

30. Organic fungicides – Mode of action-. Dithiocarbamates- characteristics and use of Zineb and Maneb

Dithiocarbamates (Organic sulphur compounds)

Investigations of the DuPont Company (USA) showed that some of the derivatives of dithiocarbamic acid $H_2N-C(=S)SH$ had insecticidal and fungicidal properties. However dithiocarbamic acid itself is not known to exist in the free state. When the primary and secondary aliphatic and aromatic amines are treated with carbon-di-sulphide in alcoholic solutions, dithiocarbamates are produced.

The hydrogen attached to S dissociates and may be replaced by a metal or other radicals producing a variety of derivatives. The group $>NCS$ is considered to be essential for insecticidal and fungicidal action. By reacting dimethylamine and CS_2 under alkaline conditions, Thiram and salts of Na, Fe and Cd were prepared. Nabam was produced by reacting ethylene diamine and CS_2 . Subsequently the heavy metal complexes of dithiocarbamates like Ziram and Ferbam and complexes of bisdithiocarbamates like maneb and zineb were developed.

A large number of derivatives of dithiocarbamic acid possess fungicidal properties. They can be classified as follows.

1. Metallic dithiocarbamates – Ziram and Ferbam
2. Thiuram disulphide (Thiram) –S-S linkage
3. Bis dithiocarbamates – Maneb, Nabam, Zineb

A) Zineb (Dithane-A 78)

Dithane-Z 78 is a white crystalline substance insoluble in water and most organic solvents; moderately soluble in pyridine. It is unstable in the presence of moisture, heat, light and alkali. Moist compound under unfavourable storage conditions may decompose to 50% in a year. To reduce the chance of explosive evolution of CS_2 , Zineb has to be stored in a well ventilated place at low temperatures. It is compatible with most insecticides like Ferbam.

It is formulated as wettable powder. Its residual effect depends on weather and season. Zineb can be of great use on Zn deficient soils.

B) Maneb (Dithane-M 45, Manzate)

It is the manganese salt of ethylene bisdithiocarbamic acid; is similar to zineb, in most physical and chemical properties. Decomposes rapidly under high temperature and moisture. It is a yellow crystalline substance insoluble in water and organic solvents. Compatibility is similar to Ferbam. When stored in bulk, Maneb is capable of

spontaneous decomposition with charring which can be avoided by diluting with an inert material. Other analogues are Dithane C-31, Propineb, Thioneb (carbathene).

Thiram as tetra methyl thiuram disulphide was the first compound to be applied as a fungicide and is still used, especially against moulds and as a seed dressing against soil fungi causing damping off. Thiram is prepared by the interaction of carbon disulphide and dimethylamine in the presence of NaOH which is subsequently oxidized to thiram.

Later work resulted in the discovery of the fungicidal activity of zinc and ferric salts of dimethyl dithiocarbamates known as ziram and ferbam respectively. Disodium ethylene bis dithiocarbamate or nabum is also fungicidal and is used to control stem rots. **Nabum** is the insoluble zinc and manganese salts known as zineb and maneb which are produced by reaction with an aqueous solution of zinc and manganese sulphate have largely replaced water soluble. These are used as protectant fungicides and are applied for the control of wide range of phyto pathogenic fungi such as downy mildews. They have very low mammalian toxicities ($LD_{50} > 7000 \text{ mg kg}^{-1}$).

Metham-sodium (N- methyl dithiocarbamate) is a valuable soil sterilant for the control of damping off diseases.

Mancozeb, a coordinated complex of zinc and manganous salts was introduced in 1962. Maneb and mancozeb are formulated with synthetic fungicides to reduce development of resistance.

The dithiocarbamates owe their fungicidal activity due to their ability to chelate with metal cations such as copper. The dithiocarbamates get metabolized to isothio cyanates which react with vital thiol compounds with in the fungal cell.

Heterocyclic N compounds

Captan (N-(trichloromethylthio)-4-cyclohexane-1,2-dicarboximide) is a very effective and persistent foliage fungicide against many soil and seed borne diseases. Analogues that have been subsequently developed as foliar fungicides include folpet and difolatan, which are most active against potato blight. These are some of the safest fungicides ($LD_{50} > 10000 \text{ mg kg}^{-1}$).

Captan interacts with cellular thiols to produce thiophosgene which poison the fungus.

Dichlofluanid, introduced by Bayer is a broad spectrum protective fungicide which is less sensitive than captan.

Phenols

The majority of phenols, especially those containing chlorine, are toxic to microorganisms, their bacterial action has been known for along time and many phenols are also fungicidal. However many are phytotoxic.

Shirlan or salicylanilide is used to inhibit the growth of moulds on cotton and against a number of leaf diseases as tomato mould.

Dinocap is a non systemic aphicide and contact fungicide which is effective for the control of powdery mildew on many horticultural crops. Low mammalian toxicity $LD_{50} > 980 \text{ mg kg}^{-1}$.

Binapacryl is closely related to dinocap and is used for the control of powdery mildew on apples.

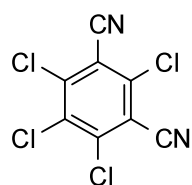
Oxine α -hydroxy quinoline is a protectant fungicide, when suitably formulated, appears to possess limited systemic action. Oxine has a striking capacity to form chelates with metals (Cu) which is effective against a range of phytopathogenic fungi.

Chlorobenzenes and related compounds

2,6-dichloro-4-nitro aniline was marketed in 1959 by Boots Ltd. Especially valuable for the control of Botrytis in tomatoes and against fungal organisms causing post harvest decay of fruits.

Penta chloro nitro benzene (PCNB) called quintazene is a widely used soil fungicide for damping off diseases. Chloroneb is used to control soil borne fungi as seed dressings or by soil application.

Chlorothalonil is a broad spectrum foliar or soil applied fungicide used in many crops. Sandoz kavach.



Chlorothalonil

Quinones

A number of quinines occur in plants and are also products of fungal metabolism.

Dichlone is more stable in light has been used as a seed dressing agent and a foliage spray against powdery mildew.

Dodine (N-dodecyl guanidine acetate) has been known as a bactericide (1941) and more recently has been shown to have fungicidal activity. Dodine is a cationic surfactant is generally formulated as wettable powder. Low mammalian Toxicity ($LD_{50} > 1500 \text{ mg kg}^{-1}$).

Guazatine is mainly used as seed dressing agent for cereals at $0.6 - 0.8 \text{ g ai kg}^{-1}$ of seed and against post harvest diseases. ($LD_{50} > 500 \text{ mg kg}^{-1}$). The fungicidal activity of these compounds probably depend on their ability to alter the permeability of the fungal cell wall, causing loss of vital cellular components such as amino acids and P compounds.

Dicarboximides

All members contain the 3,5-dichlorophenyl moiety and the fungicidal activity depends on the presence of the two chlorine atoms in 3, 5 positions.

Procymidone, hydantoin, iporodione and **vinclozolin** have been extensively used for the control of *Botrytis* and *Scelrotinia* sp in cereals, fruits and vegetables but their use is restricted due to the development of resistance.

More recently **metomedan, chlozolate** and **myclozoline** have been introduced.

Drazoxolon (ICI,1960) is a valuable seed dressing agent against damping off diseases.

The dicarboximides have low mammalian toxicities ($LD_{50} > 3500 \text{ mg kg}^{-1}$).