ETHYL FORMATE AS A FUMIGANT OF SULTANAS: SORPTION AND EFFICACY AGAINST SIX PEST SPECIES

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ABSTRACT

Ethyl formate is used in the Australian dried fruit industry as a fumigant against insect infestation. The rate of sorption of ethyl formate on sultanas was found to be independent of concentration but greatly increased with increased filling ratio and moisture content. There was a slight temperature effect. Sorption, initially rapid with 13% of gas remaining in the headspace at 12 h in containers 95% full, was followed by a more gradual reaction phase. Rate constants per full container for the reaction ranged from 0.077 h⁻¹ to 0.038 h⁻¹. At typical commercial dosage rates, concentration × time (Ct) products of 1,493 g h m⁻³ at 8 h and 3,876 g h m⁻³ at 24 h were obtained at 25°C and 60% r.h. in sealed containers. These were shown to be greater than required to control dried fruit pests.

Fumigations at 25°C of mixed-aged cultures of six pests showed that 8-h exposures were more effective than 24-h exposures with the same Ct product. In 24-h exposures, there was 100% mortality of *Oryzaephilus surinamensis*, *O. mercator*, *Plodia interpunctella* and *Carpophilus hemipterus* at 765 g h m⁻³ and of *Tribolium confusum* at 1,158 g h m⁻³; there was 94% mortality of *T. castaneum* at 1,158 g h m⁻³. All of these pests were controlled in 8-h fumigations at 541 g h m⁻³ but not at 496 g h m⁻³. Ethyl formate, where not limited by sorption behaviour, appears to have excellent potential as a replacement for methyl bromide in the treatment of durable commodities.

INTRODUCTION

Australia is the world's fourth largest producer of dried fruit, with a forecast production in 1995–96 of 59 kt of sultanas and raisins (ABARE, 1994, 1995). After harvesting and drying, fruit may be stored for up to 9 months in open crates before being processed. The fruit, generally untreated with fumigants during this period, can be subjected to heavy infestation pressure. Ethyl formate (EF) is applied to the processed fruit as it is packaged into export boxes in order to control any insects surviving the processing treatment.

EF is a versatile organic compound that can be used for a variety of purposes. It has had a long world-wide history as a fumigant used since 1927 on packaged dried fruit

(Simmons and Fisher, 1945) as well as, formerly, on wheat (Neifert *et al.*, 1925; Wilson and Mills, 1946) and other commodities (Pruthi and Singh, 1945; CFTRI, 1979; Muthu *et al.*, 1984). It has been used as a fumigant to disinfest clothing (Busvine and Vasuvat, 1966; David, 1943) and to control pests on fresh fruit, vegetables and flowers (Aharoni and Stewart, 1980; Stewart and Aharoni, 1983; Stewart and Mon, 1984; Wang, 1982) without affecting the quality or flavour of the commodity. It has also been used as a successful fungicide in cereals (Raghunathan *et al.*, 1974; Deo and Gupta, 1986) without affecting their viability or germination. Other uses are in the manufacture of artificial rum, as a flavour for lemonade and essences, as an organic solvent and as a fungicide (Merck Index, 1989).

The insect pests infesting dried fruit are generally the same as those found in cereal commodities. A recent 2-year survey of packing sheds in the Sunraysia district, Victoria (Tarr and Hilton, unpublished data) found that the major pests of dried fruit in Australia were the saw-toothed grain beetle (*Oryzaephilus surinamensis* (L.)), the Indian meal moth (*Plodia interpunctella* (Hübner)) and the raisin moth and related species (*Ephestia* spp.). Less important pests were the merchant grain beetle (*O. mercator* (Fauvel)), flour beetles (*Tribolium* spp.), the dried fruit beetle (*Carpophilus hemipterus* (L.)) and the hairy fungus beetle (*Typhaea stercorea* (L.)). While *O. surinamensis*, *P. interpunctella* and *Ephestia* spp. were the most economically important pests overall, individual outbreaks of all species occurred, depending on local conditions, in different sheds at different times. These findings duplicated those of a survey of the same sheds completed in 1928 (Myers, 1928).

