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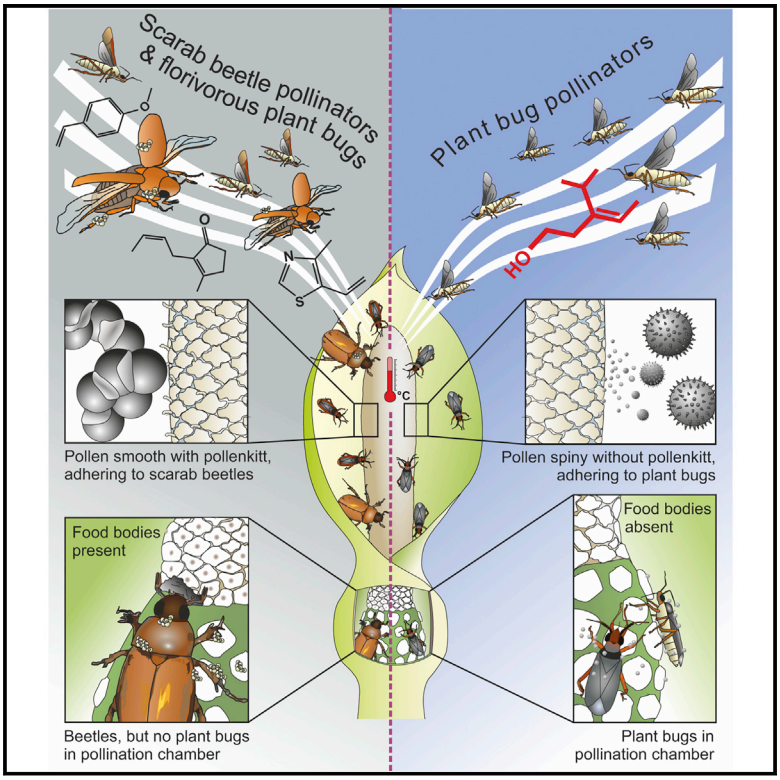
Current Biology

Evidence for the recruitment of florivorous plant bugs as pollinators

Graphical abstract



Highlights

- The aroid *Syngonium hastiferum* is pollinated by *Neella* sp. nov. plant bugs
- The plant produces a previously unknown volatile to attract the bug pollinators
- *S. hastiferum* differs in various floral traits from its beetle-pollinated relatives
- Adoption of antagonistic florivores as pollinators can drive flower diversification

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In brief

Etl et al. present a specialized angiosperm-plant bug (Heteroptera: Miridae) pollination system and identify the floral traits (e.g., thermogenesis, flower scent, and floral and pollen morphologies) that mediate the transition from florivory to a pollination mutualism.

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Evidence for the recruitment of florivorous plant bugs as pollinators

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SUMMARY

Angiosperm flowers and their animal visitors have co-evolved for at least 140 Ma, and early flowers were likely used mainly as mating and feeding sites by several groups of insects, including beetles, flies, true bugs, and thrips. Earlier studies suggested that shifts from such neutral or antagonistic relationships toward mutualistic pollination interactions between flowers and insects occurred repeatedly during angiosperm evolution. However, the evolutionary mechanisms and adaptations, which accompanied shifts toward effective pollination, are barely understood, and evidence for such scenarios has been lacking. Here, we show that *Syngonium hastiferum* (Araceae), a Neotropical representative of an otherwise beetle-pollinated clade, is pollinated by plant bugs (Miridae; Heteroptera), which are florivores of *Syngonium schottianum* and other Araceae species. We found that *S. hastiferum* differs in several floral traits from its beetle-pollinated relatives. Scent emission and thermogenesis occur in the morning instead of the evening hours, and its pollen surface is spiny instead of smooth. Furthermore, the floral scent of *S. hastiferum* includes a previously unknown natural product, (*Z*)-3-isopropylpent-3-en-1-ol, which we show to have a function in specifically attracting the plant bug pollinators. This is the first known case of a specialized plant bug pollination system and provides clear evidence for the hypothesis that the adoption of antagonistic florivores as pollinators can drive flower diversification.

INTRODUCTION

Organismal interactions are highly diverse in nature, ranging from antagonisms (e.g., predation, deceptive pollination [e.g., in orchids[1]]) to mutualisms, and occur across the entire tree of life, from bacteria that interact with plasmids[2] to plants that interact with animals or fungi. As has been suggested in earlier studies, mutualisms often evolved from antagonisms.[3,4] There is evidence that biotic pollination systems evolved from ancestrally antagonistic systems.[5] In extinct gymnosperms and other seed plant lineages, the fossil record suggests that insects feeding on pollen or pollination droplets may have been co-opted as pollinators before the first major diversification of angiosperms (flowering plants) in the Cretaceous.[6–8] For early angiosperms, flies, thrips, beetles, true bugs, and moths may have been important pollinators.[9–15] Such insect groups may ancestrally have acted as florivores that used flowers primarily for feeding (mainly on pollen) as well as mating sites.[5,9] Specialized pollination systems evolved subsequently and, through pollinator-mediated selection, led to the overwhelming diversity of flowers that we observe today.[16]

While evolutionary scenarios involving an antagonistic origin and the subsequent change to a mutualistic pollination system are intuitive and appealing, evidence for such scenarios is scarce given the fact that analyses aiming to reconstruct long past pollination interactions may be impeded by various types of uncertainty.[10,17] A potential source of information on past interactions is fossils. However, to unequivocally deduce complex past interactions from the intrinsically fragmentary fossil record may be even more difficult.[9,18–20] A tractable way to understand the evolution and diversification of pollination systems is to comparatively study extant interactions and to interpret the results in a phylogenetic framework. A prominent example of the successful use of such an approach involves the highly specialized mutualistic yucca-yucca moth pollination system, where the moths are seed predators as larvae and pollinators as adults.[21] A phylogeny of the yucca moths and related moth lineages revealed that the evolution of this pollination system required changes in the behavior and morphology of the yucca moths, which allowed for active pollination of the flowers. The study by Pellmyr and Thompson[21] showed that pollination by adult-stage moths evolved from an ancestrally florivorous system in which the moth larvae predated on yucca seeds, but the adult moths did not yet act as pollinators.

Clear examples of ''antagonist capture'' in angiosperm pollination, mediated by floral trait changes, are currently missing from the literature. Here, we focus on pollination and chemical ecology of members of the plant clade Caladieae (Araceae)

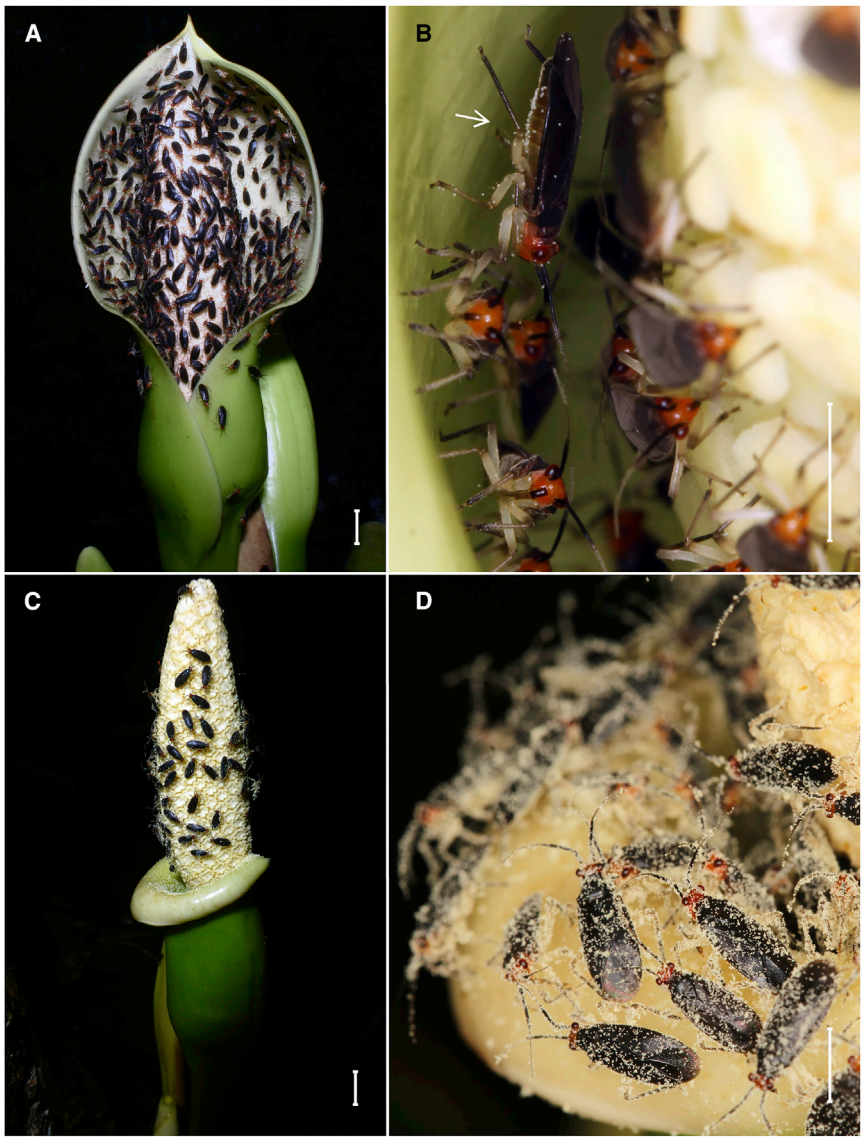

Figure 1. Anthesis of *Syngonium hastiferum* and pollinating plant bugs

(A) Inflorescence of *S. hastiferum* during the second morning of the female phase of anthesis with hundreds of individuals of the pollinating plant bug species *Neella* sp. nov. (Heteroptera: Miridae; the species is new to science and has not yet been formally described).

