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Review

Scent gland chemistry and chemosystematics in harvestmen

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Summary. This review focuses on advances in opilionid scent gland research between the years 2005 and 2012, along with an evaluation of all currently available chemical information from different groups of Opiliones from a phylogenetic perspective. To date, examples of scent gland secretions from all four suborders of Opiliones have been published, including: 4 species of Cyphophthalmi, 12 species of Eupnoi, 1 species of Dyspnoi, 4 species of insidiatorean Laniatores, and 42 species of grassatorean Laniatores. In addition, preliminary data are given for another 20 species (mainly Insidiatores and Eupnoi). From all species, more than 70 scent gland-derived components from different chemical classes have so far been identified. Secretion profiles appear to be highly specific, and well-suited for both the characterization of phyletic groups as well as for the distinction of closely related species. Secretions may contain more than 20 components (*e.g.* Cyphopththalmi), or consist of only a few, or even a single compound (*e.g.* some Insidiatores and early-derivative Grassatores). With respect to gross systematics, the suborders of Opiliones can be chemically characterized as follows: naphthoquinones and acyclic compounds (mainly ketones) appear to be widespread in the secretions of a proposed clade of Cyphophthalmi + Palpatores (Eupnoi, Dyspnoi). For this clade, naphthoquinones are considered synapomorphic, since they have not been detected in the Laniatores. Although the phyletic status of acyclic compounds in cyphophthalmid and palpatorean secretions remains unclear, these acycles may also have a common origin. A sub-class of these acycles, the so-called "sclerosomatid compounds", may represent a chemical synapomorphy of the monophyletic Palpatores. Deep chemical divergence is evident in secretions from the Laniatores, along with a split of laniatorean secretions into at least two chemically distinct groups: travunioid Insidiatores mainly produce an array of nitrogen-containing compounds, whereas phenol- and benzoquinone-rich secretions are characteristic of grassatorean Laniatores. However, a link between the chemistry of laniatoreans and the secretions of Cyphophthalmi-Palpatores is still missing.

Keywords: chemical ecology, Cyphophthalmi, Eupnoi, Dyspnoi, Laniatores.

Introduction

A characteristic feature of harvestmen (Opiliones) is the presence of a pair of large exocrine prosomal glands that are known as scent, repugnatorial, defensive or simply stink-glands in literature (*e.g.* Martens 1978). When disturbed, many opilionids discharge odorous secretions from these glands, indicating a role in chemical defense. However, these glands may serve additional functions, such as antimicrobial protection or pheromonal communication, in certain taxa (Holmberg 1970, 1986; Machado et al. 2002; Schaider and Raspotnig 2009). Since ever, the chemistry of opilionid scent gland secretions has posed a challenge to biologists and chemists, representing a source of unique (and still largely undiscovered) natural compounds, as well as an emerging pool of novel characters for opilionid taxonomy and phylogeny.

Beginning with pioneering studies in the 1950s (Estable et al. 1955), the chemistry of opilionid scent glands has consistently attracted the attention of chemical ecologists. During a particularly intense period of studies in the 1970s and 1980s, the keystones of opilionid scent gland chemistry were established (*e.g.* Blum and Edgar 1971; Eisner et al. 1971), revealing a clear chemical dichotomy between the acyclic-

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compound-rich secretions of the Palpatores and the phenolic and benzoquinonic exudates of the Laniatores. In addition, the specificity of secretion patterns was noticed by authors such as Roach et al. (1980) and Duffield et al. (1981), who recognized the potential of scent gland-derived chemical characters for investigations of opilionid phylogeny.

Around the year 2000, several independent groups of arachnologists from different countries began to revive the issue of opilionid scent gland research, sparking renewed efforts towards the development of a comprehensive understanding of opilionid scent gland chemistry. In particular, a group of South American researchers made significant contributions to scent gland research in grassatorean Laniatores (*e.g.* Gnaspini and Cavalheiro 1998; Hara et al. 2005; Machado and Pomini 2008; Pomini et al. 2010); while a second group from North America focused on basal groups of Laniatores (Shear et al. 2010a, 2010b) and Cyphophthalmi (Jones et al. 2009). A third group, from Europe, is involved in the general elucidation of the chemosystematic puzzle of Opiliones (*e.g.* Raspotnig et al. 2005, 2010, 2011, 2012). The recent advances made by these groups are considerable: a series of papers dealing with opilionid scent glands has been published since the year 2000, with at least 12 of these focusing on scent gland chemistry. Since the last review on this topic was published in the year 2007, the number of chemically investigated species has increased from 26 (as listed in Gnaspini and Hara 2007) to 85 (as listed in the present review). More importantly, information on long-standing chemically enigmatic groups such as the Cyphophthalmi, Dyspnoi and Insidiatores has been added, fundamentally contributing to a new understanding of the evolutionary traits leading to the extant chemical diversity in the scent gland secretions of opilionids in general. Thus, this review is intended to serve as an update of recent scent gland research and chemosystematics in the Opiliones.

