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Antennal Response and Field Attraction of the Predator *Elatophilus hebraicus* (Hemiptera: Anthocoridae) to Sex Pheromones and Analogues of Three *Matsucoccus* Spp. (Homoptera: Matsucoccidae)

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Abstract—The predator *Elatophilus hebraicus* is closely associated with its prey, the pine bast scale, *Matsucoccus josephi*, and utilizes the *M. josephi* sex pheromone as a kairomone. Kairomonal activity of *E. hebraicus* was studied by GC–EAD and field bioassays. The sex pheromone of *M. josephi* [(2*E*,5*R*,6*E*,8*E*)-5,7-dimethyl-2,6,8-decatrien-4-one [(*R*)-E-M.j.] elicited a strong EAD response and attracted large numbers of the predator. The sex pheromone of two allopatric *Matsucoccus* spp., *Matsucocccus feytaudi*, (3*S*,7*R*,8*E*,10*E*)-3,7,9-trimethyl-8,10-dodecadien-6-one [(*S,R*)-E-M.f.] and *Matcucossus matsumurae*, (2*E*,4*E*,6*R*,10*R*)-4,6,10,12-tetramethyl-2,4-tridecadien-7-one [(*R,R*)-E-M.m.], were also EAD-active and attracted significant numbers of *E. hebraicus* in the forest. Increasing the lure load of (*S,R*)-E-M.f. and (*R,R*)-E-M.m., in order to compensate for their lower volatility relative to (*R*)-E-M.j., resulted in similar attraction of *E. hebraicus* to each of the three pheromones. Other *Matsucoccus* pheromone stereoisomers displayed no behavioral activity. There was a significant difference in the activity of sex pheromone analogues, (6*E*/*Z*,8*E*)-5,7-dimethyl-6,8-decadien-4-one (52% *E*+48% *Z*, ANLG 1) and (6*E*/*Z*,8*E*)-2,4,6-trimethyl-1,6,8-nonatrien-3-one (60% *E*+40% *Z*, ANLG 2). The (*E*) isomer of ANLG 1 evoked a strong EAD response from *E. hebraicus* and the mixture of *E*/*Z* ANLG 1 attracted the predator in moderate numbers, whereas ANLG 2 was inactive both in EAD and field tests. Conversely, *M. josephi* males were not attracted to *M. feytaudi* and *M. matsumurae* pheromones or pheromone analogues. Cross-activity of *E. hebraicus* to *M. feytaudi* and *M. matsumurae* pheromones may be based on structural similarity of the compounds. Alternatively, *E. hebraicus* may respond specifically to the pheromones of two allopatric *Matsucoccus* spp. If true, kairomonal attraction of *E. hebraicus* to these pheromones may have evolved during speciation of the Matsucoccidae and may have been preserved despite the allopatry of *M. josephi, M. feytaudi* and *M. matsumurae*.

Introduction

The sex pheromone of *M. josephi* Bodenheimer and Harpaz has recently been isolated and identified as (2*E*,5*R*,6*E*,8*E*)-5,7-dimethyl-2,6,8-decatrien-4-one [(*R*)-E-M.j.].[1–3] For the first time, chiral capillary analysis and GC–EAD could be applied successfully to the identification of a scale pheromone.[3] Structural and chiral determination of the *M. josephi* sex pheromone[3] has revealed similarity to pheromones of allopatric *M. feytaudi* [(*S,R*)-E-M.f.][4,5] and *M. matsumurae* [(*R,R*)-E-M.m.].[6,7] All three pheromones have the same chiral ketodiene moiety, with the same absolute configuration (Fig. 1).

Elatophilus spp. occur in pine forests and are closely associated with pine bast scales, *Matsucoccus* spp.[8,9] Generally, *Elatophilus* spp. are monophagous,[8] however, there is evidence that a single Elatophilus species may prey on different pine bast scales.[10] Recently we have shown that the principal predator of *M. josephi, E. hebraicus* Pericart, is highly attracted to traps baited with the sex pheromone of its prey.[2,11] Neither *M. feytaudi* nor *M. matsumurae* occur in Eastern Mediterranean countries and therefore they are not part of the *E. hebraicus* prey spectrum.

The objective of this study was to investigate the specificity of the kairomonal and pheromonal response of *E. hebraicus* and *M. josephi* to stereoisomers and analogues of *M. josephi*, *M. feytaudi* and *M. matsu-*

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murae sex pheromones, using electrophysiological and field bioassays.

