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PYRAZOLE DERIVATIVES

PYRAZOLES FOR USE AS PESTICIDES

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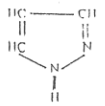
ABSTRACT

The paper gives a brief review of the synthesis of pyrazole derivatives used as pesticides. The compounds were studied mostly against agricultural pests except a few which were evaluated for housefly, mites, spider etc. which are building pests. There is good scope to explore the possibility to evaluate them for termites and cockroaches also.

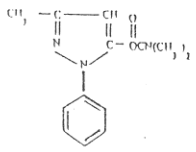
The pyrazole ring system consists of a doubly unsaturated five membered heterocyclic ring with two adjacent nitrogen atoms [I].



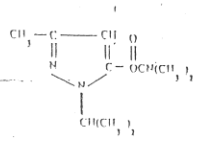
[I]

The biological activity of pyrazole is dependent upon pH and is maximum at pKa 4.0 - 7.0 (Horakova and Nemeck, 1958). Further, it also depends upon an enolizable C_4-H which is proved by the fact that the replacement of C_4-H by C_4-CH_3 results in loss of activity (Muratova and Zaharm, 1971).

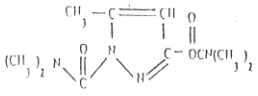
The first pyrazole was synthesised by Knoor (1883) and since then thousands of such compounds are synthesised and studied for their pesticidal and pharmaceutical activities. The common pesticides containing pyrazole ring are PYROLAN [II] or G-22008 [3-Methyl-1-phenyl-5-pyrazole dimethylcarbamate], ISOLANE [III] [1-isopropyl-3-methyl-5-pyrazole dimethylcarbamate], DIMETILAN [IV] [1-(dimethylcarbamoyl) - 5 - methyl - 3 - pyrazole dimethylcarbamate] and PYRAZOTHION [V] diethyl-3-methylpyrazole-5-ylphosphorothionate]. The above compounds were found active against aphids, bedbugs, flies in barns, stables and spider mites. They have rapid knockdown action on houseflies as studied by Morifusa Eto (1974) and Fumio Matsumora (1985).



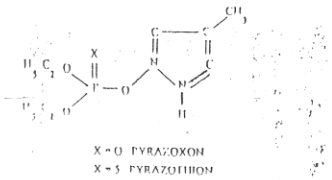
[II]



[III]



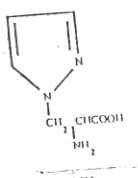
[IV]



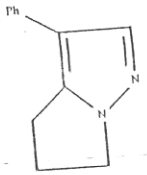
X = O PYRAZOXON
X = S PYRAZOTHION

[V]

Pyrazole derivatives normally do not occur in nature probably because of the difficulty in constructing an N-N bond by living organisms. However Kosuge *et al* (1959) isolated first natural pyrazole derivatives, 3-n-nonyl pyrazole from *Houttuynia cordate*, a plant of the piperaceae family found in tropical Asia which is inhibiting the growth of *Aspergillus niger*. Further, Noe and Fowden (1960) isolated ß-[pyrazolyl-N¹] alanine [VI] from watermelon seeds. Schorter and Neumann (1966) reported to have extracted with somanine, i.e., 4-phenyl-1,-5-trimethylene pyrazole [VII] from plant sources.



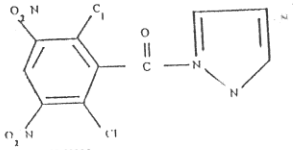
[VI]



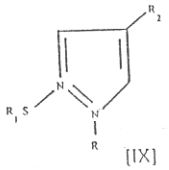
[VII]

The present paper gives a brief review of pyrazoles synthesised recently having pesticidal activity and also their scope in control of building pests.

Erik and coworkers (1982) synthesised 2,6-dichloro-3,5-dinitro-1-benzoyl pyrazole [VIII] and Anderson (1982) synthesised 3-aryl or heteroaryl - 5- mercapto substituted - 1- alkyl or arylpyrazoles [IX]. The compounds have been reported to possess fungicidal and pesticidal properties repectively.

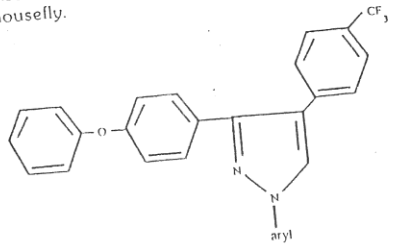


[VIII]



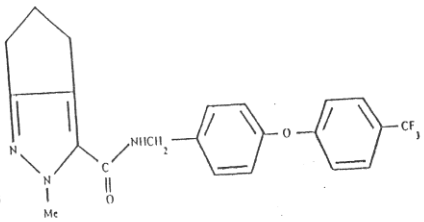
[IX]

Kitazima *et al* (1987) synthesised [N¹-Aryl-3-(aryloxy-aryl)-4-(trifluoromethylphenyl) pyrazoline [X] which demonstrated total effectiveness against insects such as tobacco cutworm, moth and housefly.



