FORUM

The Chemical Volatiles (Semiochemicals) Produced by Neotropical Stink Bugs (Hemiptera: Pentatomidae)

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Os Voláteis Químicos (Semioquímicos) Produzidos pelos Percevejos Neotropicais Hemiptera: Pentatomidae)

RESUMO - Nos últimos anos tem sido crescente a preocupação com as mudanças climáticas e com a utilização auto-sustentável dos recursos naturais, estimulando cada vez mais os estudos para a prospecção de novos produtos naturais visando minimizar o uso de pesticidas. Os percevejos produzem uma variedade de compostos químicos com potencial para o seu manejo. A composição química dos compostos defensivos dos percevejos *Chinavia impicticornis* (Stål)*, C. ubica* (Rolston), *Dichelops melacanthus* (Dallas), *Euschistus heros* (F.), *Piezodorus guildinii* (Westwod), *Thyanta perditor* (Westwood) e *Tibraca limbativentris* (Stål) foi avaliada. Os principais compostos nas glândulas dos percevejos foram: *2*-alcenais, principalmente o isômero *E*, hidrocarbonetos alifáticos saturados; e 4 oxo-(*E*)-2-alcenal. O primeiro feromônio sexual de percevejo identificado no Brasil foi do *Nezara viridula* L., que consiste na mistura dos isômeros *cis* e *trans* epóxi-bisabolenos; na sequência, o percevejo praga da soja *E.. heros* também teve seu feromônio sexual identificado. Os machos desta espécie produzem três ésteres: 2,6,10-trimetildecanoato de metila, 2,6,10 trimetildodecanoato de metila e 2*E*,4*Z* decadienoato de metila. Recentemente, mais três espécies de percevejos neotropicais tiveram a composição da mistura feromonal elucidada. Machos de *T. perditor* produzem o éster, 2*E*,4*Z*,6*Z*-decatrienoato de metila. O percevejo *P. guildinii* tem como feromônio sexual o β-sesquifelandreno, e o percevejo praga do arroz *T. limbativentris* tem também como feromônio sexual um sesquiterpenóide, o zingiberenol. Nessa revisão serão abordados os avanços obtidos no estudo do comportamento e identificação de feromônios sexuais e de alarme de várias espécies do complexo de percevejos praga da agricultura brasileira. A aplicação desses conhecimentos é discutida.

PALAVRAS-CHAVE: Feromônio, aleloquímico, agregação, comportamento, soja

ABSTRACT - In recent years the growing concern about environmental changes and how we are using the natural resources have triggered a search for natural products as alternatives to synthetic pesticides. The stink bugs produce a wide variety of chemical compounds (semiochemicals) that show potential to manage these insects. The stink bugs *Chinavia impicticornis* (Stål), *C. ubica* (Rolston), *Dichelops melacanthus* (Dallas), *Euschistus heros* (F.), *Piezodorus guildinii* (Westwood), *Thyanta perditor* (Westwood) and *Tibraca limbativentris* (Stål) had their blends of defensive compounds evaluated both qualitative and quantitatively. The main compounds identified on the glands of Brazilian stink bugs are: 2-alkenals, mainly the *E* isomer; saturated aliphatic hydrocarbons; and 4 oxo-(*E*)-2-alkenals. The first sex attractant determined from a stink bug was obtained from *Nezara viridula* L., and consists on a mix of two isomers *cis* - and *trans* bisabolene-epoxides. Later the soybean stink bug *E. heros* was also studied and its sex attractant was identified as three esters methyl : 2,6,10-trimethyldecanoate, methyl 2,6,10-trimethyldodecanoate, and methyl *E*2, *Z*4-decadienoate. Recently, three new Brazilian sting bugs were studied and had their sex attractant elucidated. Males of *T. perditor* produce the ester, methyl 2*E*,4*Z*,6*Z*-decatrienoate. Whereas, the stink bug, *P. guildinii* has as sexual pheromone, the sesquiterpene β-sesquiphellandrene, and the stink bug *T. limbativentris* produces as sex attractant the zingiberenol. In this review we discuss the advances obtained on the behaviour and identification of sex and defensive compound of stink bugs from Brazilian crops and the application of this knowledge to manage the stink bugs.

KEY WORDS: Pheromone, allelochemical, aggregation, behaviour, soybean

In recent years there has been a growing concern about environmental changes, and about how we are using the resources available in natural habitats. These concerns have triggered a search for natural products as a source of medicines, cosmetics, fuel, nutrients for humans and animals, and, especially, as alternatives to synthetic pesticides. In turn this has led to an awareness of the importance of studying natural products, and of conserving the natural habitats that remain largely unexplored in the tropics and subtropics.

Brazil, nowadays, is one of the largest producers and exporters of soybean and other crops in the world (CONAB 2007). However, millions of tonnes of grains and products are lost every year due to damage by pests, mainly due to various Pentatomidae (stink bugs) and Lepidoptera (Panizzi 1997).

The stink bugs produce a wide variety of chemical compounds that show potential to manage these insects. Among these compounds are the pheromones, which can be classified as either sexual, alarm or aggregation pheromones (Aldrich 1988). Stink-bug management by the use of semiochemicals is an alternative that has shown potential for application in soybean and others crops (Aldrich 1988; Borges *et al*. 1998a, b).

Semiochemicals mediate interactions of insects with other organisms and they can be used to directly monitor populations, mass trap pests or interfere with reproduction by sexual confusion. Indirect applications include manipulation of the natural enemies, such as parasitic wasps, for instance, that use both sex pheromones and defensive compounds during their foraging behaviour (Vinson 1985, Borges *et al*. 1998a, Bruni *et al*. 2000, Fiaboe *et al*. 2003).

In this review we report on identifications of the main semiochemicals from Brazilian stink bugs populations, illustrating the diversity of the compounds, the currents methods used for extraction and identification and the possibilities of using these compounds in pest control.

Defensive Compounds, Aggregation Pheromones and Alarm Pheromones

Pentatomids produce a mixture of chemical compounds that serve as both alarm pheromones and defence against predators, so it is important to understand the difference between defensive compounds and alarm pheromones. In the literature semiochemicals can be separated into pheromones and allelochemicals (Dicke & Sabelis 1988). Pheromones are chemical compounds that mediate interactions between individuals of the same species, and allelochemicals are chemical compounds that mediate interactions between individuals of different species. Within the allelochemicals there are three classes, depending on the interaction between the organisms involved: if the chemical mediates an interaction that provides a selective advantage to the emitter (e.g. an irritant that deters a predator), it is referred to as an allomone; if the selective advantage is to the receiver (e.g. when a predator uses a pentatomid smell to locate its prey) it is referred to as a kairomone; if both organisms receive selective advantage (e.g. herbivore damaged plant elicit volatiles that attracts an insect that kills an herbivore), it is referred to as a synomone. It is important to note that these definitions are context-dependent (Dicke & Sabelis 1988). Thus a compound can be involved in one interaction as an allomone, while in an interaction with a different organism it may be a kairomone. Here we use the term defensive compound to refer to semiochemicals produced by pentatomids that serve as allomones, or to those whose biological importance is still unknown. We use the term alarm pheromone for compounds that were shown to induce defensive behaviour (mainly dispersal and increased activity) in individuals of the same species.

The Pentatomidae are well known for producing blends of odoriferous compounds that serve mainly to directly deter predation, warn relatives of impending danger and alarm pheromones. The stink bugs produce these compounds in two different types of glands depending on their life stage (Aldrich 1988): the adults produce these compounds in the metathoracic scent glands (MTG), while nymphs produce them in the dorsal abdominal scent glands (DGAs), these glands can be retained in some Pentatomid adults as functional glands (Aldrich 1988, Aldrich *et al*. 1995).

