Outgassing of Ethylene Dibromide from Fumigated Oranges

Stephen M. Rappaport,* Wilfred Cameron, and Joseph McAllister

Measurements were made of 1,2-dibromoethane (EDB) vapor released from oranges that had been fumigated on both a laboratory scale (0.25 carton) and a large scale (400 cartons). The decay of the outgassing rate over time was approximately first order. Outgassing was significantly slowed by reducing either the temperature or the air ventilation rate. Absorption of EDB by the cardboard packing material reduced the amount absorbed by the oranges but did not otherwise affect outgassing behavior. Air concentrations of EDB in ventilated containers dropped from several ppm immediately after fumigation to a few ppb after 5–10 days; levels remained between 2 and 3 ppm for 15–20 days during unventilated, refrigerated storage. Results suggest that workers transporting and distributing fumigated citrus may routinely be exposed to airborne EDB at greater than the allowable limit of 130 ppb.

Ethylene dibromide (1,2-dibromoethane, EDB) is a commercially important fumigant that is widely used for the control of pests in a variety of commodities, particularly citrus fruit, cherries, and plumes (EPA, 1983). Demonstrations that EDB is a potent carcinogen in experimental animals (Olson et al., 1973; NCI, 1981) have motivated both the federal and California Occupational Safety and Health Administrations to reduce the allowable occupational exposure limit (in air) from the previous level of 20 ppm (as an 8-h average) to 130 ppb (OSHA, 1983; Cal-OSHA, 1982). An area of particular concern, because of the insidious nature of exposures, is inhalation of EDB outgassed from fumigated produce during transportation and distribution.

Although the outgassing behavior of EDB has apparently never been reported, it can be inferred from some published work that both the uptake of EDB during fumigation and the decay of residue levels following fumigation are governed by first-order kinetics related to diffusion (Sinclair et al., 1962; Burditt and Von Windeguth, 1976; King et al., 1980). This suggests that the outgassing rate should also reflect first-order kinetics described by the relationship

$$R_t = R_0 e^{-kt} \quad (1)$$

where R_t is the outgassing rate at time t, R_0 is the initial outgassing rate, and k is the outgassing rate constant. The purpose of this investigation was to determine whether outgassing of EDB from oranges was approximately first order and to determine the effects of several pertinent variables including ventilation rate, temperature, and the presence of packing material. Knowledge concerning these relationships would be of obvious value to the evaluation and control of airborne exposures as well as to the reduction of EDB residues in fruit.

EXPERIMENTAL SECTION

Apparatus. *Laboratory-Scale Chambers.* The apparatus used for measuring outgassing in the laboratory is illustrated in Figure 1. Chambers consisted of 16-L glass containers (Libbey Mason jars). Neoprene rubber gaskets were fitted to all inside and outside surfaces of the closure, while threads of the closure were wrapped with Teflon tape. Plastic (Tygon) tubing was attached to stainless steel tubes, which had been inserted through bulkhead fittings, to channel air into the bottom of the chamber and out of the top. Air inside the chamber was mixed with a small fan. An injection port containing a Teflon-faced rubber septum allowed liquid EDB to be deposited on a small amount of glass wool supported by a wire loop inside the chamber. Room air was drawn through the chamber at 0.16 L/min (0.6 air change/h), 0.80 L/min (3.0 air changes/h), or 2.6 L/min (10 air changes/h); the air flow rate was restricted by a critical orifice (a hypodermic needle) in the exhaust line. Air from the chamber was exhausted through 1 g of activated cocoanut charcoal (SKC, Inc., Fullerton, CA), which adsorbed the EDB vapor. A rotary-vane pump supplied the vaccuum.

