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To cite this version:
Volker Lohrmann, Michael Ohl, Peter Michalik, James Pitts, Laurent Jeanneau, et al.. Notes on rhopalosomatid wasps of Dominican and Mexican amber (Hymenoptera: Rhopalosomatidae) with a description of the first fossil species of Rhopalosoma Cresson, 1865. Fossil Record, Wiley-VCH Verlag, 2019, 22 (1), pp.31-44. 10.5194/fr-22-31-2019. insu-02135631

HAL Id: insu-02135631
https://hal-insu.archives-ouvertes.fr/insu-02135631
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Notes on rhopalosomatid wasps of Dominican and Mexican amber (Hymenoptera: Rhopalosomatidae) with a description of the first fossil species of Rhopalosoma Cresson, 1865

Volker Lohrmann1,2, Michael Ohl2, Peter Michalik3, James P. Pitts4, Laurent Jeanneau5, and Vincent Perrichot5
1Übersee-Museum Bremen, Bahnhofsplatz 13, 28195 Bremen, Germany
2Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, Invalidenstraße 43, 10115 Berlin, Germany
3Zoologisches Institut und Museum, University of Greifswald, Loitzer Str. 26, 17489 Greifswald, Germany
4Department of Biology, Utah State University, 5305 Old Main Hill, Logan, UT 84322-5305, USA
5Géosciences Rennes, Univ. Rennes, CNRS, UMR 6118, 35000 Rennes, France

Correspondence: Volker Lohrmann (v.lohrmann@uebersee-museum.de)

Received: 2 November 2018 – Revised: 11 January 2019 – Accepted: 18 January 2019 – Published: 15 May 2019

Abstract. Rhopalosomatidae are a family of aculeate wasps that are ectoparasitoids of crickets as larvae and are predominantly distributed pantropically. The published fossil record of the family is scarce. Here, we report three new fossil rhopalosomatid wasp specimens from Dominican and Mexican amber. Rhopalosoma hispaniola Lohrmann sp. nov. is described and documented from Dominican amber by two separate inclusions – one of each sex. An additional fossil female Rhopalosoma is described and documented from Mexican amber but is not named due to the insufficient preservation of the fossil. The new fossils, which are morphologically intermediate between Townes’ isopus and poeyi species groups, do not only represent the first fossil records of an extant genus of this peculiar family but also the first records of the family in Dominican and Mexican amber.

1 Introduction

The Recent New World fauna of Rhopalosomatidae is currently comprised of 35 formally described species assigned to three genera: Liosphex Townes, 1977, with 13 species, Olixon Cameron, 1887, with 5 species, and Rhopalosoma Cresson, 1865, with 17 species (Townes, 1977; Lohrmann and Ohl, 2010; Lohrmann et al., 2012). Their distribution ranges from southeastern Canada and the northeastern USA to northern Argentina and southern Brazil, with the vast majority occurring in the tropic zone. As far as it is known, female rhopalosomatids hunt for crickets (Orthoptera) that ultimately serve as hosts for their ectoparasitoid larvae (Perkins, 1908; Hood, 1913; Gurney, 1953; Lohrmann et al., 2014; Blaschke et al., unpublished results; see also Fig. 1a–b).

The recent discovery of an ectoparasitoid rhopalosomatid wasp larva attached to its cricket host in mid-Cretaceous Burmese amber revealed a remarkable constancy of the biology of Rhopalosomatidae over the last 100 million years (Lohrmann and Engel, 2017). In some way, this extraordinary fossil hides the fact that we still know little about the origin and evolution of this peculiar family of aculeate wasps. Two of the four fossil taxa previously assigned to the family, Mesorhopalosoma Darling (in Darling and Sharkey, 1990) and Paleorhopalosoma Nel et al., 2010, have been transferred to the sphecoid wasps (Osten, 2007; Archibald et al., 2018). Additionally, Propalosoma Dlussky and Rasnitsyn, 1999, has been transferred to the myrmecine ants (Archibald et al., 2018). This leaves Eorhopalosoma Engel, 2008, which is another Cretaceous Burmese amber fossil, as the sole fossil species in the family so far.

