# Volatiles from the Defensive Secretions of Two Rove Beetle Species (Coleoptera: Staphylinidae)

Konrad Dettner

Institut für Biologie II (Zoologie), RWTH Aachen, Kopernikusstraße 16, D-5100 Aachen

and

Gerhard Schwinger

Chemisches Institut, Universität Hohenheim, D-7000 Stuttgart 70

Z. Naturforsch. **41c**, 366–368 (1986); received September 10, 1985

Chemical Defence, Staphylinidae, Volatiles, Spiroketals

From the defensive secretion of the rove beetles (Coleoptera: Staphylinidae) *Ontholestes murinus* (L.) and *Xantholinus glaber* (Norden) nine volatiles have been identified by GC-MS data. From *O. murinus* a spiroketal was recorded for the first time from an arthropod defensive secretion. *X. glaber* has been found to represent the first staphylinid sequestering the monoterpenes limonen and isopulegol.

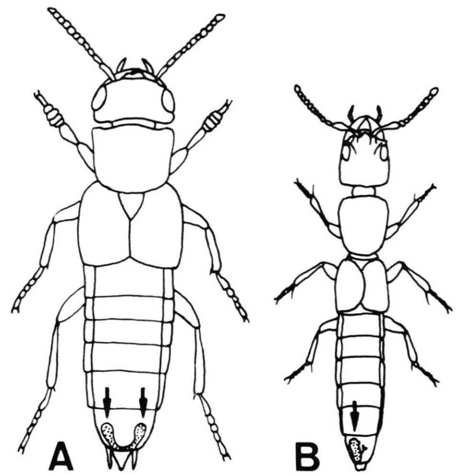

Fig. 1. Dorsal view of the rove beetle A: *Ontholestes murinus* (body length 13 mm); B: *Xantholinus glaber* (body length 7 mm). Position of paired eversible (A) and unpaired noneversible (B) defensive gland reservoirs are indicated by arrows.

## Introduction

Due to their unprotected abdomina rove beetles (Staphylinidae) have evolved a diversity of defensive glands [1–3]. According to subfamilies each taxon is characterized by its homologeous gland systems where a host of mostly terpenoid defensive chemicals or repellents are produced. On molestation both the dung inhabiting species *Ontholestes murinus* (L.) (subfamily Staphylininae; subtribe Staphylinina) and *Xantholinus glaber* (Nordm.) (subfamily Xantholininae) which is usually found from decaying wood bend their abdominal tips dorsally to emit a highly volatile material from defensive glands. The present paper reports on these unusual volatiles from the defensive glands of the two rove beetle species.

## Results and Discussion

*Secretion of Ontholestes murinus (L.)*

As with other members of the subtribe Staphylinina [2, 4], *O. murinus* is characterized by two glandular pouches which are formed by intersegmental membranes between 6th and 7th tergites (Fig. 1A). As defence against predators and other contacting arthropods, *Ontholestes* specimens partly evert their glandular pouches and emit a strong smelling secretion which was separated and analyzed by gas chromatography – mass spectrometry (GC-MS) (Fig. 2, 3A). In accordance with other Staphylinina representatives [1, 2, 4] iridodial represents the main component (**VI**; $M^+$: 168) of the defensive secretion which is accompanied by small amounts of the alcaloid actinidine (**V**; $M^+$: 147). Certainly, the aldehyde **VI** represents the active repellent principle of the *Ontholestes* defensive secretion. Furthermore the *Ontholestes murinus* gland material contains 2-heptanone (**I**; $M^+$: 114) and 6-methyl-2-heptanone (**II**; $M^+$: 128). Only compound **I** is known from ventral abdominal glands of certain cockroaches and was isolated from several gland types of Hymenoptera (see [5]). Comparisons of GC-retention values and MS

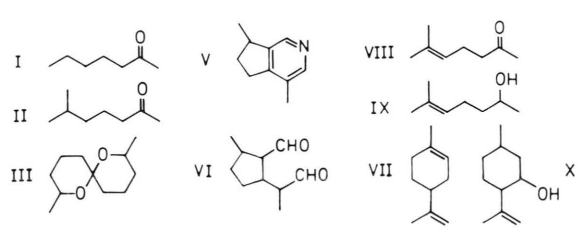


Fig. 2. Defensive components of *Ontholestes murinus* (**I–VI**) and *Xantholinus glaber* (**VII–X**, **V**); see text and Fig. 3.