Scent gland chemistry in the Opiliones: current state of knowledge

Data bias

Chemical information concerning opilionid scent gland secretions still appears to be highly biased: 1) in favor of certain higher taxa (*e.g.* the gonyleptoid

Table 1. The scattered knowledge on scent gland chemistry in the Opiliones.

Suborder & family	Species	References
<u>Laniatores – Insidiatores:</u>		
Travunioidea – "North American triaenonychids"*:	*Sclerobunus robustus*	Ekpa et al. 1984
	Sclerobunus nondimorphicus	Shear (personal communication)
	Metanonychus sp.	Shear (personal communication)
Travunioidea – Cladonychiidae:	*Holoscotolemon lessiniense*	Raspotnig et al. 2011
	Holoscotolemon jaqueti	Raspotnig et al. 2011
	Holoscotolemon oreophilum	Raspotnig et al. 2011
	Erebomaster flavescens	Shear (personal communication)
	Theromaster brunnea	Shear (personal communication)
	Cryptomaster levithian	Shear (personal communication)
	Speleomaster texi	Shear (personal communication)
Travunioidea – Briggsidae:	*Briggsus* sp.	Shear (personal communication)
Travunioidea – Travuniidae:	*Speleonychus sengeri*	Shear (personal communication)
	Travunia sp.	Raspotnig and Karaman (unpublished)
	Peltonychia clavigera	Raspotnig and Karaman (unpublished)
Travunioidea – incertae sedis:	*Trojanella serbica*	Raspotnig and Karaman (unpublished)

Table 1 (continued)

Suborder & family	Species	References
<u>Laniatores – Grassatores:</u>		
Phalangodidae:	*Bishopella lacinosa*	Shear et al. 2010a
	Texella bifurcata	Shear et al. 2010a
Stygnopsidae:	*Chinquipellobunus madlae*	Shear et al. 2010b
	Hoplobunus mexicanus	Pomini et al. 2010
Stygnommatidae:	*Stygnomma spinifera*	Duffield et al. 1981
Manaosbiidae:	*Zygopachylus albomarginis*	Eisner et al. 1977, Roach et al. 1980
Cosmetidae:	*Cynorta astora*	Eisner et al. 1977
	Eucynortula (2 spp.)	Roach et al. 1980
	Paecilaema eutypa	Eisner et al. 1977
	Paecilaemana quadripunctata	Eisner et al. 1977
	Vonones sayi	Eisner et al. 1971
Gonyleptidae:	*Acanthopachylus aculeatus*	Estable et al. 1955, Eisner et al. 2004
(species listed	*Acutisoma molle*	Hara et al. 2005
in alphabetical order)	*Ampheres leucopheus*	Hara et al. 2005
	Camarana flavipalpi	Machado and Pomini 2008
	Cobania picea	Rocha et al. 2011
	Daguerreia inermis	Hara et al. 2005
	Discocyrtus (2 spp.)	Hara et al. 2005
	Eusarcus sp.	Hara et al. 2005
	Goniosoma (3 spp.)	Gnaspini and Cavalheiro 1998, Hara et al. 2005
	Gonyleptes curvicornis	Hara et al. 2005
	Hypophyllonomus longipes	Hara et al. 2005
	Iguapeia melanocephala	Hara et al. 2005
	Iporangaia pustulosa	Hara et al. 2005, Rocha et al. 2011
	Mischonyx cuspidatus	Hara et al. 2005
	Parampheres sp.	Hara et al. 2005
	Neosadocus maximus	Hara et al. 2005, Rocha et al. 2011
	Nesopachylus monoceros	Hara et al. 2005
	Pachyloidellus goliath	Acosta et al. 1993
	Pachylus paessleri	Föttinger et al. 2010
	Proggonyleptoidellus striatus	Hara et al. 2005
	Promitobates ornatus	Hara et al. 2005
	Pseudopachylus longipes	Hara et al. 2005
	Roeweria virescens	Rocha et al. 2011
	Serracutisoma proximum	Rocha et al. 2011
	Sodreana sodreana	Hara et al. 2005
	Spherobunus pulcher	Hara et al. 2005
	Zortalia inscripta	Hara et al. 2005

Table 1 (continued)

Suborder & family	Species	References
<u>Cyphophthalmi:</u>		
Sironidae:	*Cyphophthalmus duricorius*	Raspotnig et al. 2005
	Siro exilis	Raspotnig et al. 2005
Stylocellidae:	undescribed stylocellid	Jones et al. 2009
Pettalidae:	*Austropucellia forsteri*	Raspotnig et al. 2012
<u>Palpatores – Eupnoi:</u>		
Phalangiidae:	*Phalangium opilio*	Wiemer et al. 1978
	Rilaena triangularis	Raspotnig (unpublished)
	Megabunus (5 spp.)	Raspotnig (unpublished)
	Platybunus (2 spp.)	Raspotnig (unpublished)
Sclerosomatidae:	*Leiobunum* (10 spp.)	Blum and Edgar 1971, Meinwald et al. 1971
	Hadrobunus maculosus	Jones et al. 1976, 1977, Ekpa et al. 1985
		Jones et al. 1976
	Amilenus aurantiacus	Raspotnig (unpublished)
	Gyas annulatus	Raspotnig (unpublished)
<u>Palpatores – Dyspnoi:</u>		
Nemastomatidae:	*Paranemastoma quadripunctatum*	Raspotnig et al. 2010
	Nemastoma bidentatum-complex	Raspotnig (unpublished)

*these „North American triaenonychids“ have been transferred to Travunioidea, see e.g. Derkarabetian et al. (2010).