No Rhopalosomatidae have been recorded from Dominican and/or Mexican amber, even though many of the extant aculeate families currently distributed in the neotropics are already reported from either of these contemporary outcrops. For Dominican amber, these include Andrenidae, Apidae, Bethylidae, Chrysididae, Crabronidae, Colletidae, Dryinidae, Formicidae, Halictidae, Megachilidae, Mutilli-
due to their general appearance, members of the rhopalo-
somatid wasp genus *Rhopalosoma* (see Fig. 1c), as well
as the Old World *Paniscomima* Townes, 1977, are often
mistaken for nocturnal ichneumonids, e.g., *Ophion* spp. or
*Netelia* spp. (McGown, 1998), and one is strongly encour-
gaged to go through collections of unidentified subtropical or
tropical nocturnal ichneumonids when searching for mate-
rial of the genus. This is also true for the fossil record. Dur-
ing our surveys of fossil inclusions, three adult rhopalo-
somatid wasps have been discovered in Dominican and Mexi-
can amber, and one of the fossils described herein was indeed
initially identified and advertised as a “Large Ichneumonid
Wasp”.

All three of the new fossils belong to the Recent genus
*Rhopalosoma*. The aim of the present study is to describe
and illustrate these fossils, which are not only the first fossil
records of the genus but are also the first of the family from
Dominican and Mexican amber and from the Miocene as a whole.

2 Materials and methods

2.1 Thermochemolysis–gas chromatography–mass
spectrometry

Of the three new rhopalosomatid fossils reported herein, each
is preserved in a separate amber piece. Two of these fossils
originate from the La Bucara mine in the Dominican Repub-
lic, and one comes from a mine in Mexico (Chiapas). Be-
cause the Mexican amber piece was obtained from an on-
line auction, without an indication of the exact provenance
in Chiapas, we performed a chemical analysis to ascertain its
amber vs. copal nature and its affinities with genuine Chi-
apas amber. Thermochemolysis–gas chromatography–mass
spectrometry revealed the presence of the following
components:...
spectrometry (THM-GC-MS) was performed on both the Mexican amber sample and a piece of yellowish Baltic amber as a reference chromatogram. Small portions of amber were crushed manually in an agate mortar. The powder (~ 0.1 mg) was heated with TMAH (tetramethylammonium hydroxide) at 400°C. THM was carried out using a Frontier Lab PY-2020ID pyrolyzer coupled with a Shimadzu GCMS-QP2010 Plus system operating with a split ratio of 100. Separation was achieved using a capillary column SLB-5ms. The general morphological terminology is adopted from Huber and Sharkey (1993), with additions from Mason (1986, 1990), and the following morphological abbreviations and modifications are used in the text. Cu² is the section of fore wing cubitus separating the 2Cu and 2M (not closed) cells (Fig. 4f). IOD is the interocellar distance, or the shortest distance between the lateral ocelli. LOD is the maximum diameter of a lateral ocellus. MOD is the maximum diameter of the median ocellus. M¹ is the section of fore wing media separating the R and 1M cells (Fig. 4f). M² is the section of fore wing media separating the 1M and 1Rs cells (Fig. 4e). OOD is the ocellocular distance, or the shortest distance between the lateral ocellus and eye. Rs¹ is the section of fore wing radial sector separating the 1R1 and 1Rs cells (Fig. 4e). Rs² is the section of hind wing radial sector separating the R and R1 cells (Fig. 5e). TL is the temple length, or the shortest distance between the posterior eye margin and occipital carina.

All three specimens are deposited in the amber collection of the Museum für Naturkunde in Berlin, Germany (inventory numbers: MB.I 5915, MB.I 6046, and MB.I 6549).