Relatively few modern studies specifically related to the disinfestation of dried fruit have been made on the effect of EF. Vincent and Lindgren (1972) tested examples of four dried fruit pests and found *C. hemipterus* to be the most tolerant to EF, followed by *O. surinamensis*, *P. interpunctella* and *Cadra* (= *Ephestia*) *figulilella* (Gregson). The pupa was the most tolerant stage of all species and the adult the least. Muthu *et al.* (1984) also found that the pupa of *T. castaneum* (Herbst) was the most tolerant stage to EF. All these studies were carried out on insects alone without dried fruit's being present.

This study was undertaken to confirm the effectiveness of the current treatment regime and provide a basis for improvements. It involves both a study of the sorption kinetics of EF on dried fruit under a variety of conditions and toxicological studies on six of the more common dried fruit pests.

MATERIALS AND METHODS

Sorption studies

Samples of unprocessed 'five crown' grade and commercially processed (i.e. washed, freed of sticks and debris and oiled with DURKEX 500®) 'three crown' grade Thompson seedless sultanas were obtained from the Sunraysia District, Victoria. The three series of experiments detailed below investigated the effects of processing, dosage rate, filling

ratio, temperature and moisture content (m.c.) on the sorption of EF. Each set of conditions was measured at least twice.

In the first experiment, unprocessed and processed fruit at 25°C, 60% r.h. and 0.25, 0.50 and 0.95 filling ratio was dosed with 112, 336 and 1,120 g m⁻³ EF. In the second experiment, unprocessed and processed fruit at 15, 25 and 35°C, 60% r.h. and 0.50 filling ratio was dosed with 1,120 g m⁻³ EF. In the last experiment, unprocessed and processed fruit at 25°C, 50, 60 and 70% r.h. and 0.50 filling ratio was dosed with 1,120 g m⁻³ EF.

The amount of water to be added in order to obtain a given humidity was calculated from the sorption isotherm of Pixton and Warburton (1973) together with the observed initial m.c. The fruit was allowed to equilibrate for at least 1 week before being fumigated. Relative humidities were determined by a dew point meter (MBW Model 3-D), and m.c.'s were determined by using a conductance moisture meter ('Type A', DFA of California) with standard minced samples.

Samples were dosed in 120-ml glass vials fitted with Mininert Teflon valves. EF was added by injecting measured quantities of liquid into the headspace using a gastight syringe. Samples were dosed at the stated concentration of EF calculated after making allowance for the exclusion volume of sultanas. The concentration ranges used in this study were based on the current rate used in the Australian dried fruit industry where 6 ml of EF is applied to a 15-kg box of fruit. This gives a maximum concentration of 1,120 g m⁻³ per box. Vials were filled to either 0.25, 0.50 or 0.95 of full capacity, assuming that the fruit weighed 81.00 g when the vial was 100% full. Exclusion volumes were calculated using the true density of sultanas, taken to be 1.43 kg L⁻¹.

EF concentrations were measured using a gas chromatograph (Shimadzu GC-4CM, 6-AM series) fitted with a flame ionisation detector and a 2 m \times 0.4 mm glass column packed with 5% AT-1000 on Chromasorb HP. Sample peak areas were compared to peaks of a known standard EF concentration of 50 g m⁻³ to obtain actual concentrations. The vials were shaken prior to sampling, and a sample of the headspace gas was taken using a gastight syringe.

Sorption model

The uptake of EF on sultanas was assumed to occur in two phases: an initial, rapid, reversible phase in which the fumigant was physically sorbed onto the fruitand then a second, slower, irreversible phase in which the fumigant was assumed to react with constituents in the fruit. The rate of reaction of the EF with the fruit is the slope of the linear part of the sorption curve, cast in semilogarithmic form with time after the initial rapid physical sorption phase. This rapid physical sorption phase was typically complete after about 8-h exposure. Extrapolation of the subsequent reaction phase curve back to zero time gave a concentration value (c_i) less than that originally applied (c_0) . The difference between the two values, converted into mass units, was taken to be that quantity physically sorbed and thus available for desorption or further reaction.

The curves at greater than 8 h were described mathematically by:

$$c/c_{i} = e^{-kt} \tag{1}$$

or in logarithmic form by:

$$\ln c = \ln c_i - kt \tag{2}$$

where c is the concentration at time t, c_i is the extrapolated concentration $(t = t_0 = 0)$ and k is the apparent first-order rate constant for the system.