Large-Scale Chambers. Fumigation and storage of oranges on a large scale were carried out in chambers of 12.2 m × 2.4 m × 2.4 m (72.4 m^3). The fumigation chamber was a converted "Sea-train" unit that had been modified in accordance with U.S. Department of Agriculture (USDA) criteria for fumigation (USDA, 1979). Pallets containing approximately 400 cartons of fumigated oranges were moved with a forklift to one of two adjacent storage containers. The first container, a standard refrigeration unit, maintained the temperature between 5 and 9 °C. It was unventilated except for minor leaks from doors and condensation-drainage ports. The other was a standard ambient-temperature container that was externally ventilated with an exhaust fan attached to the door. Makeup air was drawn from four 5-cm holes in the rear wall. The ventilation rate was either 4.2 m^3/min (3.5 air changes/h) or 12.4 m^3/min (10 air changes/h). The temperature inside the ambient-temperature container typically varied from evening lows of between 4 and 10 °C to daily highs of between 10 and 18 °C. The average temperature was approximately 10 °C. All chambers were fitted with sampling ports attached to polyethylene tubes to permit air from several interior points to be sampled.

Gas Chromatography. The instrument was a Perkin-Elmer Sigma 2-B gas chromatograph equipped with a ^{63}Ni electron-capture detector; the column was 1.8 m × 3.2 mm i.d. nickel tubing packed with 10% Carbowax 20M on 80/100 Chromosorb W-HP; the carrier gas was 5% CH_4 in Ar at flow rates of 30 and 60 mL/min through the column and the detector, respectively; temperatures for the column, injection port, and detector were 130, 200, and 300 °C, respectively; integration was performed on a Perkin-Elmer Model 1 digital integrator; the linear range was between 0.01 and 100 ng of EDB; the EDB retention time was 2.2 min.

Infrared Spectrophotometry. The instrument was a Miran 1A single-beam infrared spectrophotometer (Foxboro, Inc.); the analytical wavelength was 8.4 μm; the path length was 20.25 m; the time constant was 4 s; the working

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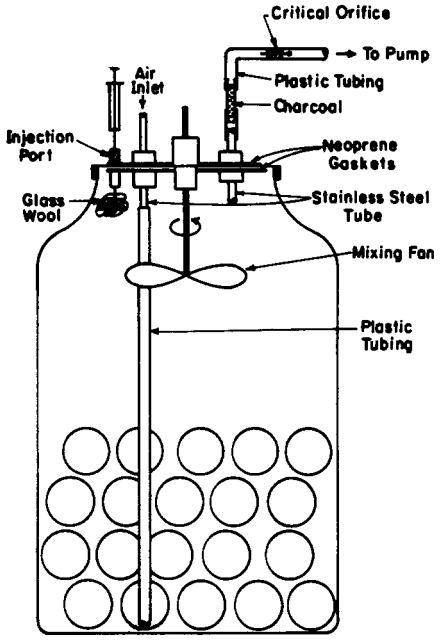

Figure 1. Apparatus used for the laboratory-scale fumigation of oranges.

range was EDB air concentrations between 0.5 and 1400 ppm.

Procedure. *Laboratory-Scale Experiments.* Fumigation was performed at 21 °C with oranges that had been maintained at that temperature for at least 24 h. Oranges used for each experiment were from the same batch, and equal numbers were contained in all chambers; the fruit volume was approximately 25% of the chamber volume. When packing material was present (unwaxed corrugated cardboard, 0.32 cm thick), the amount added to each chamber was approximately 25% of that of a standard carton. (This represented the proportion of a carton of oranges contained in each chamber.) Packing material was either cut into 5-cm squares and mixed with the fruit or cut into larger sections and shaped more or less around the fruit.

The dosage of EDB and the conditions of fumigation followed the schedule provided by the USDA (USDA, 1979) for controlling the Mediterranean fruit fly (*Ceratitus capitata*) in citrus fruit; i.e., dosage was 73 μL EDB/chamber = 160 mg/16 L = 10 mg/L for a 25% chamber load, temperature was 21 °C, duration of fumigation was 2 h with air mixing, and duration of aeration was 2 h without air mixing. At the conclusion of the 2-h fumigation phase, the mixing fan was turned off and air was drawn through the chamber at 8 L/min (30 air changes/h) for the 2-h aeration phase. Then the ventilation rate and, in one experiment, the temperature were reduced to the desired levels for the duration of the storage interval. The temperature of storage was maintained at either 21 or 10 °C. The charcoal adsorbent tube was replaced in the exhaust line periodically and analyzed for its EDB content. The two charcoal sections (800 mg in the first and 200 mg in the second) were placed in separate glass vials to which 3 mL of glass-distilled ethyl acetate (Burdick and Jackson) was added. Samples were allowed to stand at room temperature for 1 h with occasional swirling. Aliquots were then injected into the gas chromatograph. No EDB was observed in eluates of the second (200 mg) charcoal sections, indicating that there had been no breakthrough from the first sections.

