Benzimidazole Penetration, Distribution, and Persistence in Postharvest-Treated Pears

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ABSTRACT

Residues of thiabendazole (TBZ) and benomyl were determined by bioassay in postharvest-treated pears (*Pyrus communis* 'Spadona') after treatment and during cold storage. The amount of residues found in the fruit was proportional to the concentration of fungicide applied. The highest amounts remained in the peel, and a declining concentration gradient was formed in the direction of the core. In this respect, benomyl appeared to be somewhat more mobile than TBZ. There was a continuous depletion of the fungicidal residues of both compounds during storage of the fruit, and after 5 months at −1 C virtually no trace of either compound could be detected by bioassay in the flesh or core of the treated pears.

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Two benzimidazole fungicides, thiabendazole [TBZ, 2-(4-thiazolyl)-benzimidazole] and benomyl [methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate], have been found effective for controlling storage rots of pears, when applied as postharvest dips (1, 2). Both of these benzimidazoles are known to be systemic fungicides (3, 4, 6, 8), and their penetration into plants through the roots is apparently governed by the transpiration rate of the plant (6). However, when fruits are dipped in fungicidal preparations, the penetration and distribution of the material are likely to be determined chiefly by physical factors.

Benomyl reportedly is very stable as the 2-benzimidazole carbamic acid methyl ester (MBC) derivative in pea plants (8). The rate of disappearance of TBZ from pepper leaves was three to four times faster than that of MBC, which remained bound or unbound in the leaves (3). This work compares the penetration, distribution, and persistence of TBZ and benomyl, when applied to pear fruits prior to cold storage for prolonged periods.

MATERIALS AND METHODS.—Pear fruits (*Pyrus communis* L. 'Spadona') were treated one day after harvest by dipping for 1 minute in aqueous suspensions of benomyl 50% wettable powder or TBZ 60% wettable powder. The concentrations of active fungicide tested were 500, 1,000 and 2,000 μg/ml benomyl and 300, 600, and 1,200 μg/ml TBZ. [The recommended doses for commercial use are 1,000 μg/ml benomyl and 600 μg/ml TBZ (2)]. Each treatment was applied to 15 fruits, which were then divided into three equal lots. One lot was held at 20 C for 9 days, and the remaining two lots were stored at −1 C for 30 or 70 days, followed by 2 days at 20 C.

The residues of the fungicides in various parts of the fruit were determined by bioassay (5). A *Penicillium* sp. was used for benomyl assay and a *Verticillium* sp. for TBZ assay. The diameter of the inhibition zone was linearly proportional to the log of the concentration within the range of 0.05-0.5 μg for benomyl and 0.2-2.0 μg for TBZ.

The fruits were washed in detergent, rinsed in tap water, dipped in alcohol, and dried. Peel of uniform thickness was removed with a potato-peeler, and peel disks, 13-mm in diameter, were cut with a cork borer (sample "P"). With the same cork borer, two plugs were then removed from opposite sides of the pear at its widest diameter. Disks of 2 mm thickness were cut from beneath the peel ("BP"), the center ("MC"), and near the core ("C") of each plug. These disks were placed in the center of petri dishes on a thin layer of 1% potato-dextrose agar containing spores of the appropriate fungus. Similarly cut disks of each sample type were cut from the same fruits and weighed. The average disk weights of the various samples ranged from 850 to 1,055 mg. The concentration of residue in each region of the fruit was determined by plotting the diameter of the inhibition zone formed on the calibration curve, and dividing the result by the average disk weight.

In two other similar experiments, concentrations of 500, 1,000 and 2,000 μg/ml of each fungicide were used and the residues were determined after storage for 100 and 150 days.