(B) Numerous individuals of *Neella* sp. nov. on the proximal part of the spadix and on the spathe of *S. hastiferum*, where the female flowers are located (pollination chamber), during the female phase of anthesis. The arrow points to the ventral body side of a plant bug pollinator with *Syngonium* pollen, most likely from another individual of *S. hastiferum*.

(C) Inflorescence of *S. hastiferum* during the third morning of anthesis (male phase), when pollen gets released, the pollination chamber closes, and the upper half of the spathe abscises.

(D) Close-up photo of the plant bug pollinators, which are dusted with pollen grains while leaving the inflorescence on the morning of the third day of anthesis (male phase).

Scale bars, 1 cm (A and C) and 5 mm (B and D).

See also Videos S1 and S2.

and provide evidence for the recruitment of antagonistic floral visitors as pollinators. While the Caladieae were earlier considered to be exclusively pollinated by beetles,[22] here we show that a species is pollinated by plant bugs (Miridae; Heteroptera). In addition, we describe in detail the morphological, thermogenic, and chemical floral traits that distinguish this previously unknown and highly specialized plant bug pollination system from earlier described cyclocephaline scarab beetle pollination systems in Araceae, where plant bugs act as florivores. Plant bugs are known as widespread florivores in scarab beetle-pollinated Araceae and various other angiosperm lineages, where they pierce flower parts and insert saliva, producing macerations of floral tissue or pollen, which they then consume.[23–25] We provide unequivocal evidence that plant bugs are the sole pollinators of *Syngonium hastiferum* and clarify by which means these insects are attracted to the flowers. The results of our study provide novel insights into the evolution and diversification of insect pollination in angiosperms and provide an example of the evolution of a mutualistic interaction from an ancestrally antagonistic relationship.

RESULTS

Floral biology and pollinators

The numerous, small male and female flowers of a *Syngonium hastiferum* inflorescence are tightly packed along a ca. 10-cm-long upright spike (the spadix), which is enclosed by a bract (the spathe; Figure 1). The observed plants are protogynous and each of several sequentially flowering inflorescences per plant has a flowering cycle of 3 days. During the first 2 days of anthesis, the inflorescences are in the female phase (Figures 1A and 1B), and they are in the male phase on the third day (Figures 1C and 1D). On the first morning of anthesis, the spathe partly opens to reveal the apical portion of the spadix that comprises the male flowers (Figure 1A). The basal part of the spadix, which bears the female flowers, remains surrounded by the inflated lower part of the spathe to form a pollination chamber into which plant bugs enter (Figure 1B). Between the male and female parts, the spadix is slightly thinner and bears about two dozen reduced and sterile male flowers. In the inflorescences of closely related scarab beetle-pollinated *Syngonium* species and other Araceae, sterile flowers are enlarged and serve as food body rewards for the pollinators.[26,27]

Over the course of anthesis, the male part of the spadix repeatedly heats up through endogenous thermogenesis, reaching up to 16°C above ambient air temperature (Figure 2). On the first and second day of anthesis, the increase in the spadix

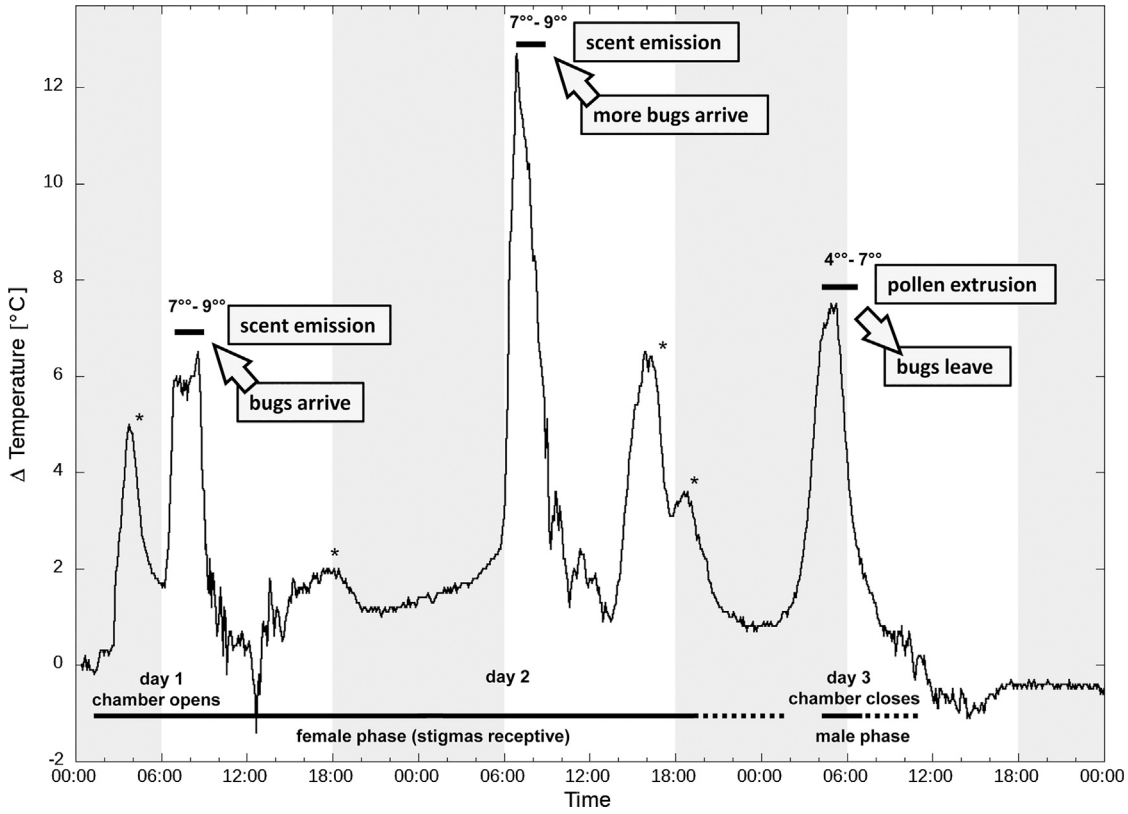

Figure 2. Thermogenesis, course of anthesis, and interaction with plant bugs of *Syngonium hastiferum*

Mean temperature difference to ambient air of five inflorescences (measured at the male part of the spadix) of different individuals of *S. hastiferum* during the 3 days of anthesis. The time periods of the main anthesis events (opening/closing of the pollination chamber, scent emission, stigma receptivity, pollen extrusion) and arrival/departure of plant bugs are shown. Gray bars indicate the duration of night, and asterisks (*) indicate thermogenic events independent of arrival/departure of plant bugs and obvious scent emission. The plant bugs arrive during the mornings of the first and second day of anthesis when a strong scent is emitted. They stay until the morning of the third day when the pollination chamber closes and pollen gets extruded.

See also Video S1.

temperature between 7:00 and 9:00 coincides with the release of a strong scent (Figure 2) emitted from the male part of the spadix. Other parts of the inflorescence do not release a scent detectable to the human nose (F.E. et al., unpublished data). At the times of combined scent and heat production, high numbers (mean, 146; min–max, 20–515) of individuals of only a single plant bug species (Miridae, Bryocorinae) arrived at all 20 investigated inflorescences while no other floral visitors were observed, except for occasional unidentified patrolling ants and a predatory *Anolis* lizard, neither of which visited the receptive female flowers (Figure 1A; Video S1). This plant bug species is new to science and has not yet been formally described; hereafter, we refer to it as *Neella* sp. nov. Male and female individuals (sex ratio determined from a subset of 200 bug individuals: 1:1) entered the pollination chamber and crawled over the female flowers. Thereby, they transferred pollen acquired during previous visits of an inflorescence in the male phase onto the moist, receptive stigmas (Figure 1B). The bugs remained on the inflorescence until the morning of the third day to mate and feed, exiting and re-entering the pollination chamber frequently throughout the day and the night (Video S1). Plant bugs generally feed on plant sap by inserting their piercing, sucking mouthparts into the plant tissue.[23] In *S. hastiferum*, their feeding behavior left small brown lesions all over the spadix and the spathe but otherwise did not cause any obvious damage to the inflorescences.

The male, pollen-extruding phase begins in the morning (ca. 4:00) of the third day of anthesis, when the spadix heats up again but does not release any scent detectable by the human nose (Figure 2). During the male phase, the distal part of the spathe wilts, turning from green to white, and usually abscises, while the inflated pollination chamber remains intact and slowly closes (Figures 1C and 1D; Video S1). Concomitant with these inflorescence changes, the plant bugs leave the chamber and move up to the heat-producing and pollen-extruding male portion of the spadix where they feed on male flowers, in particular on the anthers. Large amounts of echinate (spiny) pollen grains are extruded in pollen strands, which soon lose cohesion. The now powdery pollen grains drizzle down from the male flowers and adhere to the body surface of the *Neella* bugs (Figures 1C, 3A, and 3C; Video S2). The plant bugs, heavily dusted with pollen, leave the inflorescence between sunrise (6:00) and 8:00, potentially being attracted by other female-phase, scented inflorescences of *S. hastiferum*.