Large-Scale Experiments. Fumigation was performed according to the USDA procedures and dosage schedule (USDA, 1979). The amounts of EDB used (nominally 350 mL for a 25% load of citrus at a temperature of between 15.6 and 20.6 °C) and the storage conditions are listed in Table I. The nominal rate of 350 mL of EDB/chamber corresponded to an air concentration of 770 g/72.4 m^3 = 10.6 mg/L. EDB was dripped onto an electric hot plate where it vaporized and was rapidly mixed with the air inside the chamber with the aid of large mixing fans. The fumigation phase was initiated when all of the EDB had been added; it continued for 2 h with air mixing. Measurements of the air concentration of EDB inside the chamber, made with the infrared spectrophotometer, indicated a level of approximately 1200–1300 ppm after 5 min followed by a gradual decrease over 30 min to about 300–400 ppm where it remained for the remainder of the fumigation phase.

Table I. Conditions of Large-Scale Fumigations

run	chamber temp, °C	fruit temp, °C	vol of EDB, mL	storage conditions
A	23	20	375	refrigerated, unventilated
B	13	14	350	ambient, ventilated (3.5)[a]
C	15	13	380	refrigerated, unventilated
D	14	20	350	ambient, ventilated (10.3)[a]

[a] Air changes per hour are in parentheses.

When the fumigation phase had ended, the mixing fans were turned off and the chamber was aerated for 2 h. Air was drawn through a small vent (0.3 m × 1 m) at 170 m^3/min (138 air changes/h) and exhausted through a stack approximately 12 m above the ground level. Infrared measurements, made during aeration, showed a decline of the EDB concentration to about 20–50 ppm after 15 min and to about 1–3 ppm after 2 h. Following the aeration phase, the chamber door (2.4 m × 2.4 m) was opened and the pallets of fruit were transferred with a forklift to one of the storage containers over a period of 20–30 min. The pallets were arranged in a row in the center of the storage container with approximately 0.6 m of space above and on either side of the row.

Regular measurements were made of the EDB air concentrations inside the storage containers. The infrared spectrophotometer was used during run A; 5-L air samples were collected during runs B and C by drawing air, from a point close to the inlet of the exhaust fan in the front of the container, through 150 mg of activated cocoanut charcoal (SKC, Inc., Fullerton, CA). The adsorbents were analyzed as described in the previous section; no breakthrough of vapor was observed from the first charcoal section (100 mg) to the second (50 mg). [Recoveries of EDB, spiked from ethyl acetate solutions into 100 mg portions of charcoal from unused tubes, were 97.2% for 9.8 μg of EDB (n = 5), 97.3% for 0.98 μg of EDB (n = 5), and 94.7% for 0.098 μg of EDB (n = 4).] Measurements were made during run D by withdrawing 2 cm^3 of air, from each of several points in the chamber, into a gas-tight syringe. (Sampling lines were first purged with several liters of air to ensure that the sample represented the true concentration). Each gas sample was immediately injected through a Teflon-lined rubber septum directly into a glass vial containing 3 mL of ethyl acetate. Aliquots of the solutions were analyzed by gas chromatography as described previously.

Safety Procedures. All safety procedures and practices required by the State of California for fumigation with and the safe handling of EDB were followed (Cal-OSHA, 1982). A self-contained breathing apparatus was used in the pressure-demand mode during fumigation and unloading procedures. Full-face respirators equipped with activated