Grassatores); or 2) with respect to very small, restricted taxonomic units within a higher taxon. The latter situation is generally true for the Palpatores (Eupnoi + Dyspnoi) and for the Cyphophthalmi, and also to a lesser extent for the insidiatorean Laniatores. For example, all published chemical information on Dyspnoi and phalangiid Eupnoi relies on single species investigations only (Wiemer et al. 1978; Raspotnig et al. 2010), while chemical data on the sclerosomatid Eupnoi was inferred from 11 species of two leiobunine genera (*Leiobunum*, *Hadrobunus*; summary in Ekpa et al. 1985). Regarding the Cyphophthalmi, the scent gland chemistry of only four species has been reported (Raspotnig et al. 2005, 2012; Jones et al. 2009). Similarly, until 2010, our knowledge of insidiatorean chemistry was restricted to a single species, *Sclerobunus robustus* (Ekpa et al. 1984); although this number has meanwhile significantly increased (Raspotnig et al. 2011; Shear, personal communication; see Table 1). However, many families from many suborders remain unstudied. The most conspicuous gap in our understanding of higher-level taxa chemistry is still due to the chemically enigmatic insidiatorean Triaenonychoidea: the first data collected for these are tentative (Shear, personal communication), and therefore not included in the present review.

Current knowledge of scent gland chemistry can be summarized as follows: the secretions of 85 opilionid species have been analyzed to date (Table 1), and chemical data for at least one example of each of the four recognized opilionid suborders (Cyphophthalmi, Eupnoi, Dyspnoi, Laniatores) is available. This situation, while not entirely satisfactory, tentatively enables drawing a first general picture of opilionid scent gland chemistry. From all of these species, more than 70 compounds have been elucidated (Table 2), while a significant number of additional compounds remains to be identified (see for example Hara et al. 2005).

Scent gland derived components (or in some cases, components of putative scent gland orgin) may be roughly grouped into the following chemical classes: naphthoquinones, anthraquinones, phenols, benzoquinones, pyrans, nitrogen-containing compounds, terpenes, “gonyleptid” ketones (mainly vinyl ketones), “sclerosomatid compounds” (a group of acyclic compounds – mainly ethyl ketones – first identified in sclerosomatid Eupnoi; see below), and methyl ketones (Table 2).

Table 2. Scent gland secretion components in Opiliones.

Chemical class	References	Components*	Taxonomic distribution*
naphthoquinones & related compounds:	Wiemer et al. 1978; Raspotnig et al. 2005, 2010, 2012; Jones et al. 2009	1,4-naphthoquinone 6-methyl-1,4-naphthoquinone	Cyphophthalmi, phalangiid Eupnoi, many nemastomatid Dyspnoi
	Raspotnig et al. 2010	2-methoxy-naphthoquinone 2-methoxy-6-methyl-naphthoquinone 1,4-naphthalenediol 6-methyl-1,4-naphthalenediol	certain nemastomatid Dyspnoi (e.g. *Paranemastoma*)
	Raspotnig et al. 2005, 2012	4-chloro-1,2-naphthoquinone 4-chloro-6-methyl-1,2-naphthoquinone	Cyphophthalmi
anthraquinones:	Raspotnig et al. 2010	2-methyl-9,10-anthraquinone dimethyl-9,10-anthraquinone	certain nemastomatid Dyspnoi (e.g. *Paranemastoma*)
phenols:	Eisner et al. 1977; Roach et al. 1980; Duffield et al. 1981 Acosta et al. 1993; Hara et al. 2005; Shear et al. 2010a, 2010b; Pomini et al. 2010	2,3-dimethyl-phenol 2,5-dimetyl-phenol 2,3,4-trimethyl-phenol 2,3,5-trimethylphenol 2,3,6-trimethylphenol 2-methyl-5-ethyl-phenol 3-ethyl-5-methyl-phenol 3-methyl-5-ethyl-phenol 2,3-dimethyl-5-ethyl-phenol	some Grassatores (Phalangodidae, Stygnopsidae, Stygnommatidae, Manaosbiidae, Cosmetidae, Gonyleptidae)
	Shear (personal communication)	phenol	some American Travunioidea
benzoquinones and hydroquinones:	Eisner et al. 1977, 2004; Roach et al. 1980; Acosta et al. 1993; Gnaspini and Cavalheiro 1998; Hara et al. 2005; Föttinger et al. 2010	2,3-dimethyl-1,4-benzoquinone 2,5- dimethyl-1,4-benzoquinone 2,3,5-trimethyl-1,4-benzoquinone 2-ethyl-1,4-benzoquinone 2,3-dimethyl-5-ethyl-benzoquinone 2,3-dimethyl-hydroquinone not specified trimethyl-1,4-benzoquinone** not specified C_3H_9-1,4-benzoquinones**	some Grassatores (Manaosbiidae, Cosmetidae, Gonyleptidae)
	Raspotnig (unpublished)	benzoquinone	some Phalangiidae (Platybuninae)
pyrans:	Rocha et al. 2011	6-alkyl-3,4-dihydro-2H-pyrans	certain Gonyleptidae

