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Acetic acid esters, N-hexanol, N-octanol, and capronic acid as ingredients in the defense secretion product of whip scorpions

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RIASSUNTO

I prodotti di secrezione delle ghiandole di difesa di due specie di Uropigi sono studiati per mezzo della gas-cromatografia e della spettrometria di massa.

Oltre ad acido acetico, il prodotto di secrezione di *Thelyphonus linganus* della Malesia, contiene n-esil-estere dell'acido acetico, n-octanolo e n-octyl-estere dell'acido acetico.

Nel prodotto di secrezione di una specie della tailandia, sinora non identificata, sono stati trovati, insieme ad acido acetico, acido capronico e acido caprilico.

Parole chiave: Aracnidi, Uropigi, Secrezione di difesa, Estere dell'acido acetico, N-esanolo, N-octanolo, Acido capronico.

SUMMARY

The secretion products from the defense glands of two South East Asian species of whip scorpions were studied by gas chromatography and mass-spectrometry.

Besides acetic acid, the secretion product of *Thelyphonus* linganus from Malaysia contains acetic acid n-hexylester, n-octanol, and acetic acid n-octylester.

In the secretion product of a hitherto unidentified Thai species, capronic acid and caprylic acid were found along with acetic acid.

Key words: Arachnida, Uropygi, Defense secretion, Acetic acid ester, n-Hexanol, n-Octanol, Capronic acid.

Introduction

Whip scorpions have a somewhat misleading name, as they are more closely related to amblypygids and webspiders than to scorpions. They are also not poisonus. Nevertheless, they have a remarkable ability to defend themselves against offenders (WERNER, 1935). From large glands in the opisthosoma, they can spray a secretion product to a distance of 20 to 30 cm, accurately at a potential offender, and as a result they are usually met with respect, even by man.

In most species studied up to now, acetic acid is the major component, but several other substances may be present and improve the effectivity of the secretion product (EISNER *et al.*, 1961; HAUPT *et al.*, 1988; ITOKAWA *et al.*, 1981; ITOKAWA *et al.*, 1985; YOGI & HAUPT, 1977).

Material and method

Recently, further species of whip scorpions have been tested for the contents of their spray. For this purpose, *Thelyphonus linganus* from Malaysia and a new species from Thailand, which will be described elsewhere, were seized and their spray collected separately from each individual in separate glass tubes containing a piece of cotton imbibed with methylalcohol. 1-2 µl of each sample were used for analysis using gas chromatography and mass spectrometry as described previously (HAUPT *et al.*, 1988). Parallel analysis was made by a gas chromatograph Varian aerograph 1400, column CP sil 5 under the same conditions, and the mass spectometer VG ZAB 3 F.

Components were identified with the help of Library NBS, and results compared to synthetic products.

Results and Discussion

The gas chromatography spectrum from the secretion product of the Thai species (Fig. 1) shows three peaks, which can be referred to as acetic acid, capronic acid, and caprylic acid. The solvent methanol is labelled s.

In testing the secretion product of Thelyphonus linganus, four peaks are found in the gas chromatography spectrum (Fig. 2, 3).

Fig. 1 - Gas chromatography spectrum of secretion product from a new species of uropygi from Thailand (female). s solvent, 1 acetic acid, 2 capronic acid, 3 caprylic acid.

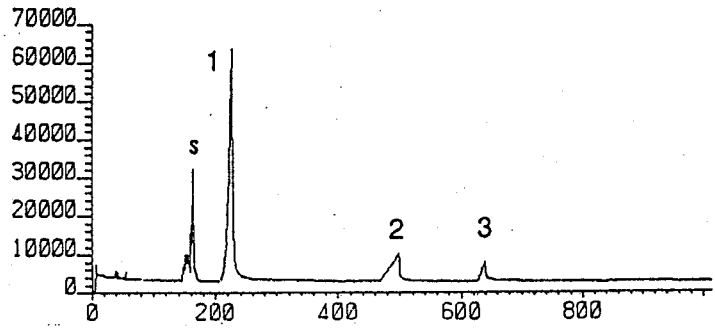
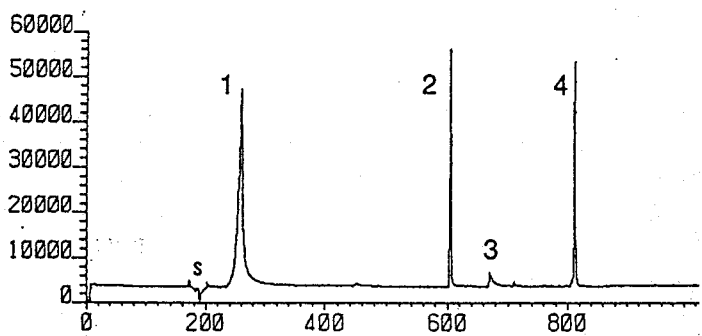
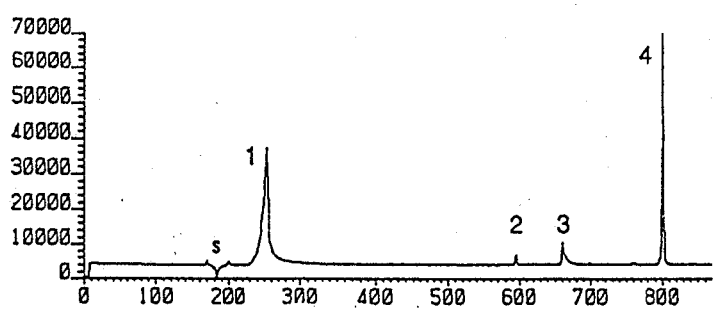