The observed value of k under a particular filling ratio, f, was standardised using the filling ratio to give a value, k_f , for the rate constant in a full container, where:

$$k_{\rm f} = k/f \tag{3}$$

A constant, K, the partition constant, was derived in which the calculated fraction of gas initially sorbed $(c_i - c_0)$ at t = 0 was corrected for concentration, mass applied and filling ratio. This gives a dimensionless measure of the tendency of a particular sample of fruit to take up EF by physical sorption. The partition constant was defined as:

$$K = \frac{(c_{\rm i} - c_{\rm 0}) \cdot V_{\rm g}}{c_{\rm i} \cdot V_{\rm f}} \tag{4}$$

where $V_{\rm g}$ is the gas volume and $V_{\rm f}$ is the volume occupied by the fruit. Regression analysis on the data was carried out using Genstat 5 and GLIM statistical packages and general data analyses using Excel 5.

Insect mortality studies

Cultures containing all life stages of six dried fruit pests, *O. surinamensis*, *O. mercator*, *C. hemipterus*, *P. interpunctella*, *T. castaneum* and *T. confusum* (Jacquelin du Val) were dosed in a fumigation chamber at 25°C with EF for 8 and 24 h. Cultures were produced by adding 50 adults (beetle species) or 25 eggs (moth species) to 200 g unprocessed sultanas at 27°C and 60% r.h. weekly for 5 weeks (7 weeks for *Tribolium* spp.). Before fumigation, cultures were divided in half to give control and test samples. These were placed in muslin bags and the controls returned to the incubation room. All test cultures were exposed simultaneously, with the total chamber load approximately 1.2 kg of cultures in 0.868 m⁻³. Test samples were placed in the fumigation chamber, the chamber sealed and the relative humidity measured using a dew point meter (MBW Model 3-D). The humidity was adjusted to 60% r.h. by addition of water if required. EF was injected into the chamber to give a concentration of 37, 73, 95 and 143 g m⁻³ for 8-h exposures and 14, 27, 35 and 52 g m⁻³ for 24-h exposures. Concentrations were measured hourly during the first 8 h and at 24 h (for 24-h fumigations), and the concentration × time (Ct) products for each fumigation calculated. Each fumigation series was replicated twice.

At the end of the exposure period, the chamber was aired for 1 h and the samples moved to a fumehood to be further aired during assessment. Test and control samples were removed from the muslin bags and the insects recorded by life stage as alive or dead

before being returned to the incubation room in glass culture jars. Samples were reassessed for mortality weekly for 3 weeks.

RESULTS

Sorption studies

Sorption of EF on dried vine fruit follows a trend similar to that seen with other fumigants on wheat and other commodities (Banks, 1986, 1990); there is an initial rapid uptake over the first 8 h followed by a more gradual subsequent sorption (Figs. 1 a, b). The curves of sorption at various concentrations at the same filling ratio for log plot of concentration over initial concentration (c/c_0) fall on the same line. This indicates that at a particular filling ratio, temperature and humidity, sorption is independent of concentration (Figs. 1 c, d). Although EF is initially taken up faster by processed fruit, at longer exposures unprocessed fruit sorbs more fumigant because the rate of reaction with unprocessed fruit is higher than that with processed fruit.

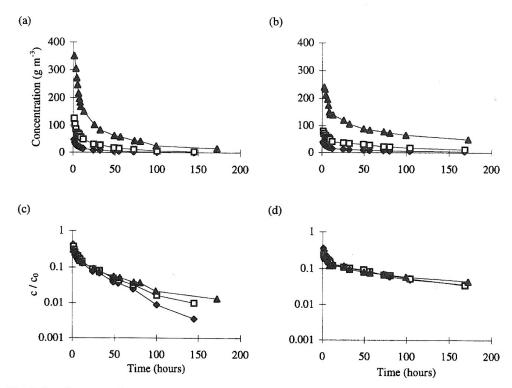


Fig. 1. Sorption curves for ethyl formate on unprocessed (a, c) and processed (b, d) sultanas at a fixed r.h. (60%), temperature (25°C) and filling ratio (0.95) illustrating the influence of concentration, with (a) and (b) showing uncorrected data as a function with time and (c) and (d) corrected on the basis of initial concentration as a logarithmic function with time. $\Rightarrow 112 \text{ g m}^{-3}$, $\Box = 336 \text{ g m}^{-3}$ and $\triangle = 1120 \text{ g m}^{-3}$ ethyl formate.