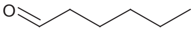
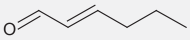
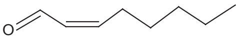
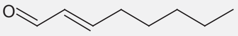
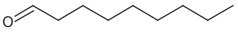
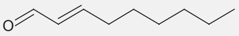
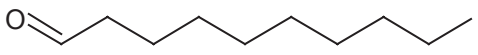
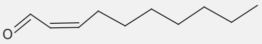
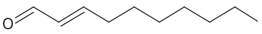
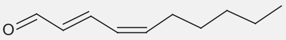
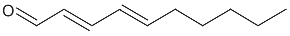
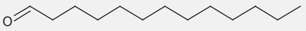
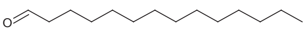
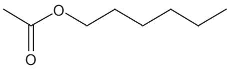
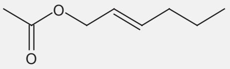
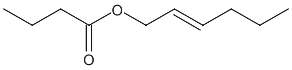
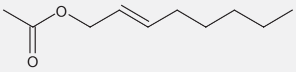
The most commonly used method for extracting compounds produced in the MTG and DAGs is direct extraction of gland contents. The adult insects can be pinned through the thorax with the dorsal side up, the edges of the abdominal cuticle and the cuticle at the junction between the thorax and abdomen are cut with dissection scissors. The viscera are then removed, revealing the big orange metathoracic gland (MTG). The gland is pierced with a flame-stretched glass capillary, causing the contents to rise through the capillary. The contents can be then emptied into solvent by immersing the tip of the capillary into the solvent and briefly passing charcoal-filtered air through the capillary (Pareja *et al*. 2007). The standard method of extraction of defensive compounds from the DAG of nymphs is by immersing the exuviae of nymphs in solvent shortly after moulting. This methodology was developed by Borges & Aldrich (1992) and, provided the exuviae are collected soon after moulting, a single moult of a fifth-instar nymph is enough to obtain analysable quantities of defensive compounds. For earlier instars several exuviae are sometimes needed. This method works because the DAG contents are shed along with the exuviae when the nymphs moult. Collection of volatiles by aeration is also a common method used, but is less likely to adequately sample minor constituents.

The semiochemicals obtained, in general, are analysed by gas-chromatography (GC) and GC coupled to mass spectrometry (GC-MS) for quantitative and qualitative analysis. These methodologies are not specific to Pentatomidae, and can be found in recent reviews and books on analysis of semiochemicals (Millar & Haynes 2000, Vilela & Dela Lucia 2001).

There are several studies detailing the qualitative differences in the blends produced by nymphs and adults (Lusby & Kochansky 1986, Aldrich & Yonke 1975, Borges & Aldrich 1992, Farine *et al*. 1992, Blatt *et al*. 1998), and between males and females (Aldrich *et al*. 1993a, Ho *et al*. 2003). More recently Pareja *et al*. (2007) conducted a study showing qualitative and quantitative differences of the defensive compounds on five different species of Pentatomidae found in Brazil.

The stink bugs *Chinavia impicticornis* (Stål), *Chinavia ubica* (Rolston), *Dichelops melacanthus* (Dallas), *Euschistus heros* (F.) and *Piezodorus guildinii* (Westwood) have had their blends of defensive compounds evaluated both qualitative and quantitatively (Table 1). All these studies showed that the blends of defensive compounds are species-specific.

Table 1. Defensive compounds and alarm pheromones identified on Neotropical estink bugs captured in Brazil: Ci - *Chinavia impicticornis*; Cu - *Chinavia ubica*; Dm - *Dichelops melacanthus*; Eh - *Euschistus heros*; Nv - *Nezara viridula*; Pg - *Piezodorus guildinii*; Tl - *Tibraca limbativentris*; Tp - *Thyanta perditor*. List based on studies from Aldrich *et al*. (1978), Lockwood & Story (1987), Borges & Aldrich (1992), Zarbin *et al*. (2000), Fucarino *et al*. (2004), Moraes *et al*. (2005), Borges *et al*. (2006) and Pareja *et al*. (2007).

Compound	Structure	Masss spectra	Species
Aldehydes			
Hexanal		82(M^+, 20), 72(26), 67(17), 56(90), 44(100)	Ci, Pg, Nv
(*E*)-2-Hexenal		98(M^+, 14), 83(46), 69(72), 41(100), 55(70)	Ci, Cu, Dm, Eh, Nv, Pg
(*Z*)-2-Octenal		126(1) 112(6), 97(19), 83(100),70(81),55(77),41(68)	Dm, Eh
(*E*)-2-Octenal		108 (1), 97 (11), 83 (47), 82 (27),70 (82), 69 (42), 57 (56), 55 (88), 41 (100)	Ci, Cu, Dm, Eh, Nv, Pg, Tl, Tp
Nonanal		124(>1), 98 (31), 95(22), 83(33), 70(50), 57 (100) 41(90)	Ci, Pg, Tl, Tp
(*E*)-2-Nonenal		41(100),70(100),43(98),55(92),83(73),96(38),111(25)	Cu, Dm
Decanal		128(3), 112(20), 110(15), 96(21), 95(23), 82(46), 70(58), 43(100), 57(95)	Tl
(*Z*)-2-Decenal		136 (2), 121(2), 110(20), 97(9), 83(82), 70(100), 55(51), 41(48)	Ci, Cu, Nv
(*E*)-2-Decenal		154(M^+, <1), 121(4), 136 (4), 110(12), 98(18), 83(46), 70(90), 55(72), 43(100), 41(88)	Ci, Cu, Dm, Eh, Nv, Tp
(*E,Z*)-2,4-Decadienal		152(M^+, 5) 123(5), 108(4), 95(15), 81(100), 67(24), 55(16), 41(31)	Ci, Cu, Dm, Eh
(*E,E*)-2,4-Decadienal		152(M^+, 2), 81(100), 95(15), 73(27), 67(22), 55(10), 41(21)	Ci, Cu, Eh
Tridecanal		180(M^+, 2), 154(5), 124(28), 110(14), 109(24), 96(47), 82(73), 67(58), 57(100), 43(77)	Cu
Tetradecanal		194(M^+, 1), 184(1), 168(3), 152(1), 138(5), 124(7), 110(13), 96(43), 82(74), 68(55), 57(99), 43(100)	Cu, Dm, Eh, Pg
Esters			
Hexyl acetate		101(2), 84(18), 73(17), 69(22) 61(25), 56(52), 43(100)	Ci
(E)-2-Hexenyl acetate		142(M^+, <1), 113(1), 100(16), 43(100), 82(26), 71(7), 67(40), 55(15)	Ci, Cu, Eh, Nv
(*E*)-2-Hexenyl butyrate		100(2), 83(10), 82(24), 71(100), 67(20), 43(47), 55(30)	Cu, Eh, Nv
(*E*)-2-Octenyl-acetate		128(M^+, 6), 110(9), 95(7), 81(20), 68(20), 67(21), 54(30), 43(100)	Ci, Cu, Dm, Eh

Continue

Table 1. Continuation.