### 2.4 Reference material studied

During the course of this research, the holotypes of *Rhopalosoma alvarengai* Townes, 1977, *R. angulare* Townes, 1977, *R. breelandi* Townes, 1977, *R. impar* Townes, 1977, *R. isopus* Townes, 1977, *R. minus* Townes, 1977, *R. obliquum* Townes, 1977, and *R. scaposum* Townes, 1977, all deposited in the Entomology Collection of Utah State University (EMUS), previously known as the American Entomological Institute (AEI), were studied. Additionally, non-type material of the EMUS, including *R. bahianum* Schulz, 1906, *R. breelandi*, *R. guianense* Schulz, 1906, *R. haitiense* Townes, 1977, *R. impar*, *R. isopus*, *R. minus*, *R. nearcticum* Brues, 1943, *R. poeyi* Cresson, 1865, and *R. simile* Brues, 1943, was also studied.
3 Results

3.1 Chemical analysis

The THM-GC-MS analysis of the Mexican resin sample (Fig. 2; see also Appendix B) revealed characteristic bicyclic products derived from polylabdanoid structures including carboxylic acids (XIIa–XIVa), analyzed as their methyl ester; alcohols (XIIIb–XIVb) partially methylated (XIIId–XIVd); and hydrocarbons (XIc, XIIIc and XIVc). Moreover, the THM of this sample also produced 1-methylbicyclic hydrocarbons (A–K) that are believed to come from A-ring defunctionalization (Anderson, 1995).

The shift in the retention times of methylic ether XIIId and XIVd between the Baltic amber and the Mexican resin (Fig. 3) indicated an enantio configuration for the latter. Consequently, it falls into the class Ic as defined by Anderson et al. (1992). The distribution of bicyclic products derived from the polylabdanoid macromolecular structure of the Mexican sample was dominated by 1-dimethylbicyclic and 1-methylbicyclic hydrocarbons (50% and 28%, respectively), while bicyclic acids and alcohols represented only 6% and 17% of those compounds, respectively (Table 1). This predominance of 1-dimethylbicyclic hydrocarbons was already observed in Sicilian amber (van der Werf et al., 2016).

The composition was compared to those of known class Ic ambers from the Eocene of Oise (France; Nohra et al., 2015) and the Miocene of the neotropics (the Dominican Republic and Mexico, from the collection of Vincent Perrichot, Univ. Rennes, unpublished results). The relative proportions of carboxylic acids, alcohols, and hydrocarbons among bicyclic products derived from polylabdanoid structures were similar in the Mexican sample and the two neotropical ambers, while the Oise amber was richer in carboxylic acids (Table 1). The proportion of 1-methylbicyclic hydrocarbons was proposed as a maturity proxy, since they are especially observed in samples of moderate thermal maturity (Anderson, 1995). The present Mexican sample (28%) falls between Oise (19%) and Dominican (22%) ambers on one side and Mexican amber (41%) on the other side, thus attesting to its amber rather than copal nature as well as its affinity with neotropical ambers.

3.2 Systematic paleontology

Order Hymenoptera Linnaeus, 1758

Family Rhopalosomatidae Ashmead, 1896

Genus Rhopalosoma Cresson, 1865

LSID (genus): urn:lsid:zoobank.org:act:F41B7AB7-0F40-40E6-AEC3-0B01AF718AF1

Rhopalosoma Cresson, 1865:58. Type species: Rhopalosoma poeyi Cresson, 1865, by monotypy.

Sibyllina Westwood, 1868:329. Type species: Sibyllina aenigmatica Westwood, 1868, by monotypy. Synonomy by Westwood, 1874: 130.

Diagnosis

Among extant and fossil rhopalosomatids, species of Rhopalosoma are characterized by the following character combination. The wings are fully developed (brachypterous in Olixon); the occipital carina is present (absent in Liosphex); the apical section of the fore wing cubitus (Cu2 in Fig. 4) is at least slightly sinuate (arched, but indented at the level of junction with CuA in Paniscomima, and almost straight in Eorhopalosoma); female pretarsal claws have a preapical tooth (as in Figs. 4b, 6c); female tarsomeres II–IV have apicolateral tarsal fenestrae (Fig. 6b); and the second preapical process of the male penis valve is narrow to broad, distad from the head of the penis valve, and is not overlapped at its apex by the third preapical process (Fig. 1d; broadly triangular, near head of penis valve, and overlapped in Paniscoma).

