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TRACE CONSTITUENTS IN THE ESSENTIAL OIL OF *THYMUS CAPITATUS*

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Key Word Index—*Thymus capitatus*; Labiatae; essential oil; terpenes; bornyl chloride; GC/MS analysis.

Abstract—The essential oil of *Thymus capitatus* was investigated by glass capillary gas chromatography in combination with mass spectrometry. In the analysis, 22 hitherto unreported trace constituents were isolated, of which 20 were identified.

INTRODUCTION

In the past, the essential oil of *Thymus capitatus* (origanum oil) has often been confused with the essential oil of *Thymus vulgaris* (thyme oil). However, origanum oil is in reality an entirely different type, distilled from the flowering herb *Thymus capitatus*, Hoffmag et Link, which is now considered a separate genus, viz. *Coridothymus capitatus* Rchb. [1–5].

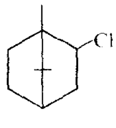
The essential oil content of *Thymus capitatus* has been extensively investigated [6–8]. Nevertheless, it was decided that a more thorough analysis was warranted, particularly as it is not known which constituents are significant from a biosynthetic and phyllogenetic point of view. Therefore, the analysis was run with the intention of including the characterization on trace (less than 0.1 %) components, so that more light could be shed upon the terpenoid distribution pattern. Also, the data obtained should prove useful in the recognition and identification of a genuine oil.

RESULTS AND DISCUSSION

The oil used in this study was obtained by steam distillation from the aerial parts of the plant, collected from the Hellenic island Thassos. Analysis and identifications were carried out using a computerized GC/MS system. Identifications of the individual components were accomplished with the aid of various computer interpretative techniques, as well as by individual interpretation of some spectra. The computer techniques included a comparison of unknown spectra with a collection of 25 409 authentic spectra, and plotting of relative intensities of significant masses ('mass chromatograms') to reveal structural isomers of compounds, or to detect some minor components and the compounds hidden by other components in an incompletely separated gas chromatographic peak.

Table 1 lists the 22 trace compounds that have been isolated and characterized for the first time in the oil of *Thymus capitatus*. The presence of bornyl chloride for the first time in natural products should be noted. Also, because of the fact that some of the essential oil constituents are very unusual, we thought it useful to cite their mass spectral data.

The compound producing peak 15a was identified as bornyl chloride (**1**). Its MS showed important peaks at m/z (rel. int.): 159 (4), 157 (13), 136 (27), 121 (22), 110 (29), 95 (100), 93 (30), 81 (19), 67 (10) and 53 (6) in accordance with the expected peaks for this structure. The occurrence of bornyl chloride as a component of an essential oil is so unusual that we should not exclude the possibility that it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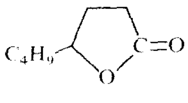
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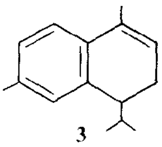
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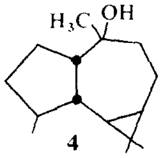
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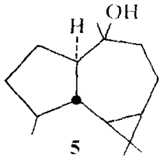
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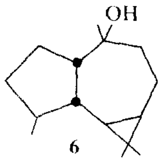
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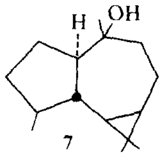
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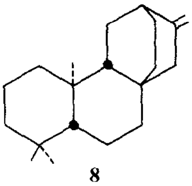
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could have been formed as an artefact. The formation of this artefact could be attributed to the presence of hydrochloric acid traces which reacted with α-pinene via a Wagner–Meerwein rearrangement.

The constituent of peak 15b was tentatively identified as 1-propenyl-2-methyl-1,3-cyclohexadiene on the basis of its MS, *m/z* (rel. int.) 134 $[M]^{+}$ (100), 91 (97), 119 (50), 117 (21), 105 (18), 92 (20), 77 (16), 79 (11). Peak 29a was produced by a compound identified as 4,8-dimethylnona-4,7-dien-2-one. Its MS showed important peaks at *m/z* (rel. int.): 166 $[M]^{+}$ (31), 123 (100), 109 (8), 95 (12), 81 (33), 55 (12) and 43 (48).

Peak 48a was a complex mixture of compounds, in which the following four components could be detected: (a) The first component was tentatively identified as 2-methyl-4-phenyl-2-butyl-acetate. Its MS showed important peaks at *m/z* (rel. int.): 146 (67), 131 (100), 91 (70) and 43 (14). (b) The second was identified as γ-octalactone (**2**). Its MS showed characteristic fragments at *m/z* (rel. int.): 142 $[M]^{+}$ (18), 124 (5), 114 (2), 100 (5) and 85 (100) in accordance with the expected fragments for this structure. (c) The third constituent was tentatively identified as 2-(3-pentyl)-phenol. Its MS showed peaks at *m/z* (rel. int.): 164 $[M]^{+}$ (62), 136 (50), 135 (92), 107 (100) and 91 (24). (d) The last component was tentatively identified as α-calacorene (**3**). Its MS showed the characteristic fragmentation pattern of dihydro-trimethyl-naphthalenes: *m/z* (rel. int.): 173 (2), 157 (100), 142 (40) and 141 (18).

