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VOLATILE MALE-SPECIFIC NATURAL PRODUCTS OF A COREID BUG (HEMIPTERA: HETEROPTERA)

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Abstract—The large coreid bug, *Pachylis laticornis* (Hemiptera: Coreidae), feeds on several mimosaceous trees in Guanacaste, Costa Rica. In addition to the presumably defensive metathoracic exocrine glands that occur in both sexes of this species, the adult males also possess a ventral abdominal gland, opening midventrally in the 7–8th abdominal intersegmental membrane, that releases volatile compounds. Two esters, (*E*)-2-hexenyl tiglate and (*E*)-2-hexenyl (*E*)-2-hexenoate, account for over 90% of the total volatiles in the ventral abdominal gland secretion of males. (*E*)-2-Octenyl tiglate and (*E*)-2-hexenyl benzoate are present at low concentrations, as are at least three other unidentified compounds. The biological role for this fragrant male-specific exudate is unknown.

Key Words—Pheromone, Hemiptera, Heteroptera, Coreidae, (*E*)-2-hexenyl tiglate, (*E*)-2-hexenyl (*E*)-2-hexenoate, (*E*)-2-octenyl tiglate, (*E*)-2-hexenyl benzoate.

INTRODUCTION

In Guanacaste Province, Costa Rica, species of the legume trees *Pithecellobium* and *Enterolobium* (Mimosaceae) are the preferred host plants of a species of coreid bug in the genus *Pachylis*, probably *Pachylis laticornis* (Hemiptera: Coreidae). The nymphs form spectacular feeding aggregations on twigs of the host plant and seem to be able to complete development on a diet of phloem alone (Aldrich and Blum, 1978). Adults are nonaposematic but large (ca. 3 cm in length), migratory (Aldrich, unpublished observation; Torre-Bueno, 1945), and have been observed feeding on *P. saman* seeds and twigs both singly and in copulo (Kinsman, personal communication). The hind femora are much larger in adult males than in adult females, an adaptation which is believed to aid in the defense of territories and the

maintenance of harems by males of other coreid species (Mitchell, 1980; Fujisaki, 1980). Field observations suggest that this species also mates in groups consisting of one male with one or more females. The males mate successively with females in the group, often remaining at one site for several days, while females move more frequently between groups (Kinsman, personal communication 1982).

Although the Hemiptera are notorious for the production of noxious defensive secretions, it is probably not generally appreciated that adult males of many hemipterans, including the Coreidae, release blends of volatile compounds from an ectodermal abdominal gland opening midventrally in the 7–8th intersegmental membrane (Figure 1) (Thouvenin, 1965). The ventral abdominal gland secretions of the coreid species analyzed to date are species-specific and contain predominantly aromatic alcohols such as benzyl alcohol (odor of cherries) and 2-phenylethanol (odor or roses) (Aldrich et al., 1976, 1979). Of the insect species whose exocrine secretions have been analyzed, these hemipteran scents are most reminiscent of the volatile compounds released during courtship by male Lepidoptera (Aplin and Birch, 1970; Petty et al., 1977) which serve as aphrodisiacs (Jacobson et al., 1976; Weatherston and Percy, 1977).

FIG. 1. The posterior sternum of a *Pachylis laticornis* adult male showing the opening (arrow) of the ventral abdominal gland in the intersegmental membrane between the last unmodified abdominal segment (segment 7) and the first genital segment (segment 8).

We report here the chemical identification of the volatile constituents from the 7–8th ventral abdominal gland of adult male *P. laticornis*.