[X]

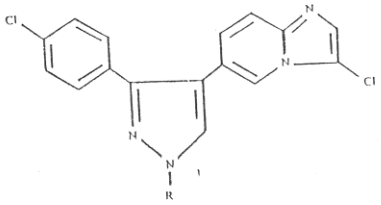
Okada and co-workers (1990) prepared carbamoyl pyrazole as miticide by the amidation of 2-methylcyclopentane (1,2-c) pyrazole-3-carboxylic acid with 4-(4-trifluromethylphenoxy) benzylamine [XI]. It was 100% active against *Tetranychus urticae*.



[XI]

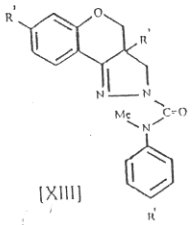
Minamida *et al* (1994) prepared a compound by dissolving 3-chloro-6-(4-chlorobenzoylmethyl) imidazo [1,2-a]pyridine in methyl alcohol followed by adding acetic acid, piperidine and formaldehyde. The resulting mixture was refluxed for 2 hours with stirring to give 1-(4-chlorophenyl)-2-(3-chloroimidazo [1,2-a]pyridine-6-yl)-2-propene-1-one. It was refluxed with hydrazine hydrate in ethyl alcohol to give 2- pyrazoline derivative [XII]. The compound was 100% effective at 100 ppm concentration to kill larvae of *Spodoptera litura* when sprayed in soybean

leaves.



[XII]

Barnette *et al* (1996) prepared benzopyranopyrazole [XIII] which exhibited more than 80% mortality against tobacco budworm, southern corn rootworm, aster leafhopper and bollweevil.



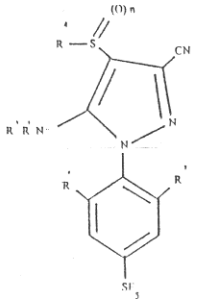
[XIII]

R^1 = Cl, Br, CF_3

R^2 = H, halo, CF_3

R^3 = CO_2Me,CO_2Et

Pilato and coworkers (1997) prepared a compound [XIV] which showed LC_{50} at less than 10 ppm concentration on cotton leaf aphid.



[XIV]

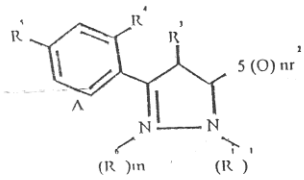
R^1 = R^3 = H, lower alkyl, alkenyl

R^2 = R^6 = H, halo, cyano

R^4 = lower alkyl

n = 1-2

Yoshnori *et al* (1997) synthesised pyrazole derivatives [XV] having low toxicity and low persistent but extremely high insecticidal property.



[XV]

A = CH

R^1 = H, lower alkyl, phenyl,

R^2 = haloalkyl, alkenyl,

R^3 = cyano,nitro,amino,

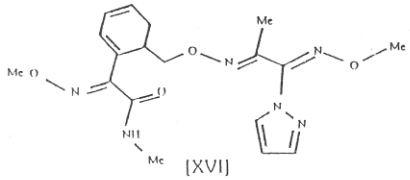
R^4 = halo,

R^5 = lower haloalkyl,

R^6 = haloalkyl, benzyl,

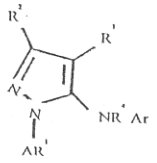
m = 0-1, n = 0-2

Herbert and coworkers (1997) synthesised a compound [XVI]. They found that in a protective test against *Erysipne graminis varetritici* on wheat seedlings, it could reduce infection upto 70%.



[XVI]

Heil *et al.* (1997) synthesised a new compound by stirring 5-amino-1-cyclohexyl - 3,4-dicyanopyrazole with sodiumhydride in dimethyl formamide followed by treatment with 1-fluoro-2,6-dichloro-4-trifluoromethylbenzene in dimethylformamide for 1 hour, at 60°C. It gave 56% yield of N-(1-Cyclohexyl-3,4-dicyanopyrazole-5-yl)-2,6-dichloro-4-trifluoromethylaniline [XVII]. it was reported that at 0.1% concentration the compound gave 100% mortality to *Plutella maculipennis* on cabbage leaves.



[XVII]

R^1 = cycloalkyl, cycloalkenyl

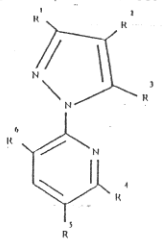
R^2 = R^3 = halo, cyano, nitro, heteroaryl,

R^4 = alkyl, alkenyl, aryloxy,

A = Bond (substituted)alkylene,

Ar = (Substituted)Ph, pyridyl

Bank and Joseph (1997) reported to have prepared parasitical pyrazole derivatives [XVIII] which are useful against arthopodes, nematodes, helminths, and protozoa. They may also have antifeeding or repellent effect on insects.



