Pestycydy/Pesticides, **2010**, 1-4, 51-57.
ISSN 0208-8703

Effect of farnesol and its synthetic derivatives on the settling behaviour of the peach potato aphid *Myzus persicae* (Sulz.)

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Abstract: The behavioural effect of *trans,trans*-farnesol and its structural derivatives on *M. persicae* was evaluated. The incorporation of carboxy group into the molecule did not alter the strong deterrent activity of farnesol. The lactonization and the epoxidation of farnesol caused the delay in expression and the loss of deterrent activity, respectively. The ester, product of Claissen rearrangement of farnesol and iodolactone did not exhibit significant biological effect.

Key words: plant protection, structure-activity relationships, farnesol, *Myzus persicae*

INTRODUCTION

Farnesol is a naturally occurring aliphatic sesquiterpenoid alcohol. It is a component of various plant essential oils, e.g., lilly of the valley (*Convallaria majalis*), citrus (*Citrus* sp.), and nutmeg (*Myristica fragrans*) [1]. Farnesol and its related compounds have an important role in signal transmission between organisms, including aphids. For example, farnesol shows effectiveness as

a repellent to the maize aphid (*Rhopalosiphum maidis*) [2]. Farnesol isomers are components of the aggregation pheromone of the spined citrus bug (*Biprorulus bibax*) and the marking substance of the Scandinavian bumble-bee (*Bombus pratorum*) [3]. (E)-β-Farnesene is the main constituent of aphid alarm pheromone [4]. (E,E)-α-Farnesene and a mixture of farnesol isomers cause a high mortality among nymphs of the black bean aphid (*Aphis fabae*) and the peach potato aphid (*Myzus persicae*) when topically applied [5].

Plants infested by aphids may be affected directly, mainly because of the fluid and nutrient removal, and indirectly, by virus transmission. *M. persicae* is a cosmopolitan and extremely polyphagous vector of more than 100 plant virus species [3] and it developed resistance to almost all available aphicides [6]. Therefore, there is an increasing demand for more specific, indirectly acting crop protection agents. Considering the high biological activity of lower terpenoids, several attempts have been made to apply these compounds or their analogues as alternatives to conventional neurotoxic chemicals in pest insect control. One of the most promising approaches is the modification of insect behaviour in a way that should lead to the termination of feeding and, in consequence, the departure from the plant or other substrate [7]. However, from the practical point of view, the use of plant-derived antifeedants on a large scale is not economic, so the synthetic analogues of natural compounds are more accessible for application. The biological activity of a given compound is species-specific and depends on its structural characteristics. Variations, such as incorporation of functional groups, epoxidation, or lactonization, can produce radical changes in activity profile [8].

The aim of the present study was to evaluate the behavioural effect of farnesol and its structural derivatives on *M. persicae*. Aphids are insects with sucking-piercing mouthparts and collect their food directly from phloem vessels, which makes the direct observation of their feeding impossible [9]. Host acceptance by aphids is manifested in settling on a given plant, i.e., the cessation of movement in consequence of prolonged feeding [10]. Hence, the willingness to settle on plants is a good indication of plant suitability and a good measure of biological activity of exogenously applied potential aphid control agents.

MATERIAL AND METHODS

Chemicals

Trans,trans-farnesol was purchased from Sigma-Aldrich Company. Iodolactone (**4**) was obtained in three-step synthesis as described elsewhere [11]. In the first step, *trans,trans*-farnesol (**1**) was subjected to Claissen rearrangement with ethyl

orthoacetate [12] and the resulted ethyl ester (**2**) was hydrolysed to carboxylic acid (**3**) in the solution of sodium hydroxide in methanol. Iodolactone (**4**) as a mixture of *trans* (84%) and *cis* (16%) isomers was the product of iodolactonization process of carboxylic acid according to Mori procedure [13]. The mixture of iodolactones was separated by column chromatography (silica gel, hexane-acetone, 6:1). In the next syntheses and biological tests, only isomer *trans* was used. Lactone **5** was obtained by reduction of iodolactone (**4**) with tributyltin hydride. Lactone with exocyclic double bond (**6**) was the product of dehydrodehalogenation of iodolactone (**4**) with 1,8-diazabicyclo[4.1.0]undec-7-ene (DBU). Epoxyfarnesol (**7**) was obtained in three-step synthesis from *trans,trans*-farnesol (**1**) *via* the bromohydrine of farnesyl acetate according to procedures described earlier [14]. The structures of the studied (i.e., synthesized) compounds were confirmed by spectral (IR, ^{1}H and ^{13}C NMR) data. The purity of the studied compounds was determined by GC (capillary column TR-5 (crosslinked 5% phenyl polysiloxane, 30 m x 0.32 mm x 1.0 μm). All compounds studied were above 97% purity.