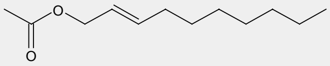
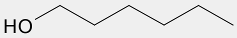
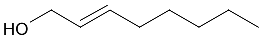
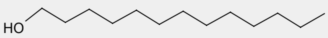
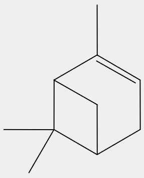
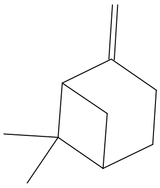
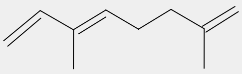
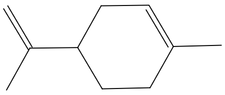
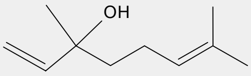
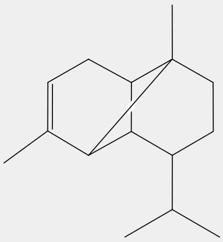
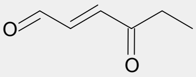
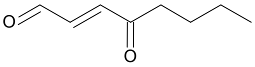
Compound	Structure	Masss spectra	Species
(*E*)-2-Decenyl acetate		156 (M$^+$,6), 127(2), 138(4), 110(11), 96(17), 81(19), 67(23), 54(29), 43(100)	Ci, Cu, Dm, Eh, Nv
Alcohols			
Hexan-1-ol		56(100),43(60),69(36),84(5)	Ci, Nv
(*E*)-2-Octen-1-ol		110(M$^+$, 4), 95(8), 81(21), 68(27), 57(100), 41(53)	Eh, Tp
Tridecan-1-ol*		154(M$^+$, 4), 125(14), 111(30), 97(51), 83(80), 69(96), 55(100), 43(81)	Ci
Monterpenoids			
α-Pinene		136(M$^+$, 6), 121 (10), 105 (10), 93 (100), 92 (38), 91 (39), 79 (23), 77 (28), 69 (<1), 67 (10), 53 (7), 41 (15)	Tl
β-Pinene		136 (M$^+$, 7), 121(10), 105 (3), 94 (4), 93 (100), 92 (11), 91 (26), 80 (12), 79 (23), 77(23), 69 (38), 53 (8), 41 (44)	Tl, Tp
α-Ocimene*		136 (M$^+$, 6), 121(15), 105(13), 93(100), 91 (29), 80 (39), 79 (40), 77 (34), 67 (17), 55 (26), 53 (28), 51 (13), 43 (36), 41 (68)	Tp
Limonene		136(M$^+$, 12), 121(21), 107(19), 94(34), 93(62), 79(33), 68(100),67(84), 53(22)	Ci, Eh, Tl
Linalool		136(M$^+$,4), 107(5), 121(14), 93(64), 80(30), 71(100), 43(65), 41(64)	Eh
Sesquiterpenoids			
α-Copaene		204(M$^+$, 9), 189 (3), 161(56), 147(30), 133(11), 119(86), 105(100), 91(43), 83(53), 81(32), 69 (15), 55(21), 41(32)	Tl
4-Oxo-(E)-2-alkenais			
4-Oxo-(*E*)-2-hexenal		83,(58),57(17),84(16), 112(12),42(3),69(2),97(1)	Ci, Cu, Dm, Eh, Nv, Pg
4-Oxo-(*E*)-2-octenal			Nv

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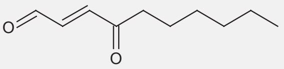
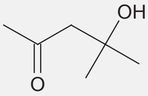
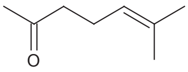
Table 1. Continuation.

Compound	Structure	Masss spectra	Species
4-Oxo-(*E*)-2-decenal		55(100),43(97),98(80),70(70),83(62),139(53),41(60),125(22),111(17)	Ci, Eh, Nv
Ketones			
4-Hydroxy-4-methyl-pentanone		43,59(53),101(16),83(3), 69(<1)	Ci, Cu, Dm, Eh, Pg
6-Methyl-5-hepten-2-one		126(M^+, 4), 111(12), 108 (35), 93(14), 69 (38), 58 (17), 55(38), 43 (100), 41(55)	Tl

On the other hand, different species may have exactly the same compounds in the blend, but these compounds are in different ratios.

This specificity can potentially play an important role in intra-specific communication and may help to understand the phylogeny of some pentatomid groups, and to understand the evolution of insect defence. For example the sister species, *C. impicticornis* and *C. ubica* are more similar to each other than the species *E. heros*, *P. guildinii* and *D. melacanthus* (Fig. 1) (Pareja *et al*. 2007).

The defensive compounds have simple chemical structures when compared with the sex pheromones produced by these insects, making their identification straight forward. Although some chromatographic and spectrometric data are not yet available (as for some of the 4-oxo-(*E*)-2-alkenals), we present spectra obtained for these compounds (Table 1).

The main compounds identified from the glands of Brazilian stink bugs are: 2-alkenals (aldehydes with an unsaturation at the second-third carbons), mainly the *E*-isomer with very small quantities of the *Z*- isomer; saturated aliphatic hydrocarbons; and 4-oxo-(*E*)-2-alkenals (C_6, C_8 and C_{10}). Esters, alcohols and unsaturated hydrocarbons are present as well, but in lower quantities and in some species, such as for the males of *P. guildinii*, various sesquiterpenes occur (Borges *et al.* 2007a). The 4-oxo-alkenals are present in higher quantities in nymphs of the pentatomids when compared with

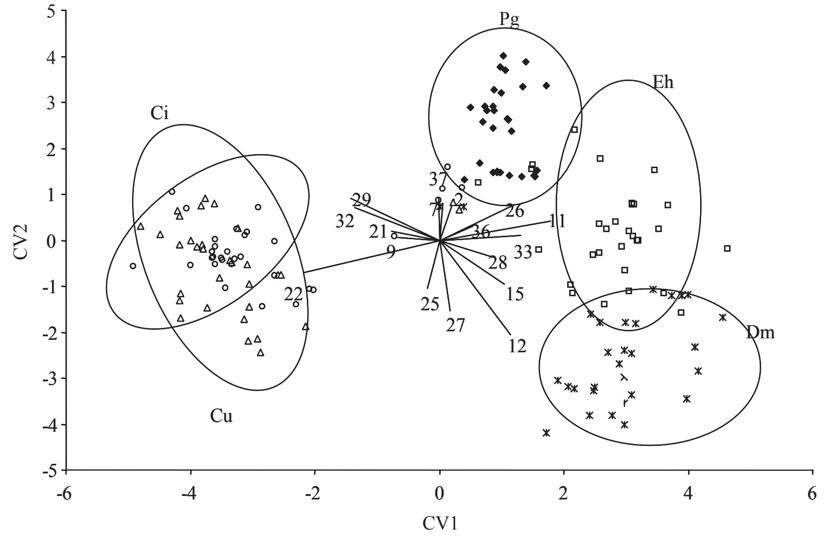


Fig. 1. Canonical variates analysis (CVA) biplot for A) the analysis differentiating between species. The points are the individual scores for each replicate, calculated from the CVA equation that maximises differences between treatments along the two dimensions defined by the two canonical variates (CV1 and CV2). The lines are the loadings for each of the variates (compounds), and the length of the line represents the relative magnitude of the importance of each compound in differentiating between treatments in the two dimensions. For A) only the first two canonical variates (representing 85% of the variability) are presented out of the four possible canonical variates. 2. 4-Hydroxy-4-methyl-pentanone; 7. Decane; 9. (*E*)-2-Hexenyl acetate; 11. (*Z*)-2-Octenal; 12. (*E*)-2-Octenal; 14. Undecane; 15. Linalool; 21. (*Z*)-2-Decenal; 22. (*E*)-2-Decenal; 23. 1-Tridecene; 25. Tridecane; 26. (E,E)-2,4-Decadienal; 27. 4-Oxo-(*E*)-2-decenal; 28. Unknown 2; 29. Tetradecene; 32. Unknown 3; 33. Pentadecene; 36. Tetradecanal; 37. Tridecan-1-ol.

MTG of adult insects (Aldrich 1988). These compounds were responsible for separating nymphal blends from adult blends of Neotropical pentatomids (Pareja *et al*. 2007).

The biological role of most of these defensive compounds still needs to be studied. Three of the compounds that were identified in higher concentrations in Brazilian species, namely (*E*)-2-octenal, (*E*)-2-decenal and (*E*)-2-hexenal, were reported initially as defensive compounds (Gilby & Waterhouse 1967) and later as alarm pheromones (Lockwood & Story 1987, Pavis 1994). In addition, some of these compounds are used as kairomones by natural enemies. For example, the egg parasitoid *Telenomus podisi* uses (*E*)-2-hexenal as a cue to find its preferred host, *E. heros*. This compound has been tested in bioassays using a Y-tube olfactometer and in the field (Peres 2004; Laumann *et al*., unpublished). However (*E*)-2-hexenal is a common plant volatile, and is produced in large amounts by soybean, a major host plant for *E. heros* (Moraes *et al*. 2008a). Thus it is not yet possible to determine whether the parasitoid responds to this compound as a cue directly associated to their host or as a means of finding the habitat of their host. These aldehydes have also been shown to have important anti-microbial action, in particular against the entomopathogenic fungus *Metarhizium anisopliae* (Borges *et al*. 1993). These blends could therefore be important in determining susceptibility of these insects to pathogens, a consideration of likely importance in biological control efforts.