Pollinator exclusion experiments showed that *Neella* sp. nov. is an efficient pollinator of *S. hastiferum*. The likelihood to set fruit (Fisher exact test: $p < 0.001$) and the number of

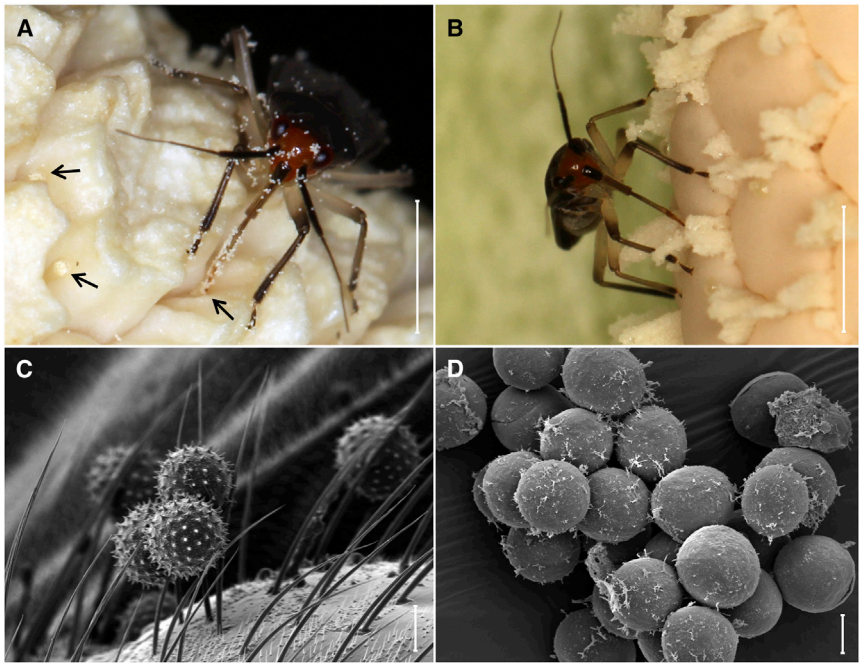

Figure 3. Male flowers and surface structure of pollen grains from different Araceae species and their adherence abilities on plant bugs

(A) An individual of the plant bug *Neella* sp. nov. gets dusted with pollen grains on a male-phase inflorescence of *Syngonium hastiferum* while feeding on the pollen-extruding male flowers (arrows point to anthers).

(B) An individual of the plant bug *Neella* sp. nov., which was experimentally transferred to a male-phase inflorescence of *Dieffenbachia aurantiaca*, a scarab beetle-pollinated species that produces pollen strands with pollen grains that stick together and do not adhere to the body surface of *Neella* sp. nov.

(C) Scanning electron microscope (SEM) image of spiny (echinate) pollen of *S. hastiferum* on the body of the pollinating plant bug *Neella* sp. nov, which was caught from a female-phase inflorescence of *S. hastiferum*.

(D) SEM image of pollen grains of *Philodendron grandipes*, a typical scarab beetle-pollinated species, sticking together due to high amounts of sticky pollenkitt covering the smooth surface of the pollen wall.

Scale bars, 5 mm (A and B) and 20 μm (C and D). See also Video S2.

developed seeds (Mann-Whitney test: $Z = 4.38$, $p < 0.001$) were significantly higher in openly pollinated inflorescences than in bagged ones. Nine out of ten inflorescences that were covered with fine meshed gauze bags to exclude the *Neella* bugs as visitors did not set any fruit/seed. The single inflorescence that set fruit produced four seeds. This strongly contrasts with the 20 non-manipulated inflorescences, which were visited by *Neella* sp. nov. They all set fruit and produced on average 51 seeds (min–max: 12–75), showing that the plants rely on *Neella* sp. nov. for fruit and seed production.

To test and compare the pollen transfer capabilities of *Neella* bugs, we experimentally transferred *Neella* sp. nov. plant bugs to *Dieffenbachia aurantiaca*, a scarab beetle-pollinated Araceae species co-occurring and co-flowering at our study site with *S. hastiferum*. We found that pollen of this species behaves differently on the surface of the bugs than does the pollen of *S. hastiferum*. In all 28 bug individuals tested, no pollen of *D. aurantiaca* stuck to their bodies (Figure 3B).

Attractiveness of floral scent to *Neella* sp. nov. and scent chemistry

Experiments that prevented the plant bugs from seeing female-phase and bud-stage inflorescences of *S. hastiferum* but allowed the scent to be released showed that floral scent is the key attractant for the plant bugs. Five female-phase inflorescences, bagged with fine meshed white gauze bags, attracted on average 71 (min–max: 30–153) individuals of *Neella* sp. nov. (Figure 4A), while none were attracted by nearby bagged, bud-stage inflorescences (Figure 4A). To test whether the white gauze bags, which potentially were resembling the visual signal of the white inner surface of the spathe (Figure 1A), served as a major cue for the bugs, we conducted similar experiments with green paper cylinders (Figure 4B). There were on average 47 (25–77) of *Neella* sp. nov. individuals on the inflorescences inside the green cylinders, while no bugs entered paper cylinders that covered bud-stage inflorescences (Figure 4B).

Gas chromatography-mass spectrometry (GC-MS) analysis of floral headspace scent samples collected during both scent-emission peaks showed a single dominant scent compound (Figure 5A; Table S1). The mass spectrum of this compound (Figure 5B) did not match with any mass spectrum in commercially available libraries for volatile organic compounds. 2D nuclear magnetic resonance (NMR) spectra of a headspace sample dissolved in deuterated chloroform allowed us to identify and characterize one dominant spin system as illustrated by ^{1}H–^{13}C and ^{1}H–^{1}H correlations (Figures 5C, 5D, and S1). The structural elucidation identified the major component as (*Z*)-3-isopropylpent-3-en-1-ol **1** (Figures 5B–5D and S1). The fact that a minor component, identified by GC-MS as 3-isopropylpentan-1-ol **2** (Figures 5A and 5B) based on published GC-MS data,[28] contains the same carbon skeleton increased our confidence in the elucidated structure.

The identity of **1** was confirmed by its independent chemical synthesis (Figure 5E). For successful synthesis, the challenge that had to be met was the stereocontrolled assembly of a sterically encumbered, trisubstituted volatile and unsaturated alcohol. After several unsuccessful attempts aiming to avoid trimethylstannylated intermediates, we synthesized vinylstannane **6** from commercially available ethyl pent-2-ynoate **3**, following a protocol that was developed by Piers and co-workers.[29,30] Unfortunately, all attempts to achieve the synthesis of **1** by a Stille cross-coupling with **6** failed. Moving to vinyliodide **7**[31] set the stage for a Negishi cross-coupling. Following the lead of Krasovsky and Lipshutz,[32] who developed the combination of $PdCl_2$ (Amphos)/*N*-MeIm in tetrahydrofuran, the coupling of **7**

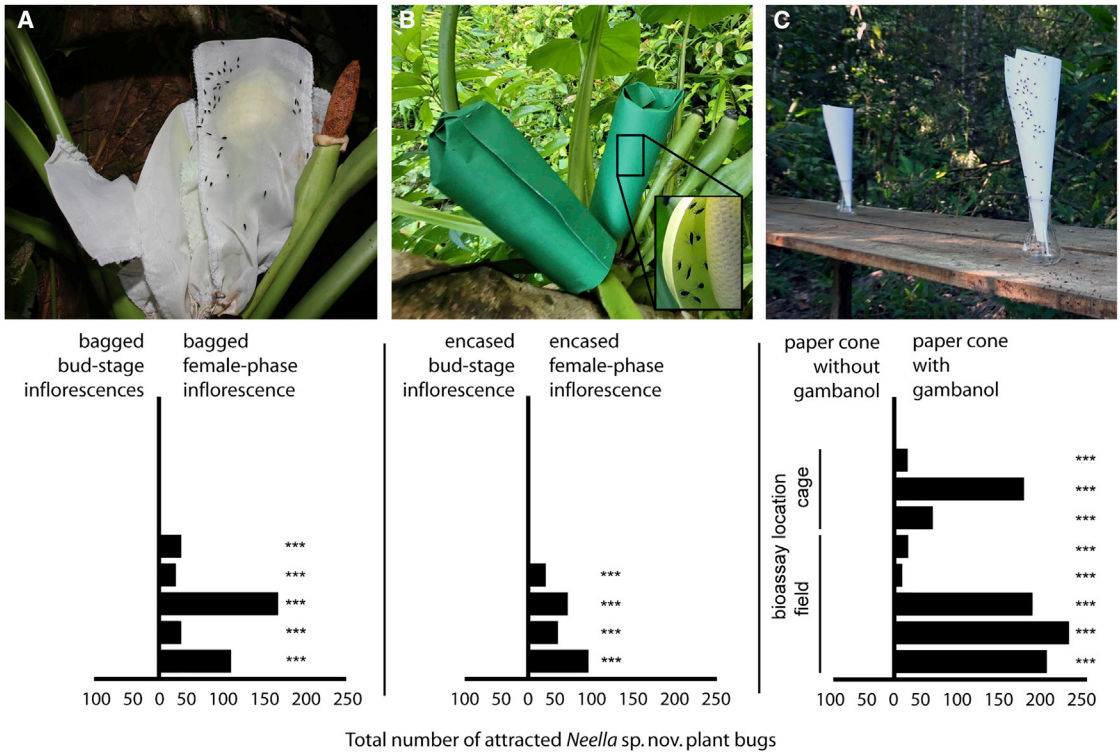

Figure 4. Two-choice bioassays with nylon-mesh-bagged and paper-encased inflorescences of *Syngonium hastiferum*, and with synthetic gambanol

(A) Plant with a female-phase inflorescence versus several bud-stage inflorescences bagged with white nylon-mesh bags to visually hide the inflorescences; note the numerous *Neella* sp. nov. plant bugs on the bag covering the female-phase inflorescence. In total five plant individuals with one female-phase and one or more bud-stage inflorescences each were tested. Only female-phase but not bud-stage inflorescences attracted *Neella* sp. nov.

(B) Plant with a female-phase versus a bud-stage inflorescence covered with green paper cylinders each to visually hide the inflorescences. Cylinders were open apically and basally to allow for scent release as well as for access of pollinators to inflorescences (four plant individuals were tested). Inset shows *Neella* sp. nov. plant bugs in a female-phase inflorescence previously covered with a green paper cylinder. Only female-phase but not bud-stage inflorescences attracted *Neella* sp. nov.

