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ScienceDirect
Journal of Stored Products Research 43 (2007) 193–201
Journal of STORED PRODUCTS RESEARCH
www.elsevier.com/locate/jspr

Oviposition attractants for *Plodia interpunctella* (Hübner) (Lepidoptera: Pyralidae) in the volatiles of whole wheat flour

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Accepted 15 May 2006

Abstract

Plodia interpunctella is attracted to whole wheat flour. Volatiles obtained from whole wheat flour by Porapak Q trapping were assayed using pitfall olfactometers, and were attractive to mated females (active at 10^{-1} gram/day equivalent, gde), but not to males or unmated females, suggesting that the volatiles are oviposition attractants for *P. interpunctella*. Silicon dioxide column chromatography of the crude volatiles revealed that the fraction recovered with 3% ether in pentane (3% EP) was active and contained at least 27 components, in which alkanals (C_6–C_{10}) and 2*E*-alkenals (C_7–C_{11}) were active as individual aldehydes or mixtures. Nonanal was most active (the lowest active limit, LAL: 10^{-2} μg), followed by 2*E*-nonenal and 2*E*-decenal (1 μg each). The synthetic mixture of the 27 components identified from 3% EP was attractive at 1.59×10^{-4} μg, which was equal in activity to the crude volatiles at 10^{-1} gde (LAL) for mated females. The ether fraction (E) showed no activity by itself but synergistically enhanced the activity of the 10% EP fraction (LAL: 10^{-4} μg). Alkanols (C_5–C_9), lactones and carboxylic acids (C_5–C_{18}) were identified from the E fraction, in which hexanol and hexanoic acid were the major components. Both hexanol and palmitic acid were synergistic in combination with the aldehyde mixture.

Keywords: Indian meal moth; *Plodia interpunctella*; Oviposition attractants; Whole wheat flour; Stored-product pest; Synergistic effect

1. Introduction

Larvae of the Indian meal moth, *Plodia interpunctella* (Hübner) (Lepidoptera: Pyralidae), are a serious stored-product pest and are distributed world-wide. They attack a wide variety of dried fruits, vegetables, nuts, chocolates and packaged foods, as well as cereals and flours, and so research into integrated pest management (IPM) of this species has become a priority (Campbell et al., 2002). The female sex pheromone of *P. interpunctella* was identified by Kuwahara et al. (1971) and Brady et al. (1971) as (*Z*,*E*)-9,12-tetradecadienyl acetate. More recently, (*Z*,*E*)-9,12-tetradecadienal (Teal et al., 1995) and two minor sex pheromone components have been reported from this species (Zhu et al., 1999). Vick and Sower (1973) reported that (*Z*,*Z*)-9,12-tetradecadienyl acetate, the geometric isomer of the sex pheromone, inhibited the responses of *P. interpunctella* to the pheromone.

In Japan, *P. interpunctella* has several generations a year. We have often observed that the moths are attracted to bagged whole wheat flour in our laboratory during summer, and so we have become interested in the volatile attractants derived from the flour. Few studies on attractants for *P. interpunctella* have been published. For example, Tamura and Miyajima (1970) reported that larvae of this species are attracted to isoamyl propionate, citral and ethyl acetate from 49 perfumes tested with a Y-shaped olfactometer. Also, Olsson et al. (2004) reported that moths of both sexes showed electroantennogram (EAG) responses to ethyl vanillin, phenylacetaldehyde and nonanal derived from chocolate, and that in a wind-tunnel, individual compounds and their mixtures induced the same behaviour and landing rates in the moth as did chocolate. To the best of our knowledge, however, there have been no published reports on attractants for these adult moths derived from cereal crops.

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0022-474X/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jspr.2006.05.002

In this paper, we report on the components of oviposition attractants for *P. interpunctella* in whole wheat flour.

2. Materials and methods

2.1. Study insect

Plodia interpunctella were reared on whole wheat flour (200 g; purchased from Tokyo Milling Co. Ltd., Tokyo, Japan) supplemented with 5% w/w brewer's yeast in a polyethylene container (24 × 39 × 11 cm) at 25 ± 2 °C, 65% r.h., and in a 16L:8D photoregime. Twenty to 30 pairs of moths were used for oviposition in the container.

