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SEMIOCHEMICAL ACTIVITY OF PHEROMONES AND ANALOGUES OF THREE *MATSUCOCCUS* SPECIES (HEMIPTERA: COCCOIDEA: MATSUCOCCIDAE).

ABSTRACT

SEMIOCHEMICAL ACTIVITY OF PHEROMONES AND ANALOGUES OF THREE *MATSUCOCCUS* SPECIES (HEMIPTERA: COCCOIDEA: MATSUCOCCIDAE).

The sex pheromone of the Israeli pine bast scale, *Matsucoccus josephi* Bodenheimer & Harpaz (Homoptera: Matsucoccidae), was identified as the ketone (*2E,5R,6E,8E*)-5,7-dimethyl-2,6,8-decatrien-4-one. The chiral diene chain is common also to the sex pheromones of *M. matsumurae* Bean & Godwin and *M. feytaudi* Ducasse. The species-specificity of the three pheromones is due to the differences in the second side chain of these ketones. Field and GC-EAD studies indicated that the sex pheromones of each of the three *Matsucoccus* spp. is a potent kairomone of both males and females of the predator *Elatophilus hebraicus* Pericart (Hemiptera: Anthocoridae). The response of *E. hebraicus* to the sex pheromones of *M. matsumurae* and *M. feytaudi* is particularly interesting since it does not occur in the distribution area of these two congeneric spp. These results prompted us to prepare a series of analogues with variations in the two side chains in order to probe the structure-activity relationship of the pheromonal/kairomonal attractancy of *M. josephi* and *E. hebraicus*. Field results indicate that alterations in the common diene moiety affected the kairomonal activity, while structural changes in the second side chain markedly reduced the pheromonal activity.

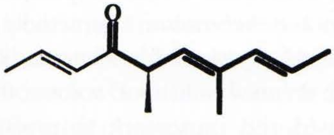
Key words: stereoisomer.

INTRODUCTION

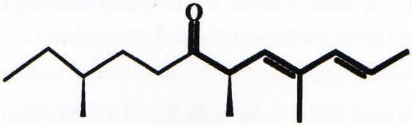
We have recently identified the sex pheromone of the Israeli pine bast scale, *Matsucoccus josephi* Bodenheimer & Harpaz (Homoptera: Matsucoccidae), as the ketone (*2E,5R,6E,8E*)-5,7-dimethyl-2,6,8-decatrien-4-one (Fig. 1 [1]) (Dunkelblum *et al.*, 1993; 1995). Structural analysis of the *M. josephi* sex pheromone has revealed a similarity to the sex pheromones of the allopatric *M. feytaudi* Ducasse (Fig. 1 [2]) (Einhorn *et al.*, 1990) and *M. matsumurae* Bean & Godwin (Fig. 1 [3]) (Lanier *et al.*, 1989). All three pheromones have the same chiral ketodiene moiety (marked in bold in Fig. 1), with the same absolute configuration *R*, while differing in the second side chain. Field tests with the *M. josephi* pheromone and its stereoisomers indicate that only the pheromone [1] is active and that the other stereoisomers are neither synergistic nor inhibitory (Dunkelblum *et al.*, 1995). In addition, it was found that the *M. josephi* pheromone is also a potent kairomone, attracting both males and females of the predatory bug, *Elatophilus hebraicus* Pericart (Mendel *et al.*, 1995; Dunkelblum *et al.*, 1996). Preliminary results indicate that the predatory bug is also attracted by the sex pheromones of *M. feytaudi* [2] and *M. matsumurae* [3] (Dunkelblum *et al.*, 1996), despite the fact that *E. hebraicus* is only associated geographically with *M. josephi* (Mendel *et al.*, 1991). These results prompted us to test a series of analogues with variations in the two side chains in order to probe the structure-activity relationship of the pheromonal response of *M. josephi* males and the kairomonal attractancy to *E. hebraicus.*

RESULTS AND DISCUSSION

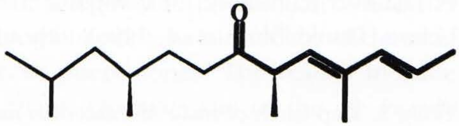
Based on earlier results, it was decided to evaluate the activity of the Z/E-racemic analogues [4A + 4B] and [5A + 5B] (Fig. 2) in relation to the chiral [1] and racemic pheromone [1A + 1B] (Fig. 2), and to include in further field tests the *M. feytaudi* pheromone [2] and chiral analogue [6] (Fig. 2). Since there is only partial overlap of flight activity of *M. josephi* and *E. hebraicus* (Mendel *et al.*, 1997), it was difficult to conduct field tests at a time when populations of both the scale and the predator were high. Several field tests were conducted in 1997 and 1998 until a proper time-window was found and satisfactory results were obtained. The results presented in Table 1 are from a field test which, in part, repeated a similar test that screened the activity of a series of analogues. The results confirmed previous tests indicating that the chiral and racemic E/Z *M. josephi* pheromones have similar pheromonal and kairomonal activity. This observation has important implications underlining the possibility of using the cheaper racemic pheromone for practical work (Mendel *et al.*, 1997). The two analogues [4] and [5] differ from the pheromone [1] in the side chain which is specific to the *M. josephi* pheromone. In earlier tests, analogue [4] revealed only kairomonal activity, attracting *E. hebraicus* and not the males of the scale (Dunkelblum *et al.*, 1996). In the 1997 and 1998 tests, this analogue attracted both insects, although its pheromonal activity was low in comparison with the activity of the true pheromone. Analogue [5], in which the propenyl side chain in the pheromone [1] was replaced by a closely related isopropenyl group, was completely inactive. The analogue [6] belongs to a new group of analogues of the *M. josephi* pheromone [1] which differ in the diene side chain which is common to all known *Matsucoccus* sex pheromones (Dunkelblum *et al.*,



