be encountered not only as seen in the crystal but also in "free" (gaseous) and in vivo situations.

All of the evidence presented points to the structure of B as being the better one to use for theoretical arguments when discussing isolated molecules.

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Registry No. Chlorpyrifos methyl, 5598-13-0.

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Methyl Bromide Residues in Fumigated Mangos

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Mangos (*Mangifera indica* Linn) were fumigated in temperature-controlled chambers with methyl bromide (MB) at 16, 48, 56, and 64 g/m^3. Gas chromatographic analysis for MB residues in the peel and flesh showed that residue concentrations were above 20 mg/kg at 0.17 h after fumigation at the highest doses. One hour after fumigation, residue levels were below 15 mg/kg. Analyses of the peel and flesh at 0.17, 1, 2, 5, 24, and 48 h after fumigation indicated that the MB residue levels followed an exponential regression, decreasing rapidly during the first hour followed by gradual decline.

The mango (*Mangifera indica* Linn, one of several subtropical fruits that is a host of the Mexican fruit fly, *Anaestrepha ludens* (Loew), requires an acceptable fumigation program prior to being imported into the United States (USDA—APHIS, 1976). The ban by the Environmental Protection Agency (EPA) on the use of the fumigant ethylene dibromide (EDB) for controlling this citrus pest (*Fed. Regist.* 1984) has necessitated finding a suitable substitute to provide quarantine security. Studies in 1979 suggested that methyl bromide (MB) could be a possible substitute for EDB (Benschoter, 1979). Reports by Benschoter et al. (1984) and Williamson et al. (1986) concluded that MB could be used successfully to fumigate grapefruit against the pests *A. suspensa* Loew and *A. ludens*.

In 1981, a rapid sensitive headspace analysis method for determining residues of MB by gas chromatography in fumigated grapefruit was developed (King et al., 1981), but no information was found in King et al. (1981) or in a full literature search on residues of MB in mangos.

This study was initiated (1) to assess the validity of the citrus method for residue analysis on and in the mango and (2) to determine residues of MB in the mango following fumigation with different doses of MB.

MATERIALS AND METHODS

Fruit. Mango variables used in this investigation were Haden, Tommy Atkins, and Kent. All were imported from Mexico.

Fumigation. Each dosage of MB, replicated five times (one fruit/replicate), was separately applied for 2 h at 16, 48, 56, and 64 g/m^3, respectively, in a 0.71-m^3 chamber, designed and constructed as described by Williamson et al. (1986). Commercially available MB in pressurized 4.54-kg tanks was passed through a chilled 2.0 m × 6.4 mm (i.d.) coiled copper tubing. A calculated amount of the liquified MB was allowed to flow into a graduated volumetric glass chamber. The MB in the glass chamber was then allowed to vent rapidly into the fumigation chamber. The temperature of the chamber was kept at 20 ± 2 °C. A halide detector was used to monitor the MB in the chamber. At 2 h after fumigation, the chamber was evacuated to the atmosphere for 5 min by an exhaust blower prior to removing the treated fruit. The fruit were then placed in a fume hood with a 24.4 m/min face velocity. At various time intervals after evacuation of the chamber fruit were removed from the fume hood and samples taken for MB residue analysis.

Headspace Analysis. At 0.17, 1, 2, 5, 24, and 48 h after fumigation at the desired dose, a 50-g peel or pulp sample and 100 mL of distilled water were blended in a 500-mL Eberbach blender container for 3 min at low speed. The container was a standard Waring glass with a modified Teflon-lined screw cap

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Table I. Analyses of MB Residues in Fortified Samples of Mangos

MB added, mg/kg	% recovered[a] peel	pulp
0	0	0
0.32	96.25	88.8
12.60	100.20	93.97
16.69	97.87	98.65
27.43	96.68	96.56
35.00	91.82	100.02
mean	96.52 ± 3.00	95.60 ± 4.43

[a] For the peel and pulp overall recoveries of 96.52 ± 3.00 SD and a 95.60 ± 4.43 SD, respectively, were obtained.

Table II. Methyl Bromide Residues (Milligrams per Kilogram) in Mango Fruit Parts after Fumigation

