Benomyl Residues in Valencia Oranges from Postharvest Applications Containing Emulsified Oil

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ABSTRACT

Residues of methyl 2-benzimidazolecarbamate (MBC) in Valencia oranges were increased 2- to 3-fold when 1% spray oil was added to nonrecovery spray applications of 500 ppm of benomyl 0 to 3 days prior to use. A treating suspension of 175 ppm benomyl with 1% spray oil provided residues similar to those obtained with an application of 500 ppm of benomyl without oil. Spray oil not only increased residues on the fruit surfaces, but it also increased those in the flavedo and albedo layers of the peel. Oil did not increase MBC residues when benomyl-oil-water emulsions were applied 7 days after preparation. However, significant increases in MBC residues were attained if the oil was added to 7-day-old benomyl suspensions immediately before application.

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Postharvest applications of benomyl provide good control of the postharvest decays of Florida citrus fruit caused by the fungi *Diplodia natalensis* P. Evans, *Phomopsis citri* Fawc., and *Penicillium digitatum* Sacc. (4). Control is achieved with applications containing 500 ppm of benomyl. In an aqueous suspension, benomyl is broken down to methyl 2-benzimidazolecarbamate (MBC) (2). Complete hydrolysis can occur within 4 days (6), but the rate is influenced by temp and pH (3). By adding emulsified oil to benomyl, disease control has been improved in certain other crops (7, 10, 12, 13), and benomyl residues have been increased (8).

In this study, I wanted to determine (i) whether the residues of benomyl in Valencia oranges could be increased by combining emulsified oil with the fungicide in a postharvest nonrecovery spray application; (ii) whether residue levels were influenced by oil concn; and (iii) the effect of oil on the distribution of benomyl on and within the fruit.

MATERIALS AND METHODS.—Oranges [*Citrus sinensis* (L.) Osbeck 'Valencia'] were washed and selected for near-uniformity in size (6.4 to 7.3 cm in diam) and freedom from blemishes. The fruit were treated with benomyl (50% WP) suspended in water (pH 5.7) with and without the addition of Ortho Volck spray oil (petroleum, 97%; inert ingredients, 3%; minimum unsulfonated residue (U.R., 91%) (Chevron Chemical Co., Richmond, Calif.). Suspensions were prepared 3 days before application, except when stated otherwise, and were stored at 18 C. Suspensions were applied through a 1.35 Steiner (William Steiner Mfg. Co., Newark, N.J.) 90°-H fuel oil nozzle which was attached to the traversing arm of a Brogdex (Brogdex Co., Orlando, Fla.) nonrecovery spray fungicide applicator. Complete coverage of the fruit was achieved using a minimum volume of the fungicide. Fruit were conveyed under the spray nozzle by revolving horsehair brushes saturated with the treating suspension and then on slats through a hot-air dryer. All residue determinations based on whole fruit were made with fruit that were immediately frozen after being treated and dried, stored, and then thawed before use. Benomyl determinations of surface, peel, and pulp were made using fruit which were dried with a polisher hot-air dryer and waxed with a commercial solvent wax. These fruit were not frozen, but were stored at 21 C and determinations were made after 1, 8, and 21 days.

Published procedures (1) were used for determining the residual amounts of benomyl on the fruit surface and in the peel and pulp. Residues in whole fruit were determined by chopping three oranges in a Waring Blendor and removing a 25-g aliquot. The sample was extracted for 3 min in 100 ml of chloroform with an Omni-Mixer, and then transferred to plastic bottles and centrifuged for 10 min at 2,500 rpm. The liquid was decanted from the fruit debris into a separatory funnel from which the chloroform fraction was recovered. This was concd under vacuum at 50 C to 5 ml. A 10 μliter aliquot was spotted on a thin-layer chromatogram sheet where methyl 2-benzimidazolecarbamate (MBC) was determined quantitatively by a bioautograph technique (6) using a solvent system of ethyl acetate/chloroform (60:40, v/v) (9). This technique was also used to detect the presence of benomyl and MBC in the treating suspensions.