Table 2 (continued)

Chemical class	References	Components*	Taxonomic distribution*
N-containing compounds:	Ekpa et al. 1984; Raspotnig et al. 2011 ; Raspotnig and Karaman (unpublished) ; Shear (personal communication)	nicotine anabaseine anabasine 3-(1-methyl-2-piperidinyl)-pyridine 2-(3-pyridinyl)-pyridine N,N-dimethylphenylethylamine N,N-dimethylisoamylamine	widespread in American and European Travunioidea
terpenes:	Ekpa et al. 1984	camphene limonene bornyl acetate bornyl propionate	certain American Travunioidea (*Sclerobunus*)
gonyleptid ketones:	Hara et al. 2005; Rocha et al. 2011	1-penten-3-one 1-hepten-3-one 4-methyl-1-hexen-3-one 4-methyl-hexan-3-one*** 5-methyl-1-hexen-3-one heptan-3-one	certain Gonyleptidae (Gonyleptinae, Hernandariinae, Sodreaninae, Progonyleptoidellinae, Caelopyginae)
sclerosomatid compounds:	Blum and Edgar 1971; Meinwald et al. 1971; Jones et al. 1976, 1977; Ekpa et al. 1985	4-methyl-hexan-3-one*** 4-methyl-4-hexen-3-one 4-methyl-3-heptan-3-one 4-methyl-4-hepten-3-one 4,6-dimethyl-6-octen-3-one 4,6-dimethyl-6-nonen-3-one 4-methyl-hexan-3-ol 4-methyl-heptan-3-ol 4-methyl-4-hepten-3-ol 2,4-dimethyl-2,4-hexadien-1-ol 2,4-dimethyl-2,4-heptadien-1-ol 2,4-dimethyl-2,4-hexadienal	some sclerosomatid Eupnoi (American Leiobuninae)
methyl ketones and related compounds	Raspotnig et al. 2005, 2012; Jones et al. 2009	undecan-2-one dodecan-2-one (2 isomers) tridecan-2-one (2 isomers) 6-tridecen-2-one 7-tridecen-2-one tetradecan-2-one (4 isomers) tetradecen-2-one (2 isomers) pentadecan-2-one pentadecen-2-one pentadecadien-2-one pentadecatrien-2-one acetophenone	Cyphophthalmi
miscellaneous compounds:	Shear (personal communication)	mellein benzothiazol salicyl alcohol	some American Travunioidea

* the compounds listed represent a pool of compounds that may occur in representatives of the given taxonomic units, but in specific patterns. **compounds are not assigned to a specific isomer; *** shared by Gonyleptidae and Eupnoi as a result of convergent evolution.

Scent gland secretions in Cyphophthalmi

Although scent glands are extremely well developed in the Cyphophthalmi, their secretions remained chemically enigmatic until relatively recently. In 2005, Raspotnig et al. (2005) analyzed the secretions of two sironid species from different genera, *Cyphophthalmus duricorius* from Europe and *Siro exilis* from Eastern North America. Both species showed multi-component secretion patterns, each consisting of more than 20 compounds. All of these compounds belong to the naphthoquinone and methyl ketone chemical classes (Table 2). Moreover, although patterns for both species turned out to be similar, they were still distinguishable by the relative abundance of chemical components. Notably, the naphthoquinone-fraction in these sironids included two chloro-naphthoquinones, which are so far unique in arthropod exocrinology.

There is growing evidence that cyphophthalmid secretions generally rely on naphthoquinone- and methyl ketone-rich chemistry. Initial data from an undescribed South East Asian stylocellid indicate a similar composition, although with a somewhat reduced naphthoquinone-fraction and a lack of chloro-naphthoquinones (Jones et al. 2009). There have been speculations that chloro-naphthoquinones might be characteristic for Sironidae only (Jones et al. 2009), but preliminary data on other Stylocellidae and initial data on Pettalidae contradict this view (Raspotnig et al. 2012). Despite the expected presence of a common overall chemistry in cyphophthalmids, there is nevertheless evidence for high chemical specificity on the species-level: for instance, a preliminary study on representatives from the genus *Cyphophthalmus* from the Balkans indicates that even closely-related species express very specific patterns, which appear to be well-suited to delineate morphologically similar species, and which could serve as novel characters for integrative taxonomy.