(C) Two-choice bioassay with non-scented versus scented (with synthetic (*Z*)-3-isopropylpent-3-en-1-ol, gambanol) white paper cones; note the numerous *Neella* sp. nov. plant bugs on the scented cone. The experiment was carried out 5 times in the field and 3 times in a flight cage (9 × 9 × 3 m). This flight cage contained ca. 200 individuals of the pollinators that were previously collected from inflorescences of *S. hastiferum* and released into the cage just before each of the three experiments. Only paper cones scented with gambanol were attractive to *Neella* sp. nov. plant bugs. ***$p \leq 0.001$ in exact binomial tests that tested for differences in the number of attracted individuals by the two choices offered to the plant bugs each.

Each bar represents the number of plant bugs attracted to one of the alternative treatments per replicate.

See also Video S3.

with 2-iodopropane was met without success (<5% yield [*Z*/*E*: 83:17] of **1**). Changing the solvent to dimethyformamide[33] turned out to be successful in allowing the synthesis of **1** in 87% yield and a *Z*/*E* ratio of 94:6 (for details on synthesis, see STAR Methods).

The NMR and mass spectra as well as the retention time of synthesized **1** were identical to the data recorded from the collected natural product (Figure S2; chemical shifts are found in Tables S2 and S3). (*Z*)-3-Isopropylpent-3-en-1-ol represents a hitherto undescribed natural product, for which we suggest the trivial name "gambanol," as a reference to the Tropical Field Station La Gamba in Costa Rica, where we conducted most of the research for this study.

In eight bioassays, performed on eight different days during morning hours (7:00–08:30), lures containing synthesized gambanol were significantly more attractive than negative controls (Figure 4C). Overall, synthesized gambanol attracted more than 900 individuals of *Neella* sp. nov. (sex ratio determined from a subset of 185 bugs: 1:1; Figure 4C; Video S3) and no other insects. *Neella* sp. nov. did not respond at all to negative controls (Figure 4C). In trapping experiments performed during evening hours (17:30–19:00), neither *Neella* sp. nov. nor nocturnal scarab beetle pollinators, nor any florivorous plant bugs of sympatric beetle-pollinated Araceae, were attracted by gambanol.

DISCUSSION

Our study is the first to document a specialized plant bug (Miridae) pollination system. Previously, plant bugs were only known as co-pollinators of primarily bee-pollinated *Arum creticum*,[34] and likely some crops,[23] and as resident floral visitors mediating self-pollination in addition to bee pollination in the carnivorous plant *Roridula dentata*.[35] Generally, specialized pollination by true bugs (Heteroptera) is extremely rare and until now had

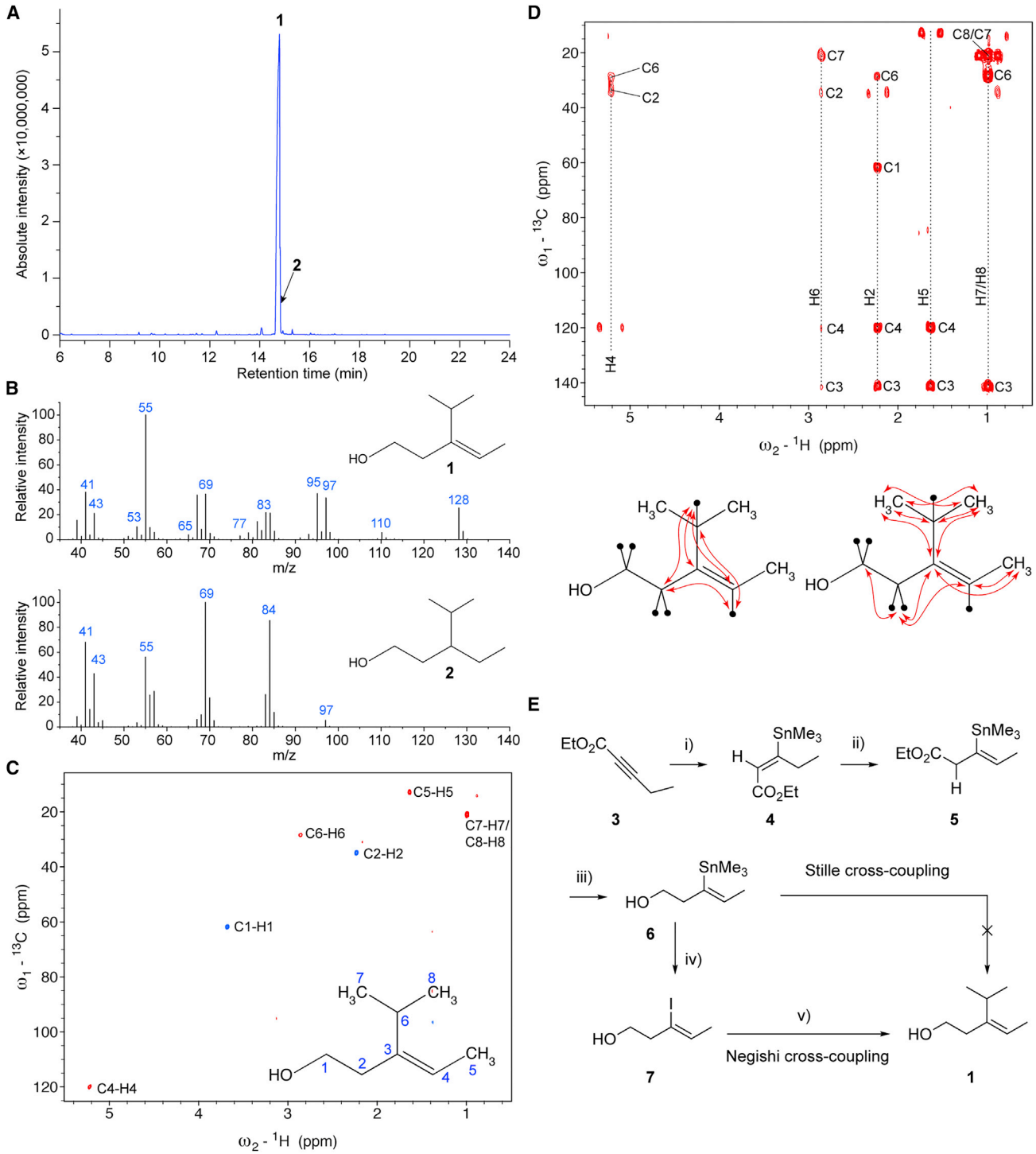

Figure 5. Analysis of the collected volatiles by gas chromatography coupled with mass spectrometry and nuclear magnetic resonance spectroscopy as well as chemical synthesis of gambanol 1

(A) Representative chromatogram (GC-MS; total ion current) of a dynamic headspace scent sample collected from an inflorescence of *Syngonium hastiferum*. The sample is strongly dominated by (*Z*)-3-isopropylpent-3-en-1-ol **1**, followed by 3-isopropylpentan-1-ol **2**, which has a retention time very similar to **1**.

(B) Mass spectra and chemical structures of the most dominant compounds 1 and 2.

(C and D) 2D NMR spectra, which correlate ^{1}H and ^{13}C resonances, established connectivities between these atoms and enabled the determination of the chemical structure of **1** as (*Z*)-3-isopropylpent-3-en-1-ol. Shown is a ^{1}H–^{13}C heteronuclear single quantum coherence (HSQC) spectrum (C) with multiplicity editing, in which CH_2 groups have an opposite sign, compared with CH and CH_3 groups; positive signals are indicated in red and negative signals in blue.

(legend continued on next page)

only been shown for flower bugs (Anthocoridae) that pollinate *Macaranga tanarius*.[36] However, true bugs may have played a major role in early angiosperm pollination.[9]

All Caladieae species studied so far,[22] including *Caladium*, the sister genus of *Syngonium*, are pollinated by beetles (Figure S3) (Coleoptera: mainly Cyclocephalini scarab beetles, Dynastinae) that feed on floral food bodies (enlarged sterile male flowers) and pollen.[37–41] These plant species are mostly co-visited by high numbers of other *Neella* plant bug species that do not enter the pollination chamber and thus cannot act as pollinators.[26,27,42] Similar communities of floral visitors, including scarab beetles as pollinators and plant bugs as abundant florivores, are found in other, more distantly related Araceae genera including *Dieffenbachia* and *Philodendron*.[24,43–46]

Anthesis and pollination biology of *S. hastiferum* differ distinctly in various properties from scarab beetle-pollinated Neotropical Araceae (Figure 6). Food bodies, which are characteristic of scarab beetle-pollinated species (e.g., *Syngonium schottianum*; species of *Caladium*, *Dieffenbachia*, and *Philodendron*[26,41,44,46–48]), are absent in *S. hastiferum*. Heat and scent production occur in the morning instead of evening hours,[24,26,47–52] and a novel, previously unknown scent compound, (*Z*)-3-isopropylpent-3-en-1-ol (gambanol), is responsible for pollinator attraction. In earlier studies, scarab beetles and non-pollinating plant bugs were shown to be attracted by compounds such as dihydro-β-ionone, 4-methoxystyrene, 4-methyl-5-vinylthiazole, and *cis*-jasmone.[24,52–54] As the number of bugs attracted by baits loaded with synthesized gambanol (Figure 4C) was similar to the number of bugs attracted by natural, thermogenic inflorescences (Figure 1A), the produced inflorescence heat itself is likely no primary attractant for the plant bugs but merely promotes scent emission.[55] The absence of food bodies in *S. hastiferum* and the combined emission of heat and scent in the morning hours do not match the needs and the activity times, respectively, of the large, nocturnal Cyclocephalini scarab beetle pollinators. Nor does the floral scent of *S. hastiferum* attract these beetles or plant bug species that occur as non-pollinating florivores in sympatric beetle-pollinated species.

The echinate (spiny) pollen grains of *S. hastiferum* are extruded as strands that quickly disintegrate. Consequently, individual pollen grains adhere to *Neella* sp. nov. By contrast, pollen grains of scarab beetle-pollinated species (Figure 3D) are psilate (smooth) or verrucate (warty) (*Philodendron grandipes*,[44] *Syngonium schottianum*[56]), remain clumped together due to high amounts of sticky pollenkitt, and are dispersed in partial pollen strands or clumps.[26,37,47,56] As demonstrated here for *D. aurantiaca*, such pollen grains do not adhere to the body of *Neella*. sp. nov. (Figure 3B), excluding these bugs as potential pollinators of this beetle-pollinated species.