(Males and females of the family can be differentiated by the number of flagellomeres – males have 11, and females have 10, by the number of visible metasomal tergites – males have 7, and females have 6, and by the form of tarsomeres II–IV – cylindrical for males and flattened for females. For a more detailed morphological description of the genus and all extant species, including a species-level identification key, the family revision of Townes (1977), should be consulted.)
Figure 2. Chromatogram from the THM-GC-MS analysis of the Mexican sample. Numbered peaks refer to identified compounds in Appendix A. TriMeNa is trimethylnaphthalene.

Figure 3. Reconstructed chromatogram (m/z = 234 + 236) of Baltic amber (solid line) and Mexican sample (dashed line). The shift in the retention times of compounds XIIIId and XIVd (Mexican amber) compared to IXd and Xd (Baltic amber) is due to the difference of configuration between the enantio and regular forms, which classifies the Mexican sample as a class Ic resinite. The box depicts the similar retention time for trimethylnaphthalene (m/z = 155).

Distribution

Distribution is predominantly in the tropics and subtropics of the Americas (eastern United States to southern Brazil and northern Argentina), including some of the Caribbean countries (Bahamas, Cayman Island, Cuba, and Haiti; Townes, 1977).

Biology

As it concerns the extant fauna, *Rhopalosoma nearcticum* Brues, 1943, has been associated with species of trigonidiine and hapithine genera (Insecta: Orthoptera), i.e., *Anaxipha* Saussure, 1874, *Hapithus* Uhler, 1864, and *Orocharis* Uhler, 1864 (Hood, 1913 – misidentified as *R. poeyi* Cresson, 1865; Gurney, 1953; Townes, 1977; Blaschke et al., unpublished results; see also Fig. 1a–b). For the remaining 16 extant species in the genus, however, no data have been published to date on their host–parasite relationships.

*Rhopalosoma hispaniola* Lohrmann sp. nov.

LSID (species): urn:lsid:zoobank.org:act:6BEECB2C-0403-4F5C-93DF-04590CF406DA

LSID (author): urn:lsid:zoobank.org:author:05A758C9-462A-422C-B8D6-DD9530E2BD05

(Figs. 4, 5)

Diagnosis

Within *Rhopalosoma*, females of *R. hispaniola* are unique in showing the following character combination: hind wing Rs* is straight and recurrent, and the apical 0.65 of fifth tarsomeres is tapered. Males of *R. hispaniola* resemble *R. minus* Townes, 1977, in having a straight, recurrent hind wing Rs* but can be differentiated by the position of the fore wing cu-a, which is distad of M1 by about 1.0 × its length (about 2.0 × in *R. minus*).
Measurements

Female (Fig. 4).

Description

Araneae. one large Isoptera wing, one unidentified Insecta, and one two Hymenoptera (Mymaridae), four Diptera, one Isoptera, fragments. The following syninclusions have been observed: characters of the fossil the amber piece has been cut into two without any significant distortions. In order to access crucial Naturkunde Berlin. The specimen is completely preserved is deposited in the amber collection of the Museum für Dominican Republic; the specimen is deposited in the amber piece containing the rhopalosomatid wasp studied here.

Currently, the genus is represented in the Caribbean only by Rhopalosoma poeyi Cresson, 1865, and R. haitiensensis Townes, 1977 (Townes, 1977). However, neither of these species has a similar hind wing Rs\(^*\).

Material

Holotype: female, MB.I 5915, in Miocene amber from the Dominican Republic; the specimen is deposited in the amber collection of the Museum für Naturkunde Berlin. The specimen is almost completely preserved without any significant distortions. However, large parts of the legs are missing. The following syninclusions have been observed: one Collombola and one Mymaridae.

Paratype: male, MB.I 6046, in Miocene amber from the La Bucara mine in the Dominican Republic; the specimen is deposited in the amber collection of the Museum für Naturkunde Berlin. The specimen is completely preserved without any significant distortions. In order to access crucial characters of the fossil the amber piece has been cut into two fragments. The following syninclusions have been observed: two Hymenoptera (Mymaridae), four Diptera, one Isoptera, one large Isoptera wing, one unidentified Insecta, and one Araneae.