METHODS AND MATERIALS

Late fifth instars of the coreids were collected during the dry season near Palo Verde field station in Guanacaste Province, Costa Rica, at the same site described for an investigation of the aposematic aggregations of the nymphs of this species (Aldrich and Blum, 1978). Originally, the species was determined to be in the genus *Thasus*, probably *Thasus acutangulus* (Aldrich and Blum, 1978). However, the publication of taxonomic revisionary work for coreid species placed in the tribe Mictini (O'Shea and Schaefer, 1978; O'Shea, 1980) prompted us to have the species redetermined. Specimens used in the present study were sent to Dr. Carl Schaefer (University of Connecticut) and redetermined to be in the sister genus of *Thasus*, the genus *Pachylis*, probably the species *Pachylis laticornis* (Fabricius). The uncertainty of the specific determination is due to the fact that this neotropical genus has never been revised (Schaefer, personal communications). Voucher specimens of adult *Pachylis laticornis* have been placed in the Cornell University Insect Collection under Lot. No. 1112.

A permit to import nymphs of *Pachylis laticornis* into the United States from Costa Rica was granted by the Animal and Plant Health Inspection Service (APHIS, USDA). Approximately 1 week after emergence, the 7–8th ventral abdominal glands were dissected from freshly sacrificed males and extracted in CS_2 as previously described (Aldrich et al., 1979).

Preliminary gas chromatography (GC) was performed on a Packard 7400 GC equipped with a flame ionization detector using a 6-ft column of 3% OV-101, temperature programed from 50° C to 250° C at 10°/min. Gas chromatographic retention times of unknowns were compared to those of authentic standards on a 3% SE-30 column and a 3% OV-275 column programed from 60° C to 250° C at 10°/min. The relative proportions of the identified components were calculated by cutting out the peaks from a GC chromatogram and weighing the pieces of paper.

Gas chromatographic–mass spectrometric analyses were conducted on two different systems: an LKB-9000 mass spectrometer using a 6-ft GC column of 0.75% SE-30 operated isothermally at 130° C, and a Finnigan 4000 mass spectrometer using a 6-ft GC column of 1% OV-17 operated isothermally at 170° C. Electron impact (EI) spectra were collected at 70 eV on both instruments. Chemical ionization (CI) spectra were also obtained with the Finnigan system using isobutane as the reagent gas.

Authentic standards of (*E*)-2-hexenyl (*E*)-2-hexenoate, (*E*)-2-hexenyl benzoate, and (*E*)-2-octenyl tiglate [(*E*)-2-octenyl (*E*)-2-methyl-2-butenoate]

were prepared by the acid chloride method. The acids (Aldrich Chemical Company) were treated with excess thionyl chloride in the presence of a few drops of dimethylformamide. The vacuum-distilled acid chloride (20 mm Hg), in ether, was added to a stirred, ice-cooled solution of the alcohol and pyridine in ether, followed by refluxing for 1/2 hr. (*E*)-2-Hexenyl tiglate was prepared from the crude acid chloride (acid + PCl_3) and (*E*)-2-hexenol or, alternatively, from tiglic acid–hexenol in benzene with *p*-toluenesulfonic acid as catalyst (Dean-Stark trap). Both methods gave equivalent products by GC, so they were combined for distillation. After washing with water, dilute acid, water, and bicarbonate, each ester was dried and vacuum-distilled. The boiling points of the esters were: (*E*)-2-hexenyl tiglate, 102–112° C (mostly 108–112° C)/13 mm; (*E*)-2-octenyl tiglate, 125–138° C (almost all 136–138° C)/10 mm; (*E*)-2-hexenyl (*E*)-2-hexenoate, 122–126° C/15 mm; and (*E*)-2-hexenyl benzoate, 148–152° C/13 mm.

RESULTS

Each ventral abdominal gland consists of two main secretory tubules, arising from the external orifice, which subdivide to form several branches. The secretory tubules are similar in appearance to Malpighian tubules except the gland tubules are bright red in color. Due to their bright color, the branches of the gland are easily traced in the abdomen; they are located ventrally and extend anteriorly nearly to the thorax.

Preliminary gas chromatography showed that the adult male ventral abdominal gland secretion contains high concentrations of two volatile compounds plus relatively low concentrations of at least five compounds (Figure 2).

Components 1–3. Unidentified.