[XVIII]

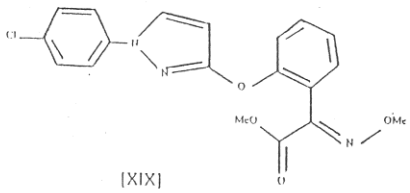
R^1 = cyano, nitro, (halo) phenyl,

R^2 = (un)substituted ethenyl, ethynyl,

R^3 = halo, alkyl, alcohal, thioalcohal

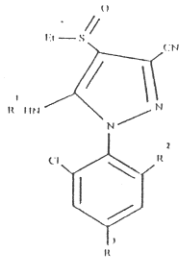
R^4 = R^5 = R^6 = H, Halo, Cyano, Amide, Thioamide

Kirstgen *et al.* (1997) prepared a series of compounds in the form of 2-(pyrazolyloxy) phenylglyoxylates [XIX]. The compounds have fungicidal and pesticidal properties. These compounds are prepared by etherifying 1-(4-chlorophenyl)-3-hydroxy pyrazole with 2-fluorobenzoyl-methylformate and the product condensed with methylhydroxylamine.



[XIX]

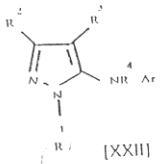
Haas and co-workers (1997) synthesised 5-amino -1-aryl-3-cyano-4-ethylsulfinyl pyrazoles which behaved as pesticides by the reaction of 5-amino 3-cyano-1-(2,6-dichloro-4-trifluoro methyl)-4-ethylthiopyrazole with Hydrogen peroxide to give final compound [XX].



[XX]

Akiyama and coworkers (1997) had prepared pyrazoline derivatives [XXI] as pesticides which at 500 ppm concentration showed fungicidal effect for *Pyricularia oryzae*.

Similarly Heil *et al.* (1997) synthesised another compound [XXII] which at 0.1% concentration gave 80% control of phaedon *Cochlearine larva* upto 7 days on cabbage leaves.



[XXII]

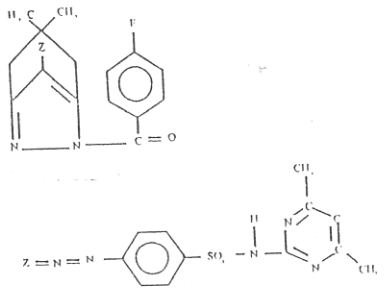
R^1 = H, alkyl, aryl,

R^2 = R^3, = H, halo, cyano, nitro.

R^4 = alkyl, aryloxy, alkenyl,

Ar = Tetra or Penta substitutedphenyl.

Recently Nayal (1997 has synthesised bicyclic heterocyclic pyrazoles such as N_1- (4-fluorobenzoyl)-5, 5'-dimethyl cyclohexane - 4-(sulpha/substituted phenylazo) -1,2-diazole [XXIII]. Preliminary investigation revealed that some of the derivatives have pesticidal and fungicidal activities.



[XXIII]

SCOPE IN BUILDINGS

Till recently Cyclodine hydrocarbons such as Aldrin, Chlordane and Heptachlor were being used to control subterranean termites in buildings. They are banned globally due to their highly toxic and environmental persistent character. The present review of literature reveals that several synthetic pyrazole derivatives were active to control agricultural pests. A few compounds were also able to control housefly, spider and mites, etc.. No work seems to have been done, to explore the possibility to study the activity of such compounds against building pests like termites and cockroaches in detail. Recently, systematic research work has been started in this institute to synthesize different bicyclic heterocyclic pyrazole derivatives to investigate them for controlling building pests.

CONCLUSION

The foregoing review of literature reveals that pyrazole and their analogues recently synthesised have been studied for their pesticidal activity. It is worthwhile to investigate them in controlling building pests such as termites, rats, cockroaches, etc. as alternative to highly toxic pesticides.

ACKNOWLEDGEMENT

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KISAN KENDRA LAUNCHED

The Minister for Chemicals and Fertilizers recently launched the Kisan Kendra set up by the Tata Chemicals Ltd. at Ujhani in Badsun district of Uttar Pradesh.

A news release said the Kisan Kendra is a one shelter stop for farmers to access all agricultural inputs, like seeds, pesticides and agricultural implements. The kendra would also provide agro services like soil testing and consultancy. While inaugurating the Kisan Kendra scheme, the minister lauded the efforts of Tata Chemicals to promote the efficient use of fertilizers where the returns from farms have been diminishing.