2.2. Bioassay

Females copulated soon after adult eclosion (copulatory rate of 2-day-old females was ca. 99% in preliminary tests). Two-day-old females, either mated or unmated, and males were used for bioassays, because our preliminary findings revealed that 2-day-old females showed the greatest responses to the wheat volatiles. Unmated females were prepared by isolating individual females from the rearing container immediately after their adult eclosion, and maintaining them for 2 days in a sample tube (12 mm diameter × 35 mm long) before bioassay. The assays were conducted using pitfall olfactometers as follows: a plastic Petri dish (90 mm diameter × 20 mm high; IWAKI, Japan) was constructed with two holes (8 mm diameter, 42 mm apart) under each of which a plastic pipetter chip (upper: 8 mm diameter, lower: 6 mm diameter, length: 2 cm; ASONE, Japan) was adhered. The chip was inserted in a glass vial (5 ml volume). Two paper discs (8 mm diameter, thin type; ADVANTEC MFS, INC., Tokyo) were treated with 10 μl of either the volatile sample in pentane or the pentane solvent (control) for each trial. After evaporation of the solvent, the papers were placed on the bottom of each vial. A single 2-day-old adult moth (unmated or mated female, or male) was released into the dish within a dark room controlled at 25 °C. The treatment of samples and introduction of moths into the Petri dishes were conducted under the illumination of a red-coloured bulb (50 watt), before being placed in the dark. After 1 h, whether the moth was in each vial or not was recorded. The assay was repeated 40–50 times using a new moth for each sample. The total number of moths attracted in a sample vial was compared with that of the control vial using a binomial test (one-tailed, $\alpha = 0.05$).

2.3. Analytical methods

Gas chromatography (GC) was performed with two capillary columns: a HP-5MS column (30 m × 0.25 mm, 0.25 μm; Hewlett–Packard) with a Hewlett–Packard 5890 (Palo Alto, CA) gas chromatograph, and a FFAP column (25 m × 0.25 mm, 0.25 μm; Quadrex) with a Hewlett–Packard 6890, using nitrogen as the carrier gas. The samples were introduced via a splitless injector in the splitless mode at 250 °C. The temperature was programmed to increase 8 °C/min from 30 °C (1 min) to 250 °C or 6 °C/min from 30 °C (1 min) to 230 °C for the 5-MS and FFAP capillary columns, respectively. A HP-5MS capillary column (30 m × 0.25 mm, 0.25 μm), fitted in a HP-6890 MSD, was used for the GC-MS analyses. The temperature was programmed to increase 10 °C/min from 30 (1 min) to 270 °C. Helium was used as the carrier gas.

2.4. Chemicals

Authentic compounds used for bioassays were commercially obtained from Wako Pure Chemical Co. Ltd. (WPC; Osaka, Japan), Nacalai Tesque (NT; Kyoto, Japan), Tokyo Kasei Ind. (TCI; Tokyo, Japan), Kanto Chemical Co., Ltd. (KC; Tokyo, Japan) and Aldrich. Alkanals (C_6–C_{10}), methyl benzoate, phytol and carboxylic acids (C_5–C_{18}) were purchased from WPC or NT. Some lactones (4-heptanolide, 4-octanolide and 4-nonanolide) were purchased from TCI and Aldrich. Red-Al was purchased from KC. 2-Alkanones (C_7–C_{13}, and C_{15}), 6-alkanones (C_{11}–C_{12}), 2*E*-alkenals (C_7–C_{11}), 5-ethyl-1-cyclopentenecarbaldehyde and phytone were synthesized as follows. 2-alkanones and 6-alkanones: the Grignard reaction of the appropriate alkyl bromides or methyl iodide and aldehydes followed by oxidation with pyridinium dichromate (PDC) in dichloromethane. 2*E*-Alkenals, (*E*)-2-heptenal and (*E*)-2-nonenal: tetrahydropyranyl (THP) ether of 2-propyn-1-ol was coupled with 1-bromobutane or 1-bromohexane in the presence of BuLi/tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA). Removal of the THP protecting group and subsequent reduction with Red-Al gave (*E*)-2-heptenol or (*E*)-2-nonenol which were oxidized with CrO_3–SiO_2 to give (*E*)-2-heptenal or (*E*)-2-nonenal, respectively. (*E*)-2-undecenal: the Wittig–Horner reaction of octanal and triethyl phosphonoacetate in the presence of NaH in THF followed by reduction with Red-Al to yield (*E*)-2-undecenol, which was oxidized with PDC to give (*E*)-2-undecenal. Phytone (hexahydrofarnesylacetone) was prepared by epoxydation of phytol with *m*-chloroperbenzoic acid followed by cleavage with orthoperiodic acid. 5-Ethyl-1-cyclopentenecarbaldehyde (Phrocanthal): cyclopentanone was converted into the corresponding dimethylhydrazone, into which one ethyl group was introduced to give 2-ethylcyclopentanone (Corey and Enders, 1976; Yamashita et al., 1985) and this was submitted to formylation with *N*, *N*-dimethylformamide (DMF) in the presence of *n*-BuLi via its tris-hydrazone to yield Phrocanthal (Chamberlin et al., 1978). Tetrahydrogeranylacetone was obtained by catalytic hydrogenation with 5% Pd/C geranylacetone, which was prepared from the acetoacetic ester synthesis of geranyl bromide (bromination of geraniol with triphenylphosphine and bromine) and ethyl acetoacetate. 2-Butyl-(*Z*)-2-octenal was synthesized