RESULTS.—Residues of both fungicides were roughly proportional to the concentrations of the applied chemicals (Fig. 1). Greatest residue concentrations were retained in the fruit peel, with a declining gradient toward the fruit core. At similar concentrations, the TBZ residues were somewhat lower than those of benomyl; e.g., 9 days after treatment with 1,200 μg/ml TBZ or 1,000 μg/ml benomyl, the residues in the peel were 2.6 and 3.3 μg/g, respectively. Moreover, benomyl appeared to penetrate more readily than TBZ—500 μg/ml benomyl leaving small residues in the middle cortex and near the core, compared with none after treatment with 600 μg/ml TBZ. At higher concentrations (1,000 μg/ml benomyl and 1,200 μg/ml TBZ), average residual amounts of the two fungicides detected in the region of the core were 0.2 μg/g and 0.14 μg/g, respectively. A chemical analysis of the residues in whole fruits, carried out in one of the experiments by the methods described by Rajzman (7), showed similar trends; e.g., fruit dipped in 500, 1,000, and 2,000 μg/ml of either fungicide contained 1.04, 2.0, and 3.5 μg/g TBZ or 1.09, 2.2, and 3.7 μg/g benomyl, respectively, after 5 months of cold storage.

The amount of active residue in the fruit diminished during storage, and the persistence of the two fungicides was of comparable magnitude at similar concentrations (Fig. 1). The percentage of residue which remained biologically active in the fruit was generally related

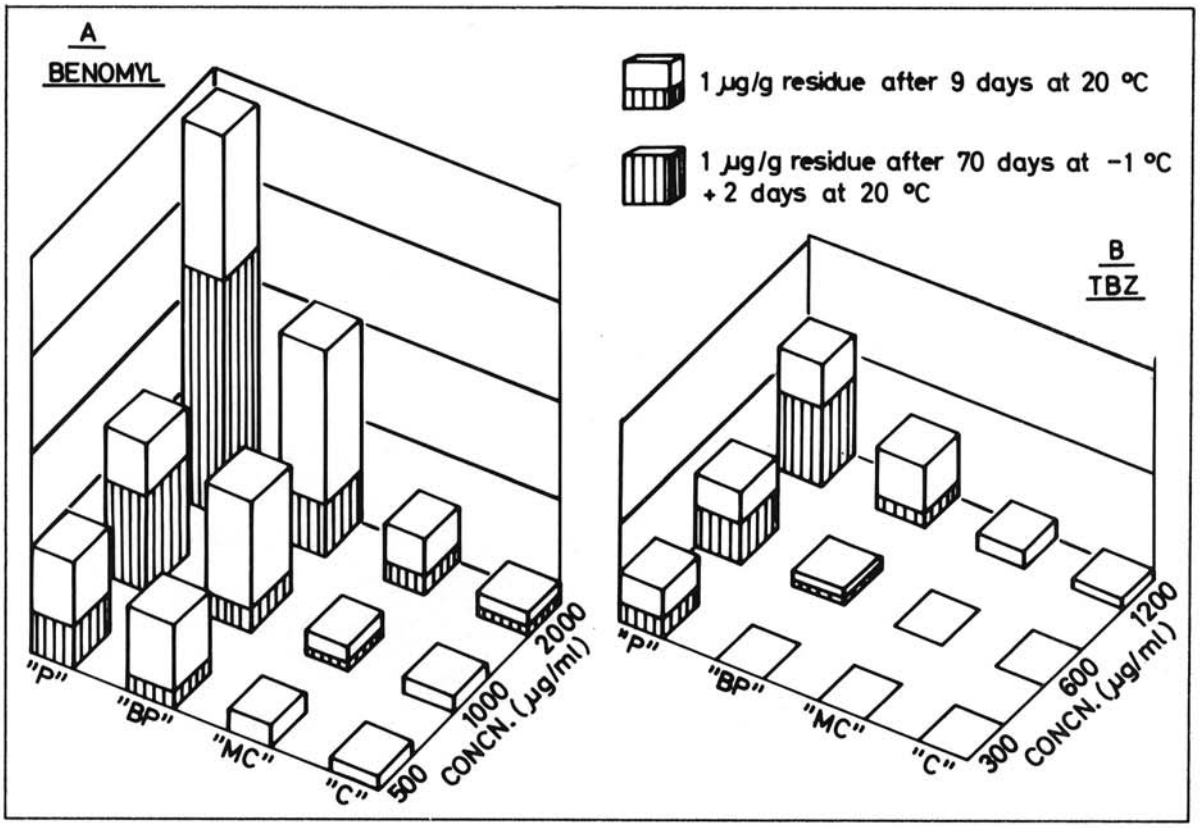

Fig. 1. The effect of concentration of postharvest fungicide treatment on the amount, distribution, and persistence of benomyl and TBZ residues in Spadona pears during storage. Abbreviations used: P = peel; BP = beneath peel; MC = middle cortex; C = core.

