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PROPYLENE OXIDE AS POTENTIAL QUARANTINE FUMIGANT FOR INSECT DISINFESTATION OF DRIED FIGS

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ABSTRACT

In this study, propylene oxide (PPO) at low pressure (100 mm Hg) was tested for rapid disinfestation of dried figs as replacement for methyl bromide by evaluating its toxicity to Indian meal moth, *Plodia interpunctella* (Hübner) and the fig moth, *Ephestia cautella* (Walker), in absence and presence of dried figs, its sorption and residue on dried figs. The complete mortality of all life stages of *P. interpunctella* and *E. cautella* was achieved at a Ct product of 45.5 and 53.2 mg h l⁻¹ for empty space fumigation (without commodity) respectively. It required a dosage of 11.4 and 13.3 mg l⁻¹ for empty space fumigation and 32.4 for and 30.2 mg l⁻¹ for fumigation in presence of dried figs to kill 99% of the larvae of *P. interpunctella* and *E. cautella* respectively. Thus, 2.85-fold and 2.27-fold higher dose of PPO required for PPO fumigation in presence of dried figs to obtain the complete mortality of the larvae of *P. interpunctella* and *E. cautella*, respectively. Sorption of PPO by dried figs after 5 h exposure time was relatively high by an average of 58% reduction of initial concentration. The PPO residue in dried figs was a maximum average of 85 ppm at 0-1 day after termination of aeration, which all was much lower than the 300 ppm maximum tolerance. Based on these data, the combination of PPO with low pressure can be a potential as fumigant for replacing methyl bromide for quarantine purposes in dried figs.

Key words: Propylene oxide, dried fig, quarantine fumigation, toxicity, sorption, *Ephestia cautella*, *Plodia interpunctella*

INTRODUCTION

Turkey is one of the most important dried figs producing and exporting country. The annual Turkish dried fig production is around 55 to 60 000 tones and comes from a single cultivar, (*Ficus carica* Sarilop (Calimyrna)), grown in the western Aegean Region. Nearly 90% of the production goes to the export market, the main period of marketing being between end of September and December (Aksoy et al., 2008). The fig moth (*Ephestia cautella* (Walker),

Lepidoptera: Pyralidae), the Indian meal moth (*Plodia interpunctella* Hübner, Lepidoptera: Pyralidae), the dried-fruit beetle (*Carpophilus* spp., Coleoptera: Nitidulidae) and the fig mite (*Carpoglyphus lactis* (L.), Acari: Carpoglyphidae) are main storage pests that play important roles in the quality and consequent trade volume of dried fig (Turanlı, 2003). Storage pests infesting fruit especially during over-ripening, drying and storage period may create cause significant problems in dried fig sector. The fig moth reduces fruit quality by feeding and damaging the fruit and contaminating by leaving its excretions and other residues as silky net weaves (Damarlı et al., 1997). Large populations can develop before being discovered and severe damage may occur (Jarratt, 2001).

Methyl bromide (MeBr) has been used as a gas fumigant for many years to fumigate the commodities that have become infested with stored-product insect pests, since it kills the insects rapidly, has a wide spectrum of activity and relatively low-cost (Fields and White, 2002). However, it has been banned in developed countries since 2005 and scheduled for worldwide withdrawal from routine use as a fumigant in 2015 under the directive of the Montreal Protocol on Substances that Deplete Ozone Layer (Schneider et al., 2003) except quarantine, laboratory and pre-shipment purposes. Various alternatives as integrated pest management, some chemicals (phosphine, carbonyl sulfide, sulfuryl fluoride, ozone, cyfluthrin) and non-chemical treatments (modified atmospheres, high pressure, heat/cold treatments, sanitation, radio frequency, long-wave energy, and irradiation) were tested (Zettler et al., 1999; Johnson et al., 2000; Fields and White, 2002; Schneider et al., 2003). Although there are a large number of suggested potential chemical and non-chemical alternatives to MeBr, each has limitations in terms of efficiency, cost, penetration or residues that prevent it from being a direct replacement for MeBr in all its current uses.

The dried-fig industry in Turkey has continued to rely on phosphine for post-harvest insect infestation. Phosphine is also under attack because of pest resistance (Bell and Wilson, 1995; Zettler and Cuperus, 1990) and its requirement of long exposure period (5 d or longer), which makes the chemical unsuitable for quarantine fumigations.

