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# 3-Oxygenated α-ionone derivatives as potent male attractants for the solanaceous fruit fly, *Bactrocera latifrons* (Diptera: Tephritidae), and sequestered metabolites in the rectal gland

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**Abstract**
A series of 3-oxygenated derivatives of α-ionone and α-ionol have been characterized as highly specific male lures for the solanaceous fruit fly *Bactrocera latifrons* (Hendel). In order to optimize the activity, we tested several analogous compounds derived from the three known attractants, 3-oxo-α-ionone, 3-oxo-α-ionol, and 3-hydroxy-α-ionone. 3-Oxo-7,8-dihydro-α-ionone and 3-oxo-7,8-dihydro-α-ionol were found to be potent attractants as well as feeding stimulants for the males in an indoor bioassay. While *trans*-3-hydroxy-α-ionone showed moderate attractant and feeding stimulant activity, the corresponding *cis*-isomer was weakly active, indicating the importance of the stereochemistry at the C-3 position. Synthetic *trans*-3-acetoxy-α-ionone exhibited lower activity than the corresponding 3-hydroxy derivative. *B. latifrons* males fed actively on 3-oxo-7,8-dihydro-α-ionone, transformed it to 3-oxo-7,8-dihydro-α-ionol, and sequestered this compound in a substantial quantity in the rectal glands. Males that fed on 3-oxo-7,8-dihydro-α-ionol incorporated the compound mostly unchanged in the rectal gland. In both cases, the rectal content was approximately 1 μg/gland at 6 h post-feeding on the chemicals, respectively. Selective accumulation of these 3-oxygenated α-ionone/α-ionol analogs suggests their possible role as a male sex pheromone.

**Key words:** *Bactrocera latifrons*; 3-oxo-7,8-dihydro-α-ionone; attractant; feeding stimulant; sequestration

## INTRODUCTION

The solanaceous fruit fly, *Bactrocera latifrons* (Hendel) (Diptera: Tephritidae) infests various solanaceous fruits, including eggplant, tomato, and chili peppers (Vargas and Nishida, 1985; Liquido et al., 1994). Males of many tephritid fruit fly species in the genus *Bactrocera* are attracted to specific phenylpropanoid substances [e.g. methyl eugenol in *B. dorsalis* (Hendel); raspberry ketone/cue-lure in *B. cucurbitae* (Coquillett)], which have been effectively used as powerful attractants in pest management programs (Steiner et al., 1965; Koyama et al., 1984; Metcalf and Metcalf, 1992). In the case of *B. latifrons*, α-ionone, α-ionol, and their mixtures with phenolic volatiles were found to act as potential lures for males of *B. latifrons*, but the attractiveness of these compounds was not nearly as strong as that of other well-known tephritid male lures (Flath et al., 1994; McQuate and Peck, 2001; McQuate et al., 2004). We recently found a series of 3-oxygenated α-ionone/ionol analogs [e.g. 3-oxo-α-ionone (**3**) and 3-oxo-α-ionol (**4**)] to be attractants as well as feeding stimulants for the males of *B. latifrons* (Ishida et al., 2008) (Fig. 1). Since *B. latifrons* has become established in subtropical Yonaguni Island, Okinawa, Japan, an eradication program using the sterile insect technique has been undertaken (Kuba et al., 2006; Shimizu et al., 2007). An effective male lure for monitoring the population and possibly as a mass trapping agent is an urgent necessity. In order to further improve the attractant potency of the lure chemicals, we have examined several analogs by modifying the 3-oxygenated α-ionone/α-ionol structures. We report here the attractiveness and

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feeding stimulant activity of several synthetic 3-oxygenated $C_{13}$-norterpenoid analogs to compare the activity with a series of related compounds previously reported by Ishida et al. (2008).