directly to the initial amount which penetrated, and also to the region of the fruit. With similar residual amounts initially, the persistence during storage was greatest in the peel. The flesh and core of the fruit retained residues after storage only at the highest concentration of benomyl used in the treatment. Determination of the two fungicides after 30 days of storage generally indicated levels intermediate between the two values shown in Fig. 1, but a consistent rate of fungicide inactivation could not be estimated. In the two experiments with pears stored for 100 and 150 days, similar residue trends were found (Table 1) and the final residue concentrations detected in the peel of fruit treated with 2,000 µg/ml fungicide were lower than in the previous experiment, not exceeding 5 and 3 µg/g, respectively, at each date. At this time, there were very low amounts (less than 0.2 µg/g) or no detectable residues, even of benomyl, in the flesh and core of the fruit.

DISCUSSION.—Penetration of benzimidazole compounds into detached pear fruits appeared to be a physical process with a declining residue gradient from peel to core and with depth of penetration proportional to concentration of fungicide-treatment. Peterson and Edgington (6) also concluded that, although accumulation of benomyl in the plant was governed by the ability of the plant to transpire, the distribution of the fungicide within the plant could be explained on the basis of physical factors. Even so, TBZ appeared to be somewhat less mobile than benomyl in the pear tissue. It is possible that this apparent difference is due partly to the lower sensitivity of the TBZ assay (four times less than that of benomyl), which did not enable detection of residues in amounts less than 0.2 µg/g.

Although TBZ has been reported to be much less stable in plants than benomyl, or its derivative MBC, the depletion of both fungicides in stored pears was of similar magnitude. This can be explained by the difference in the methods employed for residue determination. The bioassay used in the present experiments is an indication only of the change in fungicidal activity as a function of time. However, in the work of Ben-Aziz and Aharonson (3), where analytical procedures were used, it was shown that although 86.5% of MBC uptake in pepper plants could be accounted for after 10 days, the amount of unbound MBC was depleted almost as rapidly as TBZ. Moreover, there were indications that bound MBC, which had increased, was of a much lower fungicidal activity. Biehn and Dimond (4), using a bioassay test for determination of benomyl residues in treated tomato plants, also found rapid inactivation of the fungicide. Less is known of the metabolic fate of TBZ than of benomyl in the plant, but with regard to their fungitoxic activity, the bioassay employed in the present study indicates that both are being continuously degraded or

TABLE 1. The effect of postharvest fungicide treatment on the amount, distribution, and persistence of benomyl and TBZ residues in Spadona pears after prolonged storage

Postharvest treatment		Post-storage residues[a] (μg/g)							
		100 days				150 days			
Fungicide	Concn (μg/ml)	P[b]	BP	MC	C	P	BP	MC	C
Benomyl	500	2.2	0.2	0	0	0.9	0.1	0	0
	1,000	3.0	0.3	0.2	0.1	1.5	0.2	0	0
	2,000	4.8	0.5	0.2	0.2	2.3	0.4	0.1	0
TBZ	500	1.3	0	0	0	0.7	0	0	0
	1,000	2.0	0	0	0	1.4	0	0	0
	2,000	3.7	0.3	0.1	0	2.0	0	0	0

[a]Average of two experiments.
[b]Abbreviations: P = peel; BP = beneath peel; MC = middle cortex; and C = core.

bound in inactive forms.

Earlier findings (2) showed that two chief causal agents of pear storage rots, *Pencillium expansum* and *Botrytis cinerea,* were more sensitive to TBZ than to benomyl. Therefore, the weaker penetration and mobility of TBZ do not alter the effectiveness of this treatment, even though the recommended TBZ dose (600 μg/ml) leaves lower residual amounts in fruit tissues than does the similarly effective benomyl dose (1,000 μg/ml).

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