XXX. Heterocyclic compounds with three heteroatoms in the ring

General characteristics of pesticidal properties

Among heterocyclic compounds with three atoms of nitrogen, nitrogen and sulfur, or nitrogen and oxygen in the ring a number of effective materials have been found, and some of them are used in agriculture.

The five-membered heterocyclic compounds (derivatives of triazole, thiadiazole, and tetrazole, and also the corresponding benzo derivatives) are more active toward the lower and higher plants than toward insects and mites, and they, therefore, are used mainly as herbicides or fungicides. Even some organic compounds of phosphorus that contain heterocyclic radicals have predominantly fungicidal, and not insecticidal, activity. An example of such compounds is 5-amino-3-phenyl-1,2,4-triazolyl-1-bis(dimethylamido)phosphate (Wepsin) (I) (m.p. 164°–168° C., LD_{50} for rats 10–20 mg. per kg.):

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{N} & \quad \text{O} \\
\text{(CH}_3\text{)}_2\text{N} & \quad \text{NH}_2 \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\end{align*}
\]

(1)

It has been proposed for use in the control of fungous diseases of roses and powdery mildew of apple. Wepsin also shows slight acaricidal effect, but its fungicidal activity is considerably weaker.

3-Amino-1,2,4-triazole (amitrole) shows high herbicidal activity and is used to control weeds either independently or mixed with various other compounds.

Benzotriazole has interesting physiological activity. When it enters a plant through the root system, it changes the shape of the leaves (formative effect). The quaternary dialkylbenzotriazolium salts are characterized by high physiological activity for plants, and also by fungicidal and bactericidal effects. The most effective in this respect is dioctylbenzotriazolium chloride (or bromide) (II):
Compounds of this type are easily produced by prolonged heating of benzo-triazole with alkyl halides.

High fungicidal and bactericidal activities are characteristic of the quaternary salts of tetrazole and other similar compounds containing a hydrocarbon radical with 7-16 carbon atoms on a nitrogen. Higher molecular compounds are inactive. However, all these compounds are toxic to man and animals and show a curare-like effect.

Six-membered heterocyclic compounds are used as fungicides, herbicides, and soil sterilants. Of the group of six-membered heterocyclic compounds, derivatives of symmetrical triazine are used to control weeds in a great variety of agricultural crops. Since this group of compounds is very important, they are considered below in more detail.

Some use has been made also of derivatives of tetrahydrothiazine (III):

In the series of heterocyclic compounds with a seven-membered ring, endosulfan (Thiodan) (IV), a cyclic ester of sulfurous acid, is used in agriculture:

3-Amino-1,2,4-triazole (aminotriazole) and its derivatives

3-Amino-1,2,4-triazole (amitrole, aminotriazole) is a white crystalline substance, m.p. 159° C. At 23° C. 28 g. of the compound dissolves in 100 ml. of water; at 75° C. 26 g. dissolves in 100 ml. of ethyl alcohol. It is almost insoluble in ether and acetone. It is physiologically active toward plants. It is used as a herbicide, defoliant, and plant growth regulator. Amitrole forms stable salts with acids. Compounds of it with some metals and their salts also have been described.

It is resistant to hydrolysis and the action of oxidizing agents, but enters readily into condensation reactions, for example with aldehydes, ketones,