time, h	16 g/m³	48 g/m³	56 g/m³	64 g/m³
		Peel		
0.17	4.7 ± 1.3[a]	14.3 ± 2.8	16.5 ± 1.4	21.2 ± 3.9
1.0	1.1 ± 0/8	4.9 ± 1.3	4.4 ± 0.9	6.3 ± 0.6
3.0	0.01 ± 0.002	2.1 ± 0.2	2.5 ± 0.8	3.5 ± 0.3
5.0	ND[b]	1.8 ± 0.6	1.7 ± 0.4	2.6 ± 0.3
24.0	ND	ND	0.08 ± 0.003	0.01 ± 0.003
48.0	ND	ND	ND	0.01 ± 0.002
		Pulp		
0.17	2.2 ± 1.0[a]	6.2 ± 0.4	9.4 ± 2.3	20.6 ± 0.6
1.0	0.9 ± 0.7	6.1 ± 0.8	7.2 ± 1.2	8.6 ± 0.8
3.0	0.01 ± 0.004	4.8 ± 2.1	4.5 ± 0.9	6.7 ± 0.8
5.0	ND	3.0 ± 0.6	2.6 ± 1.0	4.1 ± 1.3
24.0	ND	ND	0.04 ± 0.003	0.01 ± 0.003
48.0	ND	ND	ND	0.01 ± 0.003
		Total		
0.17	6.9 ± 1.3[a]	21.1 ± 2.9	25.9 ± 3.3	41.8 ± 3.6
1.0	2.0 ± 0.7	11.3 ± 1.6	11.6 ± 1.1	14.9 ± 1.1
3.0	0.02	8.4 ± 1.3	7.0 ± 1.3	10.2 ± 1.1
5.0	ND	4.5 ± 0.7	4.3 ± 1.5	6.7 ± 1.3
24.0	ND	ND	0.12 ± 0.01	<0.01
48.0	ND	ND	ND	<0.01

[a] ±SD. [b] ND = nondetected.

as described by King et al. (1981). The container and contents were allowed to remain undisturbed for 25 min after blending to allow equal partitioning of the MB in the fruit mix phase and the vapor phase.

Gas Chromatography. A 2-mL sample from the air space above the blended liquid was removed from the blender with a 2.5-mL gas-tight syringe and the total volume injected into a 1.0-mL loop of a Valco gas valve in series with a Shimadzu 9A gas chromatograph (GC). The GC was equipped with a stainless steel 2.5 m × 0.32 cm (o.d.) column packed with 1% SP-1000 on 60/80 Carbopak B. Detection of MB was made by a nickel-63 electron capture detector. Operating parameters: detector temperature, 300 °C; oven temperature, 155 °C; injection valve, ambient temperature; carrier gas, 95% argon and 5% methane; flow rate, 40 mL/min. A Shimadzu C-RIB Chromatopac recording data processor was used for the quantitative determination of MB.

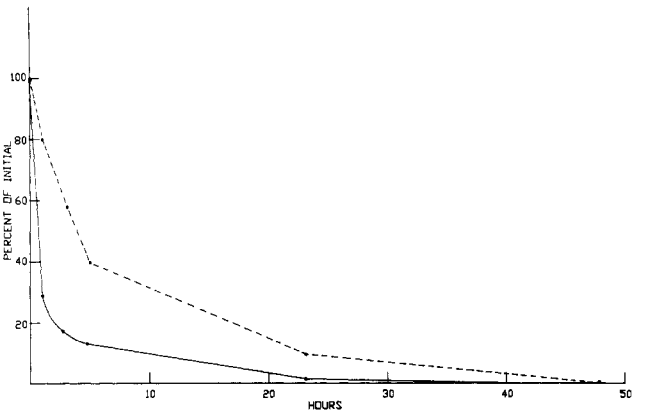

Figure 1. Percentage loss of methyl bromide from mango fruit pulp (—) and grapefruit (- - -) at a 64 g/m³ dose. Percentage loss in grapefruit was calculated from the data of King et al. (1981).

Recovery Studies. Experiments were conducted to determine the percent MB recovered by the following procedure. Fifty-gram portions of either peel or pulp were placed in 100 mL of water in a 500-mL blending jar. Gaseous MB, from a minimum of 0.32 to a maximum of 35.00 mg/kg, was injected into the blending jar through the silicon septum with use of a gas-tight syringe. The peel or pulp was blended as previously described. One-milliliter headspace samples were removed with a gas-tight syringe and injected into the sample loop of the gas chromatograph for analysis.

Analysis of Data. Mean ± SD residue levels were determined at each of the indicated times and doses tested. In addition, the exponential regression equation was applied to the time vs residue data for the peel, pulp, and total residue. At 0.17 h, the linear regression equation was applied to the dosage vs residue data to show the expected quantities of MB to be found in and on the mango fruit.

RESULTS AND DISCUSSION

Methyl bromide recovered averaged 95.60 ± 4.43% and 96.52 ± 3.00% for pulp and peel, respectively, and values are given in Table I based on the five dosages tested. These values were similar to those shown by King et al. (1981) who used similar extraction and GC methods.

There were no significant differences in MB residues at each specific time or dose among the three cultivars so the data were pooled for the results shown herein.

