Neth. J. Pl. Path. 75 (1969) 119–122

# Volatile fungitoxicants from chemicals containing haloalkylthio groups

A. TEMPEL

N.V. Philips-Duphar, Agrobiological Laboratory "Boekesteyn", 's-Graveland, The Netherlands

Accepted 31 July, 1968

**Abstract**

Addition of cysteine to the fungicides captan, folpet, dichlofluanid and captafol antagonizes the activity of these fungicides and results in the formation of volatile fungitoxicants. There is no relationship, however, between the vapour action upon reaction with cysteine and the fungitoxicity of these compounds.

## Introduction

The emission of fungitoxic vapours seems to be quite a general phenomenon among present-day fungicides. It has been reported in respect of phenylmercurichloride, maneb, mancozeb, dichlofluanid and oxythioquinox (Hislop, 1967) and of foliage fungicides used for control of powdery mildews (Bent, 1967). The fungitoxic vapours may result either from evaporation of unchanged chemicals e.g. organic mercurials, or from decomposition of the fungicides. Ferbam and nabam were found to give off a volatile sulphur compound which was taken up readily by fungus spores and green plants (Weed et al., 1953). Moje et al. (1964) demonstrated the emission of carbonyl sulphide from nabam in soil. Somers et al. (1967) concluded that the same volatile compound was emitted by captan on reaction with conidia of *Neurospora crassa* or with an aqueous solution of glutathione, used as a model thiol. This carbonyl sulphide was supposed to be a product from the rapid hydrolysis of thiocarbonyl chloride initially formed from the trichloromethylthio group. In this study the production of volatile fungitoxicants from four fungicides containing haloalkylthio groups was investigated.

## Materials and methods

The following fungicides, formulated as wettable powders, were used:
captan, containing 50% N-trichloromethylthio-4-cyclohexene-1.2-dicarboximide;
folpet, containing 50% N-trichloromethylthio-phthalimide;
dichlofluanid, containing 50% N′-dichlorofluoromethylthio-NN-dimethyl-N′-phenylsulphamide;
captafol, containing 80% N-(1.1. 2. 2-tetrachloroethylthio)-4-cyclohexene-1.2- dicarboximide.

The fungicides were finely ground in glass mortars and suspended in water. Cysteine solutions were neutralized with NaOH. The fungicidal activity and the antagonistic effect of cysteine on this activity were assessed in slide germination tests. The suspensions of the fungicides were mixed with suspensions of conidia of *Fusarium culmorum* in diluted cherry juice and with cysteine solutions. Droplets of these mixtures, containing 10,000 spores per ml, were put on glass slides; each slide was placed into a closed tube and incubated at 23 °C. After 24 h the minimum concentration at which the germination was completely inhibited (MIC) was determined.
The vapour action of the fungicide suspensions mixed with cysteine solutions was assessed with the fungus *Fusarium culmorum*, which was allowed to grow at some distance (Fig. 1). A Petri dish (diameter 7 cm, height 2 cm) with a malt agar layer (5 ml) on which conidia of the fungus were sown, was put upside down over another dish, of exactly the same diameter, in which, just before, 15 ml of a fungicide suspension was pipetted and mixed with 15 ml of a cysteine solution of the same concentration (ppm); the two dishes were sealed with transparant adhesive tape and incubated at 23 °C for 4 days, after which the mycelial growth was assessed.

**Results and discussion**

The results are summarized in Table 1 and demonstrated in Fig. 1. The fungitoxicity of captan is strongly antagonized by cysteine in the slide germination test; captan alone does not show vapour action, but the combination of captan and cysteine produces a volatile fungitoxicant. The chemically closely related folpet, however, is antagonized by cysteine to a much lower extent, and this combination does not produce a vapour with prolonged fungicidal activity (some retardation of mycelial growth was

Fig. 1. Vapour action of haloalkylthio groups containing fungicides on *Fusarium culmorum* upon reaction with cysteine

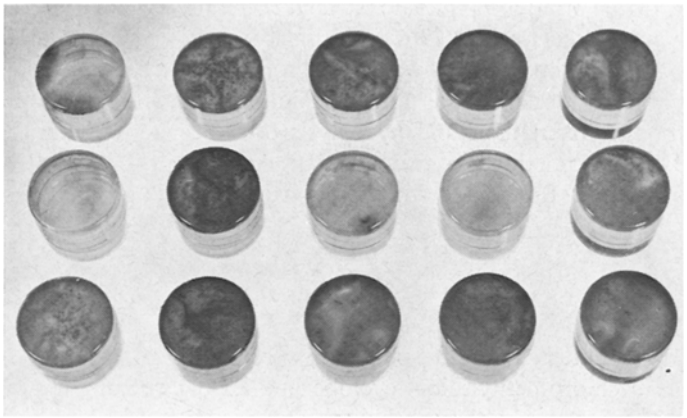
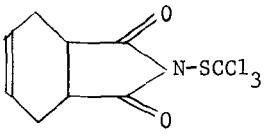
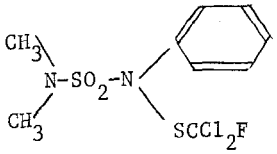