After feeding on an attractant source, males of *Bactrocera* species incorporate the chemicals selectively in their rectal glands, which are presumed to function as a reservoir of sex pheromone to attract females, as demonstrated in methyl eugenol—*B. dorsalis* association (Nishida et al., 1988; Shelly and Dewire, 1994; Hee and Tan, 1998; Tan and Nishida, 1998). It was shown that sexually mature males of *B. latifrons* that fed on a series of 3-oxygenated $\alpha$-ionone/$\alpha$-ionol analogs selectively incorporate and partially biotransform the compounds in a specific ratio and store the metabolites in the rectal gland (Nishida et al., 2009), suggesting a possible pheromonal role of the components in their life cycle. Here, we describe the sequestered metabolites in the rectal gland after ingestion of the new attractant chemicals tested above.

## MATERIALS AND METHODS

**Insects.** A *B. latifrons* colony was obtained from Okinawa Prefectural Agricultural Research Center (originally collected in Yonaguni Island) and raised at a laboratory of the Naha Plant Protection Station in Okinawa, Japan. Fruit flies were kept in an insectarium under constant conditions (26–27°C, 60–70% RH, 14L10D—light phase with dawn at 06:00–08:00 to dusk at 18:00–20:00). Adults were provided with water and a diet of four parts sucrose and one part dry yeast AY-65 (Asahi Food & Healthcare, Ltd., Tokyo, Japan). Sexually mature flies (21–27 days after eclosion, freely mated) were used for the behavioral tests in a bioassay chamber under the same environmental conditions noted above.

**Spectrometric instruments.** Proton and carbon-13 nuclear magnetic resonance ($^1$H-NMR and $^{13}$C-NMR) spectra were measured with a Bruker Avance 400 FT-NMR using TMS as an internal standard. Gas chromatography-mass spectra (GC-MS) were measured with an Agilent 5975 inert XL MSD mass spectrometer coupled with an Agilent 6890 gas chromatograph equipped with a capillary column (HP-5MS, 28 m×0.25 mm, 0.25 $\mu$m film thickness, helium as carrier gas) programmed from 60°C (1 min holding) to 280°C at a rate of 10°C/min.

**Chemicals.** (±)-$\alpha$-Ionone (**1**) and (±)-$\alpha$-ionol (**2**, a mixture of racemic diastereomeric isomers) were obtained from Sigma-Aldrich (Fluka) (St. Louis, USA) and Sankei Chemical Co., Ltd. (Kagoshima, Japan), respectively. (±)-3-Oxo-$\alpha$-ionone (**3**) and (±)-3-oxo-$\alpha$-ionol (**4**) (a diastereomeric mixture) were obtained from NARD Institute, Ltd. (Hyogo, Japan). (±)-3-Oxo-7,8-dihydro-$\alpha$-ionone (**5**) and (±)-3-oxo-7,8-dihydro-$\alpha$-ionol (**6**, a diastereomeric mixture in an approximate ratio of 1 : 1) were prepared by partial hydrogenation of compounds **3** and **4**, respectively, using palladium carbon (Pd 10% Wako Pure Chemical Industries, Japan) in hexane, followed by successive chromatographic purifications (both in a purity of >97% based on GC-MS analyses). Both (−)-(3*S*,6*S*)-*trans*-3-hydroxy-$\alpha$-ionone (**7**, $[\alpha]_D^{21.5}=-46.0^o$, $c=0.30$, methanol) and (−)-(3*R*,6*S*)-*cis*-3-hydroxy-$\alpha$-ionone (**8**, $[\alpha]_D^{21.5}=-11.2^o$, $c=0.30$, methanol) were obtained by microbial oxidation of racemic $\alpha$-ionone (Wako Pure Chemical Industries, Ltd., Japan) using *Aspergillus niger* (Yamazaki et al., 1988) (Fig. 1). *trans*-3-Acetoxy-$\alpha$-ionone (**9**) was prepared by acetylation of **7** using acetic anhydride and pyridine (room temperature). The identities of compounds **5**, **6**, **8** and **9** were confirmed by their electron impact mass spectra (EIMS) and $^1$H-NMR spectra (400 MHz) (s: singlet, d: doublet, t: triplet, m: multiplet) as assigned below.

