (40°, 1–1.5 mmHg), followed by prep. GLC (column D at 160°). Oxygenated compounds were subfractionated into light and heavy oxygenated compounds by fractional distillation *in vacuo* (Buchi–Fisher model FB-HMS-500, max. 50° at the head of column, reflux 10:1, 0.15–0.16 mmHg). Residual phenols were extracted from heavy oxygenated compounds by exhaustive extraction with 20% cold aq. NaOH soln.

Light and heavy oxygenated compounds (1 g) were subfractionated by CC (40×2 cm) on 70–230 mesh Si gel, using C_6H_6–EtOAc (19:1) as eluent. Sesquiterpene hydrocarbons were subfractionated using *n*-hexane as eluent.

Components 3d, 9d, 11d and 13d were isolated pure by repetitive GLC (column E at 160°) from suitable fractions, and collected in Pyrex capillary melting tubes, without cooling.

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