Another representative of the genus *Syngonium*, *S. angustatum*, was previously studied in the greenhouse by Chouteau et al.[47] It was found to have a similar thermogenesis pattern as *S. hastiferum*, which led the authors to suggest that *S. angustatum* is possibly pollinated by unknown, diurnal pollinators rather than by the usual nocturnal Cyclocephalini scarab beetles.[47] *S. angustatum* also has echinate pollen grains[57] and, like *S. hastiferum*, is native to Costa Rica.[58] Thus, this species may also be pollinated by plant bugs, but its pollination system remains to be investigated and documented in the field.

The novel pollination system described here is not only characterized by the specialized floral traits of *S. hastiferum* but also by the unique behavior of *Neella* sp. nov. Most importantly, *Neella* sp. nov. plant bugs respond to gambanol in the morning hours, whereas non-pollinating florivores, such as *Neella floridula*, *N. bicolor*, and *N. carvalhoi*, respond to the scent of their host plants at night.[24] *Neella* sp. nov., but not non-pollinating congeners,[24,43] enter the pollination chamber of their host plant and visit the female flowers. It appears that *Neella* sp. nov. uses the chamber as shelter during day and night and to feed on female flowers (Figures 1B and 6). One aspect in which this plant bug pollination system is similar to scarab beetle pollination in related Araceae is that pollinators leave the pollination chamber at the end of the female phase. Most likely, this behavior is induced by the combination of the contraction of the chamber and the opening of male flowers, on which *Neella* sp. nov. feeds during the male phase of anthesis. To summarize, *S. hastiferum* differs in several specific floral traits from closely related scarab beetle-pollinated Neotropical Araceae, which are often visited but never pollinated by *Neella* bugs. The combination of uncommon traits of *S. hastiferum* and of *Neella* bugs results in a highly specific interaction between *S. hastiferum* and *Neella* sp. nov.

Although shifts from one functional group of mutualistic pollinators to another have been documented and recognized as potential drivers of floral diversification in many angiosperm groups,[59–62] the recruitment of florivores as pollinators and the role of this transition in the diversification of angiosperms have so far not been well understood. A potentially promising angiosperm system to explore further might be the brood-site pollination mutualism between *Macaranga* species (Euphorbiaceae) and thrips.[63] This specialized pollination system might have evolved from a more generalized system that involved thrips mainly as florivores.[63] However, ancestral state reconstructions that focused on inflorescence morphology and pollinator rewards in *Macaranga* indicate that more work on the pollination biology of the genus is needed before any conclusion on the evolution of pollination systems in this genus can be drawn.[64] Outside angiosperms, a case that in various aspects is similar to the system described here is found in the Cycadales (cycads). Different species in this order have been shown to be pollinated by weevils (Coleoptera) and thrips (Thysanoptera), two insect groups that ancestrally likely acted mostly as plant antagonists

(D) A 2D ^{1}H–^{13}C heteronuclear multiple bond correlation (HMBC) spectrum provides ^{1}H–^{13}C long-range correlations. These correlations are shown schematically in the form of arrows and depicted on two copies of the molecule for reasons of simplicity.

(E) Synthesis of (*Z*)-3-isopropylpent-3-en-1-ol **1**, the dominant compound in the floral scent of *Syngonium hastiferum*. (i) Me_3SnCl (1.3 equiv), Li (2 equiv), naphthalene (6.6 mol %), then $CuBr \cdot SMe_2$ (1.3 equiv), **3** (1.0 equiv), 4 h, −78°C, 69%. (ii) **4** (1.0 equiv), LDA (2.3 equiv), −78°C, 45 min, then AcOH, −98°C, 72%. (iii) **5**, DIBAL-H (2.5 equiv), −78°C to 0°C, 3 h, 89%. (iv) **6**, I_2 (1.05 equiv), room temp., 30 min, 94%. (v) 2-Iodopropane (2.4 equiv), Zn (2.6 equiv), then **7** (1.0 equiv), 1-methylimidazole (2 equiv), $PdCl_2(Amphos)_2$ (2 mol %), 87%. Amphos = 4-(di-tert-butylphosphanyl)-*N*,*N*-dimethylaniline; *N*-MeIm = *N*-methylimidazole.

See also Figures S1 and S2, Tables S1–S3, and Methods S1.

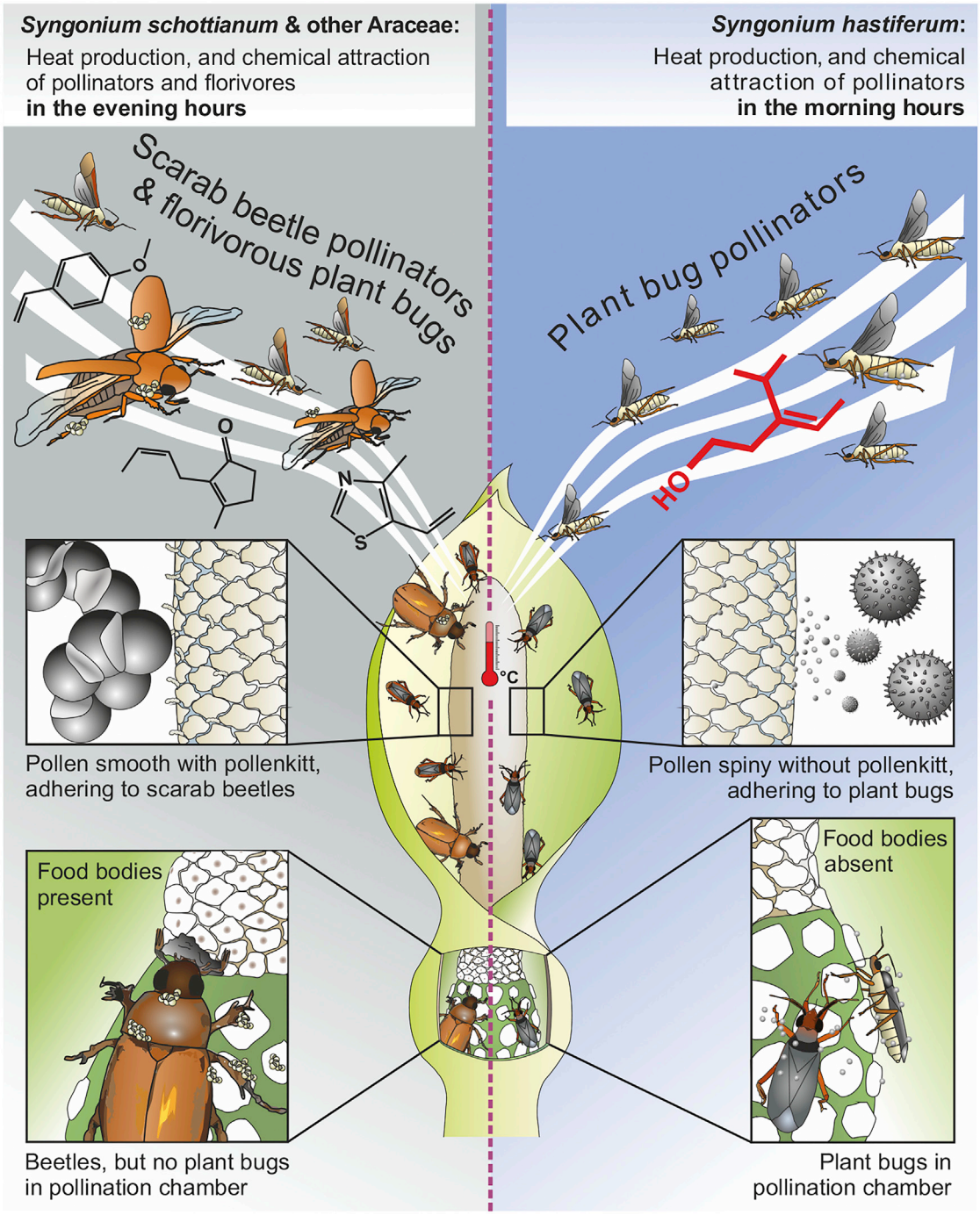

Figure 6. Main differences between plant bug and scarab beetle-pollinated Araceae

The left half of the figure shows the pollination system of typical scarab beetle-pollinated Neotropical Araceae, e.g., *Syngonium schottianum*, with nocturnal Cyclocephalini scarab beetle pollinators and florivorous plant bugs. The right half of the figure shows the close relative *S. hastiferum* with the novel plant bug pollination system. The two systems differ mainly in the timing of heat and scent production, the type of compounds involved in attracting florivores and pollinators, pollen morphology, the availability of food bodies, and the animals that enter the floral chamber.
See also Figure S3.

(feeding on pollen).[65–68] It is noteworthy that similarly to the Araceae-pollination system described here, specific pollinator behavior on different Cycadales species is mainly mediated by differences in the timing of thermogenesis and in scent composition.[65–68] These remarkable parallels present in Cycadales and Araceae indicate that similar evolutionary mechanisms may be at work in the pollination systems of very distantly related plant lineages.

The overwhelming diversity of angiosperms and their flowers evolved to a large degree in response to pollinator-mediated selection,[16] and shifts between different functional groups of pollinators are often thought to have happened gradually via a phase of more generalized pollination involving two or more almost equally effective pollinators[59,69–71] (but see Hoballah[72] and Bradshaw and Schemske[73]). In contrast to this, our results together with phylogenetic data in Araceae (Figure S3) suggest that in *Syngonium*, a highly specialized pollination system (scarab beetle pollination) was replaced with another highly specialized system (plant bug pollination). The shift was accompanied by a suite of floral changes (loss of food bodies, a change in timing of thermogenesis and scent release, emission of different floral scent compounds, and changes in pollen morphology) resulting in the fact that only plant bugs and not scarab beetles are attracted to the inflorescences of *Syngonium hastiferum* and capable of pollination.