3-Oxo-7,8-dihydro-$\alpha$-ionone (**5**): EIMS *m/z* (%) 208 (18, $M^+$), 151 (91), 135 (74), 123 (40), 109 (82), 95 (47), 91 (23), 79 (24), 77 (19), 67 (28), 44 (91), 43 (100). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 0.97 (3H, s, H-11), 1.01 (3H, s, H-12), 1.7–2.1 (3H, m, H-6, H-7), 1.99 (3H, s, H-13), 2.15 (3H, s, H-10), 2.15 (1H, d, $J$=17.4 Hz, H-2b), 2.36 (1H, d, $J$=17.4 Hz, H-2a), 2.54 (2H, m, H-8), 5.84 (3H, s, H-4). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 23.5, 24.6, 27.3, 28.8, 30.1, 36.3, 42.5, 47.0, 50.1, 125.6, 164.7, 199.0, 207.6.

3-Oxo-7,8-dihydro-$\alpha$-ionol (**6**): EIMS *m/z* (%) 210 (21, $M^+$), 177 (34), 151 (30), 150 (41), 135 (100), 123 (61), 121 (39), 111 (41), 109 (67), 108 (66), 107 (80), 95 (71), 93 (81), 84 (34), 79 (40), 69 (50), 67 (47), 55 (31), 45 (30), 43 (50), 41 (44). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.02 (3H, s, H-11), 1.07 (3H, s, H-12), 1.21 (3H, d, $J$=6.4 Hz, H-10), 1.5–1.9 (5H, overlapped m, H-6, H-7, H-8), 1.99 (3H, s, H-13), 2.03 (1H, d, $J$=17.4 Hz, H-2a), 2.40

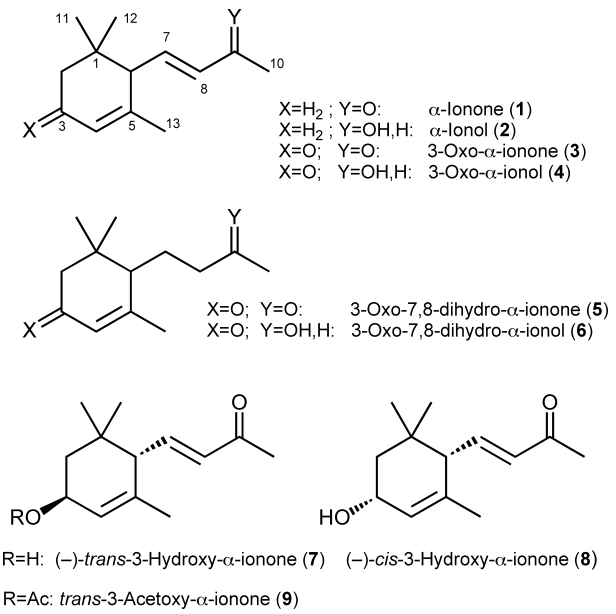


Fig. 1. Structures of 3-oxygenated $\alpha$-ionone/$\alpha$-ionol analogs tested.

(1H, d, $J$=17.4 Hz, H-2b), 3.77 (1H, m, H-9), 5.83 (1H, s, H-4). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 23.78, 23.90, 24.79, 26.34, 26.42, 27.26, 27.32, 28.93, 28.95, 36.43, 38.76, 38.83, 47.27, 47.33, 51.15, 51.24, 68.16, 68.46, 125.25, 125.29, 165.55, 165.64, 199.55.

*cis*-3-Hydroxy-$\alpha$-ionone (**8**): EIMS *m/z* (%) 208 (2, $M^+$), 175 (27), 147 (35), 109 (100), 91 (35), 43 (57). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 0.92 (3H, s, H-11), 1.00 (3H, s, H-12), 1.40 (1H, double d, $J$= 16.0, 6.5 Hz, H-2a), 1.63 (3H, s, H-13), 1.70 (1H, m, H-2b), 2.26 (3H, s, H-10), 2.28 (1H, d, $J$=7.1 Hz, H-6), 4.25 (1H, m, H-3), 5.59 (1H, s, H-4), 6.07 (1H, d, $J$=15.6 Hz, H-8), 6.64 (1H, double d, $J$=15.6, 7.1 Hz, H-7).