The esters, although in lower concentrations than the aldehydes have also been shown to have biological importance, mainly as an alarm pheromone in *N. viridula* (Lockwood & Story 1987).

The aliphatic hydrocarbons are present in large quantities, and in most species tridecane is one of the principal compounds found in gland or aeration extracts (Aldrich *et al*. 1989, 1994; Moraes *et al*. 2005a; Borges *et al*. 2007a; Pareja *et al*. 2007). However, in *Edessa rufomarginata* (Howard & Wiemer 1983) and *Edessa meditabunda* (Moraes *et al*, unpublished data) undecane is the most abundant aliphatic hydrocarbon. Lockwood & Story (1985) found that tridecane has an action as both an aggregation and an alarm pheromone for *N. viridula*, in a dose-dependent manner, though recently, Fucarino *et al*. (2004) did not find any biological activity for tridecane in *N. viridula*. Lockwood & Story (1985) only found effects at very high (alarm) and very low (aggregation) concentrations. It is difficult to determine whether these concentrations are biologically relevant, or those used by Fucarino *et al*. (2004) are more realistic, since very high amounts (up to 1 mg) of tridecane can be present in the MTG at any given time. However the aggregation effect at very low concentrations showed that these insects can detect the compound in small amounts and this is likely to be a true aggregation effect. Aldrich (1988) proposed that one of the functions of the aliphatic hydrocarbons is to serve as solvents that modulate the evaporation of the other compounds, and this can explain the high quantities of these compounds found in extracts of the stink bugs.

The 4-oxo-(*E*)-2-alkenals are compounds that have only been reported in the true bugs (Suborder Heteroptera). Borges & Aldrich (1992) identified significant quantities 4-oxo-(*E*)-2-alkenals in different instars of pentatomid mainly (*E*)-4-oxo-decenal on the first-instar nymphs, and the authors have postulated that this compound could play a role as an aggregation pheromone. Later Fucarino *et al*. (2004) showed that 4-oxo-(*E*)-2-decenal elicits aggregation behaviour in first-instar nymphs of *N. viridula*, as had been proposed by Borges & Aldrich (1992). However, there is no further information on the biological activity of these compounds, since they are unique to these species, and therefore difficult to obtain. Compounds with very similar mass spectra to, and eluting just after 4-oxo-(*E*)-2-hexenal have been detected in Pentatomidae (Pareja *et al*. 2007) and others Heteroptera (Drijfhout *et al*. 2002). However, it is not yet clear whether these are produced by the insects or are breakdown or rearrangements of 4-oxo-(*E*)-2-hexenal.

Sex Pheromones

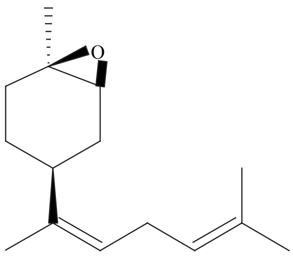
The Pentatomidae show a fantastic variety in the chemical structure of the few sex pheromones identified so far. In contrast to the Lepidoptera, the Pentatomidae do not show a structural pattern of the compounds following families or subfamilies. For Lepidoptera it is possible to classify the pheromones into either type I (75%), which are long, straight chain (C_{10}-C_{18}) alcohols and their derivatives, mainly acetates and aldehydes; type II (15%), which are polyunsaturated hydrocarbons and their epoxy derivatives with a longer straight chain ($C_{17}-C_{23}$); or miscellaneous (10%) (Ando *et al*. 2004). However, for some species of Pentatomidae it is possible to observe a characteristic structural pattern at the genus level.

So far all the studies with stink bugs have detected the male as the producer of the sex pheromone (McBrien & Millar 1999, Moraes *et al*. 2005a, Borges *et al*. 2006, Borges *et al*. 2007a). On the other hand, females are responsible for emitting substrate-borne vibratory signals that attract males during initial courtship and males respond to this by emitting a song that would bring together the partners for matting purpose (Čokl *et al*. 2000, Moraes *et al*. 2005b).

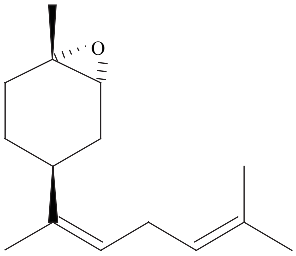
Species of *Nezara* Group

The *Nezara* group includes more of 100 species within eight genera, and they are cosmopolitan with higher diversity in Afrotropical and Neotropical regions. Schwertner (2005) conduced a new cladistic study of this group considering *Chinavia* a valid genus that includes Afrotropical, Neartic and Neotropical species formerly classified as *Acrosternum*. Following this new classification, all *Acrosternum* from the regions cited above will be refereed as *Chinavia* in this text (Table 3).

Of the species within the genera *Nezara* and *Chinavia* studied from different geographic areas in the world, the major components identified were: *trans*-(*Z*)-bisabolene epoxide (*trans*-*Z*-EBA) ((*Z*)-(1′*S*,3′*R*,4′*S*)(-)-2-(3′,4′-epoxy-4′-methylcyclohexyl)-6-methyhepta-2,5-diene) and the corresponding *cis*-isomer (*cis*-*Z*-EBA) (Fig. 2) (Baker *et al*. 1987; Aldrich *et al*. 1987,1993 b; McBrien *et al*. 2001). The *trans* and *cis* designations refer to the position between the epoxide and the pendant group on the ring. These studies



cis-(Z)-Bisabolene-epoxide (cis-Z-EBA)



trans-(Z)-Bisabolene-epoxide (trans-Z-EBA)

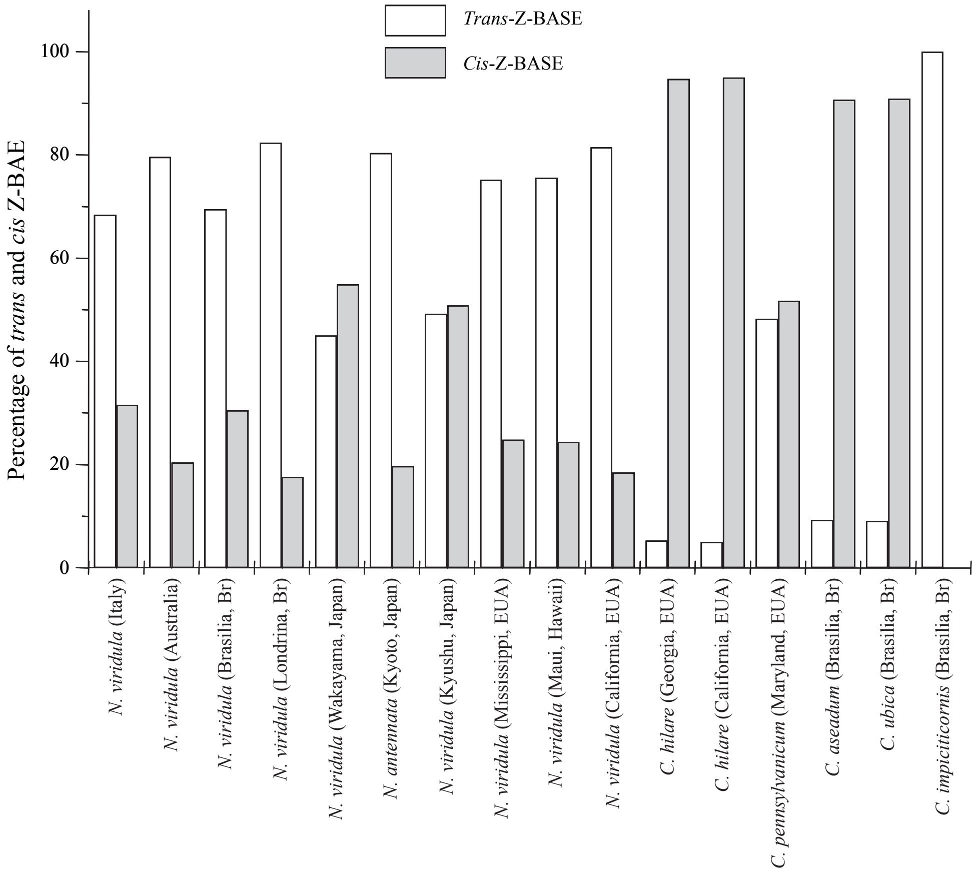


Fig. 2. Percentage of *trans* and *cis*-bisabolene-epoxide (*trans* and *cis Z*-BAE) produced by males of *Nezara* and *Chinavia* spp. from different geographic areas around the world.