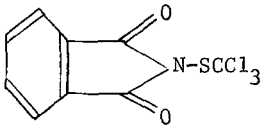

*Fig. 1. Dampwerking op Fusarium culmorum van haloalkylthio-groepen bevattende fungiciden na reactie met cysteine*



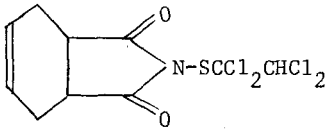
captan



dichlofluanid



folpet



captafol

observed microscopically after 24 h). The other two fungicides show higher activities in the slide germination tests, the decrease of activity and production of fungitoxic vapours on reaction with cysteine holding intermediate positions. It is very likely that the mode of action of folpet is similar to that of captan; both are very potent fungicides, not only in the laboratory but also in practical conditions. Nevertheless the amount of fungitoxic vapour released from folpet upon reaction with cysteine is too small to inhibit the growth of *Fusarium culmorum*. So there is no simple relationship as: the more volatile products are formed upon reaction with thiols, the more potent the fungicide we are dealing with. Lukens et al (1965) regarded the presence of the degradation end-products of some R-$SCCl_3$ compounds in the ambient solution likewise insufficient to account for maximum toxicity. On the other hand the production of

Table 1. Fungitoxicity of some haloalkylthio groups containing fungicides as such and after addition of cysteine. Figures in ppm; mycelial growth: – not inhibited, + seriously inhibited, ++ totally inhibited.

| | *Slide germination test (MIC)* | | *Inhibition of mycelial growth on agar by volatile products* | | |
|---|---|---|---|---|---|
| *Fungicide* | | | *1000* | *1000* | *300* |
| *cysteine added:* | *0* | *30* | *0* | *1000* | *300* |
| captan | 10 | 40 | – | ++ | + |
| folpet | 10 | 20 | – | – | – |
| dichlofluanid | 1 | 5 | – | + | – |
| captafol | 0.5 | 1 | – | ++ | – |
| Control | | | – | – | – |

*Tabel 1. Fungitoxiciteit van enige haloalkylthio-groepen bevattende fungiciden als zodanig en na toevoeging van cysteine. Cijfers in ppm; myceliumgroei: – niet geremd, + sterk geremd, ++ volledig geremd.*

fungitoxic vapours is unlikely to be considered as merely a degradation without any biological significance. Further research is needed to explain all these results.

**Acknowledgment**

The author is indebted to Mrs. O. G. ten Dolle-Kennis for able technical assistance.

**Samenvatting**

*Vluchtige fungitoxische verbindingen uit haloalkylthio-groepen bevattende chemicaliën*

Cysteine heeft een antagonerend effect op de werking van captan, folpet, dichlofluanid en captafol (Tabel 1). Bij proeven in afgesloten ruimtes (twee petri schaaltjes, waarvan de één ongekeerd op de ander, Fig. 1) bleek vooral captan als gevolg van een reactie met cysteine een voor *Fusarium culmorum* toxische damp af te geven, folpet deed dit daarentegen niet, en de twee andere fungiciden alleen in de hoogste concentratie (Tabel 1, Fig. 1). Er is dus weinig verband tussen de fungicide werking en de productie van fungicide dampen als gevolg van de reactie met thiolen.

**References**

Bent, K. J., 1967. Vapour action of fungicides against powdery mildews. Ann. appl. Biol. 60: 251–263.

Hislop, E. C., 1967. Observations on the vapour phase activity of some foliage fungicides. Ann. appl. Biol. 60: 265–279.

Lukens, R. J., Rich, S. and Horsfall, J. G., 1965. Role of the R-group in the fungitoxicity of R-$SCCl_3$ compounds. Phytopathology 55: 658–662.

Moje, W., Munnecke, D. E. and Richardson, L. T., 1964. Carbonyl sulphide, a volatile fungitoxicant from nabam in soil. Nature, Lond. 202: 831–832.

Somers, E., Richmond, D. V. and Pickard, J. A., 1967. Carbonyl sulphide from the decomposition of captan. Nature, Lond. 215: 214.

Weed, R. M., McCallan, S. E. A. and Miller, L. P., 1953. Factors associated with the fungitoxicity of ferbam and nabam. Contr. Boyce Thompson Inst. 17: 299–315.