Angiosperm flowers and their insect visitors have co-evolved over a long period of time, likely from the very start of angiosperm diversification, which was dated to at least 140 million years ago.[9,17,74] It was hypothesized that evolutionary shifts away from antagonistic relationships toward mutualistic interactions between flowers and insects have contributed considerably to the evolutionary diversification of flowers and of angiosperms as a whole.[5] Our discoveries not only expand our knowledge of angiosperm pollination by introducing a novel pollination system with plant bugs (Miridae; Heteroptera) as the only pollinators but also identify floral traits that mediate the transition from florivory to a pollination mutualism in angiosperms.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- RESOURCE AVAILABILITY
  - Lead contact
  - Materials availability
  - Data and code availability
- EXPERIMENTAL MODEL AND SUBJECT DETAILS
  - Study site and species
- METHOD DETAILS
  - Floral biology and pollinators
  - Floral scent: attractiveness to pollinators and chemistry
- QUANTIFICATION AND STATISTICAL ANALYSIS

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.cub.2022.09.013.

A video abstract is available at https://doi.org/10.1016/j.cub.2022.09.013#mmc7.

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AUTHOR CONTRIBUTIONS

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Biological samples		
Syngonium hastiferum plants	This work	Voucher at the herbarium of the University of Vienna (WU), Department of Botany and Biodiversity Research.
Dieffenbachia aurantiaca plants	This work	Voucher at the herbarium of the University of Vienna (WU), Department of Botany and Biodiversity Research.
Philodendron grandipes plants	This work	Voucher at the herbarium of the University of Vienna (WU), Department of Botany and Biodiversity Research.
Neella sp. nov. plant bugs	This work	Voucher at the herbarium of the University of Vienna (WU), Department of Botany and Biodiversity Research.
Chemicals, peptides, and recombinant proteins		
Tenax TA (60-80 mesh)	Sigma-Aldrich	11982
Carbotrap B (20-40 mesh)	Sigma-Aldrich	20287
$CDCl_3$ (99.8 atom% D) with 0.03% tetramethylsilane (TMS)	Armar Europe, Leipzig, Germany	013400.2050
3-isopropylpentan-1-ol	Private stock of Jocelyn Millar	N/A
Lithium	Sigma-Aldrich	499811
Tetrahydrofuran	Sigma-Aldrich	401757
Trimethyltinchloride	Sigma-Aldrich	146498
CuBr	Sigma-Aldrich	212865
NH_4Cl	Sigma-Aldrich	213330
NH_4OH	Sigma-Aldrich	221228
$MgSO_4$	Sigma-Aldrich	434183
Lithium diisopropylamide	Sigma-Aldrich	774766
Acetic Acid	Sigma-Aldrich	1.00062
$NaHCO_3$	Sigma-Aldrich	401676
Diethylether	Sigma-Aldrich	673811
Diisobutylaluminum hydride	Sigma-Aldrich	190306
Celite	Sigma-Aldrich	1.02693
Dichloromethane	Sigma-Aldrich	270997
$Na_2S_2O_3$	Sigma-Aldrich	72049
Zn dust	Sigma-Aldrich	96454
TMSCl	Sigma-Aldrich	92361
2-Iodopropane	Sigma-Aldrich	148938
LiCl	Sigma-Aldrich	310468
N,N-Dimethylformamide (DMF)	Sigma-Aldrich	319937
1-Methylimidazole	Sigma-Aldrich	8-05852
$PdCl_2(Amphos)_2$	Sigma-Aldrich	678740
n-Pentane	Sigma-Aldrich	1.07176
Napthalene	Sigma-Aldrich	147141
Software and algorithms		
Topspin 3.2	Bruker Biospin	https://www.bruker.com/de/service/support-upgrades/software-downloads/nmr.html

(*Continued on next page*)

Continued

REAGENT or RESOURCE	SOURCE	IDENTIFIER
SPARKY 3	University of California, San Francisco	https://www.cgl.ucsf.edu/home/sparky/
Exact binomial tests of goodness-of-fit	N/A	http://www.biostathandbook.com/exactbin.xls
GCMSolution Version 4.11	Shimadzu Corporation, Japan	N/A
Statistica Version 12	StatSoft	http://www.statsoft.com
Other		
5 mm NMR-Tubes, Type 5TA	Armar Europe, Leipzig, Germany	032100,5045
Insect cage large 9 x 9 x 3 m	Self-constructed	N/A
Insect cage small 80 x 50 x 50 cm	Papa-Papillon, Bern, Switzerland	https://www.papapapillon.ch/
Membrane pump	Gardner Denver, Germany	G12/01EB
Polyethylene oven bags	Toppits, Germany	N/A

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Florian Etl (florian.etl@univie.ac.at).

Materials availability

Plant and insect voucher specimens are deposited in the herbarium of the University of Vienna (WU), Department of Botany and Biodiversity Research, Rennweg 14, 1030 Vienna.

Data and code availability

All data are available in the main text or the supplemental information. This study did not generate a code.

EXPERIMENTAL MODEL AND SUBJECT DETAILS

Study site and species

Fieldwork was carried out during the dry season between February and April of 2013, 2014, 2016, and 2017 in the Piedras Blancas National Park, at the Tropical Field Station La Gamba, the Esquinas Rainforest Lodge, and along the road that leads from the Tropical Field Station La Gamba to the village of La Gamba in Southwest Costa Rica (8°42′03″N, 83°12′05″W).

Syngonium hastiferum (Standley & L. 0. Williams) is a climbing aroid plant endemic to the Golfo Dulce Region in Costa Rica. It frequently grows in tropical wet rain forests from sea level up to 700 m a.s.l.[58]

METHOD DETAILS

Floral biology and pollinators

Anthesis and floral visitor observations

The entire three-day anthesis (flowering cycle) and behavior of inflorescence visitors were observed on 20 inflorescences belonging to 20 individuals of *S. hastiferum*. Individual inflorescences were observed hourly for a minimum of five minutes during day and night, from the opening of inflorescences (2:00 in the morning) until the end of anthesis (11:00 in the morning, third day of anthesis). Five of these inflorescences were additionally photographed each ten minutes by a DSLR camera (Canon Eos 300D) equipped with a timer switch remote control. Arrival and departure times at inflorescences as well as the behavior on inflorescences of all insect visitors were recorded. In addition, scent emission (by sniffing with the nose), stigma receptivity (humidity of stigmas), and pollen release were documented. We used a DSLR camera (Canon Eos 60d with a macro lens Canon EF–100 mm equipped with a ring light Canon MR-14EX, Canon, Tokyo, Japan) to look for the presence of pollen grains on the body surface of visitors during the female phase and the adherence of freshly extruded pollen to the body in the male phase. The taxonomic identity of pollen was confirmed with a scanning electron microscope (see below).

Thermogenesis measurements of inflorescences

Spadix temperature was measured during the entire three days of anthesis of five inflorescences from five individuals of *S. hastiferum*. An external temperature sensor connected to a multi-sensor thermal element (NiCr/NiAl, Scantronick Mugrauer Gmbh) was inserted into the distal (male) part of the spadix, which was found to be most thermogenic in preliminary analyses.

Temperature was recorded every five minutes using a temperature data logger (Thermofox universal, Scantronick Mugrauer Gmbh), which was connected to the thermal element and simultaneously recorded ambient air temperature.

Pollen grains from Syngonium hastiferum, Philodendron grandipes *and* Dieffenbachia aurantiaca

Pollen from male-phase inflorescences of *S. hastiferum* and sympatric *P. grandipes* and *D. aurantiaca* was collected right after anther dehiscence, dried, sputter coated with gold (SCD 050, BAL-TEC Maschinenbau AG, Pfäffikon, Switzerland) and investigated under SEM (scanning electron microscope, JSM-6390, Joel, Peabody, USA). For better visibility of the surface structure, some pollen grains of each species were additionally rehydrated and critical point dried (Autosamdri-815, Tousimis, Rockville, USA) before sputter coating and investigation under SEM.

Adherence of Syngonium hastiferum *pollen to* Neella *sp. nov.*

To look for pollen grains of *S. hastiferum* on the bodies of *Neella* sp. nov., eleven plant bug individuals were collected from female-phase inflorescences of *Syngonium hastiferum* and used for microscopic investigation. These individuals were immediately frozen after collection, dried, dorsally mounted and sputter coated with gold before scanning with an SEM as described above.

Adherence of Dieffenbachia aurantiaca *pollen to* Neella *sp. nov. pollinators*

To test for the ability of pollen from a scarab beetle-pollinated aroid to adhere to the body of *Neella* sp. nov., 28 plant bug individuals were caught from a female-phase inflorescence of *S. hastiferum* and released in a 80 x 50 x 50 cm large cage containing an inflorescence of *Dieffenbachia aurantiaca*, which was about to enter the staminate (pollen extruding) phase. As all 28 bugs settled down on the inflorescence of *D. aurantiaca*, they could be observed from a close distance during pollen extrusion. Presence/absence of pollen grains on the body surface of *Neella* sp. nov. plant bugs was noted and documented by macro photography.

Importance of insect visitors for seed production

To assess the role of *Neella* sp. nov. in the development of seeds in *S. hastiferum*, we bagged a randomly selected inflorescence on each of ten individual plants (n = 10) with fine-meshed nylon gauze bags before the beginning and until the end of anthesis to exclude all visitors. Three months later, we revisited the inflorescences and recorded seed set. For positive controls, ten other inflorescences from the same ten plants plus ten inflorescences from ten other individuals (n = 20) were checked for seed set under natural conditions.

