Instability of Benomyl in Various Conditions

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The fungicide, benomyl, methyl 1-(butylcarbamoyl)-2-benzimidazole carbamate breaks down to methyl 2-benzimidazole carbamate (MBC) (HELWEG 1972, KIRKLAND 1973, PEASE and HOLT 1971, WHITE et al. 1973) in water. Benomyl is soluble in some organic solvents (DUPONT 1970, PEASE and HOLT 1971) but its stability is not well documented although PETERSON and EDGINGTON (1969) implied that it was relatively stable in chloroform and acetone. Conversely KILGORE and WHITE (1970) showed that benomyl was unstable in chloroform and identified its degradation product as MBC.

We have recently found also that benomyl is unstable in chloroform. Moreover, it is unstable in such common solvents as acetonitrile, carbon tetrachloride, methanol, 2-propanol, toluene and the others shown in Table 1. Standard solutions (2 mg benomyl/ml) were prepared with the solvents. In all cases a white precipitate formed in the solutions upon standing at room temperature (Table 1).

TABLE 1

Characteristics of breakdown of benomyl to MBC in organic solvents (100 mg benomyl/50 ml solvent) on standing at room temperature.

Solvents	Time to first evidence of precipitate	Amount of precipitate 7 days after preparing solutions
Benzene	Within 10 mins.	23.5 mg
Ethyl Ether	" 60 "	38.0
Ethanol	Approx. 20 hrs.	49.3
Acetone	" 50 "	12.9
Ethyl acetate	" 50 "	6.8
Methylene chloride	" 80 "	6.5
Chloroform	" 100 "	2.6

Table 1 shows that the quantity of precipitate is almost inversely related to the length of time needed for initial formation of precipitate. The sequence was most clearly evident with benzene; six minutes after benomyl was dissolved, the solution became cloudy and ten minutes later, precipitation commenced.

Thin-layer chromatography (Eastman chromatogram sheets with fluorescent indicator) and mass spectrometry (AEI-MS-30 double beam model) of the precipitates (Table 1) confirmed that in all cases the product was MBC.

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We did not measure the solubility of MBC in the different solvents with precision, but solubility in all the solvents tested was limited. 1,4-Dioxane is a good solvent for MBC (VON STRYK, personal communication). Because of the low concentrations it seems unlikely that MBC converted from benomyl at residue levels will precipitate from solutions. It is important to realize, however, that benomyl converts to MBC in organic solvents.

The lability of benomyl in solution dictates that quantitative analyses commence immediately after extraction if meaningful values for benomyl and MBC are to be obtained. Thin-layer chromatography (TLC) (KILGORE and WHITE 1970, PETERSON and EDGINGTON 1969, VON STRYK 1972) appears to offer an effective means of quantifying the amounts of benomyl and MBC. The choice of developing solvent, however, is important to assure the authenticity of any quantitative values, because decomposition of benomyl is possible during development e.g. in benzene containing solvent systems.

Benomyl also appears to be heat labile. With the standard sweep co-distillation procedures at 170°C (STORHERR and WATTS 1965), there was a marked decomposition of benomyl to MBC; at 100°C there was less decomposition of benomyl. LASKI and WATTS (1973) obtained no detector response for benomyl on a gaschromatograph with a column temperature of 180°C. Similarly during MS analysis benomyl decomposed completely to MBC at 180°C and 70 eV, and only a trace of the parent ion was observed at 80°C and 20 eV.

The above observations indicate major difficulties in preserving authentic benomyl in solution and in measuring it quantitatively.

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