showed that the specificity is guaranteed by the different ratios of the two components produced by the different species (Fig. 2) (Aldrich *et al*. 1989, 1993b; McBrien *et al*. 2001; MCB Moraes, RA Laumann & M Borges, unpublished data). Miklas *et al*. (2000) using solid phase micro-extraction (SPME) methodology with *N. viridula* from different parts of the world reported that there is a great variability in the quantities of the sex pheromones produced between males of the same species, but the ratio of *cis* to *trans-Z*-EBA is constant within each strain of *N. viridula*.

Only two species in the genus *Nezara, N. antennata* and *N. viridula*, had their sex pheromones identified, but nine *N. viridula* populations were studied from different geographical areas. All of these populations showed the *trans* isomer in higher quantities than the *cis* isomer. In contrast to the *Nezara* species, the *Chinavia* species presented higher quantities of the isomer *cis-Z*-EBA. The exceptions are *C. pennsylvanica*, which produces nearly equal amounts of the isomers, and *C. impicticornis*, which only produces the *trans* isomer (MCB Moraes, RA Laumann & M Borges, unpublished data). Thus C. *impicticornis* has a ratio between the components more similar to the blend identified for *Nezara* spp. than other

Chinavia species.

The function of the ratio of *trans* to *cis*-Z-EBA is still unclear. Aldrich *et al*. (1989) reported that in laboratory experiments males of *N. viridula* from Japan mated with females of *N. viridula* from the USA (Mississippi), and the offspring were fertile and produced a ratio of *trans* to *cis*-Z-EBA of 1.53, which is intermediate between the two parental blends.

Bioassays in the laboratory carried out with *N. viridula* from Brasilia, Brazil, showed that females were attracted only to synthetic EBA when both isomers are present in the correct ratio (Borges 1995). The absolute configuration was identified as being (1´*S*,3´*R*,4´*S*) (1) (Baker *et al*. 1987), and later Borges (1995) reported that females did not show the same level of response (attraction) to the racemic mixture as to the (1´*S*,3´*R*,4´*S*) enantiomer. A similar result was obtained by McBrien *et al*. (2001) working with *Chinavia hilaris* Say. Females of C. *hilaris* responded only to the pheromonal mixture containing both *cis* and *trans*-*Z*-EBA in the same ratio released by the males, additionally the absolute configuration identified for this species was the same as found by Baker *et al*. (1987).

There is a third component that is produced only by males of *Chinavia* and *Nezara* species, which is the (*Z*)-α-bisabolene (Aldrich *et al*. 1989, 1993b; McBrien *et al*. 2001). However, bioassays conducted with (*Z*)-α-bisabolene with *C. hilaris* did not provide any evidence that this compound has biological activity, and there was no evidence regarding its biological activity in other studies (Aldrich *et al*. 1993b, Borges 1997). McBrien *et al*. (2001) proposed that because of its great structural resemblance [including the (4*S*) configuration] with the EBA, the bisabolene could be a precursor to the pheromone components.

Euschistus heros

The pheromone components of *E. heros* were identified by Borges & Aldrich (1994) and Aldrich *et al*. (1994) and consists of three components: methyl 2,6,10-trimethyldecanoate, methyl 2,6,10-trimethyldodecanoate, and methyl 2*E*,4*Z*-decadienoate (Table 2, compounds 1, 2 and 3). Zhang *et al*. (2003) confirmed the ratio proposed among the three components by Borges *et al*. (1998a), as being: 53% (2*E*,4*Z*)-methyl decadienoate, 3% 2,4,6- methyl trimethyldodecanoate and 44% methyl 2,6, 10-trimethyltridecanoate. The biological activity of the three components was confirmed in a laboratory bioassay and showed that methyl 2,6,10-trimethyltridecanoate was the main component to attract females (Borges *et al*. 1998a). Costa *et al*. (2000) carried out a set of experiments that showed that the racemic mixture of methyl 2,4,6-trimethyltridecanoate was efficiently attractive to females in laboratory bioassays. Methyl 2,6,10-trimethyltridecanoate has eight possible stereoisomers. The absolute configuration of methyl 2,6,10-trimethyltridecanoate was inferred by means of bioassays using the eight stereoisomers separately, which were synthesized by Mori & Murata (1994). Costa *et al*. (2000) reported that females respond better to isomer 2*S*,6*R*,10*S* than the other isomers when compared with a solvent (Fig. 3). In addition, they showed that one of the isomers (2R,6S,10S) did not attract the insects, and most of the insects responded to the solvent when this isomer was used as a stimulus (Fig. 3) suggesting a possible repellent action. However, the presence of this component in the racemic mixture did not have an antagonist effect. Borges *et al*. (1998b), using the racemic mixture of methyl 2,4,6-trimethyltridecanoate, captured *E. heros* in field traps.

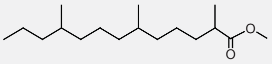
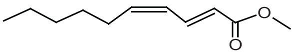
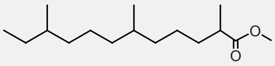
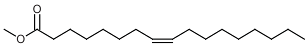
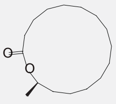
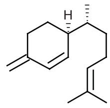
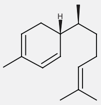
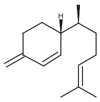
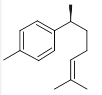
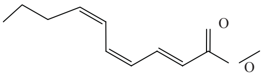
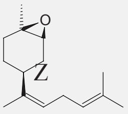
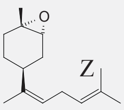
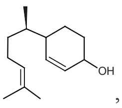
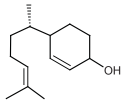
In the field, experiments were carried out in a soybean crop by placing lures with 10 µg of racemic mixture of methyl 2,6,10-trimethyltridecanoate in traps (Borges *et al*. 1998b). Traps containing the racemic mixture caught a higher number of *E. heros*, along with another pentatomid, *P. guildinii*, when compared with a trap containing only the septum with solvent (Borges *et al*. 1998b). The racemic mixture in a lure formulation attracted *E. heros* in field conditions with a potential to be used in population monitoring (Borges *et al*. 1998b, 2007b, Laumann *et al*., 2007a).

Recently, Moraes *et al*. (2008b) carried out a simple study of *E. heros* that revealed the importance of understanding the physiology and the behaviour of stink bugs in order to identify the correct sex pheromone blend. When the insects were aerated with food (*Phaseolus vulgaris* pods), males of *E. heros* released all three components in the ratio reported by Zhang *et al*. (2003) during seven consecutive days. On the other hand, when the insects were kept in aeration without food, after 48h they stopped releasing the main component of the sex pheromone (methyl 2*S*,6*R*,10*S*-trimethyltridecanoate), and they released in higher quantities the first component of the blend, methyl (2*E*,4*Z*)-decadienoate.