Scent gland secretions in the Palpatores

Eupnoi

To date, the secretions from 10 species of American *Leiobunum* and one species of *Hadrobunus* (all leiobunine Sclerosomatidae) have been analyzed (summary in Ekpa et al. 1985). The chemistry of these secretions comprises 12 characteristic acyclic compounds, mainly methyl-branched ethyl ketones, along with their corresponding alcohols and one aldehyde (Table 2). I refer to these here as "sclerosomatid compounds". Unfortunately, because of the strong data bias, it is currently not possible to draw conclusions on the characteristic chemistry of all Sclerosomatidae. However, according to preliminary investigations on further sclerosomatid taxa, "sclerosomatid compounds" may be more widespread, if not common, among the Leiobuninae and Sclerobuninae (Raspotnig, unpublished). Still, other classes of components may be expected: for instance, chemically distinct, probably aromatic compounds are present in the secretions of *Nelima* (Leiobuninae), although this data is preliminary and awaits confirmation (Raspotnig, unpublished). No published information is currently available for the sclerosomatid subfamilies Gagrellinae, Gyiinae and for the groups *incertae sedis* (*Metopilio*-group, *Dicranopalpus*-group). Interestingly, for *Gyas* spp. (Gyinae), a scenting phenomenon appears to be significant, and the emission of an awful smelling (and chemically unknown) secretion has been reported early (Stipperger 1928; also see below).

A major chemical dichotomy may be present between the scent gland secretions of sclerosomatid and phalangiid Eupnoi: although data on the scent gland chemistry of only one species of Phalangiidae (*Phalangium opilio*) has been published to date (Wiemer et al. 1978), the naphthoquinones detected in this study are widespread among phalangiid subfamilies, at least in Phalangiinae and Oligolophinae (Raspotnig, unpublished). There is, however, evidence for several further chemically distinct groups among the Phalangiidae: at least the Central European Platybuninae such as *Rilaena triangularis*, the five alpine species of *Megabunus (M. lesserti, M. rhinoceros, M. armatus, M. vignai, and M. bergomas)* as well as *Platybunus*, appear to produce hardly-soluble benzoquinonic secretions (so far considered characteristic of higher Laniatores only!). Also some eupnoans *incertae sedis* such as *Amilenus* and *Gyas* (traditionally classed within Sclerosomatidae, see above) fall into this benzoquinone-producing lineage. Interestingly, a recent molecular study supports the classification of *Gyas* with Phalangiidae rather than with Sclerosomatidae (Hedin et al. 2012). These eupnoan benzoquinones are considered having evolved independently from benzoquinones in laniatorean secretions. Since these results on benzoquinones in eupnoans are preliminary (Raspotnig, unpublished), they are not included in the chemosystematic considerations below. Chemical data is missing for all other eupnoan families, such as Caddidae, Monoscutidae, Neopilionidae and Protolophidae. In this respect, it may be interesting to note that not a single investigation on the secretions of Eupnoi has been published within the last 25 years (Ekpa et al. 1985).

Dyspnoi

The Dyspnoi show many unusual, possibly highly-derivative scent gland features such as 1) a general reluctance to discharge secretions, 2) a tendency to hide ozopores or even cover them by cuticular structures, and 3) a tendency to produce viscous, poorly-soluble or even solid secretions (*e.g.* Lopez et al. 1980; Juberthie et al. 1991; Schaider and Raspotnig 2009; Schaider et al. 2011). Production of solid secretions is a unique phenomenon among arthropods, which has possibly evolved twice in Dyspnoi: to date, solid crystals in scent gland reservoirs of certain Ischyropsalidoidea, and solid secretion-boli in Trogulidae have been reported (Juberthie et al. 1991; Schaider and Raspotnig 2009). However, it is still unclear how such secretions are released from a solid matrix: the speculative hypothesis of sublimation and subsequent gaseous exhalation from ozopores needs confirmation (Juberthie et al. 1991). A second "eco-type" of scent glands in Dyspnoi may be characteristic for a group of nemastomatid Dyspnoi such as *Paranemastoma*, *Histricostoma* and possibly others. With these, there is evidence for the production of a highly viscous secretion that has to be liquefied and diluted via specific mechanisms, possibly involving regurgitated enteric fluid (Schaider et al. 2011). The only paper on dyspnoid scent gland chemistry refers to this ecological group, demonstrating the presence of naphthoquinones, methoxy-naphthoquinones and anthraquinones (Raspotnig et al. 2010), all of these being solid at ambient temperatures. A third ecological type of scent glands in Dyspnoi indeed produces volatiles, and is realized in some nemastomatines, such as *Carinostoma* and *Nemastoma*, but also in some Sabaconidae (Ischyropsalidoidea). For this third type, only preliminary chemical data are available (Raspotnig, unpublished), but these volatiles under consideration may fall into the class of "sclerosomatid compounds" (including 4-methyl-heptan-3-one and 4,6-dimethyl-6-octen-3-one) or may represent compounds homologous to these ("sclerosomatid-like compounds").

Scent gland secretions in the Laniatores

In general, deep divergence between laniatorean scent gland chemistry and the secretions of Cyphophthalmi and Palpatores is noticeable, and has already been pointed out by early authors (*e.g.* Roach et al. 1980; Duffield et al. 1981): in the Grassatores, secretions comprise different sets of phenols and benzoquinones, whereas nitrogen-containing compounds prevail in the insidiatorean Travunioidea. Again, information on the scent glands of the Laniatores is biased: the Grassatores, and within these, the superfamily Gonyleptoidea, is the chemically best-studied group among all Opiliones (see Gnaspini and Hara 2007; Hara et al. 2005, and Table 1). In contrast, relatively little information is available for the Insidiatores, even though the secretions of a number of American and European Travunioidea have been the subject of recent chemical studies (Ekpa et al. 1984; Raspotnig et al. 2011; Shear, personal communication).