Floral scent: attractiveness to pollinators and chemistry

Importance of floral scent in attraction of pollinators

To test whether the floral scent of *S. hastiferum* is capable of attracting *Neella* sp. nov. without visual cues, we bagged, in the evening before anthesis, five inflorescences of five individuals with fine meshed white gauze bags and four individual inflorescences of four other individuals with green paper cylinders (open apically and basally to allow for scent release and access of pollinators to inflorescences). The same types of gauze bags and cylinders were used to cover bud-stage inflorescences (i.e. inflorescences not yet producing floral scent) of the same plants, and served as negative controls (two-choice setting). At 9:00 all insects that settled down on the white gauze bags were counted. Insects that were attracted to cylinder bagged inflorescences entered the paper cylinders and were exclusively present in and on the inflorescences, from which they were collected after the cylinders were gently removed.

Floral scent sampling for thermal desorption (TD) – gas chromatography/ mass spectronomy (GC/MS)

The scents of seven different inflorescences from seven individual plants of *S. hastiferum* were collected using the dynamic headspace method[75] during the period of strongest scent emission, as determined by the human nose and indicated by the attraction of plant bugs (7:00 - 9:00). All inflorescences were sampled during the first (n = 2) or second day (n = 5) of anthesis (female phase). For scent collection, a membrane pump (G12/01EB, Gardner Denver, Germany) was used with the air flow set to 200 ml/min. Inflorescences were bagged with polyethylene oven bags (10 x 20 cm; Toppits, Germany) before scent collection and their scent trapped for two minutes on adsorbent tubes (quartz glass tube: length 25 mm; inner diam. 2 mm) filled with 1.5 mg each of Carbotrap B (mesh 20 - 40, Supelco, Germany) and Tenax TA (mesh 60 - 80; Supelco, Germany). To obtain negative control samples, scent was collected for two minutes from empty oven bags.

Analysis by thermal desorption - GC/MS

Thermal desorption (TD) samples were analyzed by a GC/MS (QP2010Ultra, Shimadzu Corporation, Japan) equipped with a ZB-5 fused silica column (5 % phenyl polysiloxane; 60 m long, inner diameter 0.25 mm, film thickness 0.25 μm, Phenomenex, USA) and coupled to a thermal desorption unit (TD-20, Shimadzu, Japan). Samples were run at a column flow (carrier gas: helium) of 1.5 ml/min. The GC oven temperature started at 40 °C, then increased by 6 °C per min to 250 °C, and held for 1 min. The MS interface worked at 260 °C, and the ion source at 200 °C. Mass spectra were taken at 70 eV (in EI mode) from m/z 30 to 350. The GC/MS data were processed using the GCMSolution Version 4.11 (Shimadzu Corporation, Japan). Compounds were identified by the NIST 11, Wiley 9, FFNSC 2, Essential Oils and Adams 2007 mass spectral data bases, and wherever possible confirmed by comparison of mass spectra and retention times with those of authentic standards (available in the stock collection of SD). The total amount of scent available in the scent samples was estimated as described elsewhere.[24]

Floral scent sampling for nuclear magnetic resonance (NMR) and GC/MS (solvent $CDCl_3$ samples)

Scents of two different inflorescences from two individual plants of *S. hastiferum* were collected during the second day of scent emission with the dynamic headspace method as described above. However, scents were trapped for two hours each on a single, larger adsorbent tube (15 cm long glass Pasteur pipette, 0.5 cm in diameter) containing a larger amount (50 mg each) of Carbotrap B (mesh 20 - 40, Supelco, Germany) and Tenax TA (mesh 60 - 80; Supelco, Germany). The samples were eluted from the matrix with 600μl of

$CDCl_3$ containing 0.03 v/v% tetramethylsilane (TMS) (Armar, Germany) and the so obtained eluates where then pooled to a single sample for analysis with GC/MS and NMR.

Analysis of the solvent $CDCl_3$ sample by GC/MS

The solvent $CDCl_3$ sample was analyzed by GC/MS using a Shimadzu GCMS-QP2010 Ultra equipped with an AOC-20i auto injector (Shimadzu, Tokyo, Japan), and again a ZB-5 fused silica column (5% phenyl polysiloxane; length: 30 m, inner diameter: 0.32 mm, film thickness: 0.25 μm, Phenomenex). 1.0 μl of the samples was injected (injection temperature: 220°C; split ratio 1:1), and the column flow (carrier gas: helium) was set at 3 ml/min. The GC oven temperature was held at 40°C for 1 min, then increased by 10°C/min to 220°C and held for 2 min. The MS interface worked at 220°C. Mass spectra were again taken at 70 eV (in EI mode) from m/z 30 to 350 and data processed as described above.

Analysis of the solvent $CDCl_3$ sample by NMR spectroscopy

We directly subjected the solvent $CDCl_3$ sample to 2D NMR spectroscopy and analyzed it with analysis software, originally developed for protein and nucleic acid data. Although $CDCl_3$ is one of the most common solvents for NMR spectroscopy, chlorinated solvents are not well suited to elute volatiles from Tenax TA adsorbent traps. As judged from additional aromatic signals in the 1H NMR spectrum, $CDCl_3$ partially dissolved the Tenax TA. While these signals did not disturb the analysis in this study, better suited alternatives for future analyses would be deuterated solvents like acetone-d6 or methanol-d4.

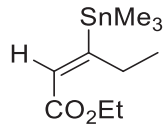
All spectra were recorded on a 600 MHz AVANCE III HDX Bruker spectrometer equipped with a QXI $^{1}H/^{13}C/^{15}N/^{31}P$ quadruple probe. A volume of ~500 μL from the solvent $CDCl_3$ sample (see above) was measured in a 5 mm standard NMR tube at 298 K. Standard 1D and 2D NMR spectra were applied. In brief, a ^{1}H 1D spectrum was recorded with 16 transients and a repetition time of 10 s; standard ^{1}H-^{1}H TOCSY spectra were recorded using 4 transients, 512 increments and 1.5 s repetition time. An ^{1}H-^{13}C HSQC spectrum was measured using the standard Bruker pulse program hsqcedetgpsisp2.2, 48 transients, 128 increments and 2 s repetition time. An ^{1}H-^{13}C HMBC spectrum was measured using the standard Bruker pulse program hmbcgpndqf, 192 transients, 96 increments and 2 s repetition time. Spectra were processed with Topspin 3.2 (Bruker Biospin, Germany). Chemical shifts were referenced to the internal tetramethylsilane (TMS). Two-dimensional spectra were analyzed using Sparky 3.115 (Goddard, T.D. and Kneller, D.G., 2008, Sparky, Version3, University of California, San Francisco, USA; https://www.cgl.ucsf.edu/home/sparky/).

Structure determination by NMR spectroscopy

A 2D multiplicity-edited ^{1}H-^{13}C HSQC spectrum revealed six carbon-proton correlations corresponding to two signals of CH_2 groups and four signals of CH/CH_3 groups (Figure 5C). With the integrals in a ^{1}H 1D spectrum it becomes apparent that the compound contains two CH-groups and three methyl groups, of which two are in an equivalent environment, resulting in two CH_3 signals with integrals of 3 and 6 compared to a CH group. The CH group $\delta^{1}H$ at 5.22 ppm and $\delta^{13}C$ at 120 ppm suggest an involvement in a carbon-carbon double bond. The neighborhood of the different groups could be established using a long-range 2D ^{1}H-^{13}C HMBC spectrum (Figure 5D), as well as 2D ^{1}H-^{1}H TOCSY and COSY (correlation spectroscopy)-type spectra (Figure S1). A comparison of the integrals with the integral of the TMS signal gives a rough estimation of the quantity, which was approx. 0.125 μmol corresponding to 16 μg.

Chemical synthesis of (Z)-3-isopropylpent-3-en-1-ol

Ethyl (E)-3-(trimethylstannyl)pent-2-enoate **4**



The procedure by Piers et al.[29] was modified as follows:

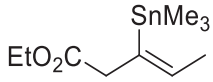
Lithium clippings (676.7 mg, 97.6 mmol, 2.0 equiv) were added to a solution of naphthalene (416.6 mg, 3.3 mmol, 6.6 mol%) in THF_{abs}. (150 mL) under N_2-atmosphere in a flame dried flask. The resulting mixture turned dark green and was stirred at room temperature for 1 h. Then trimethyltinchloride (13.0 g, 10.8 mL, 65.0 mmol, 1.3 equiv) was added dropwise and the mixture was stirred at room temperature for 3 h and the resulting trimethylstannyl-lithium solution was cooled to -48 °C. Freshly prepared $CuBr \cdot SMe_2$ (13.4 g, 65.0 mmol, 1.3 equiv) was added in one portion to the reaction mixture and was stirred for 10 min at -48 °C. The now dark red solution of the cuprate reagent was cooled to -78 °C and ethyl pent-2-ynoate **3** (6.3 g, 6.6 mL, 50 mmol, 1.0 equiv) in THF_{abs} (15 mL) was added. The solution was stirred for 4 h at -78 °C. NH_4Cl-NH_4OH (aq., sat., pH 8, 30 mL) and Et_2O (150 mL) were added, the mixture was allowed to warm to room temperature, and the mixture was stirred until the aqueous phase became deep blue. The organic layer was separated, washed twice with NH_4Cl-NH_4OH_{aq}. (aq., sat., pH 8, 75 mL), dried with $MgSO_4$ and concentrated. The residual oil was purified via Kugelrohr distillation (90 °C/0.5 mbar) and the product **4** was obtained in 69% yield (10.0 g, 34.4 mmol).

^{1}H-NMR (400 MHz, $CDCl_3$) δ= 5.89 (s, $^{3}J_{Sn\text{-}H}$ = 74 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.85 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.16 (s, $^{2}J_{Sn\text{-}H}$ = 54 Hz, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ= 174.6, 164.3, 126.9, 59.7, 28.0, 14.3, 14.2, -9.1.

The analytical data are in agreement with the literature.