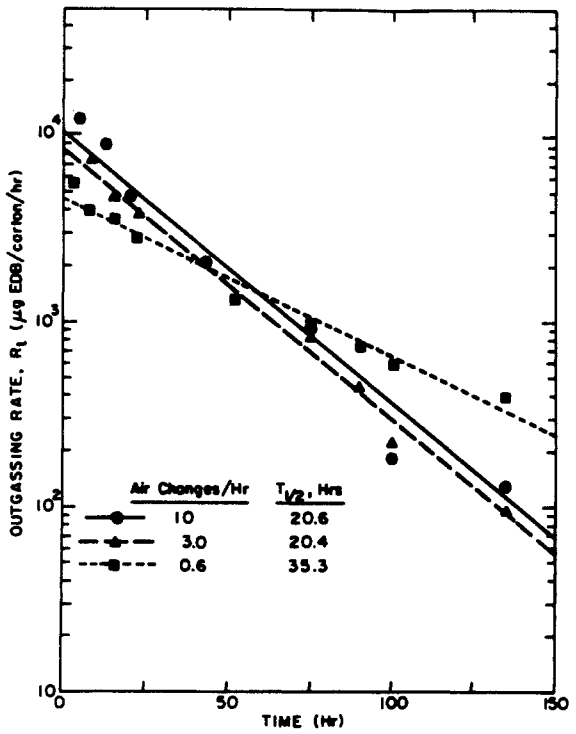

Figure 2. EDB outgassing rate, R_t, vs. time at various air ventilation rates ($T_{1/2}$ is the outgassing half-time).

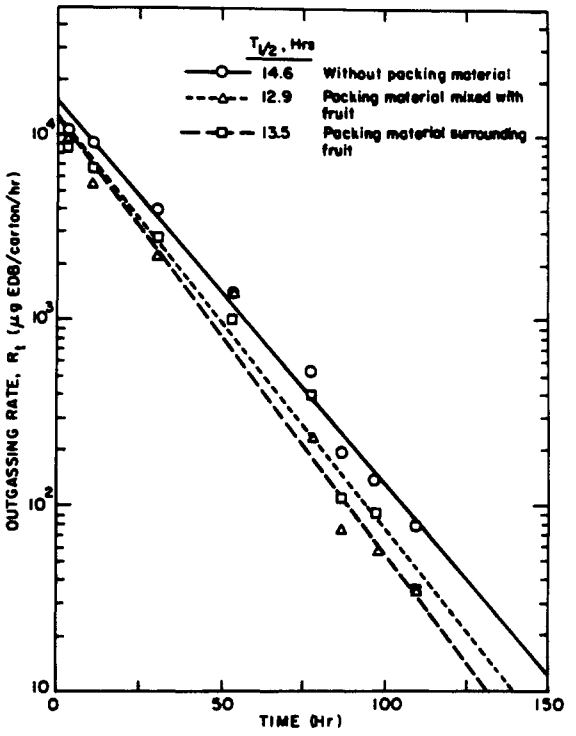

Figure 3. EDB outgassing rate, R_t, vs. time with and without packing material. The air ventilation rate was 3.0 air changes/h. ($T_{1/2}$ is the outgassing half-time).

carbon cannisters were used during those operations in which transient exposures to low concentrations of EDB were anticipated.

RESULTS AND DISCUSSION

If the relationship given in eq 1 approximates outgassing behavior of EDB, then a plot if ln R_t vs. t should be linear with slope $-k$ and intercept ln R_0. Data from the various experiments are presented as semilogarithmic plots of R_t vs. t where t is the geometric midpoint (in hours) of the elapsed storage interval [i.e., $t = (t_1 t_2)^{1/2}$, where t_1 and t_2 are the beginning and ending times of the interval respectively]. The outgassing rate, R_t, is reported as the amount of EDB released per carton of oranges per hour so that the results of both the laboratory and the large-scale experiments can be compared directly. The slopes of the curves are given in terms of the outgassing half-time, $T_{1/2}$, which is the time in hours required for R_t to decrease by half; $T_{1/2} = 0.693/k$. Values of $T_{1/2}$, R_0, and the linear correlation coefficient, r, were calculated from least-squares regressions of ln R_t vs. t.

Laboratory Experiments. Figure 2 shows the results of an experiment in which fumigated oranges were ventilated at 0.6, 3.0, and 10 air changes/h. Each value of r was greater than 0.98, indicating a strong linear correlation between ln R_t and t. The marked decrease in the outgassing half-time of the oranges ventilated at 0.6 air change/h ($T_{1/2}$ = 35.3 h) relative to those of the other groups ($T_{1/2}$ = 20.4–20.6 h) suggests that some ventilation is required to effectively remove vapor from the surface of the fruit and thereby prevent the reabsorption of EDB. However, once a minimal rate of effective removal has been achieved—this occurred in our system somewhere between 0.6 and 3.0 air changes/h—then additional increases in the air flow do not proportionately increase k; this is indicated by the similarity of behavior of the oranges ventilated at 3.0 and 10 air changes/h.