Grassatores

In addition to the meanwhile well-documented scent gland chemistry of more-derivative grassatoreans of the superfamily Gonyleptoidea (Table 1), investigations have recently focused on basally branching groups, such as Phalangodidae and Stygnopsidae. In these, component-poor and exclusively phenolic secretions were detected (Shear et al. 2010a, 2010b; Pomini et al. 2010). The same situation may be true for Stygnommatidae (Duffield et al. 1981). In more-derivative grassatoreans, a trend towards a predominance of benzoquinones is evident: mixtures of phenols and benzoquinones occur in the manaosbiid *Zygopachylus albomarginis* and in several cosmetids and a few gonyleptids (reviewed in Hara and Gnaspini 2007); whereas in the latter two families, many purely benzoquinonic secretions have been observed as well (*e.g.* Föttinger et al. 2010).

A general problem regarding component-identification in grassatorean secretions is the correct assignment of isomers. Several studies rely exclusively on mass spectrometric data, but the potential of this method to differentiate between isomeric compounds is limited. This is especially true for substituted phenols, which produce virtually indistinguishable mass spectra. In such cases, further specifications, e.g. the indication of retention indices, would be helpful and a general introduction of such indices into GC-MS based studies of opilionid scent gland chemistry is much appreciated. Still, in many papers, identifications are either tentative, or compounds are not assigned to a specific isomer. Such tentatively identified compounds may significantly increase the number of scent gland components given herein. Recent findings from Hara et al. (2005) and Rocha et al. (2011) have shown that even greater chemical diversity can be expected from grassatorean scent glands: in particular, a series of acyclic ketones has been tentatively identified in some representatives of Gonyleptidae, which appear to be superficially similar to sclerosomatid compounds in the Eupnoi (see below). Rocha et al. (2011) consider these synapomorphic for several gonyleptid subfamilies, such as Gonyleptinae, Hernandariinae, Sodreaninae, Progonyleptoidellinae, and Caelopyginae. Moreover, in the gonyleptids *Iporangaia pustulosa* and *Neosadocus maximus*, additional cyclic compounds such as pyrans were detected, revealing a new chapter in gonyleptoid chemistry (Rocha et al. 2011). Indeed, inspection of the mass spectra of several gonyleptid components indicated as “not identified” by Hara et al. (2005), already points to a wider distribution of pyrans.

Insidiatores

The scent gland secretions of Insidiatores of the superfamily Travunioidea contain compounds clearly distinct from other laniatorean secretions: tobacco alkaloids, e.g. nicotine and anabaseine, along with further nitrogen-containing substances, such as anabasine, 2,3’-bipyridinyl, and 3-(1-methyl-2-piperidinyl)-pyridine, were reported in the secretions of European cladonychiid harvestmen of genus *Holoscotolemon* (Raspotnig et al. 2011). At least nicotine and anabaseine appear to be widespread in travunioids and also predominate the secretions of further European genera such as *Travunia* and *Trojanella*. Consistently, nitrogen-containing compounds including nicotine, anabaseine, and N,N- dimethylphenylethylamine (as well as terpenes and a number of additional miscellaneous compounds; see Table 2) were found from North American Travunioidea (Ekpa et al. 1984; Shear, personal communication). According to Shear (personal communication), anabaseine appears to be prevalent in a group of travunioids from Eastern North America (*e.g. Erebomaster*, *Cryptomaster*); whereas the secretions of travunioids from Western North America (including *Sclerobunus, Briggsus, Speleonychus, Speleomaster, Cryptomaster* and *Metanonychus*) are dominated by N,N- dimethylphenylethylamine. There is evidence that the latter compound also occurs is some European travunioids of the genus *Peltonychia* (Raspotnig and Karaman, unpublished). At least for the American Travunioidea, a large number of additional compounds (see miscellaneous compounds in Table 2) is to be expected (Shear, personal communication). In contrast, chemical information on all Asian species is still missing.

Even more enigmatic are the scent gland secretions of the second insidiatorean superfamily, the Triaenonychoidea, for which only tentative information is available (Shear, personal communication): several New Zealand Triaenonychoidea contain so far unspecified ketones, along with sets of completely unidentified compounds, indicating chemical distinctness from travunioid secretions.

