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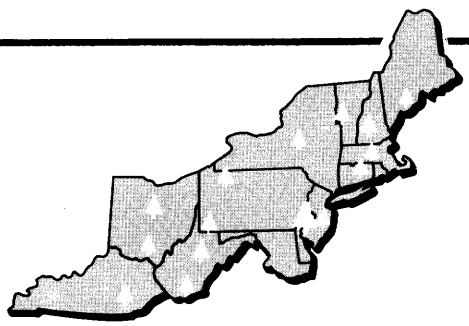

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A BENOMYL-DERIVED FUNGITOXICANT FOR TREE WILT DISEASE CONTROL

Abstract.—Methyl 2-benzimidazolecarbamate (MBC) was derived from benomyl, a relatively new broad-spectrum systemic fungicide. MBC·HCl solutions have been found to be fungitoxic, stable, suitable for injection into trees, and effective in wilt disease control.

Prospects for control of vascular-wilt disease of trees have been greatly improved by the recent development of the broad-spectrum systemic fungicide methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate—common name, benomyl.

This fungicide has been applied experimentally as a soil drench and foliar spray, and by injection into the vascular system of the tree. Benomyl applied to the root zone of American elms by soil drenching gave some protection from Dutch elm disease, but relatively large amounts were required (*1, 15*); and uptake from some soils was unsatisfactory for control (*6*). Foliar sprays of benomyl have been reported as somewhat effective for control of Dutch elm disease (*5, 15*), but spraying is viewed with considerable apprehension because of possible contamination of the environment. Solubilized benomyl injected directly into the xylem of elm, oak, and maple trees becomes distributed in the branches and twigs (*3*); and this method seems to offer many advantages over other methods while possessing few disadvantages.

Benomyl is only sparingly soluble in water and has generally been applied as an aqueous suspension. However, Gregory *et al.* (*3*) reported that only small quantities of aqueous suspension of benomyl could be injected into elms and oaks, using a pressure-injection apparatus (*7*) that introduces the fluid into the vessels of the outer two or three annual growth rings. The suspended benomyl particles quickly plugged the xylem vessels. Hence a soluble form of benomyl or a fungitoxic derivative seemed to be essential for success with this injection method.

Important properties for a chemical to be suitable for injection into trees are:

- Solubility at high concentration.
- Capacity for infinite aqueous dilution.
- Low viscosity in the required solution concentration.
- Retention and persistence of fungitoxic activity.
- Minimum phytotoxicity in solution.
- Chemical stability.

This paper is a report about the preparation of a water-soluble benomyl-derived fungi-

toxicant, confirmation of its chemical identity, and determination of its fungitoxicity and suitability for injection into trees.

Method

Three hundred twenty grams of Benlate 50 WP (the available source of benomyl) were added in portions to 2 liters of de-ionized water at 90°C., and 200 ml. of 6 N HCl were concurrently added dropwise, with continuous stirring. Stirring and temperature were maintained for 20 to 30 minutes until gas evolution ceased. The solution was treated with decolorizing charcoal, and then was filtered. Two hundred eighty-four grams of solute (89 per cent yield) were obtained. The filtrate was stirred during dropwise addition of 160 ml. of 5 N NH_4OH, which produced a precipitate assumed to be methyl 2-benzimidazolecarbamate (MBC), which was collected and water-washed, yielding 132 g. (41.5 per cent MBC).

76 g./l. of fungitoxicant solution (stock solution) was obtained by nearly saturating 0.5 N HCl with the precipitate. Appropriate dilution of this solution with water provided low-viscosity solutions suitable for injection. pH ranged from 1.0 at 50 g./l. to 2.1 at 1 g./l. pH of these solutions can be increased somewhat without precipitation.