Results and Discussion

Electroantennographic experiments

In GC–EAD recordings, the racemic (*E*) but not the (*Z*)-isomer of the *M. josephi* pheromone (formulas of all *Matsucoccus* pheromones and analogues are presented in Fig. 1) elicited antennal responses by *E. hebraicus* (Fig. 2). The chiral natural three pheromone components of *M. josephi, M. feytaudi* and *M. matsumurae* [(*R*)-*E*-M.j., (*S,R*)-E-M.f. and (*R,R*)-E-M.m.] evoked strong antennal responses, with (*R*)-E-M.j. being the most EAD-active (Fig. 3). Antennal responses were strongest, intermediate and absent for (*R*)-*E*-M.j., (*R,R*)-E-M.f. and (*S,S*)-E-M.m., respectively. In a binary mixture of (*R*)-E-M.j. and (*R,S*)E-M.f., only the *M. josephi* pheromone was EAD-active. In an exceptionally good antennal preparation, the EAD-activity of *M. matsumurae* pheromone (*R,R*)-E-M.m. exceeded those of *M. josephi* and *M. feytaudi* pheromone stereoisomers [(*S*)-E-M.j. and (*S,S*)-E-M.f.] (Fig. 4). The *E*-, but not the *Z*-ANLG 1 of *M. josephi* pheromone evoked antennal response, although slightly weaker than that of the natural pheromone (*R*)-E-M.j. (Fig. 5). Both *E*- and *Z*-isomers of ANLG 2 were EAD-inactive.

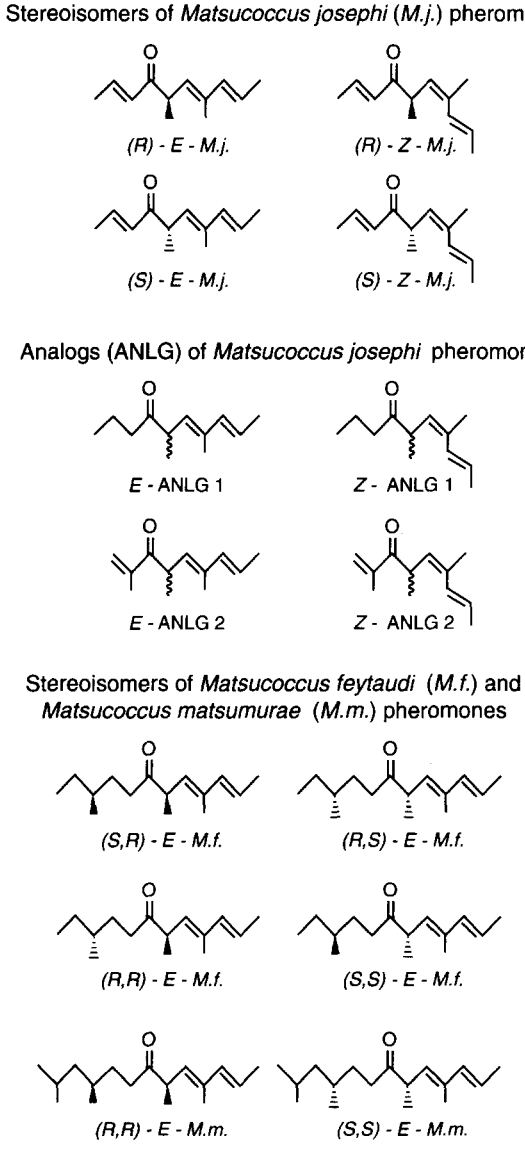

Figure 1. Pheromone stereoisomers and analogues of *M. josephi, M. feytaudi* and *M. matsumurae* sex pheromones.

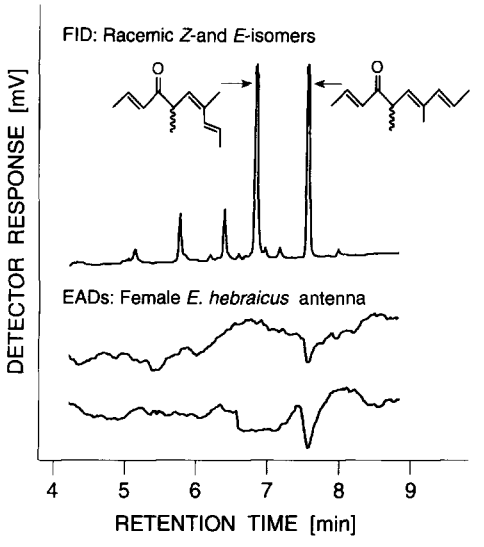

Figure 2. FID chromatogram and EAD response of female *E. hebraicus* antenna to racemic (*E*) and (*Z*) isomers of *M. josephi* sex pheromone.

