

4-Methyl-1-hepten-3-one, the Defensive Compound from *Agathemera elegans* (Philippi) (Phasmatidae) Insecta

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Insects of the genus *Agathemera* (Phasmatidae) live in the Chilean Andes over 1500 m above sea level. On disturbing, the insects release a spray that can cause temporary blindness in humans. Very little is known on the composition of chemicals used for defense by South American phasmids. Here we show that both female and male defensive secretion of *Agathemera elegans* is made up of 4-methyl-1-hepten-3-one. The compound is reported for the first time as a natural product.

Key words: *Agathemera elegans*, Phasmatidae, Defense Secretion, 4-Methyl-1-hepten-3-one

Introduction

Little is known on the composition of chemicals released as defensive compounds by insects living in the South American Andes. Insects of the genus *Agathemera* (Phasmatidae) are known under the vulgar names “chinchemolle”, “chichimol” or “tabolango” in the Coastal Cordillera as well as in the Andes of central Chile over 1500 m above sea level (Camousseight, 1995). Peasants as well as mammals living in the distribution area of the insect avoid the large female as well as the bright colored male, their irritant unpleasant smelling and long-lasting defensive spray. The Andean insect *Agathemera elegans* was first described by Philippi in 1863 from a male collected at Termas de Chillán, Chile. While the females are light brown with dark spots, the males present red or yellow spots in the thoracic and part of the abdominal segments which can be regarded as a warning coloration (Camousseight, 1995). Since no information is available on the chemical composition of the defensive *Agathemera* chemicals, a study was undertaken to identify the composition of both female and male sprays.

Materials and Methods

Insects

The insects (females and males) were captured at the valle de Las Trancas, Termas de Chillán, VIII Región, Chile, in October 2005. Insects were identified by Prof. Luis E. Parra, Departamento de Zoología, Facultad de Ciencias Naturales y Oceanográficas, Universidad de Concepción,

Chile, where both samples (females and males) were deposited. The insects were separately placed in a glass beaker and gently pressed at the abdomen, releasing a colorless, unpleasant smelling, volatile liquid (100–150 μ l). The insects were transferred to another container and the defensive sprays of both males and females were separately dissolved in deuterated chloroform for NMR measurements. A sample of the defense liquid was also kept in a glass container for GC-MS and high field MS analysis.

GC-MS analysis

Equipment: Perkin Elmer Turbo Mass. Column: fused silica capillary column, MDN-5 (Supelco), 30 m \times 0.25 μ m. Carrier: He, split flow 50.0 ml/min. Oven program: total run time: 45 min; initial temperature: 40 $^{\circ}$ C; initial hold: 1.00 min; ramp: 5 $^{\circ}$ C/min to 260 $^{\circ}$ C, hold for 0.00 min.

4-Methyl-1-hepten-3-one

Colorless liquid; $[\alpha]_D^{20}$: +2.1 $^{\circ}$ (c = 6.44, CHCl_3). – EIMS: m/z = 126.198 (calc. for $\text{C}_8\text{H}_{14}\text{O}$: 126.198). – FT-IR: ν = 2964, 2934, 2875, 1695, 1675, 1612, 1466, 1457, 1404 cm^{-1} .

Results and Discussion

The GC-MS spectrum of the colorless liquid released by the insects showed a main (>95%) compound with R_t of 8.23 min and 126 mass units. The ^1H NMR spectrum clearly indicates an α,β -unsaturated ketone moiety and an alkyl chain with a $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH--CH}_3$ sequence. The ^{13}C

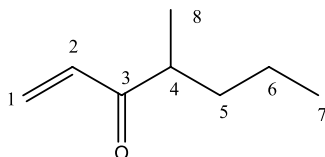


Fig. 1. Structure of 4-methyl-1-hepten-3-one from the Chilean phasmid *Agathemera elegans*.

Table I. ^1H and ^{13}C NMR spectral data of compound **1** (400 and 100 MHz, respectively, CDCl_3 , δ -values).

	H	C
1	6.30 dd (17.6, 1.5); 5.80 dd (10.5, 1.5)	127.76 t
2	6.47 dd (17.6, 10.5)	135.27 d
3	—	204.17 s
4	2.85 m (1 H) ddq	43.28 d
5	1.70 m; 1.3–1.4 m	35.23 t
6	1.3–1.4 m (2 H)	20.43 t
7	0.93 t (7.3)	14.08 q
8	1.13 d (6.9)	16.32 q

NMR spectrum presents eight signals which account for the molecular formula $\text{C}_8\text{H}_{14}\text{O}$. The structure can be assigned to 4-methyl-1-hepten-3-one (Fig. 1), the proposal being supported by HMBC correlations (Table I) and HRMS. The compound is reported for the first time as a natural product. 4-Methyl-1-hepten-3-one was described as a synthesis intermediate by Araldi *et al.* (2003) but was not found in the Dictionary of Natural Products on CD-ROM (2005).

Very little is known on the chemical defense or pheromones from South American phasmids. The structure of the defense compound from the walking stick *Anisomorpha buprestoides* was reported by Meinwald *et al.* (1962) as a monoterpene dialdehyde. A chemical analysis of the defense secretion of the phasmatidae *Sipyloidea sipyilus* was undertaken by Bouchard *et al.* (1997). They found diethyl ether, acetic acid, benzaldehyde, limonene, and benzothiazole in the mixture, the components being very different from that released by *Agathemera elegans*. *Trans,trans*-ididodial and *trans,cis*-

iridodial were reported from the defensive secretion of the phasmid *Graeffea crouani* (Smith *et al.*, 1979). Some alken-3-ones were reported as constituents of insect defense secretion such as 1-dodecen-3-one from the East African termite *Schedorhinotermes lamanianus* and 1-nonen-3-one from the tenebrionid beetle *Eleodes beamerii* (Dictionary of Natural Products on CD-ROM, 2005). The compound 1-octen-3-one was found to be part of the chemical communication system of the coleptera *Ahasversus advena*, *Cryptolestes ferrugineus*, *Oryzaephilus mercator* and *O. surinamensis* (<http://www.pherobase.com/database/com pounds-geo-delta.html>) and was also described as a mushroom flavour component and 1-undecen-3-one as a minor constituent of *Dictyopteris plagio-gramma* (Dictionary of Natural Products on CD-ROM, 2005).

Ocular injury in both humans and mammals has been reported after being sprayed in the face by the North American phasmid *Anisomorpha buprestoides* (Paysse *et al.*, 2001; Dziezyc, 1992). Severe conjunctivitis and corneal epithelial defects were the main consequences, the defects resolved over a week. In Chile, there are no published reports on eye lesions produced by the defensive chemicals of native walking sticks. The reason is that peasants and residents in areas where the insects live avoid contact with them and know that they can produce temporary blindness. With increasing recreational activities and tourism in the southern Andes, the possibilities of contact with *Agathemera* species will increase. Therefore, this insect should be approached with caution.

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