Monoterpenes from the True Bug *Harpocera thoracica* (Hemiptera)

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From the "head space"* of *Harpocera thoracica* (Miridae; Hemiptera) six monoterpenes have been isolated and identified by GLC and MS data in comparison with authentic reference substances. Predominant component was geranyl acetate. Apart from this, the alcohols geraniol and nerol, neryl acetate, and the corresponding aldehydes geranial and neral could be identified.

Introduction

The true bug *Harpocera thoracica* Fallén (Miridae; Hemiptera) can be found especially on oak trees in May and June. Adult insects have a length of 6 to 7 mm, and the females may be distinguished from the males by the lighter, yellowish colouring. Pairing adults can be collected only for some days in the second half of May, since the males are short-lived [1].

Even few specimens of *H. thoracica* (♂ and ♀ mixed) produce a perceptible fruity, sweet odour. Since no data were available on the chemical character of the compounds being responsible for this fragrancy, we decided to analyse the "head space" of *H. thoracica.*

Results and Discussion

The pentane concentrate of the "head space" volatiles of *H. thoracica* was analysed by GLC. The gas chromatogramm of this concentrate (Fig. 1) revealed six peaks. After separating the concentrate into five fractions of different polarity by modified dry-column chromatography [2], the compounds **5** and **6** appeared in the most polar fraction. The mass spectra of these two components accorded with literature spectra [3] of the isomeric monoterpene alcohols geraniol and nerol. The *trans*-isomeric geraniol (peak 6) has a quota of 19.2%, the *cis*-isomeric nerol (peak 5) 7.8% (Table I). Mass spectra and retention time data of authentic reference substances were identical with those obtained from peak 5 and peak 6, respectively.

Peaks 1 and 3 could be elucidated as neral (peak 1) and geranial (peak 3). The isomeric monoterpene aldehydes showed the typical mass spectra with a parent ion m/z 152 (M^+) and a base peak m/z 41 (4). TLC detection with the 2,4-dinitro phenyl hydrazine reagent (5) gave the expected orange colouring. The quota of the aldehydes amounts to 4.7% (neral) and 20.5% (geranial).

Peaks 2 and 4 were found in fraction 3 and identified as the acetates of geraniol and nerol. Alkaline saponification of these components led to the corresponding alcohols. Geranyl acetate (32.7%) is the predominant component of the "head space" concentrate, neryl acetate has a quota of 15.1%.

Recently, monoterpenes like the newly identified compounds from *H. thoracica* have been found in other insects, too. In ants (Formicidae) terpenoids like citral and geraniol serve as alarm and alert

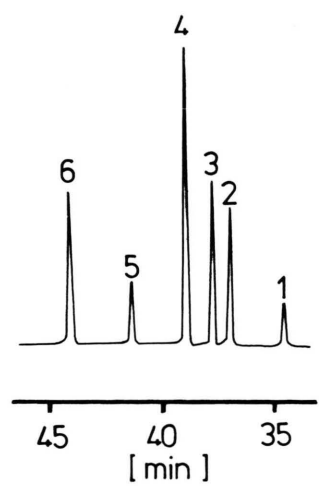

Fig. 1. Gas chromatogramm of the "head space" concentrate of *Harpocera thoracica.* GLC conditions: 22 m Carbowax 20 M capillary column. Injection and detection temperature 180 °C; temperature programme 80–200 °C; 2 °C/min.

* Concentrated sample of the volatiles produced and excreted into the environment.

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Table I. Monoterpenes identified from the "head space" of Harpocera thoracica

Peak* No.	Compound	Quota [%]
1	neral	4.7
2	neryl acetate	15.1
3	geranial	20.5
4	geranyl acetate	32.7
5	nerol	7.8
6	geraniol	19.2

* Numbers indicate order obtained on Carbowax 20 M with temperature programme.

substances (for review see [6]). In Hymenoptera, the aldehydes geranial and neral (Colletes), and geranyl acetate (Sceliphron) were recognized as aggregation pheromones [7, 8]. Moreover, in butterflies (*Pieris napi*) neral and geranial could be identified as pheromones, too [6]. Together with the corresponding alcohols and acids they seem to play a role as pheromones in bees (*Apis mellifera*) as well [9]. The possible biological function of the monoterpenes in *H. thoracica* remains uncertain and is still under investigation, as well as a presumed sex specific production and the role of the adhesive organ of the male [1].

Materials and Methods

60 specimens (♂ and ♀ mixed) of *Harpocera thoracica* were collected near Hamburg/FRG.

Insects were collected into a 50 ml-glass flask, and the flask shaken for some minutes. Subsequently, the animals were removed, and a slightly visible layer from the inner glass surface was taken up with 10 ml pentane. For separation into five fractions of different polarity by modified dry-column chromatography (2) the pentane extract was concentrated to 1 ml under nitrogen atmosphere.

Gas-liquid chromatography was performed with a Perkin-Elmer PE F 22 instrument with a computing integrator M-1 using 22 m Carbowax 20 M capillary columns and 10 m glass columns with 3% OV 101 as stationary phase on GasChrom Q. For identification a temperature programme (80–200 °C; rate 2 °C/min) and various isothermic conditions were applied.

Mass spectra were recorded on a Varian-MAT 111 (GNOM) mass spectrometer at 80 eV using a 3 m Carbowax 20 M (3%) column under isothermic conditions (125 °C). For comparison literature data [3, 4] and authentical reference substances were used.

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