Pesticidal Activities of Some Pyrazole Derivatives

Ahmed S. Abdel-Aty
Pesticide Chemistry Dept., Faculty of Agriculture, Alexandria University, Egypt

ABSTRACT

Four compounds of pyrazole derivatives: 3,5-dimethylpyrazole (**1**), 1-Benzoyl-3,5-dimethylpyrazole (**2**), 3-methyl-1-phenylpyrazol-5-one (**3**) and 3-methyl-1-(2,4-dinitrophenyl)-pyrazol-5-one (**4**) were prepared, identified by measuring their melting points, NMR and Mass spectroscopy measurements. These compounds were tested for their fungicidal activity against *Fusarium calmorum*; *Pythium debarianum*, *Rhizoctonia solani* and *Macrofomina phaseoli* comparing with Metalaxyl (Radomil) as a standard fungicide, phytocidal effects on both wheat (*Triticum aestivum*) and squash (*Cucurbita pepo*) seedlings in comparison to Metribuzin (Sencor) as a standard herbicide and insecticidal activity using *Spodoptra littoralis* (Boisid). Pyrazolone derivatives; 3-Methyl-1-phenylpyrazol-5-one (**3**) and 3-methyl-1-(2,4-dinitro-phenyl)pyrazol-5-one (**4**) were more effective than others exceeding the used standard fungicide on *R. solani*, *P. debarianum* and *M. phaseoli*. 3-Methyl-1-(2,4-dinitro-phenyl)pyrazol-5-one (**4**) overcame the standard herbicide in its phytocidal effects, while the other compounds were less effective or nearly equal to the standard herbicide against wheat and squash seedlings.

INTRODUCTION

Several derivatives of nitrogen containing compounds have been using for biological activity. Amitrol (3-amino-1,2,4-triazole) was used as a herbicide, Hostathion (Triazophos) as insecticides in addition to several structurally related 1,2,4-triazoles, which were effective against powdery mildews, rusts. Propiconazol (Tilt); Etaconazole as fungicides (Quinn *et al.*, 1985). Analgesic, antiinflamatory, diuretic and antihypertensive activities were exhibited by some benzimidazole and benzotriazole derivatives (Boido *et al.*, 1989). Their nitro derivatives showed slight activity on *Entamoeba histolytica* and *Trichomona* (Goma *et al.*, 1991). Some of 3,5-dimethylpyrazole derivatives as ethyl-2-[(3,5-dimethylpyrazol-4-yl) hydrazono]-3-oxobutyrate and ethyl-2-[(3,5-dimethylpyrazol-4-yl)hydrazono]-4-methoxy-3-oxobutyrate showed antituberculosis activity with 29 and 28% inhibition against *Mycobacterium tuberculosis*, respectively (Kocyi *et al*, 2002). So, some pyrazole derivatives: 3,5-dimethylpyrazole (**1**), 1-Benzoyl-3,5-dimethylpyrazole (**2**), 3-methyl-1-phenylpyrazol-5-one (**3**) and 3-methyl-1-(2,4-dinitrophenyl)-pyrazol-5-one (**4**) were prepared and structurally confirmed by melting points, NMR and Mass spectroscopy measurements. These compounds were studied for

their fungicidal effects against some economically important fungi, *Fusarium oxysporum*; *Pythium debarianum* and *Rhizoctonia solani* that cause welt the damping-off disease of tomato and cotton as well as against *Macrofomina phaseoli,* which causes charcoal rot of bean, winter rape, sesame, saffron, squash, cotton, potato, sorghum and cucumber. The technical grade of metalaxyl (Radomil), methyl- N-(2,6-dimethylphenyl-N-methoxyacetyl)-DL-alaninate (**6**) was used as a standard fungicide. Their phytocidal effects were determined on both wheat (*Triticum aestivum*) and squash (*Cucurbita pepo*) seedlings comparing with metribuzin (sencor), 4-amino-6-tert.butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one (**5**). The insecticidal effects were also evaluated on the 4th instar of cotton leaf worm, *Spodoptera littoralis* (Boisid.).

MATERIALS AND METHODS

I- Preparation and Identification of The Tested Compounds:

Melting points were determined on kofler block and were uncorrected. Both NMR and Mass spectroscopy were carried out in Micro analytical Center, Cairo University, Giza, ARE. The NMR spectra were recorded on Varian Mercury-VX-300 NMR Spectrometer using tetra methyl silane (TMS) as a standard. Mass spectra were recorded on a Schimadzu MS5988-mass spectrometer at 70 ev. These compounds were prepared according to Vogel (1976) with some modifications as follows:

3,5-Dimethylpyrazole (1):

In a 500 ml flat-bottomed flask, 32.5 gm (0.25 mole) of hydrazine sulfate was dissolved in 2.5 M sodium hydroxide solution and stirred at 15°C with a magnetic stirrer. Pentan-2,4-dione (26 ml, 25 gm, 0.25 mole) was added drop-wisely within 30 minutes with stirring and the reaction mixture was further stirred for an hour at 15°C. The inorganic salts were dissolved in 100 ml of water and filtered off. Pale yellow precipitate was filtered, washed with water and dried under vacuum over sodium hydroxide to give 16.5 gm (69%). Recrystallization from an equal mixture of ethyl acetate and petroleum ether (30-40) gave the pure pale yellow 3,5-dimethylpyrazole (**1**) with melting point 107.5-108°C (Ref. 107-108°C) (Vogel, 1976). **^{1}H NMR (DMSO-d_6):** δ 2.13 (3H, s, C_3-CH_3), δ 2.2 (3H, s, C_5-CH_3), δ 5.74 (C_4- H) and δ12.04 (1H, s, N-H). **EI-MS:** Molecular ion (M^+) at m/z 96 (15.77) was fragmented to fragments at m/z 95 (16.16), 81 (22.91), 67 (9.14), 66 (31.28), 65 (62.6), 63 (100), 54 (46.79) and 52 (70.40).