Field tests

All available *M. josephi, M. feytaudi* and *M. matsumurae* pheromones, streoisomers and pheromone analogues were field bioassayed in one layout (Table 1). Treat-

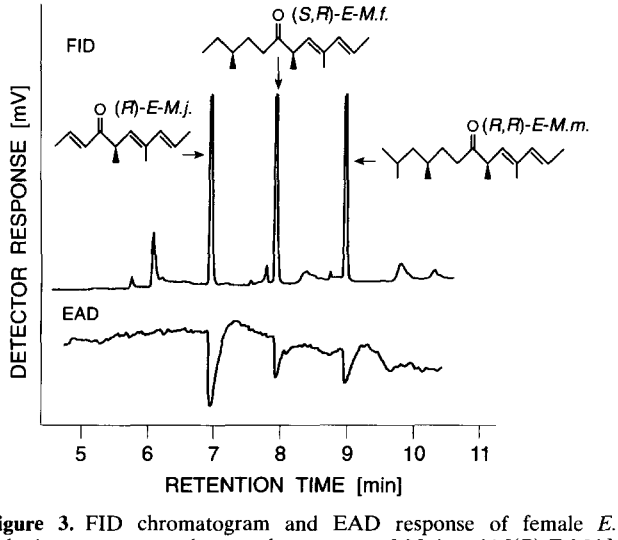

Figure 3. FID chromatogram and EAD response of female *E. hebraicus* antenna to the sex pheromones of *M. josephi* [(*R*)-E-M.j.], *M. feytaudi* [(*S,R*)-E-M.f.] and *M. matsumurae* [(*R,R*)-E-M.m.].

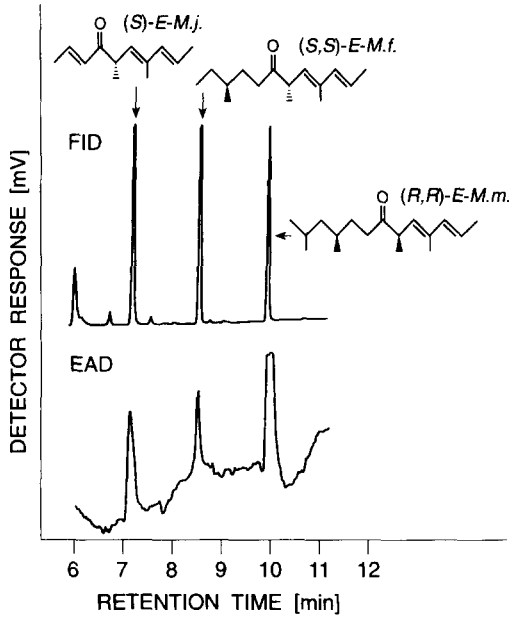

Figure 4. FID chromatogram and EAD response of female *E. hebraicus* antenna to the antipode of *M. josephi* pheromone [(*S*)-E-M.j.], to a *M. feytaudi* stereoisomer [(*S,S*)-E-M.f.] and to *M. matsumurae* sex pheromone [(*R,R*)-E-M.m.].

ments with increased concentrations of *M. feytaudi* (×4.4) and *M. matsumurae* (×12) pheromones (to compensate for lower volatilities), relative to the *M. josephi* pheromone, were also included in the test. Chiral *M. josephi* pheromone (*R*)-E-M.j., racemic (*E/Z*) *M. josephi* pheromone (containing the same amount of the natural enantiomer) and increased concentrations of *M. feytaudi* and *M. matsumurae* pheromones were equally attractive to *E. hebraicus* (Table 1). Lower amounts of natural *M. feytaudi* and *M. matsumurae* pheromones, the active *M. feytaudi* diastereoisomer (*R,R*)-E-M.f.[12] and ANLG 1 showed moderate attractancy to *E. hebraicus*. Both males and females of the predator were trapped; with a sex ratio ratio ranging between 3:1 and 6:1 (male to females). All other pheromone stereoisomers and ANLG 2 displayed negligible attractancy, similar to control. *Matsucoccus josephi* males were attracted in significant numbers only to chiral (*R*)-E-M.j. pheromone and to racemic (*E/Z*) *M. josephi* pheromone.[3]