Fruit dosed at the same concentration, temperature and humidity but different filling ratios show very different rates of sorption (Figs. 2 a, b). EF is sorbed more rapidly at the higher filling ratios. The log plot of concentration over initial concentration curves against time do not fall on a single line, showing dependence on filling ratio (Figs. 2 c, d).

Adjusting the rate constant according to Equation (3) should remove the effect of filling ratio. An average rate of sorption at specified conditions can then be found. Table 1 shows average k_f values for unprocessed and processed fruit at 25°C and 60% r.h. with the overall average for both fruit types. The sorption rate constant for unprocessed fruit is more than twice that for processed fruit, with k_f values of 0.0262 h⁻¹ and 0.0122 h⁻¹, respectively. A trend of decreasing value of k_f with increasing filling ratio at a given concentration is apparent.

The partition constant values (K), calculated using Equation 4, are shown in Table 2 for both fruit types at 25°C and 60% r.h. Samples showed little variation with change in concentration and filling ratio. The average partition constant value for processed fruit (7.78) was slightly greater than for unprocessed fruit (5.92), with a suggestion that at higher concentrations with low filling ratios the partition constant also was greater.

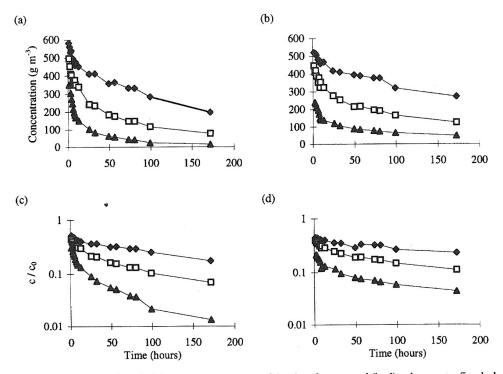


Fig. 2. Sorption curves for ethyl formate on unprocessed (a, c) and processed (b, d) sultanas at a fixed r.h. (60%), temperature (25°C) and concentration (1120 g m⁻³) illustrating the influence of filling ratio, with (a) and (b) showing uncorrected data as a function with time and (c) and (d) corrected on the basis of initial concentration as a logarithmic function with time. $\phi = 0.25$, $\Box = 0.50$ and $\triangle = 0.95$ filling ratio.

TABLE 1 Average rate constants for sorption per hour for full containers (k_f) for unprocessed (U) and processed (P) fruit at 25°C and 60% r.h., showing effect of filling ratio and concentration

EF dosage	_		Filling ratio	
$(g m^{-3})$	Fruit type	0.25	0.50	0.9
112	U	0.0383	0.0328	0.0274
336	U	0.0336	0.0309	0.0225
1120	U	0.0183	0.0183	0.0138
	Mean ±	standard deviation	$n = 0.0262 \pm 0.00$	836
112	P	0.0189	0.0155	0.0091
336	P	0.0106	0.0123	0.0097
1120	P	0.0140	0.0122	0.0077
	Mean ±	standard deviation	$n = 0.0122 \pm 0.00$	349

TABLE 2
Average partition constant values (K) for unprocessed (U) and processed (P) fruit at 25°C and 60% r.h., showing effect of filling ratio and concentration

EF dosage			Filling ratio	
$(g m^{-3})$	Fruit type	0.25	0.50	0.95
112	U	5.22	5.08	5.95
336	U	6.03	5.14	5.69
1120	U	9.34	7.29	6.99
	Me	an ± standard devia	tion = 5.92 ± 0.835	
112	P	6.38	5.84	7.26
336	P	13.07	7.97	6.70
1120	P	10.19	7.14	7.89
	Me	an ± standard devia	tion = 7.78 ± 2.260	

The effect of temperature and r.h. on sorption on sultanas at 0.50 filling ratio and $1,120 \text{ g m}^{-3}$ is shown graphically in Figs. 3 a, b and 4 a, b, respectively. Table 3 shows the rate constant for sorption in a full container (k_f) and the partition constant (K) for fruit at the different temperatures and humidities tested. Unprocessed fruit had a higher rate of reaction than processed fruit at all temperatures and humidities. The partition constant showed a slight decrease with increased temperature in both fruit types, indicating that higher temperatures increase the rate of reaction but slightly decrease the amount of fumigant sorbed. Relative humidity has a much stronger effect on sorption than temperature. At higher humidities, there was a slight increase in the rate of reaction but a dramatic increase in the amount of fumigant sorbed by the fruit which is indicated by the partition constant.