Thyanta perditor

Males of *T. perditor* produce the ester methyl 2*E*,4*Z*,6*Z*-decatrienoate ((*E*2,*Z*4,*Z*6)-10: COOMe) as the main sex pheromone component (Moraes *et al*. 2005a) (Table 2, compound 10). The same component was also identified in pheromone blend of the two neartic species *Thyanta pallidovirens* Stål and *Thyanta custator acerra* McAfee (Millar *et al*. 1997, McBrien *et al*. 2002) (Table 2, compound 7, 8 and 9). As in *Nezara* and *Chinavia* spp., *Thyanta* spp. have very similar blends, which suggests that closely related species of stink bugs share the same or similar blends as sex pheromones, with specificity possibly being due to different ratios of the compounds in the blend. GC analysis of the extracts of males showed a male-specific compound with a large and irregularly shaped peak, suggesting a thermally unstable compound (Fig. 4). Mass spectrometry analysis followed by high performance liquid chromatography (HPLC) suggested the presence of three conjugated unsaturations in the molecule, and a straight 10-carbon chain. The presence of fragments at m/z 105 and 74 suggested a McLafferty rearrangement of a methyl ester, and along with the molecular weight of 180, it appeared the compound was the same as identified for the other *Thyanta* species. Comparison of the GC retention time, peak shape and mass spectra of the unknown compound with standards of the (2*E*,4*E*,6*E*)-,(2*E*,4*Z*,6*E*)-,(2*E*,4*E*,6*Z*)-.and (2*E*,4*Z*,6*Z*) isomers of methyl (2,4,6)-decatrienoate, confirmed that the compound produced by *T. perditor* is the ester methyl

Table 2. Sex pheromone identified in stink bugs from Brazil: Eh - *Euschistus heros*; Nv - *Nezara viridula*; Pg - *Piezodorus guildinii*; Tp - *Thyanta perditor*, Tl - *Tibraca limbativentris*, and some worldwide species: Tca - *Thyanta custator acerra*, Ph - *Piezodorus hybneri*. List obtained from studies of Moraes *et al*. (2005), Borges *et al*. (2006), Borges *et al.* (2007a) and Mcbrien *et al.* (2002).

N^0	Compounds	Structure	Mass spectra	Species
1	Methyl 2,6,10-tridecanoate		270 (M^+, 3,7), 227 (1,2), 199 (1,4), 180 (5,9) 157 (14,2), 101(41,9), 88 (100), 69(16,7), 55 (30,3)	Eh
2	Methyl *E* 2,*Z*4- decadienoate		182 (17,8), 151 (17.9), 139 (7,0), 122 (12,3),111(100), 97 (25.6), 81 (92.3), 67(64.4), 55 (33,0), 41 (52.3)	Eh
3	Methyl 2,6,10-trimethyldodecanoate		256 (3,4), 203 (1,2) 152 (0,6), 119 (10,2), 101(40,3), 88(100), 69 (19,8), 55 (41,6)	Eh
4	(*Z*)-8-Methyl hexadecenoate		268 (M^+), 237 (12), 236 (14), 194 (17), 152 (14), 141 (8), 137 (11), 123 (17), 110 (23), 97 (41), 87 (48), 74 (75), 69 (61), 43 (56), 55 (100), 41 (75)	Ph
5	(*R*)-15-Hexadecanolide		254 (M^+), 236 (17), 210 (10), 194 (7), 192 (9), 152 (11), 125 (13), 111 (22), 105 (100), 97 (41), 83 (42), 71 (32), 69 (53), 43 (54), 41 (83)	Ph
6	(7*R*)-(+)-β-Sesquiphellandrene		204 (M^+, 33), 161 (66), 133 (47),120 (38), 109 (33) 93 (73), 77 (36), 69 (100), 55(17), 41(46)	Pg, Ph*
7	(7*S*)-(-)-Zingiberene		204 (M^+, 11), 161 (10) 119 (97), 93 (100), 77 (31), 69 (40), 56 (14), 55 (13), 41(49)	Tca
8	(7*S*)-(-)- β-Sesquiphellandrene		204 (15), 161 (31), 133 (26), 120 (23), 93 (53), 92 (33), 91 (47), 77 (42), 69 (100), 55 (33), 41 (99)	Tca
9	(7*S*)-(-)-α-Curcumene		202 (M^+, 26), 145 (26), 132 (74), 119 (100), 105(48), 91 (24), 83 (19), 77(16), 69 (21), 55 (31), 41 (53)	Tca
10	Methyl *E*2, *Z*4, *Z*6-decatrienoate		180 (M^+ ,63), 151 (10), 149 (11), 138 (20), 137 (11), 121 (25), 120 (18), 119 (44), 111 (18), 107 (28), 105 (30), 93 (21), 91 (100), 79 (87), 77 (38)	Tp e Tca
11	*cis*-*Z*-Epoxybisabolene *trans*-*Z*-Epoxy-bisabolene	 	*cis*-*Z*-EBA: 220 (M^+, 2), 164 (2), 133(20), 131 (8), 125 (25), 121 (18), 109 (72), 107 (41), 93 (81), 81 (55), 67 (70), 55 (43), 43 (100) *trans Z*-EBA: 220 (M^+, 2), 164 (15), 131 (35), 121 (30), 109 (95), 107 (86), 93 (100), 82 (67), 67 (76), 55 (42), 43 (94)	*Chinavia* sp. *Nezara* sp.
12	(1*R*)-Zingiberenol, (1*S*)-Zingiberenol	 , 	222(M^+), 187 207, 204, 189, 179, 161, 151, 137, 123, 119, 109, 95, 77, 69, 55	Tl

Ph did not have the absolute configuration of sesquiphellandre determined (Leal *et al*. 1998).

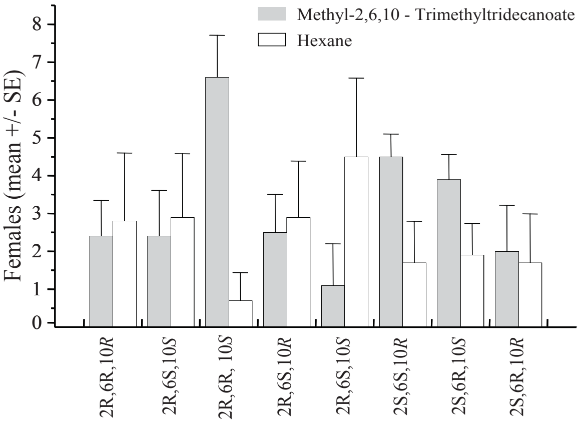


Fig. 3. Mean number of female *E. heros* responding to the eight stereoisomers of methyl 2,6,10-trimethyltridecanoate.

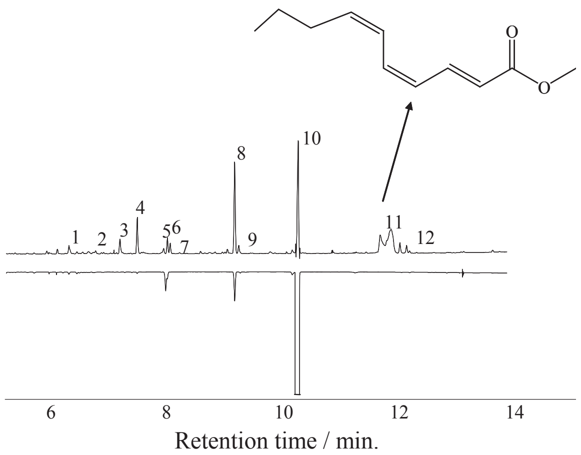


Fig. 4. Gas chromatograms of volatiles collected from live male (top) and female (bottom, inverted) *T. perditor*: 1, α-pinene; 2, β-pinene;3, α-ocimene; 4, (E)-2-octenal; 5, (E)-2-octen-1-ol; 6, undecane; 7, nonanal; 8, dodecane; 9, (E)-2-decenal; 10, tridecane; 11, distorted peak from thermal decomposition of methyl (2E,4Z,6Z)-decatrienoate; 12, pentadecane.