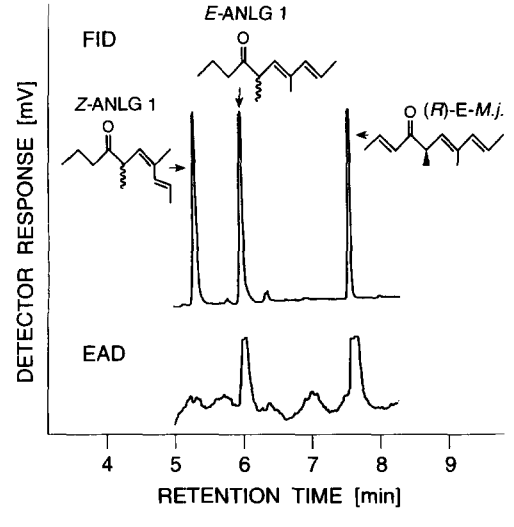

Figure 5. FID chromatogram and EAD response of female *E. hebraicus* antenna to racemic (*E*) and (*Z*) isomers of ANLG 1 and to *M. josephi* sex pheromone [(*R*)-E-M.j.].

Table 1. Captures of *M. josephi* males and of *E. hebraicus* males and females (mean number ± SE/trap/day)[a] in traps baited with *Matsucoccus* pheromone stereoisomers and analogues

Pheromone[b]	Amount (μg)	*Matsucoccus josephi*	*Elatophilus hebraicus*
Matsucoccus josephi			
(*R*)-E-M.j. (natural)	50	17.7 ± 2.5 a[c]	68.7 ± 11.7 a
(*S*)-E-M.j.	50	2.1 ± 0.6 c	7.9 ± 0.6 c
Racemic (*E/Z*)-M.j.	200	13.7 ± 3.4 b	46.4 ± 11.7 a
Matsucoccus matsumurae			
(*R,R*)-E-M.m. (natural)	50	0 d	18.9 ± 2.9 b
(*R,R*)-E-M.m. (natural)	600	0.2 ± 0.2 d	60.7 ± 8.9 a
(*S,S*)-E-M.m.	50	0.2 ± 0.0 d	3.2 ± 1.5 cd
Matsucossus feytaudi			
(*S,R*)-E-M.f. (natural)	50	0.1 ± 0.1 d	20.9 ± 4.9 b
(*S,R*)-E-M.f. (natural)	220	0.2 ± 0.1 d	48.9 ± 4.9 a
(*R,S*)-E-M.f.	50	0 d	6.9 ± 1.6 cd
(*R,R*)-E-M.f.	50	0.2 ± 0.1 d	16.9 ± 1.4 b
(*S,S*)-E-M.f.	50	0.0 ± 0.0 d	2.7 ± 1.1 cd
Analogues			
Racemic (*E/Z*)-ANLG 1	200	0.7 ± 0.2 d	25.0 ± 3.5 b
Racemic (*E/Z*)-ANLG 2	200	0.3 ± 0.1 d	5.5 ± 1.8 cd
Control	—	0.0 ± 0.0 d	1.3 ± 0.2 d

[a]Test was conducted between 18 May 18–1 June 1995 with five replicates for each treatment.
[b]Formulas of all pheromone stereoisomers and analogues are presented in Figure 1.
[c]Means followed by the same letter are not significantly different at $P < 0.05$ according to Student–Newman–Keuls test.

Relative volatilities of *Matsucoccus* pheromones

The three investigated *Matsucoccus* pheromones have different molecular weights, resulting in different release rates. The release rates obtained in a flow system under laboratory conditions are not equivalent to the release rates from the pheromone dispensers in the forest. However, we assume that the release ratio of the three *Matsucoccus* pheromones will be very similar under differing conditions. Approximately equal release rates of the three pheromones from rubber septa were obtained by loading septa with *M. josephi*, *M. feytaudi* or *M. matsumurae* pheromones; in a ratio of 1:4.4:12, respectively (Table 2).