Reprint requests to Dr. K. Dettner.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0341–0382/86/0300–0366 $ 01.30/0

data with authentic compounds (**I, II**) or beetle secretions where some of these constituents had been recorded previously (**V**, **VI**; [2, 3]) confirmed the identity of **I**, **II** and **V**, **VI**. Compound **III** showed a molecular mass of 184 and its mass spectrum with diagnostic peaks at *m/z* 112 and 115 (184(6%), 115(100), 114(39), 113(37), 112(89), 97(59), 70(30), 69(57), 58(60), 57(28)) was identic with MS data of *E,E*-2,8-dimethyl-1,7-dioxaspiro (5.5) undecane [6]. Such spirocompounds are very erratically distributed within arthropods [6, 7] and now could be recorded for the first time from the defensive secretion of an insect. Likewise, *O. murinus* secretes a second spiroketal (**IV**) with a molecular mass of 198 which showed a fragmentation pattern similar to constituent **III** (**IV**; 198(4%), 129(54), 128(32), 115(53), 112(90), 111(55), 97(31), 83(58), 71(31), 69(100), 58(39), 55(81)). At the moment, however, the exact structure of compound **IV** could not be found conclusively. So far spiroketals act as aggregation pheromones of the bark beetle *Pityogenes chalcographus* and as sex pheromone of the olive fly *Dacus oleae* [7]. Moreover, these compounds are probably used as scent marks in solitary bees of the genus *Andrena* and their function as alarm pheromones in *Paravespula* species has been discussed [6, 7]. Forthcoming studies must show whether pure spiroketals (as **III**) show a specific repellency or defensive activity against arthropods or if they represent mere biogenetic admixtures of the iridodial preventing a polymerization of the main component **VI** [3]. Those constitutents eluting beginning from 270 sec of the *Ontholestes* secretion (Fig. 3A) have been found to represent irodoids of unknown chemistry.

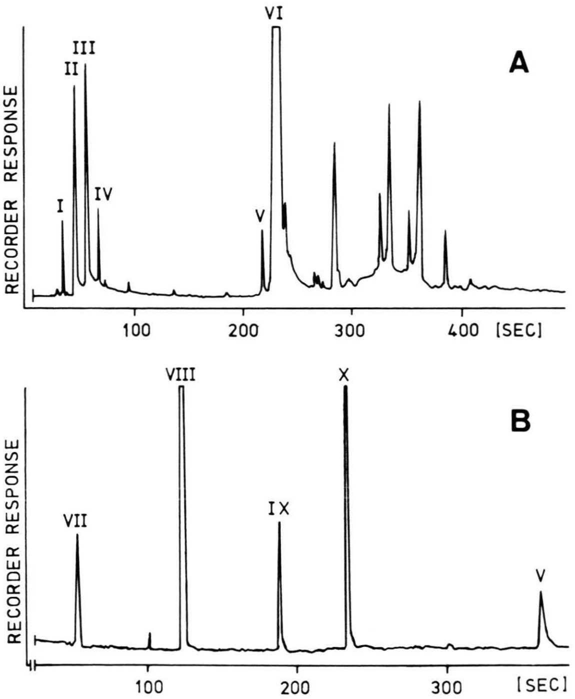


Fig. 3. Total ion current chromatogram of a solid injected single defensive gland reservoir of *O. murinus* (A) and the abdominal secretion of *X. glaber* (B); see Materials and Methods.