Description

Female (Fig. 4). Measurements. Total body length (head, without antenna, plus mesosoma plus metasoma) in lateral view 12.0 mm. Maximum head width in dorsal view 2.0 mm. Flagellar length (measured on left antenna with the last segment added from the right antenna) 11.4 mm (including pedicel and scapus 12.1 mm). Mesosomal length in lateral view 3.2 mm. Fore wing length 8.9 mm. Hind wing length 6.5 mm. Metasomal length in lateral view 7.8 mm.

Head. (Base of right flagellum and last flagellomere of left flagellum not preserved.) FI–FV each with a pair of apical bristles. FI shorter than FII, which is about as long as flagellomeres III–V. FVI–FX becoming sequentially shorter from base to apex. Inner margin of compound eye emarginate. Depth of eye notch about the same size as the width of torulus. FI 5.0 ×, FII 8.2 ×, and FVII 9.5 × as long as wide. TL 0.6 ×, OOD 0.25 ×, and MOD 1.0 × LOD.

Mesosoma. Scutellum about half as long as mesoscutum and approximately 3 times as long as metanotum. Mesosternal lobes present, separated from mesosternum by slight constriction.

Fore wing. With eight enclosed cells: C, R, 1Cu, 1R1, 2R1, 1Rs, 1M, and 2Cu. Costal cell very narrow, apically slightly wider, over complete distance narrower than bordering veins. Cell 1Rs about 1.05 × as long as cell 1R1. Vein 1cu-a slightly bowed, distad of M\(^1\) by about 1.0 × its length. Distance between 1cu-a and M\(^1\) about half the distance between 1cu-a and m-cu. Vein Rs\(^1\) straight, about 0.8 × length of M\(^2\). Pigmented traces of 2m-cu present. Anal cell without longitudinal spurious vein at its center (present in some Recent Asian Paniscomima). Pterostigma narrow.

Hind wing. Rs\(^*\) straight, recurrent, its anterior section meeting Sc + R at an angle of about 55°. M diverging far beyond cu-a. With two clusters of hamuli. Basal hamuli straight. With 13 distal hamuli, all of same size and curved-and/or hook-like.

Legs. (The following parts of the legs are not preserved: tarsomeres III and following of right fore leg, tarsomere II and pretarsus of left fore leg, distal two-thirds of tarsomere I and tarsomere II of right mid leg, tarsomeres II–IV of left mid leg, distal half of tarsomere I and following of both hind legs.) Fore leg with one tibial spur. Mid leg and hind leg each with two tibial spurs, inner spur of hind tibia at base with dorsal tuft of bristles (calcar). Tarsomeres II–IV with apicobasally broadened. Tarsomeres II–IV with apico-lateral fenestrae. Pretarsal claws toothed medially (Fig. 4c). Arolia large.

Metasoma. Segment I about as long as mesosoma. Sting upcurved (Fig. 4a).

Pilosity. Body and wing membranes covered with regular distributed fine, short setae.

Male (Fig. 5). Measurements. Total body length (head, without antenna, plus mesosoma plus metasoma) about 7.3 mm. Maximum head width in oblique ventral view about 1.0 mm. Flagellar length (measured on left antenna in ventral view) 5.7 mm (including pedicel and scapus: 6.2 mm).

Table 1. Relative proportions of characteristic bicyclic products derived from polylabdanoid macromolecular structures of the present Mexican sample compared with three classes of three class-Ic ambers. Amber from Dominican Republic and from Mexico are from the personal collection of Vincent Perrichot (VP coll.), and their chemical fingerprints have not yet been published. In bold: the Mexican amber piece containing the rhopalosomatid wasp studied here.

|                | Dominican Republic (VP coll.) | Oise, France (Nohra et al., 2015) | Mexico (VP coll.) | Mexico (this study) |
|----------------|-------------------------------|----------------------------------|------------------|---------------------|
| Bicyclic acids\(^a\) | 15                            | 59                               | 4                | 6                   |
| Bicyclic alcohols\(^b\) | 17                            | 14                               | 2                | 17                  |
| Bicyclic hydrocarbons | 47                            | 7                                | 53               | 50                  |
| 1-Methylbicyclic hydrocarbons | 22                            | 19                               | 41               | 28                  |

\(^a\) Analyzed as methyl ester. \(^b\) Sum of alcohols and methyl ethers.
Mesosomal length in lateral view is about 2.3 mm. Fore wing length about 5.6 mm. Hind wing length about 3.8 mm. Metasomal length about 4.3 mm.

