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IDENTIFICATION OF SCENT VOLATILES FROM THE EUROPEAN FIRE BUG *PYRRHOCORIS APTERUS.* L.

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Summary

Secretion from the metathoracic adult scent gland, and from the third abdominal scent gland of the fifth instar larva of *P. apterus* has been analysed by technique of coupled gaschromatography mass spectrometry. Three compounds were identified;oct - 2 - enal, hex - 2 - enal and 4- oxo- oct- 2- enal.

Introduction The scent substances are for the most part short to medium unbranched carbon- chain aliphatic substances, acid, aldehydes, ketoaldehyde, Keton, alcohols and esters. They have been fully listed by (Dazzini and Finzi 1964)and other authors for example (Gilby and Waterhouse 1965),(Baggini, Bernardi,Carnati,pavan and Ricca, 1966),(Calam and youdeowei, 1968).

When disturbed, many species of Hemiptera produce defensive secretion from exocrine gland. The nature of these glands has been studied by (Remold, 1963), (Waterhouse and Gibly, 1964),(Stein and Schumacher , 1969) and the componts of their secretions have been identified for nearly 40 species (Weatherston, 1967).

In the larvae, the scent abdominal glands are located middorsally at sites under abdominal tergites III, IV, V,

The adults tipically possess a ventrally located metathoracic scent gland (Remold, 1962, 1963), (Daroogheh 1978), it has been accepted generally that the scent volatiles are produced primarily for purposes of defence against predators.

The present paper gives a report of chemical investigation on the secretion of scent glands system of *P. apterus*.

Materials and Methods

The culture of *P. apterus* was mai ntained under insectory conditions or in an incubator at a temprature of26 C°, and with a 16 L: 8 D photoperiod. The insects were fed on mallow seed (Malva). They drank from a pad of water coton wool.

The gas chromatography carried out with a varian 1400 gas chromatograph equipped with a flame ionization detector. Samples were injected by open column injection(Staddon er al 1979),(Staddon and Daroogheh,1981), (Daroogheh and Olagbemiro,1982). The excised gland in a small droplet of saline (200m M Nacl, ca, o. 1 μl) was interoduced into the 6 inch × 4mm i. d.glass precolumn in the embrace of the coils of a copper wire spoon. The 6 ft × 2 mm i.d. glass column (a permanent glass joint connected procolumn and column) was packed with 3 % ov 225 on 60-80 mesh Gas chrom Q.

Temperatures were maintained for every analysis as follows, injector block, 180 C° ; detector, 230 C° ; oven, 80 C°; The supply flow rate of carrier gas to the column was 30 ml/min^{-1}.

The components of the scent glands were identifed by combined(GC-MS). This was achieved by injecting a 20 glands sample in a minimum of saline into the spectrometer using the solventless wire coil spon technique as above. The finnigan

4000 quadrupole mass spectrometer Wasequipped with a 9610 microprocessor gas chromatograph,INCOS real time data system(32K core)and printronix data plotter was used, Chemical ionization(CI)with methane as the reagent gas, source temperature 240 C°,and electron impact (EI) with source temperature 260 C°, modes were employed in the analysis of the scent materials. The usual column packing material (3% ov 225 on 60-80 mesh Gas chrom Q) was employed in the 6 ft × 2 mm i.d. column of the gas chromatograph.

Results

Metathoracic gland secretion proved to be a mixture of at least two major and three minor components. (fig.1 A), (fig.1 B) show a chromatogram obtained from the posterior abdominal scent gland of fifth instar larvae, from the mass spectral analysis of the scent materials.

From the metathoracic scent and abdominal scent gland of p. apterus, the following spectral data were obtained.

Actual mass spectra are shown in figs. 2 and 3.

Peak 1(R.T., 1.5; R.A., 86); m/e EI 98 (M^+,27), 83 (55), 69 (42), 55 (47), 41 (100). M.W., 98. Proposed identity: hex - 2- enal.

Peak 2.3.4. Unidentified very small Peaks and not always present.

Peak 5. (R.T.,6, R.A., 11); m/e EI 126 (M^+, 1), 97 (13), 83 (42), 70 (58),55 (64), 41 (100). M.W., 126. Proposed identity: oct - 2 - enal.

Fig. 1 B shows a chromatogram obtained from the Posterior abdominal scent gland of fifth instar larvae. The abdominal scent gland of the larva yielded the following mass - spectral data.

Peak 1. (R.T., 6.4; R.A., 47) m/e 126 (M^+, 1), 108 (6), 97 (15), 83 (58) , 70 (65), 55 (78), 41 (100). M.W., 126. Proposed identity: oct - 2 - enal.

Peak 2. This peak was often the second major individual compound (M.W. 154) tentatively identified as a C9, monounsaturated ketone.

Peak 3.(R.T., 32; R.A., 34), m/e EI 140 (M^+, 1), 125 (12), 111 (70),98 (100), 83 (68),70 (43),55 (87), 41(68). M.W. 140. Proposed indentity: 4-oxo - oct - 2 - enal.

The amount of secretion in the metathoracic scent gland and the abdominal scent gland in P. aptrus was estimated by an external standard technique using the equation.

$$X = \frac{\text{Vol, standard } (\mu_1)}{\text{Peak area response of standard } (cm^2)} \times \text{total peak area response of scent oil } (cm^2).$$

The standard consisted of a solution of dodecane in acetone (dilution of dodecane , 1/1000) : 1 u l of the standard soltion was injected into the chromatograph.

By this technique the metahoracic scent gland(the two half - glands) was found to contain 2.6×10^{-4} μ_1 and the 3 rd abdominal scent gland of the larva $5.5 \times 10^{-4} \mu_1$ of volatile material.

Attempts to provide chemical structure for peak 2, 3, 4 (metathoracic gland), and peak 2 (abdominal gland) were unsuccessful.

Abbreviation: R.T. Retention time; R.A. Percent Relative amount (%);
M.W. Molecular weight; EI. Electron impact;
m/e (%) mass charge (% relative peak intensity);

CI, chemical ionization

Discussion

All the compounds that were found in the abdominal metathoracic scent glands of *P. apterus* have previously been identified in defensive secretions from the other Heteroptera. Schumacher (1971 C)reports that the secretion of *Dysdercus intermedius* and *pyrrhocoris - apterus*, though having a contact poison effect on ants of the *Formica* and *Lasius* genera, has no defensive power

whatsoever against vertebrate predators. secnt volatiles from the (European fire bug) *P.apterus*(Heteroptera pyrrhocoridae)have been analysed by combined gas chromatography and mass - spectrometry.

Analysis of the scent materials was made(1)from the adult metathoracic gland, and (2) from the larval (fifth instar) posterior abdominal gland . GC-MS analysis of the metathoracic scent gland from. *P. apterus* showed the present of hex - 2 - enal and oct - 2 - enal in the adult, and oct - 2 - enal , 4- oxo-oct-2 - enal and unknow compounds in the larva.

The discovery of hex -2- enal in the metathoracic scent gland of *P. apterus* is interesting in view of the absence of an accessory gland in the wall of the median reservior Daroogheh (1987).

This indicates perhaps that hex-2-enal is formed in the secretory tubule and not in the median reservoir as in some other Heteroptera (e.g, *O. fasciatus*, Games and Staddon, 1973b). Unfortunately attempts made to obtain gas chromatograms of isolated tubules of P. apterus were unsuccessful.

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