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Short Communication

Sex Pheromone Activity of Synthetic (±)-Periplanone-A and (±)-Epiperiplanone-A to Males of *Periplaneta* and *Blatta*

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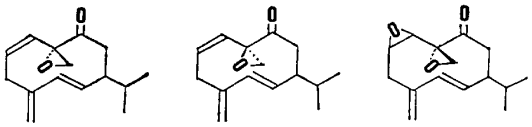
Abstract: Sex pheromone activity of synthetic periplanone-A (PA) and its epimer (EPA) was bioassayed in six species of genera *Periplaneta* and *Blatta*. The activity of PA was about one thousandth that of periplanone-B (PB) in males of *P. americana*, and that of EPA was a further one thousandth lower than that of PA. PA, EPA and mixtures of PA and PB showed low pheromone activity in males of *P. joponica*, *P. brunnea*, *P. australasiae* and *B. orientalis*.

INTRODUCTION

Two sex pheromones of the American cockroach *Periplaneta americana*, periplanone-A and periplanone-B, were isolated and identified by Persoons *et al.*[1] The absolute configuration of periplanone-B was unambiguously determined by its synthesis.[2] Since Persoons *et al.* reported in 1982 that the chemical structure of periplanone-A as a second component was to be 7-methylene-4-isopropyl-12-oxatricyclo[4.4.2.$0^{1,5}$]-9-dodecen-2-one,[3] the structure of the component was reexamined using primarily a synthetic approach. Recently, the compound was synthesized by Shizuri *et al.* and found to elicit no response from male *P. americana*.[4] Concerning to the structure of periplanone-A, Hauptmann *et al.* isolated an epoxygermacrone (**1**) from extract of female *P. americana* feces and postulated that it is periplanone-A.[5] They also synthesized periplanone-A of the structure and the epimer at C_1 (epiperiplanone-A) (**2**), and the spectral data of the former were found to be identical with those of the natural periplanone-A. Macdonald *et al.*, on the other hand, synthesized epiperiplanone-A (**2**) from a germacratriene epoxide with the epi-C_1 epoxide stereochemistry relative to periplanone-B (**3**).[6] Hauptmann *et al.* confirmed its biological activity in structure **1** but not in **2**, whereas Macdonald claims the pheromone activity of synthetic epiperiplanone-A (**2**).



1 **2** **3**

We have been working on the structure and pheromone activity relationship since our first identification of pheromonal activity in germacrene-D.[7] The quantitative comparison of the sex pheromone activity of (±)-periplanone-B (PB) (**3**) among the genera *Periplaneta* and *Blatta* was recently reported.[8] In this paper we report the pheromone activity of the synthetic (±)-periplanone-A (PA) (**1**) and (±)-epiperiplanone-A (EPA) (**2**) to the males of the six *Periplaneta* and *Blatta* species.

MATERIALS AND METHODS

1. *Insects*

Colonies of *P. americana*, *P. japonica*, *P. australasiae*, *P. brunnea*, *P. fuliginosa* and *Blatta orientalis* were fed mouse food and water, and maintained in a light cycle of 12L-12D at 25± 2°C. After imaginal ecdysis, males were separated from the colony two weeks before bioassay.

2. *Bioassay*

About 100 males were kept in a sheltered container (34×49×27 cm). The method and criterion were the same as described earlier.[8]

3. *Synthetic Pheromones*

Hauptmann's PA (**1**) and Macdonald's PA (**2**) were synthesized in the following way. The exocyclic enone **5** was prepared from the endocyclic enone **4**.[9] Epoxidation of the enone **5** (*t*-BuOOH/KH) at 0°C in THF gave a mixture of **1** and **2** in a ratio of 56: 44.[10] The ^{1}H-NMR spectral data of the synthetic **1** and **2** were identical with those previously reported.[5,6] Although Hauptmann reported that this epoxidation provided a high stereoselectivity (99%), our

Table 1 Behavioral responses of six species of genera *Periplaneta* and *Blatta* to periplanone-A (PA).