Matsucoccus josephi [1]

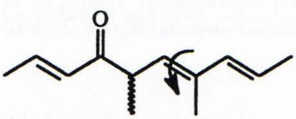


Matsucoccus feytaudi [2]

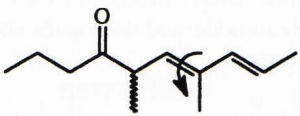


Matsucoccus matsumurae [3]

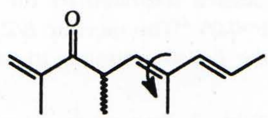
Fig. 1. The structure of the known sex pheromones of *Matsucoccus* spp. The common keto-diene moiety, common to all three pheromones, is marked in bold.



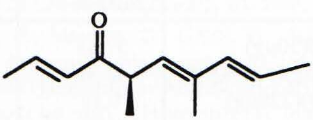
1A + 1B



4A + 4B



5A + 5B



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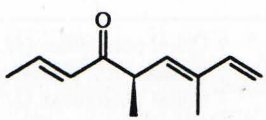

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Fig. 2. The structure of analogues of the *Matsucoccus josephi* sex pheromone.

1995). Its activity is surprising as it behaves like a parapheromone, attracting only males of *M. josephi* and not *E. hebraicus*. The activity of the pheromone, the new analogue [6] and the *M. feytaudi* pheromone [2] were assessed in another test (which included an evaluation of some other parameters not presented here). It was considered important to reaffirm the activity of analogue [6], due to its specific pheromonal attractancy. The results (Table 2) did indeed confirm the previous findings. The *M. feytaudi* pheromone [2] displayed kairomonal activity and attracted the predatory bug only. The activity of [2], as a kairomone in comparison with [1], was lower than that observed before (Dunkelblum *et al.*, 1996), although its specificity remained the same.

Table 1. Trap catch of male *Matsucoccus josephi* and males and females of *Elatophilus hebraicus* (mean/trap/day) with *Matsucoccus josephi* pheromone and analogues. Yatir forest, 14-22nd July 1998 (8 days), each treatment with five replicates*.

Pheromone/analogue (amount)**		*Matsucoccus josephi*	*Elatophilus hebraicus*
[1]	- Chiral pheromone (50μg)	56.0a	26.2a
[1A + 1B]	- Racemic *E/Z* pheromone (200μg)(~25%*E-R*)	37.8ab	20.9a
[4A + 4B]	- Racemic *E/Z* analogue (200μg)(~25%*E-R*)	8.0c	10.3b
[5A + 5B]	- Racemic *E/Z* analogue (200μg)(~25%*E-R*)	0.1d	0.4c
[6]	- Chiral analogue (50μg)	34.4b	0.5c
	Control	0.8d	0.5c

*Means followed by the same letter for columns are not significantly different at P>0.05 **The racemic *E/Z* pheromone and analogues contained approximately 25% of the *E-R* stereoisomer in each case.

Table 2. Trap catch of male *Matsucoccus josephi* and males and females of *Elatophilus hebraicus* (mean/trap/day) with *Matsucoccus josephi* pheromone and analogues. Yatir forest, 14-20th May - 1st June 1998 (12 days), each treatment with five replicates*.

Pheromone/analogue (amount)**		*Matsucoccus josephi*	*Elatophilus hebraicus*
[1]	- Chiral pheromone (*M. josephi*)(50μg)	57.8a	46.3a
[1A + 1B]	- Racemic *E/Z* pheromone (200μg)(~25%*E-R*)	42.9a	25.6ab
[2]	- Chiral pheromone (*M. feytaudi*)(220μg)	0.1c	13.3b
[6]	- Chiral analogue (50μg)	26.3b	0.9c
	Control	0.3c	0.3c

*Means followed by the same letter for columns are not significantly different at P>0.05

**The racemic *E/Z* pheromone contained approximately 25% of the *E-R* stereoisomer in each case. The amount of chiral *M. feytaudi* pheromone [2] was adjusted to compensate for its lower volatility as compared with that of *M. josephi* [1].

The activity of analogues is always lower than that of the natural pheromone or kairomone. In the case of the *M. josephi/E. hebraicus* complex, the pheromone of the female *M. josephi* [1] is both a male attractant and a potent kairomone for both males and females of the predatory bug, *E. hebraicus*. The *M. feytaudi* pheromone [2] can be considered as an analogue of [1] and, in this case, the tested analogues may be classified into two groups. The first group consists of analogues [2], [4] and [5] and the second group of analogue [6]. The first group is characterized by changes in the specific propenyl side chain of the *M. josephi* pheromone [1], while the second group is characterized by a change in the structure of the diene side chain common to the three *Matsucoccus* pheromones. The results indicate that alterations in the propenyl side chain, characteristic of the *M. josephi* pheromone, adversely affect the pheromonal activity, whereas changes in the diene side chain adversely affect the kairomonal activity. Analogue [5] is unique among all the analogues, being devoid of any activity, probably due to the introduction of a methyl group α to the ketone. Preparation and testing of more analogues is necessary in order to generalize on this very interesting observation.

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