Head, mesosoma, and metasoma as in female except the following. Fore wing cell 1Rs about 0.85 × as long as cell 1R1. Vein Rs1 about 1.25 × length of M 2. Distance between 1cu-a and M 1 about the same length as the distance between 1cu-a and m-cu. Hind wing Rs* meeting Sc + R at an angle of about 50°. With eight distal hamuli. Plantar lobe present on tarsomeres I–IV. Pretarsal claws bifid. Metasomal segment I only two-thirds the length of mesosoma. Cuspis with ~ 12 peg-like bristles on apical section and ~ 6 apical setae. Digitus with ~ 33 peg-like bristles on apical section. Paramere spine-like, upcurved. Cercus paddle shaped and with apical setae.

Note

The intraspecific variation between the non-sex-specific characters (e.g., ratio of the length of fore wing veins Rs 1 and
**Figure 5.** Rhopalosoma hispaniola sp. nov.: male, paratype, MB.I 6046, Miocene Dominican amber. (a) Overview. (b) Posterior metasoma with genitalia. (c) Details of right fore wing. (d–e) Details of right fore and hind wing with labeling of fore wing cells and venation (d) and labeling of hind wing venation (e). Abbreviations used in (b): ce – cercus, cu – cuspis, di – digitus, pa – paramere, pv – penis valve, tg6 – tergite 6, and tg7 – tergite 7.

M², ratio of the length of fore wing cells 1Rs and 1R1) seems to be slightly higher than in the Recent species of *Rhopalosoma*. However, we chose a conservative approach by assigning both specimens to the same species rather than describing two species based on only a single specimen of each sex.

**Etymology**

The specific epithet refers to the island of Hispaniola in the Caribbean where the fossils were found. It is a noun in apposition.
Figure 6. Rhopalosoma sp.: female, MB.I 6549, Miocene Mexican amber. (a) Overview. (b) Left hind tarsus. (c) Pretarsus with claws. (d–e) Details of left fore wing. (f) Details of right hind wing. Abbreviations used in (b) and (e): pat – preapical tooth, tc – tarsal claw, tf – tarsal fenestrae, t1 – tarsomere 1, t2 – tarsomere 2, t3 – tarsomere 3, t4 – tarsomere 4, and t5 – tarsomere 5.

**Rhopalosoma sp.**

(Fig. 6)

**Material**

Female, MB.I 6549, in Miocene amber from Chiapas, Mexico; the specimen is deposited in the amber collection of the Museum für Naturkunde Berlin. The specimen is almost completely preserved, except for part of the antennae, but it is largely distorted, except for the wings and legs. In order to access the crucial characters of the fossil the amber piece has been cut into three fragments. The following synincclusions have been observed: one Hymenoptera (Braconidae), six Diptera, one Heteroptera, and one Thysanoptera.

**Description**

Head, mesosoma, and metasoma as in *R. hispaniola* except the following.
Measurements. Due to the heavy distortion of the specimen all measurements except for those of the wings, should be treated rather as an estimate of the general size. Body length (head, without antenna, plus mesosoma plus metasoma) in dorsal view 10.4 mm. Head width in dorsal view 1.4 mm. Mesosomal length in lateral view 2.9 mm. Fore wing length 8.2 mm. Hind wing length 6.3 mm.

Fore wing. 1Rs cell about 0.85 × as long as cell 1R1. 1cu-a slightly curved, distad of M1 by about 1.0 × the length of 1cu-a. Distance between 1cu-a and M1 about 0.7 × the distance between 1cu-a and m-cu.