Male	Dose (g)					Behavior observed
	4×10^{-11}	4×10^{-10}	4×10^{-9}	4×10^{-8}	4×10^{-7}	
P. americana	++	++	+++	+++	+++	Attracted to the source
P. japonica	−	−	−	+	+	Walking around the source, not attracted, a few raised wings
P. brunnea	−	−	−	+	++	Slowly attracted
B. orientalis	−	−	−	+	++	Running around
P. australasiae	−	±	+	++	++	Running around, not attracted, a few raised wings and short flight
P. fuliginosa	−	−	−	−	−	Antennal waving

Table 2 Behavioral responses of six species of genera *Periplaneta* and *Blatta* to epiperiplanone-A (EPA).

Male	Dose (g)					Behavior observed
	4×10^{-10}	4×10^{-9}	4×10^{-8}	4×10^{-7}	4×10^{-6}	
P. americana	−	+	++	++	+++	Attracted to the source
P. japonica	−	−	−	−	+	Walking around, a few raised wings
P. brunnea	−	−	−	−	+	Slowly attracted, a few raised wings
B. orientalis	−	−	−	−	+	Running around
P. australasiae	−	−	−	±	+	Running around, a few raised wings
P. fuliginosa	−	−	−	−	−	Antennal waving

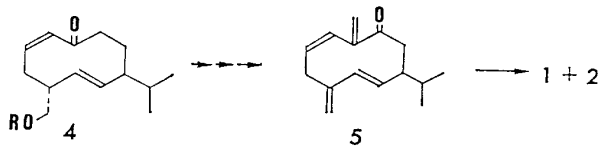
Table 3 Behavioral responses of six species of genera *Periplaneta* and *Blatta* to mixtures of periplanone-A and -B.

Male	PA(4×10^{-8} g)+PB(4×10^{-8} g) (1 : 1)	PA(1.2×10^{-7} g)+PB(1.2×10^{-6} g) (1 : 10)
P. americana	+++	+++
P. japonica	++	+++
P. brunnea	++[a]	++[d]
B. orientalis	+[b]	+[e]
P. australasiae	++[c]	++[f]
P. fuliginosa	—	—

a) Slowly attracted.
b) Running around.
c) Running around.
d) Running around, a few raised wings.
e) Running around.
f) Running around, a few raised wings.

experimental results and the prediction of this epoxidation based on MM2 calculation showed a lower stereoselectivity.

A series of decadal dilutions of pheromone solution was prepared in hexane.



RESULTS AND DISCUSSION

The threshold amount of (±)-periplanone-A (PA) (1) to elicit response in male *P. americana* was 4×10^{-12} g. The activity was 1000 times more active than EPA. The behavior elicited by PA was very similar that elicited by PB. Bioassay results of the six species are shown in Tables 1 and 2. Compared with the activity of PB, PA showed about 1000 times less activity to male *P. americana*. EPA was another 1000 times

less active than PA. Other than the conspecific males, male *P. australasiae* responded most to PA and EPA among the five species. Both PA and EPA were active to male *P. brunnea* and *Blatta orientalis* but at much less intensity.

Male *P. australasiae* responded by running around in the bioassay container but were not attracted to the pheromone source. Some of the responding males showed short flight and wing raising behavior about 10 cm away from the pheromone. Seelinger reported that a 1: 3 or more ratio of PA to PB inhibited the response of male *P. americana*.[11] Table 3 shows our results using mixtures of PA and PB at ratios of 1: 1 to 1: 10. By mixing the two compounds the male responses increased in males of all five species. The result indicates that the mixture can be used as an attractant for a survey of *Periplaneta* populations.

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要　約

合成 (±)-ペリプラノン A および (±)-エピペリプラノン A の *Periplaneta* 属, *Blatta* 属雄ゴキブリに対する性フェロモン活性

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ワモンゴキブリの性フェロモンの一つペリプラノン A(PA) とそのエピマー (EPA) を使って，*Periplaneta* 属，*Blatta* 属 6 種の雄に対する性フェロモン活性を実験室内で生物検定した．PA のワモンゴキブリに対するフェロモン活性はペリプラノン B(PB) の約 1/1000 で，EPA の活性は PA の約 1/1000 であった．PA，EPA および PA と PB の混合物はワモンゴキブリ以外にヤマトゴキブリ，トビイロゴキブリ，コワモンゴキブリ，トウヨウゴキブリの雄にもフェロモン活性があった．