Kairomonal response of *E. hebraicus* to different *Matsucoccus* pheromone streoisomers and analogues was demonstrated using GC–EAD analysis and by a field bioassay. Generally, the kairomonal attraction of *E. hebraicus* to various *Matsucoccus* stereoisomers and analogues, in the forest related fairly well with their EAD activity, indicating that GC–EAD can be used for assessing kairomonal activity. As expected, *E. hebraicus* responded to the pheromone of its principal prey, *M.*

Table 2. Release rate of *Matsucoccus* pheromones from rubber septa[a]

Pheromone	Mean release ± SE (ng/h)	Release ratio
Racemic *M. josephi*[b]	736 ± 35	1
Natural *M. feytaudi*	167 ± 6	1/4.4
Natural *M. matsumurae*	60 ± 2	1/12.3

[a]Four replicates, at 25 °C, each septum loaded with 1 mg pheromone. [b]It is assumed that all isomers have a very similar volatility.

josephi,[11] and (*R*)-E-M.j. elicited the strongest EAG signal (Fig. 3). Interestingly, *E. hebraicus* responded by cross-attraction to the pheromones of allopatric *M. feytaudi* and *M. matsumurae*, which do not naturally belong to the *E. hebraicus* prey spectrum. Consistent with their EAD-activity (Fig. 3), (*S,R*)-E-M.f. and (*R,R*)-E-M.m. attracted significant numbers of the predator. Increasing the amount of (*S,R*)-E-M.f. and (*R,R*)-E-M.m., to compensate for their lower volatilities relative to (*R*)-*E*-M.j. (Table 2), resulted in the same level of attractancy of *E. hebraicus* to the three natural *Matsucoccus* pheromones (Table 1).

Kairomonal attraction of natural enemies to sex pheromones of scale insects is rare. The parasitic wasps *Aphytis africans* and *Aphytis melinus* respond to the pheromone of their host. However, these parasites are equally attracted to yellow unbaited traps and to traps baited with the pheromone of the California red scale, *Aonidiella aurantii*.[13] Moreover, *Aphelenid* parasitoids of the San Jose scale, *Quadraspidiotus perniciosus*, are strongly attracted to colored traps baited with the San Jose sex pheromone. These examples indicate that both olfactory and visual cues are involved in host location of parasites.[14] However, none of these cases is as striking as the observed kairomonal response of *E. hebraicus* to *Matsucoccus* pheromones.

Antennal response of *E. hebraicus* to the (*E*) but not the (*Z*) isomer of *M. josephi* pheromone (Fig. 2) and to (*E*) but not (*Z*) ANLG 1 (Fig. 5) indicates that the geometric configuration of the molecule is critical for sensory recognition. Lack of, or smaller antennal responses to scale pheromone antipodes (Fig. 4) further implies enantiospecific recognition of chirality in the ketodiene moiety in the three *Matsucoccus* pheromones. However, no EAD response to (*E*)-ANLG 2 and negligible attraction of the predator to (*E/Z*)-ANLG 2 baited traps provides evidence that the ketodiene moiety per se does not impart kairomonal activity. The presence of the ketodiene moiety with the (*R*) configuration (common to all three known *Matsucoccus* pheromones) is a precondition for kairomonal activity of *E. hebraicus*, but the other part of these molecules is also of importance. Replacing the crotyl chain in (*R*)-E-M.j. or the propyl chain in ANLG 1 with a methacryl chain in ANLG 2 eliminated kairomonal activity. Transformation of the crotyl chain into a propyl chain preserved a high degree of kairomonal activity, whereas replacement with a methacryl chain destroyed the kairomonal response (Table 1). Introduction of a methyl next to the chiral ketodiene moiety in ANLG 2 adversely affected sensory recognition by *E. hebraicus*.

The three *Matsucoccus* species, *M. josephi*, *M. feytaudi* and *M. matsumurae* are geographically well isolated and only *M. josephi* is preyed upon by *E. hebraicus*.[9] Cross-attraction of *E. hebraicus* to *M. feytaudi* and *M. matsumurae* pheromones may be based on chemical similarity of the three pheromones. This hypothesis is further supported by a rather strong EAD response (Fig. 5) and by attraction of *E. hebraicus* to the (*E*) isomer of ANLG 1 (Table 1), which resembles all three *Matsucoccus* pheromones. However, *M. josephi* males were not cross-attracted to *M. feytaudi* and *M. matsumurae* pheromones and *E. hebraicus* may indeed respond to distinct pheromones of three allopatric *Matsucoccus* species. If true, kairomonal attraction of *E. hebraicus* to these pheromones may have evolved during speciation of the genus *Matsucoccus* and may have been preserved despite the separation of the three *Matsucoccus* species.