The compounds were applied as 0.1% solutions in 70% ethanol.

Aphid and Plants

Aphids (*M. persicae*) and plants (Chinese cabbage *Brassica pekinensis*) were reared in laboratory at 20 °C, 65% r.h., and L16:8D photoperiod. Young, 2-3 days old viviparous apterous females were selected for experiments. Cabbage plants used in the bioassays were 5-6 weeks old.

Aphid settling

The aphid settling assay was a choice test, in which the aphids were offered a choice between treated and control leaves. Leaves cut from cabbage plants, were dipped for 10 s in the solution of the studied compound or control solution (70% ethanol) and dried at room temperature for 1 h. Two leaves (test and control) were transferred to Petri dishes. Afterwards, twenty apterous females of *M. persicae* were placed between the leaves at the centre of the Petri dish (the distance between the two leaves approximately 2.0 cm). Aphids that settled on each leaf were counted at 1, 2 and 24 h intervals after the beginning of the experiment. This experiment was replicated 8 times for each treatment (total number of insects per treatment = 160). The data were analyzed using one way ANOVA ($P \leq 0.05$). The relative index of deterrence (DI) was calculated from the total number of aphids counted on treated (T) and control (C) leaves at each time interval:

$$DI = (C–T)/(C+T)$$

Possible values for the index therefore range between 1 (complete deterrent) and −1 (complete attractant), with a value at or close to zero indicating no effect.

RESULTS AND DISCUSSION

The natural compound, *trans,trans*-farnesol (**1**) appeared a very strong deterrent to *M. persicae*. The application of this terpenoid caused the avoidance of plants by the peach potato aphid (Table 1). The structural modifications of farnesol molecule had a significant effect on biological activity. The epoxy derivative of farnesol (**7**) was absolutely inactive, while the activity of the carboxylic acid (**3**) was comparable to that of the natural compound. Aphids avoided the leaves treated with **3** as soon as one hour after application. The effect was relatively strong (high values of relative index of deterrence DI=0.5÷0.7) and stable: the deterrent activity was observed for at least 24 hours, i.e., until the end of experiment. However, the ethyl ester of the carboxylic acid **3** (compound **2**) did not show any activity (Table 1, Figure 1). The lactonized derivatives of *trans,trans*-farnesol (**5** and **6**) were also active deterrents (DI: 0.3 and 0.4, respectively), but the negative effect on aphid settling was delayed. Moreover, at the beginning of the experiment, i.e., 1-2 hours after application, the compounds showed a weak attractant properties. It is very well documented that natural antifeedants are lactones with one or more additional functional groups [15, 16]. The halogenation of the lactonized derivatives, i.e., the incorporation of iodine into the molecule (compound **4**) caused the loss of activity (Table 1, Figure 1).

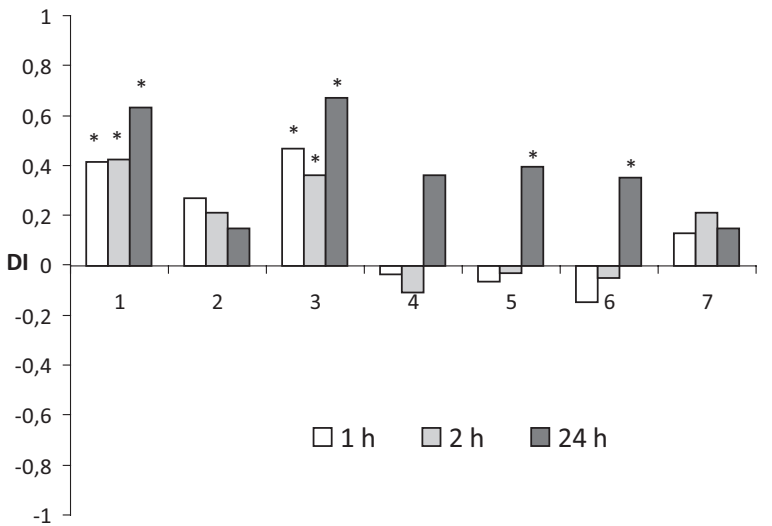
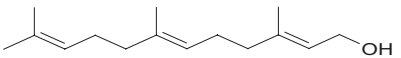
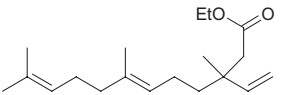
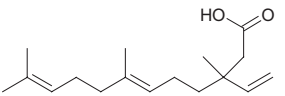
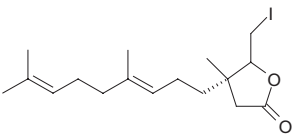
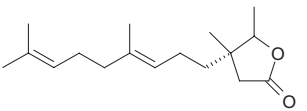
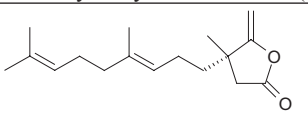
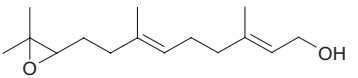