RESULTS.—By adding oil to the benomyl spray suspension, significantly higher amounts of MBC were recovered from the fruit (Table 1). A concn of 1% (10 ml/liter) of spray oil was optimum; MBC residues from the use of less oil were lower, while applications of higher concns of oil did not increase residues significantly. No phytotoxicity was evident from the use of oil at any of the concns tested.

Oil at 1% was added to suspensions of benomyl at concns of 200 ppm and less to determine which concn in the presence of oil would provide residues comparable to those obtained with a treating suspension of 500 ppm benomyl without oil (Table 2). Concns of 150 to 175 ppm of benomyl with 1% oil gave residues in the whole fruit similar to the residue obtained with an application of 500 ppm benomyl alone.

In an earlier experiment, the amount of MBC on fruit surfaces and in the peel and pulp was compared between treatments of benomyl without and with 0.25% oil (Table 3). The addition of oil to benomyl not only increased the surface residues, but also increased those found in the flavedo and albedo. Significant changes in MBC content occurred on the fruit surfaces and in the albedo and pulp during 21 days of storage at 21 C. These changes followed similar trends in both treatments; the most striking being the constant decrease in the amount of MBC recovered from fruit surfaces with time in storage. Where benomyl was applied with oil, the albedo contained significantly less MBC while the pulp had more at 21 days than was present in these tissues after 1 day of storage.

In Table 4, data are shown which illustrate the effect of the age and method of preparation of the benomyl-oil-water emulsions on residues of MBC in the fruit. After 7 days at 34 C, the preparations either with or without oil were found to contain primarily MBC due to hydrolysis of the benomyl. The stimulatory effect of oil with benomyl was not evident when the two materials were combined in a water emulsion for 7 days. However, by adding the oil to a 7-day-old benomyl suspension just prior to applying it to fruit, the residues of MBC were again increased with the use of oil. Lack of the stimulatory activity of oil was also noted with a 7-day-old benomyl-oil-water emulsion held at 18 C before applying it to fruit and in a 7-day-old preparation held at 34 C

TABLE 1. Residues of methyl 2-benzimidazolecarbamate (MBC) in 'Valencia' oranges treated with nonrecovery sprays of benomyl[a] containing different concns of Ortho Volck oil

ml oil/liter (ml/liter)	MBC/fruit[b] (μg/g)
0.0	0.35 w[c]
2.5	0.62 x
5.0	0.87 x
7.5	1.04 y
10.0	1.33 z
12.5	1.36 z
15.0	1.36 z
17.5	1.36 z
20.0	1.40 z

[a]500 μg/ml.
[b]Mean of three samples each containing three fruit.
[c]Values followed by unlike letters are significantly different, $P = 0.05$.

TABLE 2. Residues of methyl 2-benzimidazolecarbamate (MBC) in 'Valencia' oranges treated with nonrecovery sprays of different concns of benomyl containing Ortho Volck oil[a]

Benomyl concn (μg/ml)	MBC/fruit[b] (μg/g)
75	0.08
100	0.14
125	0.23
150	0.29
175	0.39
200	0.51
500[c]	0.33

[a]10 ml/liter.
[b]Mean of three samples each containing three fruit.
[c]Applied without the addition of oil.

TABLE 3. Residues of methyl 2-benzimidazolecarbamate (MBC) on the surface and in the peel and pulp of 'Valencia' oranges receiving a nonrecovery spray of benomyl[a] or benomyl[a] and Ortho Volck oil[b]

Treatment	Storage at 21 C (days)	MBC on fruit components[c]			
		Surface ($\mu g/cm^2$)	Flavedo ($\mu g/g$)	Albedo ($\mu g/g$)	Pulp ($\mu g/g$)
Benomyl-water suspension	1	0.17 x[d]	1.13 y	0.10 x	0.00 y
	8	0.14 x	1.22 y	0.24 y	0.01 y
	21	0.01 w	0.83 y	0.05 x	0.05 y
Benomyl-oil-water emulsion	1	0.83 z	2.32 z	0.51 z	0.01 y
	8	0.52 y	2.75 z	0.61 z	0.03 y
	21	0.13 x	2.39 z	0.15 xy	0.14 z