Ethyl (Z)-3-(trimethylstannyl)pent-3-enoate 5



The procedure by Piers and Gavai[30] was modified as follows:

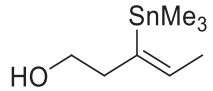
A solution of the ester **4** (8.7 g, 30.0 mmol, 1.0 equiv) in $THF_{aq.}$ (15 mL) was added to a cold (-78 °C), stirred solution of lithium diisopropylamide (LDA) (7.4 g, 69.0 mmol, 2.3 equiv) in $THF_{abs.}$ (150 mL). The solution was stirred at -78 °C for 45 min and at 0 °C for 1.5 h. After the solution was cooled to -78 °C, it was transferred via cannulation to a vigorously stirred, cold (-98 °C) solution of acetic acid (20 mL) in Et_2O (100 mL). The mixture was warmed to room temperature, and $NaHCO_3$ (aq., sat., 50 mL) and Et_2O (50 mL) were added. The organic phase was separated and the aqueous layer was washed with Et_2O (3 x 100 mL). The combined organic extracts were washed with H_2O (50 mL), brine (50 mL), dried with $MgSO_4$ and the solvent was evaporated. The residual oil was purified via Kugelrohr distillation (95 °C/0.5 mbar) and product 5 was obtained in 72% yield (6.3 g, 21.7 mmol).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.14 (qt, J = 6.5, 1.3 Hz, $^3J_{Sn-H}$ = 130 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.19 (d, J = 1.1 Hz, $^3J_{Sn-H}$ = 52 Hz 2H), 1.75 (dt, J = 6.6, 1.0 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 0.28 – 0.10 (s, $^2J_{Sn-H}$ = 52 Hz, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ= 173.1, 138.5, 137.3, 60.5, 45.1, 19.6, 14.3, -8.3.

The analytical data are in agreement with literature.

(Z)-3-(Trimethylstannyl)pent-3-en-1-ol 6



The procedure by Piers and Wong[31] was modified as follows:

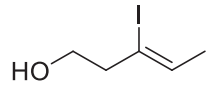
A solution of diisobutylaluminum hydride (DIBAL-H) (45 mL, 45 mmol, 2.5 equiv) in hexanes was added to a cold (-78 °C), stirred solution of ester **5** (5.24 g, 18.0 mmol, 1.0 equiv) in $Et_2O_{abs.}$ (180 mL), and the resulting clear solution was stirred at -78 °C for 1.5 h and at 0 °C for 1.5 h. NH_4Cl-NH_4OH (aq., sat., pH 8, 5 mL) was added and the white slurry was allowed to stir at room temperature for 1 h. $MgSO_4$ (1 g) was added and the slurry was filtered through a column of Celite (10 g). The column was washed with Et_2O (300 mL). The solvent of the combined filtrate was evaporated and the residual oil was purified via Kugelrohr distillation (65 °C/0.5 mbar) and product 6 was obtained in 89% yield (4.0 g, 16.1 mmol).

^{1}H-NMR (400 MHz, $CDCl_3$) δ= 6.18 (q, J = 6.5 Hz, $^3J_{Sn-H}$ = 137 Hz, 1H), 3.55 (q, J = 6.1 Hz, 2H), 2.42 (t, J = 6.2 Hz, $^3J_{Sn-H}$ = 55 Hz, 2H), 1.76 (dt, J = 6.6, 0.9 Hz, 3H), 1.45 – 1.38 (m, 1H), 0.19 (s, $^2J_{Sn-H}$ = 137 Hz, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ= 140.8, 138.4, 61.7, 43.1, 19.8, -8.5.

The analytical data are in agreement with literature.

(Z)-3-Iodopent-3-en-1-ol 7



The procedure by Piers and Wong[31] was modified as follows:

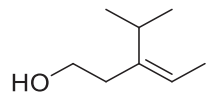
A solution of alcohol **6** (3.7 g, 15.0 mmol, 1.0 equiv) in $DCM_{abs.}$ (15 mL) was added to a stirred solution of iodine (4.0 g, 15.8 mmol, 1.05 equiv) in $DCM_{abs.}$ (150 mL) at room temperature, and the mixture was stirred for 30 min. $Na_2S_2O_3$ (aq., sat., 20 mL) was added and the phases were separated. The aqueous phase was extracted with Et_2O (4 x 50 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated. The residual oil was purified via column chromatography (hexanes/Et_2O: 3:1) and subsequent Kugelrohr distillation (60 °C/0.5 mbar) and gave rise to 94% yield (3.0 g, 14.2 mmol) of product 7.

^{1}H-NMR (300 MHz, $CDCl_3$)) δ= 5.70 (qt, J = 6.3, 1.2 Hz, 1H), 3.71 (q, J = 5.9 Hz, 2H), 2.68 (tt, J = 5.9, 1.2 Hz, 2H), 2.00 (t, J = 5.9 Hz, 1H), 1.74 (dt, J = 6.3, 1.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ= 133.0, 105.9, 61.0, 47.9, 22.3.

The analytical data are in agreement with literature.

(Z)-3-Isopropylpent-3-en-1-ol 1



The 1.0 M organozinc halide solution was prepared as follows:

Dibromoethane (50 μL) was added to Zn dust (1.08 g, 16.5 mmol, 1.1 equiv) in $THF_{abs.}$ (15 mL), and the suspension was heated until reflux and then cooled down to room temperature. TMSCl (50 μL) was added to the suspension, heated until reflux and cooled down to room temperature again. 2-Iodopropane (2.6 g, 1.5 mL, 15.0 mmol, 1.0 equiv) was added slowly to the suspension under vigorous

stirring and the reaction mixture started to boil and was stirred until the reaction mixture cooled down to room temperature (30 min). The obtained organozinc halide solution was titrated with a solution of iodine in 0.5 M LiCl in THF to receive a 1.0 M solution.

The Negishi coupling reaction[32] was carried out as follows with modified conditions:

DMF_{abs}. (2 mL) followed by iodide **7** (212.0 mg, 1.0 mmol, 1.0 equiv) and 1-methylimidazole (162.2 mg, 159 μL, 2.0 mmol, 2.0 equiv) were added to $PdCl_2(Amphos)_2$ catalyst (14.2 mg, 20.0 μmol, 2.0 mol%) under vigorous stirring. The preformed organozinc halide solution (2.4 mL, 2.4 mmol, 2.4 equiv) was added slowly and stirred at room temperature for 30 min. Then the reaction mixture was heated to 100 °C for 3 h until the reaction was complete (checked by TLC). The mixture was cooled down to room temperature and quenched with NH_4Cl (aq., sat., 5 mL) and the organic layer was separated. The aqueous phase was extracted with Et_2O (2 x 25 mL) and the combined organic layers were dried with Na_2SO_4 and concentrated. The residual oil was purified via column chromatography (*n*-pentane/Et_2O: 2:1) and product **1** was received in 87% yield (111.2 mg, 0.87 mmol).

^{1}H-NMR (400 MHz, $CDCl_3$)) δ= 5.22 (q, *J* = 6.8 Hz, 1H), 3.68 (dt, *J* = 6.3, 5.5 Hz, 2H), 2.86 (sep, *J* = 7.0 Hz, 1H), 2.23 (t, *J* = 6.7 Hz, 2H), 1.64 (d, *J* = 6.8 Hz, 3H), 1.48 (t, *J* = 5.4 Hz, 1H), 1.00 (d, *J* = 7.0 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ= 141.2, 119.8, 61.8, 34.9, 28.4, 20.9, 12.8.

IR (ν/cm^{-1}): 3332, 2959, 2870, 1655, 1464, 1383, 1181, 1103, 1028, 962, 883, 824, 746.

HRMS (EI) exact mass calc. for C8H16O: *m/z* 128.1196, found: *m/z* 128.1198.

For NMR spectra of compounds, see Methods S1.

Two-choice bioassays with synthetic (Z)-3-isopropylpent-3-en-1-ol

To test whether (*Z*)-3-isopropylpent-3-en-1-ol **1** is responsible for attracting *Neella* sp. nov., we tested synthetic gambanol (trivial name of **1**) in ethyl acetate (1:10 ratio), offering 50 μl on a filter paper, in a series (n = 8) of two-choice bioassays against negative controls (same amount of ethyl acetate on the same type of filter paper). The gambanol added to filter paper resulted in a scent that was similar, but weaker than the one perceived from natural inflorescences. Five of the eight bioassays were conducted under open field conditions, and three were set up in a 9 x 9 x 3 m fine-meshed cage. This cage contained ca. 200 individuals of the pollinators that were previously collected from fresh inflorescences of *S. hastiferum* and released into the cage just before the experiments. Lures and controls were offered at 7:00 in the morning, ca. two meters from each other (in the cage bioassays, lures and controls were placed in the center of the cage). Over a period of 90 min, we counted and collected all plant bugs that settled down on the filter paper.

To test if *Neella* plant bugs or *Cyclocephala* scarab beetles (the pollinators of beetle-pollinated relatives of *S. hastiferum*) are attracted to (*Z*)-3-isopropylpent-3-en-1-ol **1** at night, we conducted three additional bioassays in the field, following the same procedure as described above for daytime bioassays under open field conditions. However, lures were offered from 17:30 – 19:00 instead, which is the main natural activity time of the nocturnal scarab beetles and *Neella* florivores.[24]

QUANTIFICATION AND STATISTICAL ANALYSIS

A Fisher exact test was used to test whether the likelihood to set fruit differed between open pollinated and pollinator excluded inflorescences, and a Mann-Whitney test was applied to compare the number of seeds between the treatments (STATISTICA version 12, https://www.tibco.com/products/data-science).

Exact binomial tests of goodness-of-fit were used to test the hypothesis that white gauze or green paper bagged, female-phase and bud-stage inflorescences attracted the same number of plant bugs. (http://www.biostathandbook.com/exactbin.xls). The same test was used to test the hypothesis that gambanol attracted the same number of plant bugs as negative controls.