3-Acetoxy-$\alpha$-ionone (**9**): EIMS *m/z* (%) 250 (0.2, $M^+$), 109 (100), 43 (62). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 0.89 (3H, s, H-11), 1.03 (3H, s, H-12), 1.50 (1H, double d, $J$=14.0, 6.2 Hz, H-2a), 1.64 (3H, s, H-13), 1.85 (1H, double d, $J$=14.0, 4.2 Hz, H-2b), 2.04 (3H, s, $CH_3COO$), 2.26 (3H, s, H-10), 2.50 (1H, d, $J$=9.8 Hz, H-6), 5.33 (1H, broad s, H-3), 5.57 (1H, broad s, H-4), 6.09 (1H, d, $J$=15.8 Hz, H-8), 6.53 (1H, double d, $J$=9.8, 15.8 Hz, H-7).

**Behavioral bioassay.** The attractant and feeding stimulant activities were examined by the method reported previously (Ishida et al., 2008). Sexually mature adults (50 males and 50 females) were introduced into a screen cage (30×30×45 cm). A sample solution (100 $\mu$g in 10 $\mu$l of ethanol) was applied to the center of filter paper (a diameter of 90 mm, Advantec No. 2) and dried at ambient temperature. The test filter paper was placed on a plastic cup (45 mm height from the bottom) at the center of the cage. Ethanol (10 $\mu$l) was used as a control. Starting 10 min after the introduction of the filter paper (08:45 in the morning), the number of males and females "attracted" (sighted on the filter paper) and "feeding" (licking with extended proboscis) at the sample area were recorded during 10 sec of observations every 10 min for 60 min (i.e. 6 times). In order to pre-examine the responsiveness of males, a brief bioassay was conducted for the known attractant, 3-oxo-$\alpha$-ionone (**3**) under the same conditions employed for Ishida et al. (2008). Although qualitative, the sensitivity of males was the same as that observed for compound **3** in the previous paper (dose: 100 $\mu$g/filter paper, see Table 1). Data collected at the 10 min intervals were summed to yield a grand total for a replicate. Total counts were square root-transformed [sq rt ($x$+ 0.5)] to normalize the distribution before analysis. Means of the transformed values were compared by Tukey-Kramer HSD multiple comparison test ($\alpha$=0.05) with the statistical package JMP (ver. 5.0.1J, SAS Institute Inc., 2001).

**Rectal sample preparation and quantification of volatiles.** *B. latifrons* males (3 weeks old, unmated) were exposed to each compound separately on a thin film (30 $\mu$g per male) in a Petri dish (85 mm in diam.), allowed to feed for 2 h in the morning, and then moved to a screen cage (18× 18×22 cm) with food and water until rectal sampling. Rectal glands were dissected from flies at 6 h after treatment and extracted with 250 $\mu$l ethanol/gland. Quantifications of volatile chemicals were performed using an HP5890 Plus gas chromatograph (Hewlett Packard, Wilmington, DE, USA) with a capillary column (HP5-MS, 15 m×0.25 mm, 0.25 $\mu$m film thickness, helium as carrier gas) programmed from 60°C (2 min holding) to 250°C at a rate of 10°C/min (flame ionization detection). A 1-$\mu$l portion of each rectal gland sample obtained above was subjected to GC quantification, using 1-pentadecanol as an internal standard.

Table 1. Mean total number (±SD) of males and females of *Bactrocera latifrons* attracted to and feeding on the chemical source