Hind wing. Rs* very slightly curved (almost straight), its anterior section recurrent, meeting Sc + R at an angle of ∼45°, posterior section almost vertical. With 11 distal hamuli (Fig. 6f).

Note

This specimen resembles the female from Dominican amber. Unfortunately, many important characters, such as the size and position of the ocelli, form of the inner eye margin, etc., cannot be examined due to the insufficient preservation of the fossil. However, we do not include this specimen in the type series of Rhopalosoma to emphasize its different geological origin and the slightly different wing venation as an indication of a separate distinct species which might be properly described and named after new material becomes available.

Currently, the genus is represented in Mexico only by Rhopalosoma simile Brues, 1943, and R. obliquum Townes, 1977 (Townes, 1977). However, neither of these species has a similar hind wing Rs*.

4 Discussion

Based on the presence of a median tooth on the tarsal claws, females of Rhopalosoma are easily identified, and there is no doubt about the generic placement of the new species described herein. Townes (1977) divided Rhopalosoma into three species groups – the isopus, poeyi, and lanceolatum groups (comprising two, 14, and one species, respectively). Whereas the identification of Rhopalosoma at the species level remains a challenge, the new species likely belongs to the poeyi group based on the characters provided by Townes: front spur of mid tibia and hind tibia without narrow basal neck (as present in the lanceolatum group), and the form of tarsomere V, which is gradually tapered at its apical 0.65 (parallel-sided in the isopus group). Nevertheless, the new species has some affinities with a member of the isopus group, and with R. minus in particular, by having the hind wing Rs* straight and recurrent. But because this state is also found in Eorhopalosoma gorgyra, all Liosphex, and several Paniscomima (Lohrmann and Ohl, 2010; Lohrmann, 2011; Volker Lohrmann, personal observation, 2014), it can be assumed that this is the plesiomorphic character state compared to the angular or strongly bowed form found in many Recent species of Rhopalosoma. Townes (1977) regarded the isopus group as the “primitive species group”. His assumption is based on the similarities of the morphology of the fifth tarsomeres with those found in Paniscomima, a genus he regarded as “definitely more primitive”. Thus, the fossils likely do not represent the most archaic forms in the genus but represent either basal members of the poeyi group or an intermediate link between the isopus and the poeyi species group.

Note

The current contribution includes revised parts of a chapter used earlier in the PhD thesis of Volker Lohrmann, i.e., the description and discussion of the female of R. hispaniola (including Figs. 1d and 4b). Because the thesis includes a statement disclaiming all relevant nomenclatural acts from taxonomic use, the new taxon is formally described here to make its name available according to the ICZN (1999).

Data availability. No data sets were used in this article.
Appendix A

Table A1. List of identified compounds and their retention times in Mexican amber. Target compounds were identified based on \( m/z \) int and \( m/z \) identification. Areas were integrated using the \( m/z \) int, and the area on the total ion chromatogram was estimated using the mass spectra factor (MSF).

| Bicyclic methyl esters                      | Retention time (min) | \( m/z \) int | \( m/z \) identification | MSF | Area (\( m/z \) int) |
|--------------------------------------------|----------------------|---------------|--------------------------|-----|----------------------|
| XLa                                        | 42.781               | 236           | 161 177                  | 57  | 11 992               |
| XIIa                                       | 43.581               | 236           | 176 121 161              | 121 | 5630                 |
| XIIIa                                      | 47.362               | 250           | 175 191 235              | 67  | 56 279               |
| XIVa                                       | 47.899               | 248           | 173 133 188              | 58  | 70 849               |

| Bicyclic alcohols                          |                       |               |                          |     |                      |
|--------------------------------------------|----------------------|---------------|--------------------------|-----|----------------------|
| XIb                                        | 208                  | 95 177        | 158                      | nd  |                      |
| XIIb                                       | 208                  | 55 109 177    | 95                       | nd  |                      |
| XIIIb                                      | 47.704               | 222           | 95 191 207               | 62  | 187 935              |
| XIVb                                       | 48.385               | 220           | 91 132 187               | 49  | 188 631              |

| Bicyclic methyl ethers                     |                       |               |                          |     |                      |
|--------------------------------------------|----------------------|---------------|--------------------------|-----|----------------------|
| XId                                        | 222                  | 95 107 177    | 152                      | nd  |                      |
| XIIId                                      | 222                  | 105 119 190   | 130                      | nd  |                      |
| XIIIId                                     | 44.435               | 236           | 109 121 189              | 79  | 33 935               |
| XIVd                                       | 45.109               | 234           | 132 187                  | 62  | 65 870               |