Propylene oxide (PPO) is a liquid fumigant under normal temperature pressure (NTP) with a boiling point of 35°C and a noticeable ether odor. As a fumigant, PPO has reduced environmental risks compared with MeBr. It is not an ozone depleter and degrades into nontoxic propylene glycol in the soil and in the human stomach. PPO is commonly used as a sterilant to reduce bacteria, mould and yeast contamination on processed spices, cocoa and processed nutmeats except peanuts. A disadvantage of PPO is that it is flammable from 3% to 37% in air and therefore, to avoid flammability it should be applied under low pressure or in a CO₂-enriched atmosphere. Several studies reported by Creasy and Hartsell (1999), Isikber et al. (2006) and Navarro et al. (2004) have shown that PPO has insecticidal properties under vacuum conditions as a fumigant by killing all stages of various stored-product insects within a short exposure time. These reports on insect toxicity indicated that PPO would be an effective replacement for methyl bromide in some postharvest situations (Creasy and Hartsell, 1999; Isikber et al., 2006; Navarro et al., 2004).

The loss of methyl bromide could have a significant negative impact on the dried fig industry, particularly because of non-availability of alternatives to methyl bromide currently exist for rapid disinfestation of dried figs. Thus, there is a critical need to develop new fumigants for quarantine purposes. PPO is considered here for rapid disinfestation of the dried fig as a replacement for methyl bromide by evaluating its toxicity against major insect pests of dried fig, and its sorption and residue on the dried fig.

MATERIALS AND METHODS

Test insects

Toxicity tests were carried out on all life stages of the most common insect pest, *Plodia interpunctella* (Hübner) (Indianmeal moth) and *Ephestia cautella* (Walker) (Fig moth). All stages were obtained from laboratory cultures reared at 26 ± 1 °C and 70 ± 5 % r.h. using standard culture techniques (Donahaye, 1990). Eggs for exposure to treatments were transferred into "pits" drilled into Perspex exposure slides, each slide containing 50 pits. When filled, the slides were covered with a cover glass to retain the eggs. Two slides containing 100 eggs aged 1-2 days were exposed to each treatment. Two days old pupae, 17-19 d old larvae and newly emerged adults were removed from culture jars and exposed to the treatment.

Commodities

Sun-dried fruit of Sarılop (Calimyrna) fig variety with a m.c. of 21 ± 1 %, harvested in 2011 season and delivered to TARIŞ, Farmers' Sales Cooperative (İzmir, Turkey), was used in the tests.

Fumigation chambers

Test chambers consisted of 3 liter glass jar, each metal lid capped with a ground-glass stopper equipped with entry and exit tubing. A magnetic stirrer placed in the bottom well beneath a wire-mesh disc served to mix the air with the fumigant. Two pieces of rubber tubing, 5 cm long, 6.2 mm ID, were attached to the tubing and sealed with pinch-clamps.

The fumigant

The fumigant was 99% pure liquid PPO that was withdrawn from a sealed vial fitted with a rubber septum, using a gas-tight syringe.

Dosing and fumigation procedures

Propylene oxide was introduced as a liquid into the test chamber using 50 or 250 μ L gas-tight syringes. Pressure in each glass jar was measured using a 0 to 800 mm Hg vacuum gauge (Celesco SE-2000, U.S.A.). The 100 mm Hg measure referred to herein is absolute pressure, with 760 mm Hg considered as atmospheric pressure. Prior to each test, 50 larvae, pupae or adults were confined, separately, inside 3 cm diameter by 8 cm long wire-mesh cages. For eggs, two exposure slides each holding 50 eggs were used per fumigation. For fumigations at low pressure, the insects were first placed in the empty test chamber and then, prior to the introduction of the required PPO concentration, 100 mm Hg of low pressure was obtained by evacuating air. PPO at 100 mm Hg was tested at four to five dosages varying from 1 to 20 mg l^{-1} . Each test was replicated at least three times. The Exposure time was 4 h for all the experiments. The gas mixtures in the test chambers were stirred for at least 20 min. The r.h. and temperature were maintained at 65 ± 5 % at atmospheric pressure and 26 ± 1 °C respectively.

