

TERPENOID CONSTITUENTS OF THREE TAXA OF *MONARDELLA*

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Key Word Index—*Monardella crisper*, *M. undulata* var. *undulata*; *M. undulata* var. *frutescens*; Lamiaceae; chemotaxonomy; monoterpenoids; sesquiterpenoids.

Abstract—Essential oils from the leaves of three closely related taxa of *Monardella* (*M. crisper*, *M. undulata* var. *undulata*, *M. undulata* var. *frutescens*) were analysed by GC and GC-MS. All three taxa showed highly similar qualitative chromatographic profiles. *Monardella crisper* and *M. undulata* var. *frutescens* apparently show closer affinities qualitatively to each other than either taxon did to *M. undulata* var. *undulata*. The chemical data suggest, however, in addition to morphological and ecogeographical data, that *M. undulata* var. *frutescens* may represent a stabilized hybrid derivative between *M. crisper* and *M. undulata* var. *undulata*.

INTRODUCTION

Monardella Benth comprises a highly variable and taxonomically problematic assemblage of approximately 25 species found in western North America [1, 2]. Relatively little taxonomic work has been done in the genus and this has been confined principally to morphological and ecogeographical studies [3]. Several studies of the terpenoid constituents of various genera of the Lamiaceae have proven to be valuable in understanding taxonomic and evolutionary relationships within these groups [4–7]. We have initiated studies of the terpenoid constituents in three closely related taxa of *Monardella* to aid in the eventual delineation of their taxonomic position.

RESULTS AND DISCUSSION

Twenty-eight mono- and sesqui-terpenoid compounds were isolated and identified from the steam distillate of three closely related taxa, *Monardella crisper* Elmer, *M. undulata* Benth var. *undulata*, and *M. undulata* var. *frutescens* Hoover. The three taxa displayed highly similar chromatographic profiles (Table 1). *Monardella crisper* had two major monoterpenoid components, piperitenone and pulegone, whereas *M. undulata* var. *undulata* and var. *frutescens* had a single major monoterpenoid component, pulegone. However, var. *undulata* had two major sesquiterpenoids, a caryophyllene isomer and *trans*- β -farnesene, that were found to be minor constituents in the other taxa. Of further interest is the occurrence of piperitenone, α -phellandrene, an unidentified monoterpenoid alcohol, and β -caryophyllene in var. *frutescens* and *M. crisper* that were lacking in var. *undulata*. Nine of the 28 compounds investigated showed intermediate values for var. *frutescens* in comparison to the other two taxa.

The occurrence of δ -3-carene is unusual for the family, but has been found in *Lepichinia calycina* [8] and *Monardella hypoleuca* [9]. The pinenes and other low-

boiling constituents are major components of some genera of mints [4, 7], but are relatively minor components in these taxa. Piperitenone is relatively rare in most lamiates in which a number of populations of each species have been examined [10] and, thus, the large percentage in *M. crisper* may be taxonomically useful.

The taxonomic and nomenclatural status of these three taxa are in flux at present (D. Smith, unpublished results). *Monardella crisper* and *M. undulata* var. *frutescens* share a similar habit (herbaceous perennials), contiguous distribution, and ecological preferences. *Monardella undulata* var. *undulata* is an annual, and is found more inland and in more xeric situations than the other two taxa. The terpenoid chromatographic profiles suggest that these three taxa are closely related. However, the apparent differences in qualitative terpenoid composition between the varieties of *M. undulata*, in combination with morphological and ecogeographical differences, suggest that these taxa are artificially allied. Observations from morphological data suggest further that *M. undulata* var. *frutescens* may be a stabilized diploid hybrid. A taxonomic judgement is reserved at present until a broader chemosystematic survey is completed.

EXPERIMENTAL

Three separate isolation techniques were performed [9]. 25 g of air-dried stems and leaves each of *M. crisper*, *M. undulata* var. *undulata*, and *M. undulata* var. *frutescens* (collected by DMS and Dr D. L. Koehler, vouchers at UCSB) were water-distilled using a modified Clevenger apparatus. A 3.0 μ l injection (three replicate injections) was placed in an HP 5831A GLC equipped with a 1.8 m \times 4 mm glass column packed with either 3% SE-30 or 3% OV-17 and dual FID. Chromatographic conditions were: inj temp 280°, detector temp 300°, and an initial oven temp of 100°. Program conditions were: 1.0 min hold, 10° min, to a final temp of 270° and a final hold of 5.0 min. Integrator parameters were attenuation 8, slope sensitivity 1.0, He carrier gas flow rate was

Table 1. Composition of essential oil of *M. crispa*, *M. undulata* var. *undulata* and *M. undulata* var. *frutescens*

Compound*	Composition (% total oil)		
	<i>M. crispa</i>	<i>M. undulata</i> var. <i>frutescens</i>	<i>M. undulata</i> var. <i>undulata</i>
α -Pinene	2.7	1.4	0.2
β -Pinene	0.5	0.6	0.7
Camphene	1.1	0.4	tr
Myrcene	1.0	0.5	0.2
α -Phellandrene	0.1	tr†	—
β -Phellandrene	0.2	—	tr
α -Thujene	tr	tr	tr
δ -3-Carene	0.3	1.3	1.5
γ -Terpinene	—	tr	—
Limonene	tr	tr	tr
β -Caryophyllene	0.4	1.6	—
Caryophyllene isomer	0.2	1.7	23.4
<i>trans</i> - β -Farnesene	1.3	2.2	15.4
Linalool	0.2	tr	0.2
1,8-Cineole	tr	tr	tr
Unknown alcohol	1.0	1.7	—
Citronellal	0.5	—	—
Isoborneol	2.0	tr	0.5
Piperitenone	29.6	4.8	—
α -Terpineol	1.0	1.2	1.8
Thymol	—	—	0.3
Carveol	—	tr	—
Pulegone	57.0	70.5	54.5
Piperitone	0.6	tr	1.0
Carvacrol	tr	tr	—
Dihydrocarveol	tr	tr	tr
4-Terpineol	tr	tr	—
Caryophyllene oxide	—	tr	—

* Compounds identified by GC-MS or GC(1,8-cineole, thymol, piperitone, carvacrol, 4-terpineol).

† tr = trace component (< 0.1 %).

27 ml/min. Mass spectrometry was performed on an HP 5992A GC-MS equipped with a 12 m fused silica WCOT capillary column coated with methyl silicon and interfaced with an HP 9825 data system.

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