Experimental

Chemicals

The racemic *M. josephi* pheromonal components (2*E*, 6*E*,8*E*)-5,7-dimethyl-2,6,8-decatrien-4-one and (2*E*,6*Z*, 8*E*)-5,7-dimethyl-2,6,8-decatrien-4-one as a mixture (56% *E* + 44% *Z*) were available from previous work.[2] The two (*E*) enatiomers (2*E*,5*R*,6*E*,8*E*)-5,7-dimethyl-2,6,8-decatrien-4-one [(*R*)-E-M.j.] (96.6% ee) and (2*E*,5*S*,6*E*,8*E*)-5,7-dimethyl-2,6,8-decatrien-4-one [(*S*)-E-M.j.] (99.0% ee) have been recently prepared.[15] The racemic analogues, (6*E*/*Z*,8*E*)-5,7-dimethyl-6,8-decadien-4-one (52% *E* + 48% *Z*, ANLG 1) and (6*E*/*Z*,8*E*)-2,4,6-trimethyl-1,6,8-nonatrien-3-one (60% *E* + 40% *Z*, ANLG 2) were prepared by the same procedure as the racemic (*E*/*Z*) mixture of the *M. josephi* pheromone,[2] starting from butyraldehyde and methacrylaldehyde, respectively. The *E*/*Z* ratio in both analogues was determined on a Carlo Erba 5300 GC instrument equipped with a capillary DB5 column (30 m × 0.25 mm; J&W Folsom, California), as it was accomplished for the (*E*/*Z*) mixture of the *M. josephi* pheromone.[2] The column was kept at 50 °C for 2 min, then programmed to 145 °C at 10 °C/min and after 8 min it was programmed to 200 °C at the same rate. The column was operated in the splitless mode, the purge valve was opened 1 min after injection and the carrier gas (helium) pressure was maintained at 1 atm. The (*Z*) isomers always eluted first.

The four *M. feytaudi* stereoisomers, (3*S*,7*R*,8*E*,10*E*)-3,7,9-trimethyl-8,10-dodecadien-6-one, (*S,R*)-E-M.f. (99.3%), (3*R*,7*S*,8*E*,10*E*)-3,7,9-trimethyl-8,10-dodecadien-6-one, (*R,S*)-E-M.f. (98.3%), (3*R*,7*R*,8*E*,10*E*)-3,7,9-trimethyl-8,10-dodecadien-6-one, (*R,R*)-E-M.f. (98.4%), and (3*S*,7*S*,8*E*,10*E*)-3,7,9-trimethyl-8,10-dodecadien-6-one, (*S,S*)-E-*M.f.* (98.2%),[5] and the two *M. matsumurae* stereoisomers, (2*E*,4*E*,6*R*,10*R*)-4,6,10,12-tetramethyl-2,4-tridecadien-7-one [(*R,R*)-E-M.m.

(99.6%) and (2*E*,4*E*,6*S*,10*S*)-4,6,10,12-tetramethyl-2,4-tridecadien-7-one (*S,S*)-E-M.m. (99.2%),[7] were obtained from K. Mori. Percentages in brackets represent the streoisomeric purity of *M. feytaudi* and *M. matsumurae* pheromone stereoisomers (Fig. 1).

Insects

Predators: *E. hebraicus* were collected from Aleppo pines, *Pinus halepensis* in the Beqoa forest (Judean foothills) and reared on eggmasses and adult female *M. josephi* in the presence of Aleppo pine saplings as an oviposition substrate. Males and females were shipped by special delivery to Simon Fraser University for the GC–EAD analysis.