2*E*,4*Z*,6*Z*-decatrienoate. Bioassays in the laboratory showed that 4 µg of the methyl 2*E*,4*Z*,6*Z*-decatrienoate was attractive to females of *T. perditor* (Moraes *et al*. 2005a). Traps baited with 1 mg (*E*2,*Z*4,*Z*6)-10: COOMe, protected and non-protected from sunlight, were more efficient in capturing *T. perditor* than traps baited with the isomer (*E*2,*E*4,*Z*6)-10: COOMe, the pheromone of a Neartic pentatomid species, *Plautia stali* (Scott), and control traps. Additionally, traps baited with the sex pheromone captured a significantly higher number of insects than the sampling cloth technique, as well as some tachinid parasitoids of stink bugs. Results from field tests showed that the (*E*2,*Z*4,*Z*6)-10: COOMe has a great potential in monitoring populations of *T. perditor*, and this technique is more easily performed than the traditional cloth sampling (Laumann *et al*., unpublished).

Piezodorus guildinii

The Neotropical redbanded stink bug, *P. guildinii* is one species of the complex of stink bugs that are serious pests of soybean in Central and South America, especially in Brazil (Panizzi & Rossi 1991). The first pheromone study of the genus *Piezodorus* was carried out by Leal *et al*. (1998), working with *P. hybneri,* a species distributed in Thailand, Korea, Taiwan, Japan and some regions of India and Australia (Shepard *et al*. 1983, Singh *et al*. 1989), which reportedly produces three compounds: β-sesquiphellandrene, (*R*)-15-hexadecanolide and methyl (*Z)*-8-hexadecenoate (Table 2, compounds 4, 5 and 7) in the proportion of 10: 4: 1. Laboratory bioassays revealed that this blend is an aggregation pheromone, attracting both sexes.

Recently, Borges *et al*. (2007a) identified a new compound specific to males when gas chromatograms of extracts of volatiles collected from sexually mature virgin males and females were compared. This compound was not found in aerations of sexually immature females or males, and its retention time and mass spectra matched the sesquiterpene β-sesquiphellandrene. This identification was confirmed using an authentic standard, and the absolute configuration was determined as (*R*)-β-sesquiphellandrene (Borges *et al*. 2007a). The quantitative analysis of 10 extracts obtained from volatile collection of 20 males resulted in a mean liberation of sexual pheromone of approximately 40 ng/24h. The bioassays showed that females of *P. guildinii* responded preferentially to (7*R*)-β-sesquiphellandrene, but the authors did not test the attraction power of the compound in the field, and the females also showed response to isomer (7S)-β-sesquiphellandrene.

Tibraca limbativentris

The Brazilian rice stalk stink bug *T. limbativentris* has three sesquiterpenoid isomers that were identified as compounds specific to males, called 1´*S* zingiberenol, with a chemical structure of (1*RS*, 4*RS*, 1´*S*)-4-(1´,5´-dimethylhex-4-enyl)-1-methylcyclohex-2-en-1-ol (Borges *et al*. 2006) (Table 2, compound 12). Because zingiberenol has three chiral centers (positions 1´,1 and 4), there are eight isomers (four enantiomeric pairs of diastereomers). The non-selective synthesis produced two groups of isomers: zingiberenol I, containing the four isomers of (1*RS*. 4*RS*, 1´*R*)-4-(1´,5´-dimethylhex-4-enyl)-1-methylcyclohex-2-en-1-ol; and zingiberenol II, containing the four isomers of (1*RS*. 4*RS*, 1´*S*)-4-(1´,5´-dimethylhex-4-enyl)-1-methylcyclohex-2-en-1-ol). Females of *T. limbativentris* responded to zingiberenol II better than to zingibrenol I, suggesting that males produce the isomer 1´*S* zingiberenol (1*RS*. 4*RS*, 1´*S*)-4-(1´,5´-dimethylhex-4-enyl)-1-methylcyclohex-2-en-1-ol) (Borges *et al*. 2006).

Conclusions and Future Directions

Within the Heteroptera there are about 38,000 described species, and an estimated minimum of 25,000 undescribed species (Panizzi *et al*. 2000). Of the described species less than 1% have some type of semiochemical identified, usually only the defensive compounds (Table 3).

From the small sample of species presented here, it is clear that a fascinating diversity and complexity of chemical compounds are produced by these insects. The specificity provided by the stereochemistry of the sex attractant pheromones indicate a complex evolutionary scenario for chemical communication and behavioral ecology of pentatomid bugs and has biochemical implications. The enzymes responsible for biosynthesis of these compounds must be stereospecific, and the identification of the enzymes involved will provide information on stereo-specific catalysis, and may suggest precursors for development of stereo-specific methods of synthesis.

The defensive compounds produced by these insects are not as chemically interesting as the sex pheromones, but their biological roles are proving very important. Borges *et al*. (1993) showed that (*E*)-2-decenal and (*E*)-2-hexenal, both present in the allomones of several Brazilian pentatomids, have anti-microbial properties, inhibiting the germination and development of the entomopathogen *M. anisopliae*. Thus the presence or absence of these compounds could be very important in mediating the success of biological control efforts using pathogenic fungi. In aerations of *T. limbativentris* these components were not detected (Borges *et al*. 2006), nor were they found in preliminary MTG extracts (M.C.B. Moraes, unpublished data). Interestingly, in the field this species appears to suffer higher infection by *M. anisopliae* than *E. heros, N. viridula* or *P. guildinii* (Sosa-Gómez & Moscardi 1998, Da Silva Martins *et al*. 2004), species in which these compounds have been detected (Zarbin *et al*. 2000, Fucarino *et al*. 2004, Pareja *et al*. 2007). In future studies it could be interesting to look at how variation in MTG compounds affects mortality by fungi, both within and between species.

Defensive compounds also mediate interactions of the stink bugs with many different natural enemies. For certain species it has been shown that the egg parasitoids *Trissolcus basalis* Wollaston and *Telenomus podisi* Ashmead use compounds present in defensive blends to orient towards their hosts (Borges &Aldrich 1994; Borges *et al*. 1997, 2003; Conti *et al*. 2004). Furthermore, *T. basalis* can distinguish between male and female blends of *Nezara viridula* (Colazza *et al*. 1999) and this could be influenced by the different composition of stink bugs MTG of males and females (Pareja *et al*. 2007). Additionally, some defensive compounds such as aldehydes can attract spiders and kelptoparasitic flies (Milichiidae and Chloropidae) (Aldrich & Barros 1995) and (*E*)-2-decenal isolated from MTG of *N. viridula*, stimulates oviposition in the egg parasitoid, *T. basalis* (Mattiacci *et al*. 1993).

The diversity of pentatomid semiochemicals makes them an ideal system for studying the evolution of insect defence and of sex pheromone specificity. Blends of defensive compounds are species-specific, even though many of the compounds are shared between species (Pareja *et al*. 2007). Males and females also differ in their blends, and differ from nymphs. Nymphs are commonly gregarious, and this could be correlated with some of the chemical differences. Males are likely to be more exposed to natural enemies than females, since they produce the sex attractant pheromone and vibratory signals to attract the female (Moraes *et al*. 2005b) that can be exploited by natural enemies (Laumann *et al*. 2007b). Future work could determine whether this difference in exposure has had an effect on the defensive blends of males, and in resulting alarm behaviour. The pattern of differentiation of sex pheromones can also provide information on the ecological conditions that generate pheromone specificity. In particular the group of genera comprising *Nezara* and *Chinavia* could provide interesting insights into pheromone specificity, since their pheromones consist of isomers of *Z*-EBA in different ratios. For example *C. ubica* has a similar blend to the North American *Chinavia* species, while *C.*

Table 3. Number of species from different genera of Pentatomidae studied whose semiochemicals have been investigated. BR indicates the Brazilian species studied, “*” indicate the species which their sex pheromones were studied and laboratory bioassays or field tests were carried out to test the sex pheromone. “^{1}” new classification of *Acrosternum* from the regions cited in this text is referred as *Chinavia*.