Chemosystematics

The impact of scent gland chemistry on opilionid phylogeny

The chemistry of opilionid scent gland secretions is not only a rich source of rare natural compounds, but also represents a potential pool of phylogenetically informative data: scent glands are present in all lineages of Opiliones, and are considered an important and complex synapomorphic character of this group. Presumably originating from a common chemistry in ancestral opilionids, the extant chemical heterogeneity of opilionid secretions is considered the result of evolutionary modifications during species diversification spanning several hundreds of millions of years. Thus, it seems likely that opilionid phylogeny is somehow reflected in the specific chemistry of extant groups. Along with recently compiled information (*e.g.* Shear et al. 2010a, 2010b; Föttinger et al. 2010; Raspotnig et al. 2005, 2010, 2011, 2012), scent gland chemistry clearly has emerged as a pool of phylogenetic characters independent from the traditional morphological and genetic data used to date. Such a novel set of characters seems to be of uppermost importance to further resolve the contradictory hypotheses on opilionid gross phylogeny currently debated in the literature: including the classical opilionid system stating basal Cyphophthalmi and monophyletic Palpatores (*e.g.* Shultz and Regier 2001), the Dyspno-Laniatores-hypothesis of Giribet et al. (1999, 2002), and the Cyphopalpatores-concept of Martens (*e.g.* Martens 1986; Shultz 1998).

Tracing the evolution of scent gland chemistry

One major problem regarding phylogenetic chemosystematics in opilionids is the scarce evidence for an evolutionary reading direction of chemical information, and the problematic interpretation of plesiomorphic and apomorphic states in scent gland chemistry. De facto, outgroup comparison with other arachnid orders is impossible, since prosomal scent glands are autapomorphic for Opiliones. At least with respect to a proposed lineage of Cyphophthalmi and Palpatores, the Cyphophthalmi may offer valuable clues to this problem: although the Cyphophthalmi may be apomorphic in several traits (Karaman, personal communication), most authors regard them as an early-branching group of Opiliones (*e.g.* Shultz 1998; Giribet and Kury 2007), possibly even representing the sister taxon to all other harvestmen. Cyphophthalmids are considered still primitive in many respects, and thus, they may also reflect an ancestral opilionid scent gland condition. Consistently, their scent glands display some character states that may be classified as ancestral, such as the multi-component structure of their secretions (a condition regarded to be primitive by Blum 1981), or the rich muscle equipment of their glands (a condition considered to be primitive by Juberthie 1961). Moreover, cyphophthalmids apparently display only minor modifications of a common chemistry between genera, or even families, as evidenced by comparisons of secretions of Sironidae (Raspotnig et al. 2005), Stylocellidae (Jones et al. 2009), and Pettalidae (Raspotnig et al. 2012). Thus, cyphophthalmid secretions appear to be highly conserved, and possibly still display an ancestral scent gland condition. In these terms, cyphophthalmids indeed may provide a reading direction for scent gland chemistry, at least for the possibly derivative chemistry of Eupnoi and Dyspnoi.

Naphthoquinones: synapomorphic for a clade of Cyphophthalmi and Palpatores?

The scent gland secretions of the Cyphophthalmi and Palpatores clearly rely on a homogenous overall chemistry, comprising common chemical classes such as 1) naphthoquinones *sensu latu* (see Table 2), and 2) a group of acyclic components (see the next chapter).

While naphthoquinones may characterize the secretions of all Cyphophthalmi, they appear to be dichotomically split to different palpatorean groups: while naphthoquinones were found in Dyspnoi (Raspotnig et al. 2010) and in certain phalangiid Eupnoi (Wiemer et al. 1978; see preceding paragraph), they may be missing in other palpatoreans (e.g. in eupnoan Sclerosomatidae). Although information on their occurrence in the Palpatores is based only on studies of two species (*Phalangium opilio* and *Paranemastoma quadripunctatum*), there is evidence for a widespread occurrence of naphthoquinones throughout the Dyspnoi and Eupnoi. In a series of preliminary investigations, naphthoquinones were found in many phalangiid Eupnoi, throughout dyspnoan Nemastomatidae and also in certain Sabaconidae (Raspotnig, unpublished). Regarding their obviously wide distribution in both cyphophthalmids and palpatoreans, naphthoquinones are likely to represent phylogenetically old scent gland components of a clade of Cyphophthalmi and Palpatores, and possibly were already present in cyphophthalmid-palpatorean ancestors. Since they are otherwise rare in the exocrine secretions of arthropods, an independent origin of naphthoquinones in several subgroups of Opiliones is unlikely. On the other hand, naphthoquinones have not (yet) been detected in the secretions of sclerosomatid Eupnoi, although a comprenhensive study is missing. If we consider naphthoquinones es as ancestral compounds of Cyphophthalmi and Palpatores, the apparent lack of naphthoquinones in certain eupnoan taxa (e.g. in Sclerosomatidae) would be due to apomorphic regression.

Interestingly, no trace of naphthoquinones has ever been detected in the secretions of Laniatores, neither in basal groups, such as insidiatorean Travunioidea, nor in the Grassatores. This may either be due to their complete reduction in laniatorean secretions, or naphthoquinones might indeed be considered synapomorphic for a clade of Cyphophthalmi plus Palpatores. In the latter case, the phyletic position of the Laniatores would need reconsideration, and the laniatorean split-off from the opilionid stem line might have happened much earlier than hitherto proposed, i.e. before naphthoquinones in opilionid secretions evolved. Such a scenario clearly contradicts several concepts of opilionid phylogeny (*e.g.* both the classical concept and the Dyspno-Laniatores-hypothesis), but would be roughly consistent with the Cyphopalpatores hypothesis of Martens (1986).