Peak 50 was due to a compound tentatively identified as ledyl acetate. Its MS showed important peaks at *m/z* (rel. int.): 122 (22), 109 (40), 107 (32), 81 (32), 69 (58), 55 (41), 43 (100) and 41 (71). Peak 50a arose from a mixture of two individual components: (a) The first one was identified as γ-nonalactone. Its MS showed important peaks at *m/z* (rel. int.): 138 (4), 114 (4), 100 (4), 85 (100), 71 (13) and 57 (11). (b) The other compound was tentatively identified as ledol (**4**). Its MS, *m/z* (rel. int.): 122 (66), 109 (66), 107 (44), 81 (50), 69 (63), 55 (44), 43 (100) and 41 (44), showed the characteristic fragmentation pattern of ledol stereoisomers and may be well correlated with the MS of globulol (**5**), *epi*-globulol (**6**) and viridiflorol (**7**).

The compound in peak 60 was tentatively identified as atisirene (**8**). Its MS showed important peaks at *m/z* (rel. int.): 272 $[M]^{+}$ (23), 257 (100), 105 (10), 93 (5), 91 (8), 81 (4), 69 (10) and 55 (5).

EXPERIMENTAL

Preparation of the essential oil. Thymus capitatus from the island Thassos region, Hellas, was identified by Dr. G. Pavlidis

Table 1. Trace* constituents found in the oil of *Thymus capitatus.*

Peak No.	R_t† (min)	Components	Reference
2a	10.24	2,5-Diethyltetrahydrofuran	n.c.
4a	14.21	Hexyl acetate and	n.c.
		butylbenzene isomer	n.c.
11	20.34	Methyl hexyl ketone	n.c.
15a	25.57	Bornyl chloride	n.c.
15b	29.19	1-Propenyl-2-methyl-1,3-cyclohexadiene	n.c.
18a	31.01	α-Copaene	n.c.
19a	32.09	Sesquiterpene	—
19b	32.57	Isogeranial	[7]
28	37.44	Sesquiterpene	—
29a	38.32	4,8-Dimethyl-nona-4,7-dien-2-one	n.c.
44a	44.42	Hydrocinnamic aldehyde	n.c.
44b	45.44	Piperitenone	n.c.
48a	48.59	2-Methyl-4-phenyl-2-butyl acetate,	n.c.
		γ-octalactone,	n.c.
		2-(3-Pentyl)-phenol and	n.c.
		α-calacorene	n.c.
50	51.30	Ledyl acetate	n.c.
50a	52.49	γ-Nonalactone and	n.c.
		ledol	n.c.
58a	60.59	γ-Undecalactone	n.c.
60	64.24	Atisirene	n.c.

* Less than 0.1%

† The compounds are listed in order of increased R_t [8].

n.c. = New component.

and S. Kokkini of the Department of Botany, University of Thessaloniki. The aerial parts of the plant, at the flowering state, were air-dried, then 200 g of plant material was subjected to steam distillation in an all-glass assembly for 2 hr yielding 3.2 % of essential oil.

GC/MS analysis. Analysis and identifications were carried out using a computerized GC/MS. Gas chromatographic separations were performed on a W WCOT SP-2100 column, 30 m, with about 95 000 theoretical plates. He flowed at 1.8 ml/min, temp. 70–270° at 6°/min. The detectors FID and TCD were operated simultaneously after 1:100 split ratio. Mass spectra were taken every 0.6 sec over the range m/z 34–420, utilizing an ionizing voltage of 70 eV.

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THREE EUDESMANOLIDES FROM *PLUCHEA ROSEA**

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Key Word Index—*Pluchea rosea*; Compositae; sesquiterpene lactones; eudesmanolides.

Abstract—Three eudesmanolides of *Pluchea rosea* were found to be structurally related to the eudesmane, cuauthemone, earlier reported from plants of the same genus.

So far, the investigations of *Pluchea* species (Compositae, tribe Inuleae) have shown that eudesmane derivatives like cuauthemone (**1**) are characteristic [1–5]. The aerial parts of *Pluchea rosea* Godfrey also afforded **1**. Furthermore, lactones were present in small amounts, the eudesmanolides **2**–**4**. The structures followed from the ^{1}H NMR data (Table 1). From the spectra of **2** and **3** the presence of an axially orientated ester group at C-3 could be deduced; its nature also followed from the typical ^{1}H NMR signals. The difference in the chemical shift of H-3 in the spectra of **2** and **3** is characteristic [2, 4] and is obviously due to the deshielding effect of the 4α-acetoxy group. As the signals of H-5 and H-6 could also be assigned unambiguously, the presence of an 8,12-lactone was obvious too. The chemical shift of H-9 and of H-13 further supported the proposed structures. The spectrum of **4** (Table 1) was very similar to that of **3**. However, the olefinic singlet at 5.49 ppm was missing. As already clear from the molecular formula, an additional hydroxy group was present, which only could be placed at C-8, most probably β-orientated, as the chemical shift of H-14 obviously was influenced by a deshielding effect of the hydroxyl. Again, the 3α-orientated ester group clearly followed from the couplings observed. The 8,9-dihydro compound of **2** we have named ixtlixochilin.

EXPERIMENTAL

The Soxhlet extract (petrol) of the air-dried aerial parts (2 kg) (Voucher 7733) afforded after column chromatography (Si gel) and TLC (Si gel) 5 mg **1**, 3 mg **2**, 10 mg **3** and 3 mg **4** (separated

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* Part 364 in the series 'Naturally Occurring Terpene Derivatives'. For Part 363 see Bohlmann, F., Singh, P., Borhtakur, N. and Jakupovic, J. (1981) *Phytochemistry* **20**, (in press).