Figure 1. Effect of farnesol (1) and its derivatives (2-7) on the settling of the peach potato aphid *Myzus persicae* expressed as the Relative Index of Deterrence (DI).

Table 1. Effectiveness of farnesol and its derivatives as aphid settling deterrents. Numbers represent mean number of aphids (±SD) that settled on treated ('test') and control leaves 1, 2, and 24 hours after application of the studied compounds. P value represents statistical significance of difference (ANOVA).

Compound		Time after access to plants		
		1h	2h	24h
 *Trans, trans*-farnesol (**1**)	Control	12.8 (±1.5)	11.1 (±1.2)	14.6 (±1.8)
	Test	5.3 (±1.3)	4.5 (±1.0)	3.3 (±0.7)
	P	0.0023	0.0008	0.0000
 *Ethyl trans*-3,7,11-trimethyl-3-vinyldodece-6,10-dienoate (**2**)	Control	7.5 (±1.8)	6.5 (±1.8)	5.4 (±2.0)
	Test	4.3 (±0.9)	3.0 (±0.7)	2.8 (±0.9)
	P	0.1214	0.0936	0.2410
 *trans*-3,7,11-trimethyl-3-vinyldodeca-6,10-dienoic acid (**3**)	Control	11.9 (±1.5)	10.6 (±1.6)	14.8 (±1.1)
	Test	4.4 (±0.7)	5.0 (±1.1)	2.9 (±0.4)
	P	0.0005	0.0128	0.0000
 *trans*-4-(4',8'-dimethylnona-3'*E*,7'-dienyl)-5-iodomethyl-4-methyldihydrofuran-2-one (**4**)	Control	6.8 (±2.8)	6.4 (±3.3)	8.3 (±3.3)
	Test	7.3 (±3.2)	8.0 (±3.7)	3.9 (±5.1)
	P	0.7428	0.3747	0.1036
 *trans*-4-(4',8'-dimethylnona-3'*E*,7'-dienyl)-4,5-dimethyl-dihydrofuran-2-one (**5**)	Control	5.6 (±3.0)	6.4 (±2.1)	10.1 (±4.4)
	Test	6.4 (±2.5)	6.8 (±3.4)	4.4 (±3.8)
	P	0.5938	0.7960	0.0139
 4-(4',8'-dimethylnona-3'*E*,7'-dienyl)-4-methyl-5-methyldihydrofuran-2-one (**6**)	Control	6.0 (±3.2)	6.3 (±3.6)	8.1 (±3.4)
	Test	8.1 (±2.7)	7.0 (±3.5)	3.9 (±3.4)
	P	0.1701	0.6800	0.0262
 (±)-10,11-epoxyfarnesol (**7**)	Control	7.4 (±2.0)	6.6 (±1.9)	4.6 (±1.5)
	Test	5.4 (±1.7)	4.3 (±1.7)	3.4 (±1.9)
	P	0.4609	0.3657	0.4795

The results of experiments presented here illustrate three major aspects of biological activity of the studied compounds that depend on their substituents and stereochemistry, i.e., the variation in the stability of deterrent effect, a switch from attractant to deterrent properties or otherwise. The change in stability and nature of behavioral effect of exogenously applied chemicals may be caused by the alteration of local conditions in the plant tissues in the course of time due to plant and aphid metabolism [17]. The highest activity of *trans,trans*-farnesol is worth of notice. *Trans,trans*-farnesol, and more probably, the essential oils in which farnesol is detected have a chance for practical application in aphid population regulation. In the further studies, the activity of essential oils with farnesol as a component should be evaluated.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education, Grant No. N N310 146835.

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