1-Dimethylbicyclic hydrocarbons

| XIc                                        | 33.605               | 192           | 8 195 107 177            | 23  | 186 559              |
| XIIc                                       | 33.605               | 192           | 95 121 177               | 16  | nd                   |
| XIIIc                                      | 38.780               | 206           | 95 121 191               | 19  | 693 963              |
| XIVc                                       | 39.257               | 204           | 105 119 161              | 15  | 1452 344             |

1-Methylbicyclic hydrocarbons

| A                                          | 31.006               | 163           | 81 107 178               | 9   | 60 884               |
| B                                          | 31.053               | 163           | 95 178                   | 17  | 50 732               |
| C                                          | 32.209               | 163           | 81 107 178               | 14  | 40 681               |
| D                                          | 32.511               | 163           | 95 178                   | 13  | 19 600               |
| E                                          | 36.240               | 177           | 95 121 192               | 9   | 131 382              |
| G                                          | 37.492               | 177           | 95 121 192               | 11  | 194 635              |
| F                                          | 36.449               | 175           | 108 190                  | 12  | 448 787              |
| K                                          | 36.641               | 175           | 119 133 190              | 25  | 645 555              |
| H                                          | 37.284               | 175           | 93 190                   | 13  | 1549 998             |

Aromatic hydrocarbons

| Dimethyltetralin                           | 32.398               | 145           | 145 160                  | 5   | 107 826              |
| Trimethyltetralin                          | 38.077               | 159           | 159 174                  | 4   | 755 296              |
| Trimethylindene                            | 34.526               | 158           | 143 158                  | 12  | 100 696              |
| Dimethylnaphthalene                        | 36.120               | 156           | 141 156                  | 8   | 272 332              |
| Trimethylnaphthalene                       | 41.652               | 155           | 155 170                  | 7   | 3210 319             |
| Dimethylphenanthrene                        | 54.904               | 206           | 191 206                  | 4   | 203 288              |

\( \text{nd} \) – not detected
Figure B1. Molecules identified in the pyrolysates of Mexican amber. Individual compounds are labeled according to the identification of peaks in Fig. 2 and Appendix A.
Author contributions. VL designed the study. VP carried out the preparation of the fossil amber samples for the THM-GC-MS analysis and for microscopic studies of the fossils. LJ did the chemical analysis. VL, VP, and PM prepared the photographs of the fossils. VL, VP, LJ, MO, and JPP wrote the paper. All authors contributed to the discussion and proof-reading of the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. We are sincerely thankful to Judy Gallagher (Woodbridge, Virginia) and Robert Lord Zimlich (Mobile, Alabama) for their kind permission to use their photographs, Jeremy Blaschke and his team (Jackson, Tennessee) for sharing their knowledge of the new host record of Rhopalosoma, Keith Luzzi (New Jersey) for making the two Dominican amber fossils available, and Christian Neumann (Museum für Naturkunde, Berlin) for allowing the study of all three inclusions. Partial support in the initial and the final stage of this project was provided by the “Studienstiftung des Deutschen Volkes” (to Volker Lohrmann) in the initial and the final stage of this project was provided by the “Studienstiftung des Deutschen Volkes” (to Volker Lohrmann) and the OSUR grant from program AO2 2018 for visiting researchers (to Vincent Perrichot, enabling Volker Lohrmann’s work at the University of Rennes 1) respectively. Finally, we thank Denis J. Brothers and Mónica Solórzano Kraemer for their valuable comments on the manuscript.

Edited by: Torsten Scheyer
Reviewed by: Denis J. Brothers and Mónica Solórzano Kraemer

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