The phyletic status of acyclic compounds

The phyletic status of acycles in opilionid secretions is even more difficult to interpret. In cyphophthalmids, acycles are represented by methyl ketones, and similar acyclic ethyl ketone components are produced by some Palpatores (certain Sclerosomatidae). Although a common ancestry of these acycles may be assumed, a convergent evolution of acyclic compounds in a presumed clade of cyphophthalmids + palpatoreans cannot be excluded.

One specific class of these acycles, namely the “sclerosomatid compounds” (see Table 2) were originally found in some sclerosomatid Eupnoi (*e.g.* Ekpa et al. 1985), but also occur in some nemastomatid Dyspnoi and in certain Ischyropsalidoidea (Raspotnig, unpublished). These findings may indicate a possible chemical synapomorphy of Eupnoi and Dyspnoi, thus chemically supporting the monophyly of Palpatores, as stated in the classical concept of opilionid phylogeny (*e.g.* Shultz and Regier 2001). Though speculative, it is possible that both cyphophthalmid methyl ketones and palpatorean ethyl ketones (along with some corresponding compounds) have evolved from a hypothetical fraction of ancient acycles. The modification to ethyl ketones might have happened early in basal Palpatores, explaining the occurrence in both Eupnoi (i.e. Sclerosomatidae) and in Dyspnoi (i.e. certain nemastomatid Troguloidea and some Ischyropsalidoidea). In phalangiid Eupnoi, however, sclerosomatid compounds seem to be missing, possibly as a result of apomorphic reduction, or they simply have not yet been detected in this group. Thus, the actual distribution of sclerosomatid- and sclerosomatid-like compounds among the Palpatores remains to be studied in much more detail.

The recent findings of ethyl ketones similar to sclerosomatid compounds in the secretions of some Gonyleptidae (Hara et al. 2005; Rocha et al. 2011) may complicate the phyletic interpretation of scent gland-derived acycles. Regarding opilionid relationships currently discussed in the literature (*e.g.* Shultz and Regier 2001), gonyleptoid acycles might be explained as a result of independent evolution (Hara et al. 2005; Rocha et al. 2011). Moreover, gonlyleptid ethyl ketones largely lack the characteristic substitution pattern of sclerosomatid compounds (i.e. methyl groups in position 4). However, at least one compound, 4-methyl-3-hexanone, is shared by both Gonyleptidae and Sclerosomatidae. Ethyl ketones showing the sclerosomatid compound substitution pattern are quite rare in nature with 4-methyl-heptan-3-one being an exception: this compound is also known from non-opilionid sources, including the secretions of some hymenopterans, such as ants and wasps (*e.g.* Byers and Levi-Zada 2011), and has obviously evolved several times independently in exocrine secretions of different arthropods.

The divergent chemistry of Laniatores

It is currently not evident how to logically include laniatorean chemistry into the overall picture of Opiliones. The deep chemical divergence between the group of Cyphophthalmi-Palpatores and the Laniatores appears to be the most significant gap in our ability to trace evolutionary trends based on scent gland chemistry. This gap between the naphthoquinone- and acyclic compounds-rich chemistry on the one hand,

and the alkaloidal, phenolic and benzoquinonic secretions of Laniatores on the other hand, is not easily explained, and may even call for a fundamental reconsideration of hypotheses of opilionid phylogeny. A further question question refers to the internal chemical heterogeneity of Laniatores, namely to the gap between the nitrogenic compound-rich secretions of laniatorean Insidiatores (at least in Travunioidea) and the phenolic and benzoquinonic secretions of the Grassatores. Groups showing transitional chemical states are largely missing, or poorly supported, although preliminary findings of a phenolic compound in American travunioids (Shear, personal communication) may represent a first link to the phenolic chemistry of basal Grassatores (Shear et al. 2010a, 2010b). In addition, the phyletic state of the unusual nitrogenic-compounds in insidiatorean travuniods is difficult to evaluate at present. Tobacco alkaloids such as nicotine and anabaseine are unique compounds in arthropod exocrinology, but appear to be widespread in insidiatorean travunioids, and are shared by many European and American species (Ekpa et al. 1984; Raspotnig et al. 2011; Shear, personal communication). These alkaloids may represent ancestral components of the Laniatores in general, or an autapomorphy of Travunioidea in particular. The same may be true for N,N-dimethylphenylethylamine, which, although more restricted in its distribution, characterizes a large clade of travunioids from Western North America as well as of at least one European taxon from the Pyrenees (*Peltonychia clavigera*; Raspotnig and Karaman, unpublished). According to recent phylogenies (*e.g.* Derkarabetian et al. 2010), American anabaseine-producing *Erebomaster* and *Theromaster* may form a clade that is derived from N,N-dimethylphenylethylamine-producing travunioids. In spite of the promise of these preliminary data, much more research in insidiatoreans remains to be done: especially the inclusion of chemically enigmatic groups such as the Triaenonychoidea might provide important information towards a comprehensive understanding of evolutionary traits in laniatorean scent gland chemistry.

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