For PPO fumigation in presence of the commodity only larval stage which was found to be the most tolerant stage to PPO was used. Each test chamber was filled up with 1.5 kg of dried figs and then 50 larvae confined separately inside the wire-mesh cages were placed into the commodity. For fumigations at low pressure, prior to the introduction of the required PPO concentration, 100 mm Hg was obtained by evacuating air. PPO at 100 mm Hg was tested at

four to five dosages varying from 5 to 35 mg l⁻¹. Each test was replicated at least three times. The exposure time was 4 h for all the experiments. The r.h. and temperature were maintained at 65±5 % at atmospheric pressure and 26±1 °C respectively.

Measurement of sorption and residue in the commodity

Dried figs weighing 1.5±0.2 kg were placed into the fumigation chamber and the lids of each fumigation chamber were tightly closed. The fumigation chambers before treatment were held for two or three hours for preconditioning of the commodities at 26°C. Sorption profiles of PPO were determined for dried fig at a dose of 68.7 mg l⁻¹ applied over a 5 h period. The calculated volumes of PPO were introduced as a liquid into the desiccators containing the commodities using 50 µL gas-tight syringes. Controls consisting of sealed, empty fumigation chambers were also dosed to determine the “chamber effect” on fumigation concentrations to see any loss or reduction of gas concentration. All exposures were conducted at 26±1 °C and 60±5 % relative humidity, ambient conditions. PPO was sampled from the free-space of each chamber to determine the decrease in fumigant concentration due to sorption. The gas concentration of PPO was measured using a Shimadzu 17A GC fitted with an FID (Flame Ionization Detector) and an ECTM–WAX capillary column (30 m length x 0.25 mm ID x 0.25 µm Film Thickness) run at 170 °C isothermal. The PPO residues in dried figs were measured after 5 h fumigation at 26°C at a sole dose of 112 mg l⁻¹ PPO. The levels of PPO residue on dried figs were determined at the end of the fumigation and following a 3-day aeration period. The levels of PPO residue in the commodities were determined by analytical laboratory service of Kahramanmaraş Sutcu Imam University following the analytical method that was a modification of the ASTA analytical method of the Official Methods of Analysis of the AOAC (Anonymous, 2000).

Data processing and analysis

After each treatment, larvae, pupae, and adults were transferred to 200-mL jars containing food medium and were held at 26±1 °C and 65±5 % r.h. until examined for mortality. Mortality counts for all life stages of the insects were made after each treatment. Zero dose control and dose-mortality responses were subjected to probit analysis by the POLO-PC computer program (LeOra Software, 1987) to determine LC₅₀s, LC₉₉s and their respective 95% confidence intervals. Required concentrations x time (Ct) products to obtain 50 % and 99 % mortality of all insect stages of each insect were calculated using the LC₅₀ and LC₉₉ concentrations derived from probit analyses.

RESULTS AND DISCUSSION

PPO at 100 mm Hg was toxic to all life stages of *P. interpunctella* and *E. cautella*. Eggs and larvae of *P. interpunctella* by LC₉₉ values of 12.24 and 11.37 mg l⁻¹ respectively were more tolerant than the adults and pupae by LC₉₉ values of 4.65 and 6.98 mg l⁻¹, respectively (Table 1). On the other hand, larvae and pupae of *E. cautella* LC₉₉ values of 13.31 and 8.98 mg l⁻¹, respectively were more tolerant than the eggs and adults LC₉₉ values of 7.11 and 4.15 mg l⁻¹, respectively (Table 1). The complete mortality of all life stages of *P. interpunctella* and *E. cautella* were achieved at a Ct product of 45.47 and 53.24 mg h l⁻¹ respectively. These findings may be compared with several studies of the two most commonly used fumigants, methyl bromide (MB) and phosphine, for control of *P. interpunctella*. Methyl bromide requires CT products of 21, 25 and 35 mg h l⁻¹ to obtain complete mortality of eggs, larvae and pupae, respectively, at 30 °C (Bell, 1976a), while phosphine requires Ct products of > 9.4,

0.9 and 1.3 mg h l⁻¹ to achieve complete mortality of eggs, larvae, and pupae, respectively, at 30 °C (Bell, 1976b).