Component 4. This compound is the most abundant component of the secretion, accounting for 73% of the identified volatiles. The EI mass spectrum showed a small molecular ion (1.5%) at *m/e* 182, which was confirmed by the CI mass spectrum [base peak at *m/e* 183, $(M+H)^+$], and characteristic ions at *m/e* 167, 153, 137, 125, 83 (base peak), 67, 55, and 41. The spectrum was not in the computer file of mass spectra (Heller 1972), nor could a matching published spectrum be found. However, the spectrum was similar to the published mass spectrum of the allyl ester of tiglic acid; therefore, it was suspected that the compound could be a hexenyl ester of tiglic acid. The spectrum of the unknown is identical to the mass spectrum of the synthesized standard of (*E*)-2-hexenyl tiglate, and the GC retention times of the unknown and the authentic standard are identical on SE-30 and OV-275 columns.

Component 5. This compound accounts for 19% of the identified volatile compounds in the secretion. The EI mass spectrum had a small molecular ion (1.5%) at *m/e* 196, confirmed as the molecular ion by the CI spectrum, with

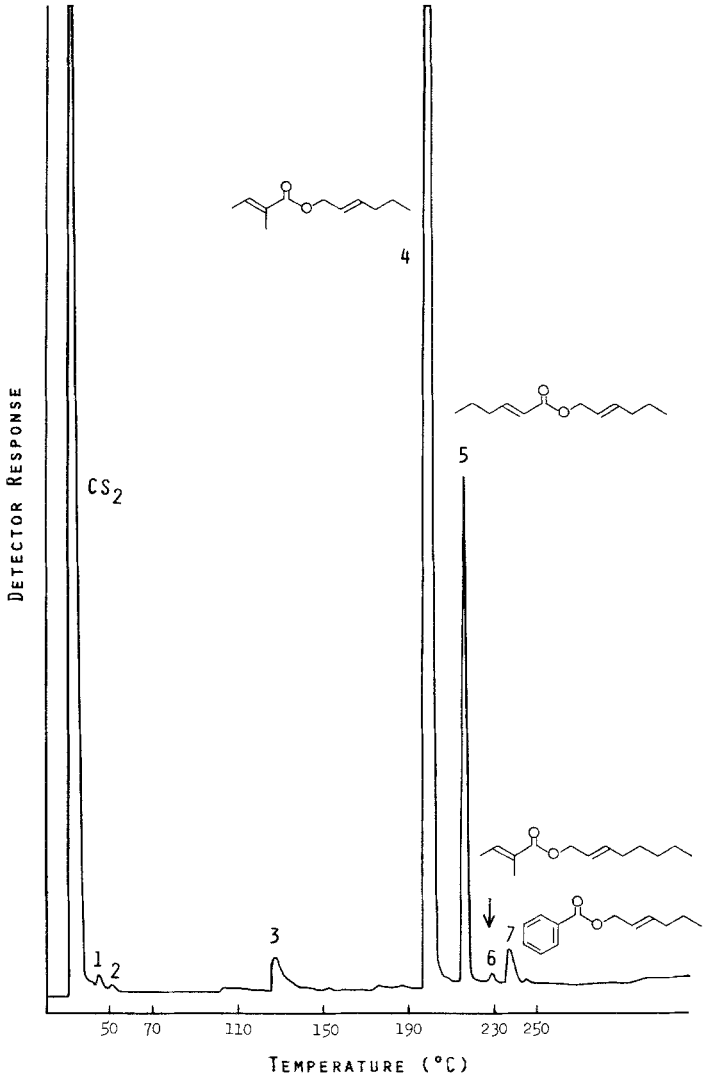

FIG. 2. Gas chromatogram (3% OV-101 column programed from 50° to 250° C at 10° C/min) of a carbon disulfide extract of the ventral abdominal glands from *Pachylis laticornis* adult males.

characteristic ions at *m/e* 167, 153, 139, 125, 111, 97 (base peak), 82, 67, 55, and 41. The EI mass spectrum matches the spectrum of the synthetic standard of (*E*)-2-hexenyl (*E*)-2-hexenoate and the spectrum of this compound in the computer file (Heller, 1972). The GC retention times of the unknown matched the retention times of authentic (*E*)-2-hexenyl (*E*)-2-hexenoate on SE-30 and OV-275 columns.