*Secretion of Xantholinus glaber (Nordm.)*

As compared with species of the Staphylininae the rove beetle *Xantholinus glaber* (Nordm.) of the Xantholininae is characterized by an unpaired noneversible abdominal gland sac which opens at the anus ([**1**]; Fig. 1B). On molestation *Xantholinus* specimens bend their abdominal tips towards an aggressor and release an intensely smelling defensive droplet which was analyzed by GC-MS (Fig. 2, 3B). Chemically there is no conformity with defensive secretions of other Xantholininae species of the genus *Thyreocephalus* [1]. The *Xantholinus glaber* secretions have been found to contain 6-methyl-5-hepten-2-one (**VIII**; $M^+$: 126) as main constituent which is accompanied by the biogenetically related 6-methyl-5-hepten-2-ole (**IX**; $M^+$: 128). Especially compound **VIII** is widespread and abundant within exocrine glands of insects (see [5]). Mass spectral data from compounds **VII** and **X** have been found to be identic with the mass spectra of the authentic monoterpenoids limonen (**VII**; $M^+$: 136) and isopulegol (**X**; $M^+$: 154). Both constituents have not previously been reported from rove beetle defensive secretions. Within Coleoptera limonen was only isolated from the defensive secretion of the tenebrionid beetle genus *Artystona* [8] whereas isopulegol is unknown from beetle defensive secretions and was only reported from *Formica*-gasters the only insect source for this terpenoid known till now [5].

In accordance with defensive secretions from the paired eversible glands of the Staphylininae the *Xantholinus glaber* gland reservoir contains actinidine (**V**) which might be biogenetically derived from iridodial.

The present investigation on the defensive chemistry of *Ontholestes* and *Xantholinus* and the recently found chemical data of *Creophilus* [4] amply illustrate a significant evolutionary trend which is evident when all chemically known members of both rove beetle subfamilies are considered [1, 2, 9, 10]: There is an extreme tendency toward chemical diversification which is hitherto unknown from other Coleoptera. Only the presence of iridoid constituents within members of both Xantholininae and Staphylininae seems to be an indication that both subfamilies share a common ancestor.

## Materials and Methods

Specimens of *Ontholestes murinus* were caught from dunghills in the vicinity of Aachen/FRG. *Xantholinus glaber* specimens could be extracted from rotten wood in the near of Calw, Blackforest/FRG. *Ontholestes* gland reservoirs had been prepared into the groove of a wire plunger in order to inject them into the injector of a gaschromatograph [2, 3]. Specimens of *Xantholinus glaber* were induced to push their abdominal tips towards a minute filter paper triangle. By addition of a trace of water the minute filter paper triangles were inserted into the groove of the aforementioned wire plunger and were injected in to the gaschromatograph [3]. Splitless capillary gaschromatography – mass spectrometry (GC-MS) was performed on a Varian 3700 capillary gaschromatograph coupled to a MAT 44 quadrupole mass spectrometer which operated at 80 eV and was connected to a Varian SS 200 computer system. For GC-MS the following glass capillary columns and temperature programs were used: Ontholestes (Fig. 3A) 8 m CW 20 M, 65 °C–210 °C, 12.5 °C/min); Xantholinus (Fig. 3B) 8 m CW 20 M, 50 °C 2 min isothermal, 50 °C–210 °C, 12 °C/min.

*Acknowledgements*

We wish to thank the Deutsche Forschungsgemeinschaft for financial support (De 258/4–4,4–5).

[1] C. Gnanasunderam, C. F. Butcher, and R. F. N. Hutchins, Insect Biochem. **11,** 411 (1981).
[2] K. Dettner, Z. Naturforsch. **38c,** 319 (1983).
[3] K. Dettner, G. Schwinger, and P. Wunderle, J. Chem. Ecol. **11,** 859 (1985).
[4] M. Jefson, J. Meinwald, S. Nowicki, K. Hicks, and T. Eisner, J. Chem. Ecol. **9,** 159 (1983).
[5] M. S. Blum, Chemical Defenses of Arthropods, Academic Press, New York 1981.
[6] W. Francke, W. Reith, G. Bergström, and J. Tengö, Naturwissenschaften **67,** 149 (1980).
[7] W. Francke, Structural concepts in the chemistry of aliphatic pheromones, in: Advances in Invertebrate Reproduction 3 (W. Engels *et al.* editors), Elsevier, Amsterdam 1984.
[8] C. Gnanasunderam, H. Young, and R. F. N. Hutchins, J. Chem. Ecol. **7,** 889 (1981).
[9] T. E. Bellas, W. V. Browne, and B. P. Moore, J. Insect Physiol. **20,** 277 (1974).
[10] L. J. Fish and G. Pattenden, J. Insect Physiol. **21,** 741 (1975).