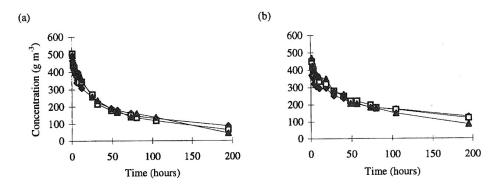


Fig. 3. Sorption curves for ethyl formate on unprocessed (a) and processed (b) sultanas at a fixed r.h. (60%), filling ratio (0.50) and concentration (1120 g m⁻³) illustrating the influence of temperature. Both graphs show uncorrected data as a function with time. $\blacklozenge = 15^{\circ}\text{C}$, $\Box = 25^{\circ}\text{C}$ and $\triangle = 35^{\circ}\text{C}$.

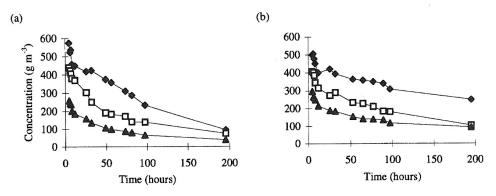


Fig. 4. Sorption curves for ethyl formate on unprocessed (a) and processed (b) sultanas at a fixed temperature (25°C), filling ratio (0.50) and concentration (1120 g m⁻³) illustrating the influence of humidity. Both graphs show uncorrected data as a function with time. $\blacklozenge = 50\%$, $\Box = 60\%$ and $\triangle = 70\%$ r.h.

TABLE 3
Average rate constants for sorption per h for full containers (k_f) and partition constants (K) for unprocessed and processed fruit at 1120 g m⁻³ EF and 0.50 filling ratio showing effect of temperature and r.h.

Temperature		Unpro	cessed	Proce	essed
(°C)	r. h. (%)	$k_{ m f}$	K	$k_{ m f}$	K
15	60	0.0141	8.20	0.0081	9.60
25	60	0.0183	7.29	0.0121	7.14
35	60	0.0224	6.05	0.0153	7.27
25	50	0.0100	4.28	0.0067	4.51
25	60	0.0183	7.29	0.0122	7.18
25	70	0.0179	15.66	0.0100	13.44

Insect mortality studies

Fumigation of six dried fruit pests showed that 8-h exposures with higher initial concentration were more effective at controlling all pest species than with 24-h exposures at the same Ct product (Tables 4 and 5). There was 100% mortality of all species at 541 g h m⁻³ in the 8-h exposures, corresponding to an initial concentration of 73 g m⁻³ (Table 4). The duplicate fumigation with a lower Ct product of 496 g h m⁻³ had a 99.8% mortality of both *O. surinamensis* and *O. mercator* and complete kill of *P. interpunctella* and *C. hemipterus*, indicating that this Ct product is only just achieving control. Eggs and pupae were the only stages surviving any 8 h treatment, with pupae more tolerant than eggs. *Tribolium* spp. showed no survival at any Ct products tested in 8-h exposures.

In 24-h treatments, as compared to 8-h exposures, a higher Ct product was required to control all species. There was complete mortality of all stages of *O. surinamensis*, *O. mercator*, *P. interpunctella* and *C. hemipterus* at 765 g h m⁻³, corresponding to an initial concentration of 27 g m⁻³ (Table 5). In contrast to their relative susceptibility in 8-h exposures, *Tribolium* spp. were the most tolerant species in 24-h exposures. Larvae and pupae of *T. castaneum* survived at the maximum Ct product tested (1,158 g h m⁻³). As with the 8-h exposures, eggs and pupae of *O. surinamensis*, *O. mercator*, *P. interpunctella* and *C. hemipterus* were the most tolerant life stages to the fumigant. Larvae and pupae were the most tolerant stages of *Tribolium* spp.