Genus	Species studied	References
Aelia	*A. fieberi* (Scott)	Tsuyuki *et al*. 1965
Apodiphus	*A. amygdali* (Germar)	Everton *et al*. 1974
Aspongopus	*Aspongopus* sp.	Prestwich 1976
Banasa	*B. calva* (Say), *B. dimidiata* (Say)	Aldrich *et al*. 2007
Biprorulus	*B. bibax* (Breddin)	MacLeod *et al*. 1975; Oliver *et al*. 1992; James *et al*. 1996, 1994
Brochymena	*B. quadripustulata* (F.), *Brochymena* sp.	Blum 1961, Leskey & Hogmire 2005
Caura	*C. rufiventris* (Germar)	Prestwich 1976
Chlorochroa	*C. ligata* (Say)*, *C. sayi* (Stål)*, *C. uhleri* (Stål)*	Ho & Millar 2001a, b, c
Chinavia	*C. ubica* (Rolston) ^{BR*}, *C. impicitcornis* (Stål)^{BR*}, *C. aseada* (Rolston) ^{BR*1}, *C. hilais* (Say)^{*1}, *C. marginata* (Palesot & Bearvois)^{*1}, *C. pennsylvanica* (DeGeer)^{*1}	Aldrich *et al*. 1993b, McBrien *et al*. 2001

Continue

Table 3. Continuation.

Genus	Species studied	References
Coridius	*C. janus* (F.)	Gunawardena & Herath 1991
Cosmopepla	*C. bimaculata* (Thomas)	Krall *et al*. 1999
Cyclopelta	*C. siccifolia* (Westwood)	Sagar *et al*. 2000
Delegorguella	*D. lautus* (Stål)	Prestwich 1976
Dichelops	*D. melachantus* (Dallas)[BR]	Marques *et al*. 2007, Pareja *et al*. 2007
Dolycoris	*D. baccarum* (L.)	Schildknecht 1964
Edessa	*E. rufomarginata* (DeGeer)	Howard & Wiemer 1983, Howard 1987
Eocanthecona	*E. furcellata* (Wolff)	Ho *et al*. 2003
Erthesina	*E. fullo* (Thunberg)	Kou *et al*. 1989
Eurogaster	*Eurogaster* sp.	Schildknecht 1964
Eurydema	*E. oleraceum* (L.)[*], *E. pulchrum* (Westwood), *E. rugosa* (Motschulsky), *E. ventrale* (Kolenati)[*]	Ishiwatari 1974, 1976; Aldrich *et al*. 1995a, 1996b
Euschistus	*E. conspersus* (Uhler)[*], *E.heros* (F.) [BR*], *E. ictericus* (L.), *E. obscurus*, (Palisot & Beavois), *E. politus* (Uhler), *E. servus* (Say), *E. tristigmus* (Say)	Aldrich *et al* 1991,1994, 1995, 2007; Borges *et al*. 1994, Krupke 2001, Leskey, 2005
Eysarcoris	*E. parvus* (Uhler)[*]	Men *et al*. 1999
Graphosoma	*G. rubrolineatum* (Westwood)	Tsuyuki *et al*. 1965
Halyomorpha	*H. halys* (Stål)	Lee *et al*. 2002, Khrimian 2005, Aldrich *et al*. 2007
Lincus	*L. malevolus* (Roleston), *L. spurcus* (Roleston)	Nagnan *et al*. 1994
Mecidea	*M. major* (Sailer), *M. minor* (Ruckes)	Keaster *et al*. 1996
Murgantia	*M. histrionica* (Hahn) [*]	Aldrich *et al*. 1996
Nezara	*N. antennata* (Scott)[*], *N. viridula* (L.) [BR*], *N. viridula smaragdula* (F.)	Waterhouse *et al*. 1961, Tsuyuki *et al*. 1965, Baker *et al*, 1987, Lockwood & Story 1987, Aldrich *et al*. 1989, Brezot *et al*. 1994, Borges 1995
Oebalus	*O. pugnax* (F.)	Blum *et al*. 1960, Keaster *et al*. 1996
Oechalia	*O. schellenbergii* (Guérin-Meneville)[*]	Aldrich *et al*. 1996a
Oplomus	*O. severus* (Breddin)[*]	Aldrich *et al*. 1986a
Palomena	*P. viridissima* (Poda)	Schildknecht *et al*. 1964
Perillus	*P. bioculatus* (F.)	Aldrich *et al*. 1986a; Weissbecker *et al*. 1999, 2000
Piezodorus	*P. guildinii* (Westwood) [BR*], *P. hybneri* (Gmelin)[*], *P. teretipes* (Stål)	Gilchrist *et al*. 1966; Leal *et al*. 1998; Borges *et al*. 1999, 2007a; Zarbin *et al*. 2000; Endo *et al*. 2003; Endo *et al*, 2006, Huh *et al*. 2006
Plautia	*P. stali* (Scott)	Sugie *et al*. 1996
Podisus	*P. acutissimus* (Stål), *P. fretus* (Olsen), *P. maculiventris* (Say), *P. nigrispinus* (Dallas)	Aldrich 1978, 1984a, b; Aldrich *et al*. 1986b; Keaster *et al*. 1996; Sant' Ana & Dickens 1998
Poecilometis	*P. strigatus* (Westwood)	Waterhouse *et al*. 1961
Rhoecocoris	*R.. sulciventris* (Stål)	Park & Sutherland 1961, Waterhouse *et al*. 1961, MacLeod *et al*. 1975
Scotinophara	*S. lurida* (Burmeister)	Tsuyuki *et al*. 1965
Stiretrus	*S. anchorago* (F.)	Aldrich *et al*. 1986a, Kochansky *et al*. 1989
Thyanta	*T. accera* (McAtee)[*], *T. custator accera* (McAtee)[*], *T. pallidovirens* (Stål)[*], *T. perditor* (F.) [BR]	Keaster *et al*. 1996, Millar 1997, McBrien *et al*. 2002, Moraes *et al*. 2005a, Aldrich *et al*. 2007
Tibraca	*T. limbativentris* (Stål) [BR*]	Borges *et al*. 2006
Veterna	*V. patula* (Distant)	Prestwich 1976
Vitellus	*V. insularis* (Stål)	Smith 1974

impicticornis shows a complete absence of the *cis* isomer. Understanding the mechanisms generating these differences is likely to be a rich area of evolutionary research, perhaps leading to new hypothesis on Pentatomidae phylogeny.

Two major difficulties in the study of insect semiochemicals is the unequivocal determination of behavioural activity, and the development of simple, low-cost synthetic procedures that make the use of semiochemicals economically viable and practical. Purification and structural elucidation are no longer the limiting factors with the improvement of analytical equipment. However it must be noted that insects can be much more sensitive to chemical substances than our analytical equipment. This is most clearly seen in the study of insect response to plant volatiles, where insects can detect changes that are invisible to us, even with the most advanced techniques (van Dam & Poppy 2008).

Determination of biological activity requires rigorous testing of different behavioural circumstances to understand whether the chemical compound of interest is mediating the interaction being studied. Despite new methodologies to monitor behaviour (i.e. computational automatized systems of capture and analyses of insect behaviour), simple bioassays are often critical to highlight the importance of semiochemical. In addition, it is important to consider how feeding conditions can affect the resulting pheromone blend and activity (Moraes *et al*. 2008b). Determination of biological activity is complicated by the difficulty of rearing many species in the laboratory, and the resulting changes in behaviour and general biology, even under strict rearing conditions. We can never be certain that insects reared in the laboratory will behave in the same manner as the wild insects. However, use of field-collected insects is also not ideal, since we do not know each individual´s semiochemical history, plus insect behaviour studies in the field are hard to conduct. Thus, by necessity, the only solution is to use a combination of chemical, laboratory and field studies for correct determination of biological activity. This highlights the importance of the interaction between biologists, chemists and biochemists in the study of chemical ecology.

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