GC–EAD experiments

All *Matsucoccus* pheromone stereoisomers were analyzed isothermally (135 °C) on a Hewlett Packard (HP) 5890 GC instrument equipped with a chiral Cyclodex-B column (30 m × 0.25 mm, J&W). Pheromone enantiomers of *M. josephi* but not of *M. feytaudi* or *M. matsumurae* separated on this column.[3] Subsequently, pheromones and analogues were subjected to GC–EAD analysis[16] on a DB-23 column (30 m × 0.25 mm; J&W). The column was kept at 100 °C, after 1 min it was programmed at 10 °C/min to 200 °C. The column was operated in the splitless mode, the purge valve was opened 1 min after injection and the carrier gas (helium) pressure was maintained at 1 atm. Like moth antennae, the fine *E. hebraicus* antennae were suspended between glass capillary electrodes for GC–EAD recordings. Antennae of females rather than males gave the best responses and were used for all analyses.

Seven mixtures of *Matsucoccus* sex pheromone stereoisomers or analogues (Fig. 1), containing about 6 ng of each compound, were analyzed: (1) racemic (*E*) and (*Z*) isomers of *M. josephi* pheromone (Fig. 2); (2) pheromones of *M. josephi, M. feytaudi* and *M. matsumurae* [(*R*)-E-M.j. + (*S,R*)-E-M.f. + (*R,R*)-E-M.m.] (Fig. 3); (3) *M. josephi* pheromone, diastereomeric (same chirality in the ketodiene moiety) *M. feytaudi* pheromone and the antipode of *M. matsumurae* pheromone [(*R*)-E-M.j. + (*R,R*)-E-M.f. + (*S,S*)-*E*-M.m.]; (4) the major *M. josephi* pheromone and the antipode of *M. feytaudi* pheromone [(*R*)-E-M.j. + (*R,S*)-E-M.f.]; (5) antipode of *M. josephi* pheromone, second diastereoisomer of *M. feytaudi* pheromone and *M. matsumurae* pheromone [(*S*)-E-M.j. + (*S,S*)-E-M.f. + (*R,R*)-E-M.m.] (Fig. 4); (6) pheromone of *M. josephi* and ANLG 1 [(*R*)-E-M.j. + (*E*)- and (*Z*)-ANLG 1] (Fig. 5); (7) pheromone of *M. josephi* and ANLG 2 [(*R*)-E-M.j. + (*E*)- and (*Z*)-ANLG 2].

Field bioassay

The timing of high *E. hebraicus* population levels for field bioassays was determined in preliminary small scale field tests during the whole year. Subsequently, a comprehensive five-replicate field test was set up in a randomized complete block in Shaharia Forest (Judean foothills) plantations of Aleppo pine, *P. halepensis* Mill, and brutia pine, *Pinus brutia* Ten. All available *Matsucoccus* pheromone stereoisomers and analogues were tested in this field experiment. Triangular sticky traps baited with rubber dispensers,[17] impregnated with the various compounds, were used. They were suspended from tree branches, 1.8–2 m above ground, at least 25 m apart. Trapped male *M. josephi* and male and female *E. hebraicus* were counted using a stereomicroscope.

Relative evaporation rates of the three *Matsucoccus* pheromones from rubber septa

Release rates of racemic (*E/Z*)-M.j. pheromone, (*S,R*)-E-M.f. or (*R,R*)-E-M.m., from rubber septa (Maavit Products, Tel Aviv, Israel; distributed by Rimi, Tel Aviv), were measured in an airborne collection system as described previously.[18] Purified air at a rate of 2 L/m (wind speed of approximately 6.5 cm/s) was pulled over the dispensers, each loaded with 1 mg of either pheromone, at 25 ± 2 °C for 1 h. Pheromones were trapped on a Porapak Q trap (200 mg) and were eluted with dichloromethane until 0.5 mL was collected. After adding 500 ng of 2-undecanone as internal standard, the solutions were concentrated and analyzed by capillary GC on a DB5 column (30 m × 0.25 mm; J&W) under the same conditions described above. The release rate of each pheromone was measured in four replicates.

Statistical analysis

Analysis of the field data was conducted employing a SAS program. Data were transformed to $\sqrt{x}+0.01$ and subjected to analysis of variance, followed by Student–Neuman–Keuls test at $P<0.05$.

Conclusions

The *M. josephi/E. hebraicus* sex pheromone/kairomone system constitutes a special case of predator–prey relationship. *Elatophilus hebraicus* exploits the sex pheromone communication channel of its prey and, in addition, responds very efficiently to the sex pheromones of two allopatric *Matsucoccus* species, despite the fact that it is associated with *M. josephi* only. These findings indicate that the kairomonal activity of *E. hebraicus* has probably evolved during speciation of the genus *Matsucoccus.*

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