Fig. 2 and 3 - Gas chromatography spectrum of secretion product from Thelyphonus linganus (Fig. 2, male; Fig. 3, female). s solvent, 1 acetic acid, 2 acetic acid n-hexylester, 3 n-octanol, 4 acetic acid n-octylester.





As the spectra do not contain any information about molecule-ions, their identification proves difficult. Only by using the chemical ionization method could two acetates be identified. Thus, the secretion product of this species contains acetic acid, acetic acid n-hexylester, n-octanol with a spectrum of low significance, and acetic acid n-octylester. The loss of 60 ($MH^+ = 145 \rightarrow 85$), molpeak 144 (peak 2) and $MH^+ = 173 \rightarrow 113$ (peak 4) reveals a loss of acetic acid, i.e. the substances are acetates.

In order to evaluate this assessment, acetic acid n-hexylester and acetic acid n-octylester were synthesized, and both substances were used in mixtures with genuine secretion product. The gas chromatography and mass spectrometry spectra reveal the identity. The third component could be identified only with the help of Library NBS of the VG 11-250 system, analyzed with a ZAB 3F produced by VG Inc. This assessment was evaluated by comparison to commercial n-octanol.

The relative concentration of components may be varying with different specimens (Fig. 2, 3).

The comparison of secretion products from whip scorpions from different genus and regions shows a relatively similar product in species at the periphery of the distribution area: *Mastigoproctus giganteus*, which is widely distributed from the South Eastern part of North America down South to Brazil, sprays the same products in a very similar concentration (EISNER *et al.*, 1961) as species of the genus *Typopeltis* from Kyushu and the Ryukyu-Islands (ITOKAWA *et al.*, 1981; ITOKAWA *et al.*, 1985; YOGI & HAUPT, 1977): acetic acid, caprylic acid and water.

Most species of whip scorpions live in South East Asia, and quite unique constituents are produced by a *Typopeltis* species from Guangxi province in Southern China: in addition to acetic acid, three different 2-ketones have been found, 2-heptanone, 2-octanone, and 2-nonanone (HAUPT *et al.*, 1988). Together with the present new results, it may be worth to discuss the biological significance of this spectrum of products.

As shown previously (EISNER *et al.*, 1961; HAUPT *et al.*, 1988), the main component acetic acid is used as a repellent while additional substances may ease application and penetration. At present, it can be excluded that special prey may contribute to the composition of the secretion product. The latter contains the same substances whether the specimens were brought to the laboratory directly from their natural

habitate or whether they were kept in captivity for several months or even years and fed upon a diet of crickets and flies. Thus, the secretion products are produced by the whip scorpions themselves and in some cases prove to be specific characters, although at present there is no evidence of any correlation to higher taxa than species.

A possible sex-related difference in relative concentrations of secretion products (Fig. 2, 3) will have to be the subject of further investigation, as in the case of *Thelyphonus linganus*, so far only a single male could be studied.

The wide distribution of acetic acid, caprylic acid and water, which occurs in the genus *Mastigoproctus* (EISNER *et al.*, 1961) and in some species of *Typopeltis* (ITOKAWA *et al.*, 1981; ITOKAWA *et al.*, 1985; YOGI & HAUPT, 1977), reveals that these substances may represent the plesiomorphous status. Acetic acid has now also been found in a representative of the genus *Thelyphonus*, supporting this hypothesis.

The occurence of esters as additional secretion products in *Thelyphonus linganus* can easily be explained resulting from the reaction of acetic acid and n-octanol, or acetic acid and n-hexanol, respectively.

It seems unlikely, that evolutionary relationships in whip scorpions, presently revealed on the basis of morphology and ethology (WEYGOLDT, 1988), could critically be reviewed by biochemical results on the chemical composition of secretion products as proposed by ITOKAWA *et al.* (1981). Nevertheless, it is obvious that in South East Asia as the main geographical center of uropygid evolution, a greater variety of secretion products has evolved than elsewhere. Since most species have not yet been studied in their natural surroundings so far, nothing is known about the possible ethological relevance of special ingredients of the secretion product.

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