| Test chemicals | Number of males attracted | Number of males feeding | Number of females attracted | Number of females feeding | *n* |
|---|---|---|---|---|---|
| α-Ionone (**1**)[a] | 26.5±12.9 c | 12.8±6.9 c | 0.3±0.6 b | 0.0±0.0 a | 21 |
| α-Ionol (**2**)[a] | 42.2±17.4 bc | 24.9±10.5 b | 0.1±0.2 b | 0.0±0.0 a | 19 |
| 3-Oxo-α-ionone (**3**)[a] | 105.1±26.0 a | 91.6±23.9 a | 1.7±1.5 a | 0.2±0.6 a | 40 |
| 3-Oxo-α-ionol (**4**)[a] | 100.7±19.2 a | 86.0±17.6 a | 1.6±2.1 a | 0.4±0.7 a | 31 |
| 3-Oxo-7,8-dihydro-α-ionone (**5**) | 122.6±19.3 a | 104.0±16.9 a | 1.4±1.3 ab | 0.0±0.0 a | 5 |
| 3-Oxo-7,8-dihydro-α-ionol (**6**) | 101.0±26.1 a | 85.3±24.6 a | 1.0±1.0 ab | 0.0±0.0 a | 3 |
| *trans*-3-Hydroxy-α-ionone (**7**)[a] | 35.0±22.1 b | 28.0±18.0 b | 0.6±0.8 ab | 0.0±0.0 a | 21 |
| *cis*-3-Hydroxy-α-ionone (**8**) | 26.5±13.2 c | 13.6±6.9 c | 0.9±2.6 ab | 0.4±1.4 a | 12 |
| *trans*-3-Acetoxy-α-ionone (**9**) | 12.7±2.1 c | 4.7±3.8 c | 1.0±1.0 ab | 0.0±0.0 a | 3 |
| Control | 0.7±0.9 d | 0.0±0.0 cd | 0.4±0.6 bc | 0.0±0.0 a | 20 |

The values with different letters indicate significant differences within the same column by Tukey-Kramer HSD test of the square-root transformed data ($p<0.05$).
[a] Data from Ishida et al. (2008).

Table 2. Contents (μg/male) (mean±SE) of the rectal gland volatiles in *Bactrocera latifrons* males 6 h post-feeding on 3-oxo-7,8-dihydro-α-ionone (**5**) or 3-oxo-7,8-dihydro-α-ionol (**6**)

| Treatment | 3-Oxo-7,8-dihydro-α-ionone (**5**) | 3-Oxo-7,8-dihydro-α-ionol (**6**) | *N*-3-Methylbutyl acetamide | *n* |
|---|---|---|---|---|
| 3-Oxo-7,8-dihydro-α-ionone (**5**) | 0.06±0.01 | 0.91±0.24 | 2.54±0.39 | 6 |
| 3-Oxo-7,8-dihydro-α-ionol (**6**) | 0.09±0.03 | 1.29±0.39 | 2.18±0.35 | 6 |
| Control (unfed) | 0 | 0 | 2.62±0.50 | 5 |

## RESULTS

### Attractant and feeding stimulant activities of compounds

Table 1 shows mean total numbers of males and females of *B. latifrons* attracted and feeding on α-ionone/α-ionol analogs **5**, **6**, **8** and **9**, comparing those with preceding bioassay data for **1**, **2**, **3**, **4** and **7** (Ishida et al., 2008). 3-Oxo-7,8-dihydro-α-ionone (**5**) and 3-oxo-7,8-dihydro-α-ionol (**6**) elicited levels of both attraction and feeding similar to those noted for the corresponding 7,8-unsaturated derivatives (**3** and **4**) in males. Most males attracted to **5** and **6** persistently licked the chemical source for more than 10 min, leaving clear salivation marks on the filter paper. Both the attractant and feeding stimulant activities of *cis*-3-hydroxy-α-ionone (**8**) and *trans*-3-acetoxy-α-ionone (**9**) were significantly lower than those of *trans*-3-hydroxy-α-ionone (**7**), eliciting responses similar to the level of α-ionone (**1**). Females did not display strong responses towards any of the test compounds (Table 1).

### Contents of rectal volatiles after feeding on chemicals

Sexually mature *B. latifrons* males possessed substantial quantities of *N*-3-methylbutyl acetamide as an endogenous volatile in the rectal gland regardless of whether they fed on the lure chemicals or not (Table 2). After ingestion of either synthetic attractants **5** or **6**, the most abundant rectal metabolites was found to be **5** followed by **6** in both cases.