The effect of packing material can be inferred from Figure 3, which compares two experimental groups with a control group (without packing material). As in the previous experiment, all three values of r were large (greater than 0.99), indicating strong linear correlation of ln R_t and t. The relative position of the curve corresponding to the control group above those of the two experimental groups indicates that significant amounts of EDB were absorbed by the packing material during fumigation and rapidly release during aeration. Indeed, about 37% of the total EDB charge was released from the experimental groups during aeration compared with 20% from the control. Similar behavior had previously been reported by King et al. (1979) from investigations of EDB residues in packing materials and grapefruit. Thus, oranges fumigated without packing material would be expected to absorb greater amounts of EDB during fumigation than those fumigated in packing cartons. The similarities in the behavior of the two experimental groups (lower curves in Figure 3) indicate that the disposition of the packing material (either mixed with or shaped around the fruit) was not important.

It should also be noted that the half-time of the control group in this case ($T_{1/2}$ = 14.6 h) was smaller than the comparable value obtained during the first experiment at the same ventilation rate of 3.0 air changes/h ($T_{1/2}$ = 20.4 h, Figure 2). This difference in the outgassing characteristics of identically treated oranges of the same type but from different batches suggests that intracommodity variability can affect outgassing behavior.

Figure 4 shows the effect of reduced storage temperature. The outgassing half-time which had been 14.6 h at 21 °C (the oranges were from the same batch as those in the second experiment, Figure 3), increased to 46.2 h during storage at 10 °C. This suggests that refrigerated transport of fumigated produce will substantially retard the outgassing of EDB at a given level of ventilation.

Large-Scale Experiments. Results of the large-scale experiments provide an interesting complement to the laboratory-scale trials described above. The outgassing behavior of 400-carton loads of oranges stored at ambient temperature (4–18 °C) with ventilation is shown in Figures

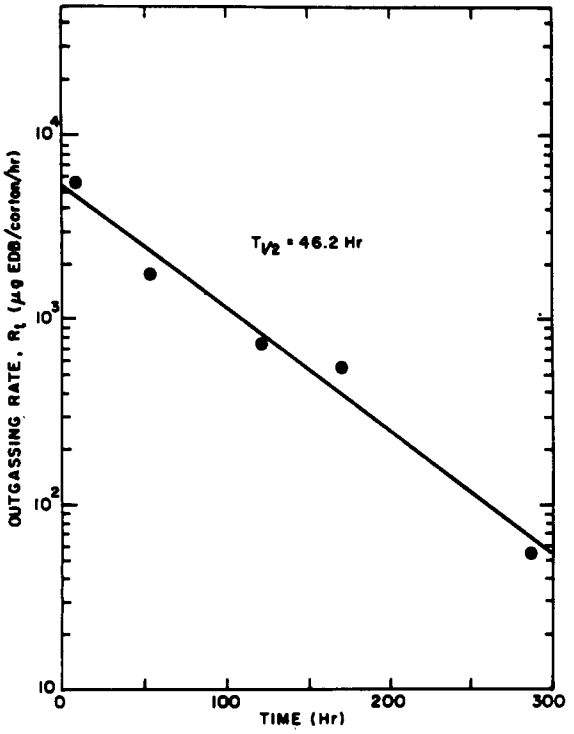

Figure 4. EDB outgassing rate, R_t, vs. time at 10 °C. The air ventilation rate was 3.0 air changes/h. ($T_{1/2}$ is the outgassing half-time).

