

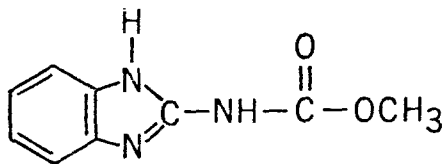
Decomposition of the Systemic Fungicide 1991 (Benlate)

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During the past few years considerable effort has been devoted to the development of effective and economically useful systemic fungicides. One compound in particular, 1-(butylcarbamoyl)-2-benzimidazole carbamic acid, methyl ester (DuPont F-1991 or "Benlate") has received considerable attention because of its broad spectrum fungicidal properties (1,2,3,4). We have found that this fungicide is relatively unstable and decomposes to a highly insoluble compound also having fungicidal properties. Because of the relative importance of F-1991 a study of the decomposition product was therefore undertaken. The degradation product was isolated, characterized and subsequently tested for fungicidal activity.

The degradation product was initially recognized and afterwards isolated by thin-layer chromatography. A standard chloroform solution of F-1991 (1 mg/ml) was found to develop a cloudy appearance after standing for several hours at room temperature. A 5- μ l aliquod of the resultant suspension was chromatographed on a commercially prepared silica gel film containing a fluorescent indicator. Petroleum ether and acetone (90:10) were used to develop the chromatogram, and ultraviolet light (2537 Å) was used for detection. Two spots having R_f values of 0.0 and 0.5 were clearly visible. A freshly prepared chloroform solution of F-1991 served as a reference and exhibited a single spot having an R_f value of 0.5. Further tests revealed that precipitation of the decomposition product from solution was enhanced upon exposure to sunlight and/or heat. Utilizing this procedure, a larger amount of the degradation product was isolated and was subjected to several physical analytical techniques appropriate for structure elucidation.



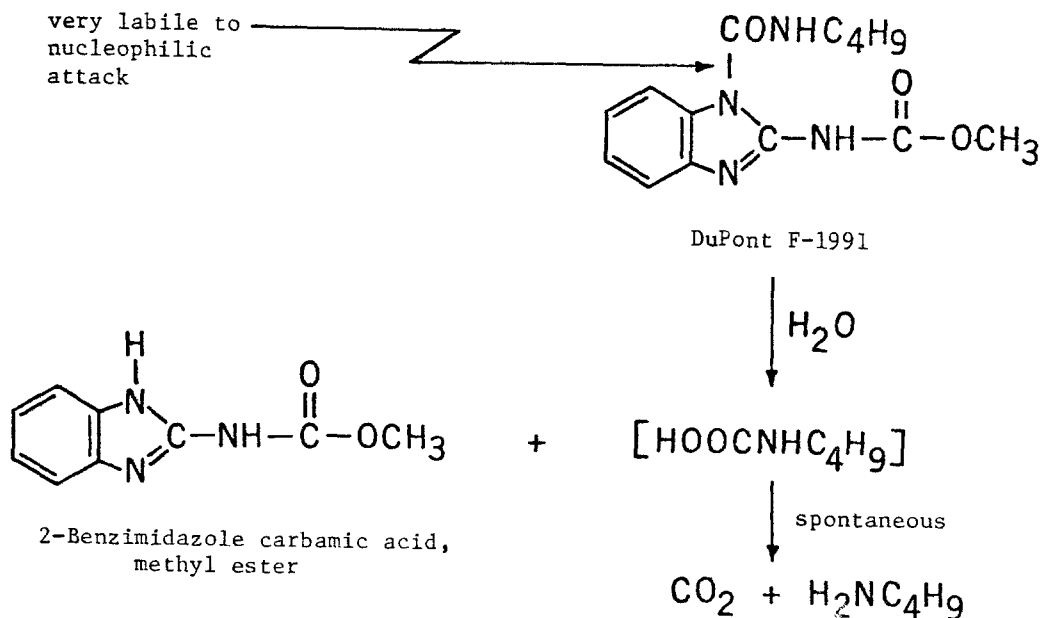
2-Benzimidazole carbamic acid, methyl ester
(I)

The degradation product was assigned structure (I) on the basis of physical evidence derived from IR, Mass and NMR spectra. The relative mass determined by mass spectrometry for the decomposition product was 191.0681, whereas, the calculated mass of the proposed structure was 191.0693. The elemental percentages as found for the degradation product and as calculated for the proposed structure are contained in Table I. Final structural confirmation was accomplished by synthesizing 2-benzimidazole carbamic acid, methyl ester (5) and comparing its IR, mass and NMR spectra to the corresponding spectra of the degradation product. In each instance, the spectral data obtained with both substances were

Table I
Elemental Percentages

Element	Found	Calculated
C	56.10	56.60
H	4.83	4.72
N	21.82	22.00
O	17.25	16.85

identical. As these results clearly indicate that the 2-benzimidazole carbamic acid, methyl ester is formed from F-1991, the most probable route of degradation would be as follows:



The degradation product was also tested for fungicidal activity by using the standard paper disc assay procedure. Penicillium expansum (a citrus fungus), Alternaria tenuis, and Monilinia fructicola (brown rot) were used as test organisms. The chemical showed nearly complete inhibition of P. expansum and M. fructicola. It showed no effect on A. tenuis. These data are identical to those obtained with F-1991 and suggest that the breakdown product may actually be the active component.

Acknowledgments

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