Confirmation of the benomyl-derived fungitoxicant as methyl 2-benzimidazolecarbamate (MBC) was made by elemental analysis of the prepared hydrochloride, picrate, and 3.5-dinitrosalicylate salts, as follows:

MBC·HCl was prepared by dissolving the assumed MBC prepared by the foregoing processes in an excess of 1 N HCl. Evaporation produced crystalline needles, which were put into solution, charcoaled, and dried, yielding a melting point of 163 to 167°C. Elemental analysis showed percentages of C, 47.21; H, 4.50; Cl, 15.46; and N, 18.21; compared to the theoretical percentages C, 47.50; H, 4.74; Cl, 15.58; and N, 18.46.

MBC picrate was prepared as follows. One gram of assumed MBC·HCl prepared as described was dissolved in 15 ml. of warm 95-percent EtOH, then 36 ml. (1.2 mol.) of 4-percent ethanolic picric acid were added. A yellow crystalline mass was obtained, which decomposed at 228 to 232°C. Elemental analysis showed percentages of C, 43.06; H, 2.77; and N, 20.19; whereas theoretical percentages are C, 42.89; H, 2.88; and N, 20.01.

MBC·3,5-dinitrosalicylate was prepared by dissolving 1 g. of the foregoing preparation of assumed MBC·HCl in 20 ml. of hot 95-percent EtOH and then adding 12 ml. of 10-percent ethanolic 3,5-dinitrosalicylate acid. A yellow crystalline mass was obtained, which gave an elemental analysis percentage of C, 46.00; H, 3.16; and N, 16.91; compared to the theoretical percentages of C, 45.82; H, 3.35; and N, 16.71.

Results and Discussion

Elemental analysis of hydrochloric, picric, and 3.5-dinitrosalicylic acid salts of the reaction product obtained by heating Benlate 50 WP with dilute hydrochloric acid and precipitating with ammonium hydroxide confirmed the assumption that this product is MBC.

MBC·HCl solutions varying from 0.5 to 50 g./l. were bioassayed for fungitoxicity, using *Penicillium*-seeded potato dextrose agar petri plates. Periodic tests during 7 months in the laboratory showed no loss of fungitoxic activity. Also, there was no visible evidence of chemical change such as precipitation or color change.

Solutions of MBC·HCl are capable of infinite dilution and have low viscosity. Furthermore, this MBC·HCl solution seems to have advantages over previous solutions (*13*), which contained excess acid, solubilized carrier, and contains reaction byproducts (benomyl hydrolyzes to give MBC, CO_2, and butylamine, which can be phytotoxic to injected trees).

McWain and Gregory (*10*) reported the ease with which aqueous acids convert benomyl into soluble fragments that can be measured to estimate the amount of benomyl (*11*, *12*). Furthermore, hydrolysis of benomyl is known to produce relatively stable MBC (*2*), which apparently is the mobile species in plants (*12*). MBC is considered to be the benomyl-derived fungitoxic chemical in plants following application of benomyl to leaves or roots (*13,14*). Certain types of benzimidazolecarbamates were introduced as fungicides

in patents by Klopping (*8*). Benomyl itself is covered by U. S. 3,541,213 (use claims) and by U. S. 3,631,176 (compound claims). Littler *et al.* (*9*) patented the use of MBC and some of its fungitoxic salts as foliar fungicides.

MBC·HCl has been tested for the control of vascular wilt diseases of red oak (*4*) and American elm. Excellent protection against oak wilt infection was obtained by injection of either 4 or 40 mg. of MBC·HCl into red oak seedlings (*4*). Similar treatment of diseased red oak seedlings resulted in symptom remission in some of the seedlings (*4*).

The requirement that a fungicide be in solution for efficient injection into trees for disease control was met for benomyl by forming the water-soluble derivative MBC·HCl. This salt appears to be chemically stable in solution in the laboratory for at least 7 months. Also, no loss in fungitoxicity was observed during 7 months. No foliar phytotoxicity was observed. MBC·HCl appears to have the chemical, fungitoxic, and injection characteristics desired.

Field trials for control of Dutch elm disease and oak wilt showed effective disease prevention and promising results for disease therapy. A report on this is being prepared.

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