DISCUSSION

Understanding the sorption kinetics of a fumigant on a commodity is important, as the rate of sorption affects the insecticidal efficacy of the fumigant. Sorption onto dried fruit, independent of the initial concentration, was dependent on the filling ratio of the container. There was a greater uptake of EF at 0.25 filling ratio with increasing concentrations (close to point of saturation), probably due to condensation of the fumigant on the fruit. An increase of 10° C increased the rate of reaction by a factor of 1.5 but slightly decreased the amount of fumigant sorbed. Higher humidities have a stronger effect on sorption than does temperature. An increase of 20% in r.h. resulted in a slight increase in the rate of reaction and a fourfold increase in the amount of fumigant sorbed. The very high solubility of EF in water (118.0 g L^{-1}) may explain this trend.

Processed fruit had a reaction rate almost half that of unprocessed fruit over the range of conditions tested. Despite an initial high level of sorption, at long exposures processed fruit sorbed less fumigant than did unprocessed fruit. The dressing oil used to coat sultanas after processing may have caused the increase in the initial amount of fumigant sorbed. Results not reported here indicate that different varieties of unprocessed fruit, ranging in size from small currants (0.20-cm berry) to natural muscatels (1.07-cm berry), showed no significant differences in the rate of reaction or amount of sorption from those of the unprocessed sultanas studied here. The results thus appear to be a general indication of sorption and reactivity of dried vine fruit rather than being specific to the fruit tested.

TABLE 4 Initial concentration, Ct product, mortality (M) and stage surviving fumigation 1 of the six species fumigated with EF for 8 h

O. mercator P. interpunctella C. hemipterus M (%) Stage M (%) Stage 99.8 E 100 * 94.1 E 100 * 100 * 78.1 P - - - - - - - - - - - - 99.8 P 100 * 100 * 100 * 100 * - - 100 * 100 * - - - - - - - - - 100 * 100 * - - - 100 * 100 * - - - - - - - - - - - - - - - - - - - - -			, 1 - (, I	- 1)							
M (%) Stage M (%) Stage M (%) Stage M (%) Stage 91.1 E, P 99.8 E 100 * 94.1 E 99.8 P 100 * 78.1 P 99.8 P 99.8 P 100 * 100 100 * 100 * 100 * 100 * 100 * 100 * 100 * 100 * - - - - - - - - - 100 * 100 * 100 * - 100 * 100 * - - - - - - - - - - - - - 100 * 100 * - - - - - - - -	Concentra-	ŭ	O. surine	amensis		cator	P. interp	unctella	C. hemi	pterus	T. castaneum	пешт	T. confusum	nsnm
99.8 E 100 * 94.1 E 100	tion $(g \text{ m}^{-3})$	product $(g h m^{-3})$	M (%)	Stage	M (%)		M (%)		M (%)	Stage	M (%)	Stage	M (%) Stage	Stage
100 * 100 * 100 * 4 100	37	248	91.1	E, P	8.66		100		94.1	田		Ţ	ı	1
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	142	920	1	Ī	1	ī	1	1	I	I	100	*	100	K

 $^{1}E = egg$, L = larva, P = pupa, A = adult, * = no stage surviving.

Initial concentration, Ct product, mortality (M) and stage surviving furnigation 1 of the six species furnigated with EF for 24 h

Concentra-	Ct	O. surin	ıamensis	O. mercator	cator	P. interpunctella	unctella	C. hemipterus	pterus	T. castaneum	aneum	T. confusum	fusum
tion	product												
(g m ⁻³)	(g h m ⁻³)	M (%)	Stage	M (%)	Stage	M(%)	Stage	M (%)	Stage	M (%)	Stage	M(%)	Stage
14	321	45.3	all	59.3	all	93.3	L, P	87.5	A. P	I	1	1	
14	321	8.89	all	61.7	all	95.7	L.P	94.1	. Д	ı	ı	1	
27	572	1	Ţ	1	I	J	. 1	ı	. [46.9	II.	71.9	П О
27	583	1	ı	ı	I	I	1	1	ı	56.5	all le	77.1	H, I, I
27	592	7.76	E, P	99.1	Ь	100	*	100	*) 	į	: 1	
27	628	6.86	Ь	8.66	Ь	8.86	Щ	100	*	1	ı	ı	1 1
35	765	100	*	100	*	100	*	l	ı	I	ı	1	
35	783	100	*	100	*	100	*	ŀ	I	1	ı	ı	î
52	911	ı	1	ŀ	ī	1	I	I	ı	92.9	<u>, </u>	7 00	-
52	1158	1	1	ı	1	I	Ι	ſ	Ī	94.4	L, P	100	1 *

 $^{1}E = egg$, L = larva, P = pupa, A = adult, * = no stage surviving.