## DISCUSSION

We previously reported 3-oxo-α-ionone (**3**) and 3-oxo-α-ionol (**4**) as potent attractants and feeding stimulants for *B. latifrons* males (Ishida et al., 2008). Here, we have demonstrated that the two corresponding 7,8-dihydro-analogs (**5** and **6**) elicited equally strong responses from the males. Although there were no significant differences in the potencies among the four analogs (**3**–**6**) in this experiment, the superiority of compound **5** over its 7,8-unsaturated derivative **3** was observed in a sim-

ilar test conducted in Hawaii (Todd E. Shelly, personal communication). While (−)-*trans*-3-hydroxy-$\alpha$-ionone (**7**: 3*S*, 6*S*) showed moderate attractant/feeding stimulant activity, its *cis*-isomer (**8**: 3*R*, 6*S*) was found to be less active, indicating the importance of the stereochemistry. It should be also noted that both 3-oxo-$\alpha$-ionol (**4**) and 3-oxo-7,8-dihydro-$\alpha$-ionol (**6**) have two chiral centers at C-6 and C-9, respectively. Both **4** and **6** used here are racemic diastereomeric mixtures, respectively, in that the diastereomeric compositions are unknown. *trans*-3-Acetoxy-$\alpha$-ionone (**9**) was tested in comparison with hydroxy-analog **7**, because it could possibly increase the vaporizability and hence the activity, but the compound exhibited lower activity than **7**. Both the attractancy and feeding stimulant activity of **9** appeared to be the same level as that of $\alpha$-ionone (**1**), which lacks the 3-oxygenic function.

Originally, *trans*-3-hydroxy-$\alpha$-ionone (**7**) was found as an attractant/feeding stimulant of *B. latifrons* males from a cultivar of eggplant, *Solanum melongena* (Nishida et al., 2009). 3-Oxo-7,8-dihydro-$\alpha$-ionone (**5**) is known from various plant parts, such as leaves of *Tilia flos* (Tiliaceae), flowers of *Aptenia cordifolia* (Aizoaceae), fruits of *Mammea americana* (Guttiferae), aerial parts of *Chenopodium album* (Chenopodiaceae) and *Helianthus heterophyllus* (Asteraceae), and root and root exudate of *Zea mays* (Poaceae), often together with **6** (Morales and Duque, 2002; DellaGreca et al., 2004, 2007; Park et al., 2004; Radulescu and Oprea, 2008). However, **6** has been reported more frequently as glycosidically bound volatiles together with 3-oxo-$\alpha$-ionol (**4**) and other related analogs, which are liberated enzymatically: e.g. garlic mustard, *Alliaria petrolata* (Brassicaceae), varieties of grapes, *Vitis vinifera* (Vitaceae), and bay leaves, *Laurus nobilis* (Lauraceae) (Strauss et al., 1987; Wirth et al., 2001; Kilic et al., 2005; Blažević and Mastelić, 2008). Interestingly, these $C_{13}$-norterpenoids are found in fruit tissues of many plant species (e.g. tomato, mango, papaya, star fruit, apricot, raspberry and acerola fruit) as degradation products of carotenoids, most likely as glycosidically bound forms as listed in the preceding paper (Nishida et al., 2009 and refs. therein). However, the ecological association between *B. latifrons* and such ubiquitous phytochemicals in nature is totally unknown.

The male rectal gland of *B. latifrons* is a suspected pheromone reservoir similar to other *Bactrocera* species (Little, 1992). We have previously reported that after consumption of either 3-oxo-$\alpha$-ionone (**3**) or 3-oxo-$\alpha$-ionol (**4**), *B. latifrons* males sequestered **4** and **6** in an approximate ratio of 3 : 1 with a trace amount of **3** in the rectal gland (Nishida et al., 2009). In contrast, after ingestion of either **5** or **6**, the ratios of **5** and **6** were roughly 1 : 15 regardless of the substrate chemicals (Table 2). Neither one of the 7,8-unsaturated analogs (e.g. **3** and **4**) were formed when the 7,8-dihydro analogs (**5** and **6**) were ingested. There seems to be a kind of reductive-oxidative enzymatic equilibration in these biotransformation processes (Nishida et al., 2009). Selective incorporation of these metabolites suggested their possible role as a male sex pheromone component and/or allomone to deter predators, similar to other cases of *Bactrocera* species that use phenylpropanoid volatiles to attract conspecific females as well as defense substances (Nishida and Fukami, 1990; Shelly and Dewire, 1994; Shelly and Villalobos, 1995; Tan and Nishida, 1998; Khoo et al., 2000; Wee and Tan, 2005; Wee et al., 2007). An artificial mixture of major rectal volatiles (*N*-3-methylbutyl acetamide+3-oxo-$\alpha$-ionol (**4**)) induced some short-range attraction in virgin females in lab cage tests (Nishida, unpublished), and further behavioral tests are in progress to clarify the possible role of these pharmacophagously acquired rectal metabolites in the mating and/or defense system of *B. latifrons.*