Residues of MB in the peel and pulp of the mango fumigated for 2 h at all the MB dosages tested are given in Table II. Total MB residues at 0.17 h after fumigation dosages of 48, 56, and 64 g/m³ are above the tolerance level of 20 mg/kg. Rapid decrease of MB residue was observed at all dose levels for both peel and pulp,

Table III. Exponential Regression Equations and R^2 Values of Methyl Bromide Residues in Mango Fruit Parts

dose, g/m³	peel	pulp	total
16	$0.99y = 6.13e^{-2.10x}$	$0.96y = 3.4e^{-1.87x}$	$0.98y = 9.62e^{-2.01x}$
48	$0.84y = 9.76e^{-0.40x}$	$0.93y = 6.75e^{-0.16x}$	$0.93y = 17.21e^{-0.27x}$
56	$0.92y = 6.67e^{-0.19x}$	$0.99y = 8.81e^{-0.23x}$	$0.98y = 15.81e^{-0.21x}$
64	$0.83y = 6.19e^{-0.16x}$	$0.99y = 11.77e^{-0.15x}$	$0.79y = 14.02e^{-0.17x}$

Table IV. Linear Regression Equations, R^2 Values, and Expected Residues (Milligram per Kilogram) of Methyl Bromide in and on Mangos at 0.17 h

residue location	R^2	$y = -a + bx$	16 g/m³	48 g/m³	56 g/m³	64 g/m³
peel	0.98	$y = -0.89 + 0.33x$	4.39	14.95	17.59	20.23
pulp	0.68	$y = -4.67 + 0.31x$	0.29	10.21	12.69	15.17
total	0.66	$y = -5.56 + 0.64x$	4.68	25.16	30.28	35.40

[a] Data taken from Table I. For 0.17 h, the linear regression equation was applied to the dosage vs residue data to determine the expected quantities of MB shown here in and on the mango.

with most of the loss occurring between 0.17 and 1 h after fumigation. This disappearance curve was generally different from the curve observed for citrus (King et al., 1981) at the 64 g/m^3 dose, due to the fact that the rate of loss (b = 0.17 g/m^3 per h) from mango is greater than for grapefruit (b = 0.084 g/m^3 per h) (King et al., 1981) as determined by exponential regression equation. In addition, the intercept for grapefruit is greater (25.36) as determined by King et al. (1981) than the 14.02 shown for mango in Table III. Also, the loss curve data for grapefruit gave a better fit (R^2 = 0.98) by the exponential regression equation than that indicated by the same equation for mango (R^2 = 0.79). However, both values were statistically significant (P = 0.05).

If total residue concentration of MB in mangos is used to compare with the established grapefruit levels of 20 mg/kg, then at 1 h after evacuation of the MB from the chamber and thereafter, MB residues in mangos of all dosages tested are below the tolerance level for grapefruit. If residue levels in the peel or pulp are the only criteria for comparison, mangos may be fumigated for 2 h at MB dosages of 16, 48, and 56 mg/kg without exceeding the acceptable levels established for grapefruit at 10 min after evacuation of MB from the chamber.

The fumigation method and the headspace analysis procedure for citrus (King et al., 1981) provide a means to treat and determine MB residues in mango fruit. The exponential regression equations can be applied to calculate the MB loss curve in mangos at the specified treatment dose while the linear analysis equations in Table IV can be used to calculate expected residues levels at the zero hour, in this case 0.17 h.

Registry No. MB, 74-83-9.

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Structure–Activity Studies on the Inhibition of Photosystem II Electron Transport by Phenylbiurets

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The inhibition of photosynthetic electron transport by phenylbiurets has been investigated. The chemical structure of this class of molecules bears some similarity to that of other well-known photosystem II (PS II) inhibitors, such as the carboxy anilides and the phenylureas. However, some important differences have been found in the structural requirements for maximum inhibition by these PS II inhibitors and the phenylbiurets. For example, some ortho-substituted phenylbiurets show enhanced activity. In contrast ortho substitution in the phenylureas considerably reduces activity. Moreover, electronic effects are important in increasing the ability of the phenylbiurets to inhibit electron transport. Finally, the biological activity of the phenylbiurets has been compared to that of other well-known PS II inhibitors, and it appears that, as in the case of the latter compounds, a log P maximum of about 3 is required for optimum biological activity.

Members of a large group of compounds that inhibit photosystem II (PS II) electron transport belong to a number of different chemical classes but have the common structural features, shown in I. Examples are carboxy anilides (R_3 = alkyl), phenylureas (R_3 = mono- or dialkylamino), phenyl(methoxymethyl)ureas (R_3 = (methoxyalkyl)amino), and carbamates (R_3 = alkoxy). These compounds are thought to bind to an integral membrane protein component of the PS II reaction center called the 32-kDa or D1 protein. An important requirement for the binding of these molecules to the protein is a nitrogen atom attached to a hydrophobic phenyl group and an electron-deficient carbon atom.

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