Table 1. Probit analysis data and Ct products (mg h l⁻¹) for propylene oxide at low pressure of 100 mm Hg for all life stages of *Plodia interpunctella* and *Ephestia cautella* resulting from 4-h laboratory fumigations at 26°C.

Life stage	n ^a	Slope ^b ±SE	LC ₅₀ (Fiducial limit) ^c (mg l ⁻¹)	LC ₉₉ (Fiducial limit) ^c (mg l ⁻¹)	H ^d	Ct product for LC ₉₉ (mg h l ⁻¹)
<i>Plodia interpunctella</i>						
Egg	350	4.20 ± 0.35	3.42 (3.07 – 3.75)	12.24 (10.57 – 14.89)	0.86	24.48
Larva	140	16.85 ± 3.07	8.28 (7.79 – 8.61)	11.37 (10.57 – 13.1)	0.63	45.47
Pupa	140	11.05 ± 2.21	4.41 (4.12 – 5.52)	6.98 (6.52 – 9.70)	0.70	27.92
Adult	140	4.23 ± 0.81	1.48 (1.06 – 2.02)	4.65 (3.44 – 8.15)	0.86	18.58
<i>Ephestia cautella</i>						
Egg	350	7.23 ± 0.62	3.39 (3.18 – 3.59)	7.11 (6.45 – 8.09)	0.32	28.44
Larva	140	4.93 ± 0.61	3.81 (3.37 – 4.21)	13.31 (9.33 – 15.31)	0.59	53.24
Pupa	140	2.85 ± 0.21	1.37 (0.69 – 1.04)	8.98 (6.58 – 14.34)	0.23	35.92
Adult	140	2.01 ± 0.15	0.29 (0.23 – 0.36)	4.15 (2.69 – 7.77)	0.27	13.18

^a Number treated, excluding controls; ^b Slope ± Standard Error; ^c Numbers in brackets give the 95% confidence range; ^d Heterogeneity factor

The LC₅₀ and LC₉₉ levels for PPO at 100 mm Hg against larval stage of *P. interpunctella* and *E. cautella* resulting from 4-h laboratory fumigations in empty space and presence of 1.5 kg of dried fig are presented in Table 2. There was a significant difference in toxicity of PPO at 100 mm Hg against the larvae fumigated in empty space and presence of dried figs. It required a dosage of 32.40 and 30.21 mg l⁻¹ to kill 99 % of the larvae of *P. interpunctella* and *E. cautella* when fumigated in empty space and in presence of dried figs, respectively (Table 2). The results indicated that there were 2.85 and 2.27-fold increase in LC₉₉ value of PPO at low pressure respectively when *P. interpunctella* and *E. cautella* larvae were fumigated in the presence of dried figs as compared to those fumigated in the empty space. Thus, the present study indicates that a much higher dose of PPO is required for fumigation in the presence of dried figs to obtain complete mortality of *P. interpunctella* and *E. cautella* larvae. This could be due to a high sorption of PPO by dried figs. It is a well-recognized fact that a much higher dose of fumigants is required to kill an insect in a container filled with a commodity than in an empty one, owing to the sorption of the gas by the product. Just as, Punj (1969) reported that LC₅₀ value of different fumigants against *T. castaneum* in presence of paddy and groundnut kernels varied from 2.7 to 7.5 times as in empty space.

Sorption of PPO by dried figs after a 4-h exposure time was high with 58% of the initial concentration (Fig. 1). In all cases, there was an initial rapid decrease in concentrations of PPO during the first hour of exposure followed by a more gradual subsequent drop (Fig. 1). The drop in concentrations during the first hour for dried figs was 50% of the initial dosage

indicating a rapid sorption of PPO by dried figs. These data also support those of Zettler et al. (2002) who showed that PPO rapidly sorbed into the commodities, with 97.3, 99.2 and 98.6 % sorbed in the almonds, pecans and walnuts, respectively, at 48-h after initiation of the fumigation. The PPO residue in dried figs was a maximum average of 85 ppm at 0-1 day after termination of aeration, which was below the 300 ppm maximum tolerance determined by US FDA (Table 3). A very low 22 ppm of PPO residue was detected at 3 days after termination of aeration (Table 3). This data indicate that the PPO rapidly desorbs from the commodity at conditions of NAP and 30-35 °C. Thus, it is clear that most of the sorption of PPO by the commodity was physical. These data also support those of Zettler et al. (2002) who showed that the PPO residues among almonds, pecans and walnuts immediately after 4-h fumigations were well below the 300 ppm tolerance and that residues could not be detected following three days aeration.