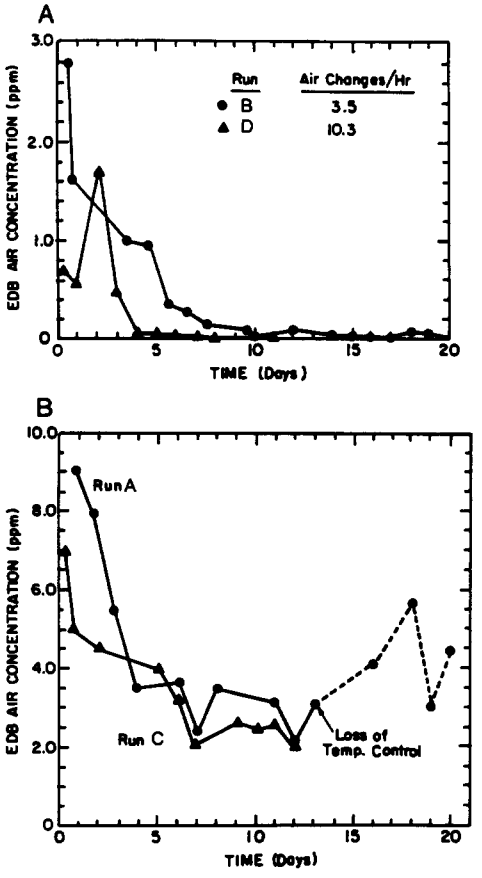

Figure 5. Air concentration of EDB vs. time for 400 cartons of fumigated oranges: (A) stored in a ventilated container at ambient temperature (4–18 °C); (B) stored in a refrigerated, unventilated container at 5–9 °C.

5A and 6. These data also showed linear correlation of ln R_t and t (Figure 6) with r values of 0.97 and 0.89 for runs B and D, respectively. Some of the fluctuations in these data undoubtedly reflect changes in the ambient temperature that occurred from day to day. This was particularly the case during run D, where the standard deviation of daily high temperatures was 4.5 °C (mean = 12.8 °C) compared to 1.5 °C (mean = 12.2 °C) during run B. Values of R_0, which reflect outgassing rates immediately after aeration, were 12 and 14 mg of EDB carton^{-1} h^{-1} for runs B and D, respectively; these are very close to the mean of the six laboratory runs, which was 11 mg carton^{-1} h^{-1}. The half-times for runs B and D, 51.4 and 31.6 h, respectively, bracket the value of 46.2 h observed in the laboratory at 10 °C.

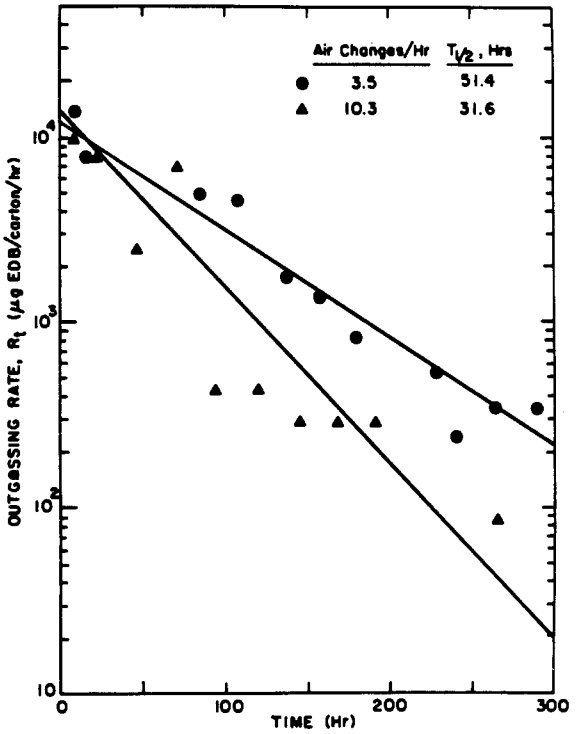

Figure 6. EDB outgassing rate, R_t, vs. time for 400 cartons of oranges stored in a ventilated container at ambient temperature (4–18 °C). ($T_{1/2}$ is the outgassing half-time).

Collectively, these comparisons of laboratory-scale and large-scale data indicate that simple and relatively inexpensive experiments performed in the laboratory can provide reasonable predictions of the outgassing behavior of produce fumigated commercially.