Short exposure periods with a higher initial concentration of EF were found to be the most effective way of controlling the six insect species tested. In 8-h fumigations, C. hemipterus was controlled at 73 g m⁻³ (Ct product of 496 g h m⁻³), which is consistent with the results of 95% mortality of the pupae at 72 g m⁻³ in 6-h fumigations (estimated Ct product of 432 g h m⁻³) reported by Vincent and Lindgren (1972). Also in agreement were the results with P. interpunctella. Our results showed no survival at any concentrations tested (lowest 37 g m⁻³), compared to the 95% mortality of pupae at 36 g m⁻³ observed by Vincent and Lindgren (1972). The pupa was the most tolerant stage for both O. surinamensis and O. mercator, with a 99.8% mortality at 73 g m⁻³ (Ct product of 496 g h m⁻³), but 100% mortality in the duplicate fumigation (Ct product of 541 g h m⁻³) indicated that this is the borderline for complete control. Vincent and Lindgren (1972) found 95% mortality of O. surinamensis pupae at 48 g m-3 in 6-h exposures (estimated Ct product of 288 g h m⁻³). No Tribolium spp. survived at any concentration (lowest 73 g m⁻³) in 8-h exposures. Shepard et al. (1937) found 50% mortality of T. confusum at 24.5 g m⁻³ in 5-h fumigations (estimated Ct product of 122.5 g h m⁻³). In the present work, a Ct product of 541 g h m⁻³ gave complete control in 8-h fumigations of all species tested.

Complete control of O. surinamensis, O. mercator, P. interpunctella and C. hemipterus was achieved with an initial concentration of 35 g m⁻³ (Ct product of 765 g h m⁻³) in 24-h exposures. Pupae of the beetle species and eggs of P. interpunctella were the most tolerant. No comparable results for 24-h exposures were found in the literature. Larvae and pupae of Tribolium spp. were the most resistant in 24-h fumigations, with 100% mortality of T. confusum and 94.4% mortality of T. castaneum at the highest concentration tested (52 g m⁻³, Ct product of 1,158 g h m⁻³). Neifert et al. (1925) achieved 80% mortality of T. confusum adults in one experiment at 36.4 g m⁻³ for 24 h (estimated Ct product of 874 g h m⁻³), which is consistent with our findings. Muthu et al. (1984) found pupae of T. castaneum to be the most resistant stage, requiring a concentration of $27.9~g~m^{-3}$ (estimated Ct product of 669 g h $m^{-3}\!)$ for 24 h to obtain a 95% mortality, a slightly lower concentration than in our results. In the present work, a Ct product of 765 g h m⁻³ gave complete control of the more common dried fruit pests tested in 24-h fumigations and 1,158 g h m⁻³ were needed to control Tribolium spp. In a gastight fumigation, the commercial dose of 6 ml per 15-kg box of fruit was found to give a Ct product of 1,493 g h m⁻³ at 8 h and a Ct product of 3,876 g h m⁻³ at 24 h. This is well above the Ct product expected to kill all dried fruit pests.

As demonstrated in this study, EF appears to be an effective fumigant of dried fruit (the use to which it is currently put in the Australian industry). It is effective against dried fruit pests, leaves no 'off' odours or tastes, is easy to handle and has a low mammalian toxicity. It is grouped under 'formates' as a food additive for human consumption (FDA, 1979) and is considered to be only mildly toxic by skin contact and inhalation (Sax and Lewis, 1989). Though receiving little attention recently in stored-product literature, EF appears to be well-suited as a fumigant for a variety of dried foodstuffs unless it is too highly sorbed to give insecticidal gas concentrations. Further sorption studies will need to be undertaken to address this point. With the current need for replacements for methyl bromide, EF

appears worthy of reassessment. It seems to have good potential as a 'rediscovered', rapidly-acting fumigant for some durable commodities.

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