[a]500 $\mu g/ml$.
[b]2.5 ml/liter.
[c]Mean of two samples each containing 10 fruit.
[d]Values within each column followed by unlike letters are significantly different, $P = 0.05$.

which contained oil and technical benomyl rather than the 50% WP formulation.

DISCUSSION.—Approximately a 2- to 3-fold increase in residues of MBC in Valencia oranges was obtained by adding 1% spray oil to treating suspensions of benomyl. Increased residues were due not only to greater surface deposits, but also to higher amounts of MBC in the peel and pulp (Table 3). Improved dispersion of benomyl on fruit surfaces by oil may account at least partly for the increase in surface deposits, which in turn would increase fungicide diffusion through the cuticle (11), and thus enhance the residues recovered from within the peel. Penetration of benomyl through the cuticle and/or stomata may also be improved by the action of oil.

Residues of MBC in the oranges were increased by adding oil either to benomyl suspensions that were applied immediately after preparation (and which therefore contained principally benomyl), or to suspensions prepared 7 days previously (and which were therefore composed primarily of MBC). However, no increase was observed where the benomyl-oil preparations were allowed to stand for 7 days before use. This may have been due to some deterioration of the emulsion as the oil particles did not remain suspended in the water as long after agitation at 7 as they did at 1 or 3 days. Larger oil particles in such older emulsions may not effectively improve the dispersion of benomyl on orange fruit surfaces.

Inclusion of oil with the benomyl application always increased the residues significantly, but not always in the same proportion. For example (Table 1), we see that 1% oil increased MBC residues almost 4-fold. But only ca. a 2-fold increase in residues was obtained in the experiment reported in Table 4. Further studies are needed to determine why such variation occurs. Fairly consistent residues of 0.30 to 0.35 $\mu g/g$ were recovered however, from fruit which received only benomyl without oil.

Cost of treatment would be materially reduced if some of the benomyl in a postharvest treating formulation could be replaced with the less expensive spray oil, assuming equivalent residues from applications of benomyl and benomyl with oil provide comparable disease control. In some instances, higher residues obtained by adding oil to standard concns of benomyl may be useful; e.g., to improve disease control in the decay-prone specialty fruits or to reduce soilage by retarding sporulation of *Penicillium digitatum* on infected fruit. The only limiting factor would be that the treating suspension would have to be used within 2-3 days after adding the oil.

Some degradation of benomyl was evident during storage of Valencia oranges at 21 C, especially that on the surface and in the albedo. Some of this loss was apparently due to a slight accumulation of MBC in the fruit pulp, but presumably most of the MBC that was being lost was metabolized into form(s) not fungitoxic to the bioassay organism. Similar losses in residues of thiabendazole (TBZ) have been reported (5) during the storage of citrus fruit.

TABLE 4. Residues of methyl 2-benzimidazolecarbamate (MBC) in 'Valencia' oranges, as influenced by the age and method of preparation of benomyl[a]-oil[b]-water emulsions before nonrecovery spray application

Treatment	MBC in fruit[c] ($\mu g/g$)
Benomyl-oil-water emulsion prepared and applied immediately	0.55 z[d]
Benomyl-oil-water emulsion prepared and held 7 days at 34 C before application	0.31 y
Benomyl suspension prepared and held 7 days at 34 C with oil added immediately before application	0.52 z
Benomyl suspension prepared and applied immediately[e]	0.30 y

[a]500 $\mu g/ml$.
[b]10 ml/liter.
[c]Mean of three samples each containing three fruit.
[d]Values followed by unlike letters are significantly different, $P = 0.05$.
[e]Applied without the addition of oil.

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