The air concentrations of EDB inside the refrigerated, unventilated, storage container (Figure 5B) stabilized after approximately 1 week at 2–3 ppm. Apparently the natural sinks for sorption of EDB in the container (such as the walls and other surfaces) became saturated during this period and the net flux of vapor was negligible thereafter. Figure 5B also shows that with the loss of temperature control (resulting from a breakdown in the refrigeration unit on day 13 of run A) and the subsequent warming of the fruit, the levels of EDB in the air increased to 4–6 ppm. This indicates that EDB is stable in fumigated oranges confined within a closed storage container at 4–10 °C, conditions that predominate in the commercial transport of fumigated fruit.

The results of these investigations of EDB outgassed from fumigated oranges have implications to the regulation and control of airborne exposures. First, it should be clear that air concentrations of EDB in facilities that contain large quantities of fumigated citrus can easily exceed the federal and California limit of 130 ppb. Whether average 8-h exposures of personnel in these facilities exceed this level depends largely upon the amount of ventilation that is present and upon the nature of the work. However, it

is not difficult to envision situations in which daily exposures could be much greater than 130 ppb. Populations of workers that appear to be a greatest risk from prolonged exposure to EDB during outgassing include truck drivers and warehousemen. It is recommended that these exposures be investigated so that the extent of the problem can be understood and effective controls instituted.

If airborne exposures, and indeed residues of EDB in fumigated fruit, are to be minimized, it is important that both temperature and ventilation be considered during transport and storage. Since reduced temperature retards outgassing, the amount of EDB remaining in refrigerated fruit would be relatively great; outgassing could be significant upon warming of the fruit, even if many days have elapsed since fumigation. Essentially the same behavior would be expected for produce transported at ambient temperature without ventilation. It should be obvious that the transient ventilation of produce (transported without ventilation) immediately prior to unloading would not significantly alter either the magnitude or the duration of subsequent outgassing.

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Heterocyclic Analogues of Substituted [1,1′-Biphenyl]-3-methylpyrethroid Insecticides

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The effect of substitution on a series of 3-heterocyclic benzyl pyrethroid esters was investigated. Since 2-methyl-[1,1′-biphenyl]-3-methanol had been shown in earlier studies to produced the most active esters in the biphenyl series, the equivalent 2-methyl-3-heterocyclic esters were prepared first. The most active of these, the 1-pyrrole analogue, was then studied further for substituent effects. The alcohol that produced the most active esters in this series, 2-methyl-3-(1*H*-pyrrol-1-yl)benzenemethanol, was then esterified with a series of common pyrethroid acids. The synthesis of all the intermediate alcohols is presented as well as the activity of the final esters against *Spodoptera eridania* (SAW), *Epilachna varivestis* (MBB), *Oncopeltus fasciatus* (MWB), *Heliothis virescens* (TBW), *Trichopulsia ni* (CL), *Acyrthosiphon pisum* (PA), and *Tetranychus urticae* (TSM). The 2-methyl-3-heterocyclic benzyl esters are, in general, more active than their parent esters and like the analogous biphenyl esters have broader spectra of activity than permethrin.

It has been demonstrated that highly active pyrethroid insecticides can be prepared from benzyl alcohols with phenyl substituents in the meta position even if no bridging atom separates the two aromatic rings (Plummer and Pincus, 1981). It has also been demonstrated that the meta phenyl group can be replaced by a number of heterocyclic rings with a change in activity proportional to the lipophilicity of the heterocyclic ring (Plummer, 1983). Recently we reported (Plummer et al., 1983) the effect of substitution on the activity of pyrethroid esters derived from [1,1′-biphenyl]-3-methanol. It was found that substitution in the 2- and 2′-positions was most efficacious and further that 2-fluoro- and 2-methyl[1,1′-biphenyl]-3-methanol not only produced esters of increased activity against insects that are classical targets of synthetic pyrethroids but also provided broader spectrum insecticides and acaricides than other synthetic analogues of the pyrethrins. We now report the effect of substitution on a number of "B" ring heterocyclic analogues of the substituted [1,1′-biphenyl]-3-methyl pyrethroid esters.

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MATERIALS AND METHODS

Analysis of Products. Nuclear magnetic resonance (NMR) spectra were determined on a Varian T-60 spectrometer. Analyses by gas–liquid chromatography (GLC) were performed on Model 5830A Hewlett-Packard in-

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