Table 2. Probit analysis data for propylene oxide at low pressure of 100 mm Hg for the larvae of *Plodia interpunctella* and *Ephestia cautella* resulting from 4-h laboratory fumigations with 1.5 kg of dried fig and empty spaces

Treatments	n ^a	Slope ^b ±SE	LC ₅₀ (Fiducial limit) ^c (mg l ⁻¹)	LC ₉₉ (Fiducial limit) ^c (mg l ⁻¹)	H ^d
<i>Plodia interpunctella</i>					
PPO at 100 mm Hg with Dried Fig	240	21.2±3.16	19.80 (15.70 – 23.53)	32.40 (29.95 – 38.25)	0.51
PPO at 100 mm Hg with Empty Space	140	16.85 ± 3.07	8.28 (7.79 – 8.61)	11.37 (10.57 – 13.1)	0.63
<i>Ephestia cautella</i>					
PPO at 100 mm Hg with Dried Fig	240	19.8±3.77	21.21 (18.84– 24.66)	30.21 (26.67 – 35.60)	0.45
PPO at 100 mm Hg with Empty Space	140	4.93 ± 0.61	3.81 (3.37 – 4.21)	13.31 (9.33 – 15.31)	0.59

^a Number treated, excluding controls; ^b Slope ± Standard error; ^c Numbers in brackets give the 95% confidence range; ^d Heterogeneity factor

Although sorption of PPO by dried figs was relatively high, the fumigation still enables a sufficient build up of gas concentrations to achieve insect mortality. Based on its high and rapid toxicity to insects, and its rapid desorption from dried figs, the combination of PPO with low pressure can become a potential fumigant for replacement of MB for quarantine purposes where rapid disinfestation of dried figs is essential. However, further research is needed to obtain data on its penetration through the mass of commodities, its phytotoxicity and its impact on commodity quality.

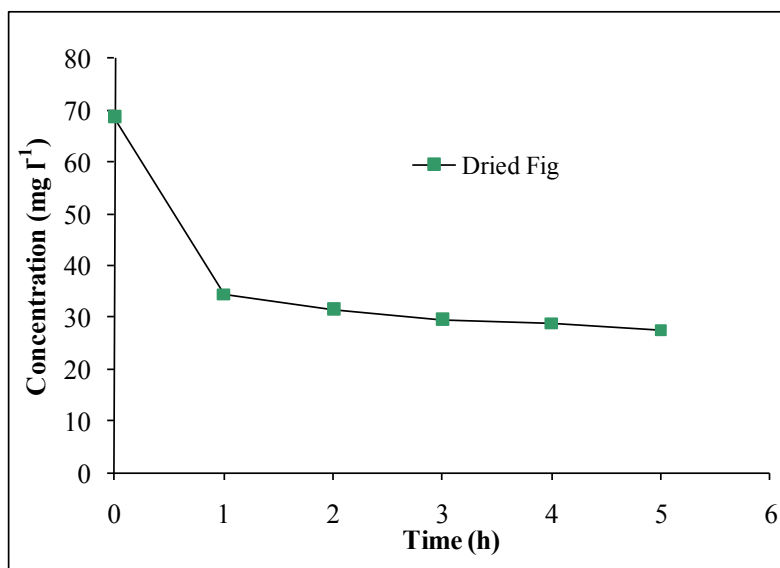


Fig. 1- Concentrations of PPO (mg l^{-1}) in fumigation chamber of 3 l during five hours of exposure after the application of PPO dose of 68.7 mg l^{-1} to 1.5 kg of dried fig at 26°C and $60\pm 5\%$ relative humidity.

Table 3. PPO residues (ppm) on dried figs at 0-1 day and 3 days after termination of aeration when exposed to 4-h fumigation at 26°C and atmospheric pressure with a dose of 112 mg l^{-1} PPO

Commodity	Average PPO Residue (ppm) in sample during aeration	
	0-1 day	3 days
Dried fig	85	22

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