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## REFERENCES

Blažević I. and J. Mastelić (2008) Free and bound volatiles of garlic mustard (*Alliaria petiolata*). *Croatica Chem. Acta* 81: 607–613.

DellaGreca, M., C. Di Marino, A. Zarrelli and B. D'Abrosca

(2004) Isolation and phytotoxicity of apocarotenoids from *Chenopodium album*. *J. Nat. Prod*. 67: 1492–1495.

DellaGreca, M., A. Fiorentino, A. Izzo, F. Napoli, R. Purcaro and A. Zarrelli (2007) Phytotoxicity of secondary metabolites from *Aptenia cordifolia*. *Chem. Biodivers.* 4: 118–128.

Flath, R. A., R. T. Cunningham, N. J. Liquido and T. P. McGovern (1994) Alpha-ionol as attractant for trapping *Bactrocera latifrons* (Diptera: Tephritidae). *J. Econ. Entomol.* 87: 1470–1476.

Hee, A. K. W. and K. H. Tan (1998) Attraction of female and male *Bactrocera papayae* to conspecific males fed with methyl eugenol and attraction of females to male sex pheromone components. *J. Chem. Ecol.* 24: 753–764.

Ishida, T., H. Enomoto and R. Nishida (2008) New attractants for males of the solanaceous fruit fly *Bactrocera latifrons*. *J. Chem. Ecol.* 34: 1532–1535.

JMP (2001) *User's Manual, version 5.0.1j.* SAS Institute, Cary, NC.

Khoo, C. C. H., K. H. Yuen and K. H. Tan (2000) Attraction of female *Bactrocera papayae* to sex pheromone components with two different release devices. *J. Chem. Ecol.* 26: 2487–2496.

Kilic, A., H. Kollmannsberger and S. Nitz (2005) Glycosidically bound volatiles and flavor precursors in *Laurus nobilis* L. *J. Agric. Food Chem.* 53: 2231–2235.

Koyama, J., T. Teruya and K. Tanaka (1984) Eradication of the oriental fruit fly (Diptera: Tephritidae) from the Okinawa Islands by a male annihilation method. *J. Econ. Entomol*. 77: 468–472.

Kuba, H., T. Matsuyama and N. Mougi (2006) Current status of the solanaceous fruit fly control project in Yonaguni Island. In *FFTC-OPARC Joint International Symposium on Area-Wide Management of Insects Pests.* Proceeding of the Symposium. October 2–3, 2006. Okinawa Prefectural Agricultural Research Center, Okinawa, Japan, pp. 41–51.

Liquido, N. J., E. J. Harris and L. A. Dekker (1994) Ecology of *Bactrocera latifrons* (Diptera: Tephritidae) populations: Host plants, natural enemies, distribution, and abundance. *Ann. Entomol. Soc. Am*. 87: 71–84.

Little, H. F. (1992) Fine structure of presumed pheromone glands of *Dacus cucurbitae* and *D. latifrons* (Diptera: Tephritidae). *Ann. Entomol. Soc. Am.* 85: 326–330.

McQuate, G. T. and S. L. Peck (2001) Enhancement of attraction of alpha-ionol to male *Bactrocera latifrons* (Diptera: Tephritidae) by addition of a synergist, cade oil. *J. Econ. Entomol.* 94: 39–46.

McQuate, G. T., Y. S. Keun, C. D. Sylva, Q. X. Li and E. B. Jang (2004) Active ingredients in cade oil that synergize attractiveness of $\alpha$-ionol to male *Bactrocera latifrons* (Diptera: Tephritidae). *J. Econ. Entomol.* 97: 862–870.