Component 6. This minor component (2%) had an EI mass spectrum very similar to that of peak 4, but with a small molecular ion (1.0%) at *m/e* 210 instead of 182. Other characteristic ions occurred at *m/e* 181, 165, 125, 95, 83 (base peak), 69, 55, and 41. The EI mass spectrum matches the spectrum of the synthesized standard of (*E*)-2-octenyl tiglate, and the retention times of the unknown and standard matched on SE-30 and OV-275 columns.

Component 7. The EI mass spectrum of this minor component (6%) exhibited a base peak at *m/e* 105, suggesting a benzoate moiety, and a small molecular ion (1.3%) at *m/e* 204 which was confirmed by the CI mass spectrum. Other characteristic ions were present in the EI spectrum at *m/e* 123, 82, 77, 67, 55, 51, and 41. The EI mass spectrum of the unknown matches the spectrum of authentic (*E*)-2-hexenyl benzoate, and the retention times matched on SE-30 and OV-275 columns.

DISCUSSION

Two esters, (*E*)-2-hexenyl tiglate and (*E*)-2-hexenyl (*E*)-2-hexenoate, account for over 90% of the total volatiles in the 7–8th ventral abdominal gland secretion from adult males of the coreid bug, *P. laticornis*. (*E*)-2-Octenyl tiglate and (*E*)-2-hexenyl benzoate are also present in the secretion at low concentrations, as are at least three other unidentified compounds. Tiglate esters have not, to our knowledge, been previously found in arthropods.

Tiglate esters are known to occur naturally in plants and are used for perfumes and as flavoring agents. Geranyl tiglate, for example, is a major constituent of the oil of geranium (Geraniaceae) and butyl tiglate is present in the oil of the Roman chamomile, *Anthemis nobilis* (Compositae) (Windholz, 1976). Tiglic acid [(*E*)-2-methyl-2-butenoic acid] and methacrylic acid (2-methylpropenoic acid) are synthesized and used defensively as chemical irritants by many species of carabid beetles (Schildknecht, 1970). Of the many hemipterans whose metathoracic gland secretions have been analyzed, only the broad-headed bug, *Megalotomus quinquespinosus* (Alydidae), has been found to produce methyl-branched esters in this secretion (Aldrich and Yonke, 1975). Interestingly, this is a species in which the 7–8th ventral abdominal gland is absent.

Esters were the only class of compounds identified in the ventral abdominal gland secretion of the young *P. laticornis* males examined here. Although it is conceivable that compositional changes occur with age in a male's exudate (Aldrich et al., 1978), it appears that the chemical theme expressed in the ventral abdominal glands of *P. laticornis* is distinct from the aromatic alcohol-dominated secretions of other coreid bugs (Aldrich et al., 1979). As such, this secretion from *Pachylis* males more closely resembles the

blends of acetate esters liberated as sex pheromones by many female moths than the aphrodisiacs produced by male moths (Blum, 1977).

At this point we can only speculate that the esters produced in the ventral abdominal glands of adult male *P. laticornis* constitute some type of pheromone. In at least one species of Pentatomidae (the southern green stink bug, *Nezara viridula*), males are responsible for the production of an aggregation pheromone (Harris and Todd, 1980). Perhaps the male-specific secretion of *P. laticornis* functions as an attractant pheromone. Alternatively or concurrently, the secretion could serve as a territorial marker or as a mating stimulant during courtship. These seem to be the most likely functions; other functions may exist.

Our identification of the distinctive array of esters from *P. laticornis* males and the relative ease with which the compounds can be synthesized should provide impetus for future research on the biology of this interesting coreid species.

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