Metcalf, R. L. and E. R. Metcalf (1992) *Plant Kairomones in Insect Ecology and Control*. Chapman & Hall, New York, NY. 168 pp.

Morales, A. L. and C. Duque (2002) Free and glycosidically bound volatiles in the mammee apple (*Mammea americana*) fruit. *Eur. Food Res. Technol.* 215: 221–226.

Nishida, R. and H. Fukami (1990) Sequestration of distasteful compounds by some pharmacophagous insects. *J. Chem. Ecol.* 16: 151–164.

Nishida, R., K. H. Tan, M. Serit, N. L. Lajis, A. M. Sukari, S. Takahashi and H. Fukami (1988) Accumulation of phenylpropanoids in the rectal glands of males of the Oriental fruit fly, *Dacus dorsalis*. *Experientia* 44: 534–536.

Nishida, R., H. Enomoto, T. E. Shelly and T. Ishida (2009) Sequestration of 3-oxygenated $\alpha$-ionone derivatives in the male rectal gland of the solanaceous fruit fly, *Bactrocera latifrons*. *Entomol. Exp. Appl.* 131: 85–92.

Park, S., Y. Takano, H. Matsuura and T. Yoshihara (2004) Antifungal compounds from the root and root exudate of *Zea mays*. *Biosci. Biotechnol. Biochem.* 68: 1366–1368.

Rădulescu, V. and E. Oprea (2008) Analysis of volatile compounds of officinal *Tiliae flos* by gas chromatography coupled with mass spectrometry. *Farmacia (Bucharest, Romania)* 56: 129–138.

Shelly, T. E. and A. Dewire (1994) Chemically mediated mating success in male oriental fruit flies, *Bactrocera dorsalis* (Diptera: Tephritidae). *Ann. Entomol. Soc. Am.* 87: 375–382.

Shelly, T. E. and E. M. Villalobos (1995) Cue lure and the mating behavior of male melon flies (Diptera: Tephritidae). *Fla. Entomol.* 78: 473–482.

Shimizu, Y., T. Kohama, T. Uesato, T. Matsuyama and M. Yamagishi (2007) Invasion of solanum fruit fly *Bactrocera latifrons* (Diptera: Tephritidae) to Yonaguni Island, Okinawa Prefecture, Japan. *Appl. Entomol. Zool*. 42: 269–275.

Steiner, L. F., W. C. Mitchell, E. J. Harris, T. T. Kozuma and M. S. Fujimoto (1965) Oriental fruit fly eradication by male annihilation. *J. Econ. Entomol.* 58: 961–964.

Strauss, C. R., B. Wilson and P. J. Williams (1987) 3-Oxo-$\alpha$-ionol, vomifoliol and roseoside in *Vitis vinifera* fruit. *Phytochemistry* 26: 1995–1997.

Tan, K. H. and R. Nishida (1998) Ecological significance of male attractant in the defense and mating strategies of the fruit fly *Bactrocera papayae*. *Entomol. Exp. Appl.* 89: 155–158.

Vargas, R. I. and T. Nishida (1985) Survey for *Dacus latifrons* (Diptera: Tephritidae). *J. Econ. Entomol*. 78: 1311–1314.

Wee, S. L. and K. H. Tan (2005) Male endogenous pheromonal component of *Bactrocera carambolae* (Diptera: Tephritidae) deterred gecko predation. *Chemoecology* 15: 199–203.

Wee, S. L., K. H. Tan and R. Nishida (2007) Pharmacophagy of methyl eugenol by males enhances sexual selection of *Bactrocera carambolae.* *J. Chem. Ecol.* 33: 1272–1282.

Wirth, J., W. Guo, R. Baumes and Z. Günata (2001) Volatile compounds released by enzymatic hydrolysis of glycoconjugates of leaves and grape berries from *Vitis vinifera* Muscat of Alexandria and Shiraz cultivars. *J. Agric. Food Chem.* 4: 2917–2923.

Yamazaki, Y., Y. Hayashi, M. Arita, T. Hieda and Y. Mikami (1988) Microbial conversion of $\alpha$-ionone, $\alpha$-methylionone, and a-isomethylionone. *Appl. Environ. Microbiol*. 54: 2354–2360.