1-Benzoyl-3,5-dimethylpyrazole (2):

The prepared 3,5-dimethylpyrazole (I) (3 gm, 0.31 mole) was dissolved in 150 ml of 10% aqueous sodium hydroxide solution with shaking at room temperature. Benzoyl chloride (5.39 gm, 4.5 ml, 0.0385 mole) was added in five portions in 30 minutes to the solution with vigorous shaking (Benson *et al.*, 1952). Concentrated hydrochloric acid was dropped to the cooled reaction mixture with stirring until separating the product as off white crystals. The yield was dried over phosphorus pentoxide (P_2O_5) to 3.13 gm (47.5 %). Recrystallization from 95% aqueous ethanol gave the pure 1-benzoyl-3,5-dimethylpyrazole (2) as an off-white amorphous crystalline powder with melting point 122.5-123°C. **^{1}H NMR (DMSO-d_6):** δ 7.57 (3H, s, C_3-CH_3), 7.59 (3H, s, C_5-CH_3), δ 7.47 (1H, s, C_4-H) and δ 7.95 (5H, m, Ph). **EI-MS:** Molecular ion (M^+) was fragmented to fragments at m/z 123 (3.65), 122 (40.41), 105 (55.82), 78 (9.0), 77 (100), 74 (28.12) 66 (4.21), 53 (13.54) and 51 (57.74).

3-Methyl-1-phenylpyrazol-5-one (3):

In a porcelain evaporating dish, a mixture of ethyl acetoacetate (50 gm, 49 ml, 0.384 mole) and 40 gm (36.5 ml, 0.37 mole) of phenyl hydrazine was placed. The reaction mixture was heated on a boiling water bath for two hours in the fume cupboard with stirring by a glass rod and left overnight at room temperature, heavy syrup appeared. Diethylether (100 ml) was added with vigorous stirring to separate the insoluble product as a precipitate. The product was filtered under vacuum and washed with ether to remove the colored impurities to give 51.71 gm (79.6%) of yellow powder that was recrystallized from 80% aqueous ethanol (10 ml/gm) to the pure compound with melting point 127.5-128°C. (ref.127°C). **^{1}H NMR (DMSO-d_6):** δ 2.05 (3H, s, 3-CH_3), δ 5.35 (1H, s, 4-H), δ 11.39 (1H, s, N-H) and aromatic protons at δ 7.68 (2H, d, *ortho*-2H, J = 10.3 Hz), δ 7.34 (1H, d, *para*-H, J = 10.3 Hz) and δ 7.41 (2H, dd, *meta*-2H, J = 8.33, 2.0 Hz). **EI-MS:** m/z 175 (8.47) ($M+1^+$), 174 (73.45) (M^+), 159 (4.44), 132 (7.14), 105 (28.48), 91 (63.09), 78(14.39), 77 (100), 64 (20.08), 52 (10.32) and 51(51.04).

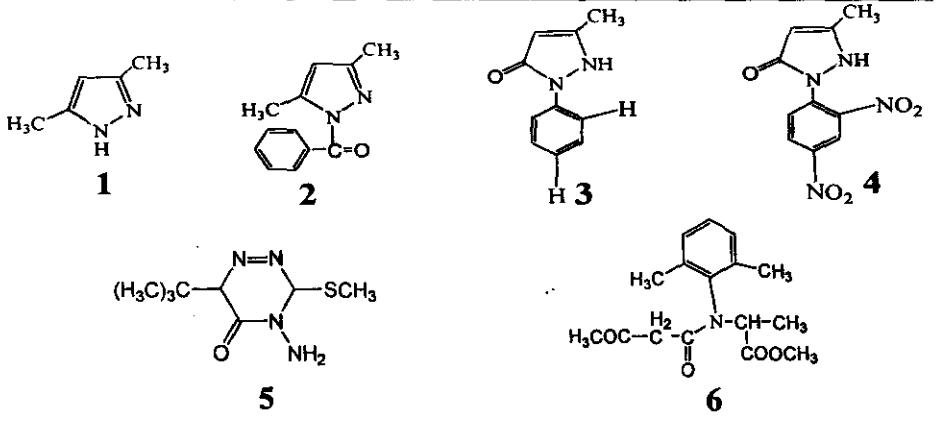

Figure (1): Chemical structures of the prepared compounds and the used standard pesticides

3-Methyl-1-(2,4-dinitrophenyl)pyrazol-5-one (4):

10 gm (0.07 mole) of 2,4-dinitrophenylhydrazine and 10.95 gm (10 ml, 0.098 mole) of ethyl acetoacetate were mixed in an evaporating dish and heated whilst stirring as in case of compound **3**. The product was separated as yellow hygroscopic crystals (11.2 gm, 85.2 %), recrystallized from ethylacetate and washed with diethyl-ether three times to produce the pure yellow crystalline powder with melting point 78-80°C. **^{1}H NMR (DMSO-d_6):** δ 3.2 (1H, s, C4-H), δ 1.23 (3H, t, C3-CH_3) and aromatic protons at δ 8.4 (1H, dd, C3-H, J = 10.33 Hz), δ 7.82 (1H, dd, C5-H, J = 10.33) and δ 8.5 (1H, d, C6-H, J = 3.0 Hz). **EI-MS:** m/z 265 (15.10) ($M+1^+$), 264 (15.93) (M^+), 237 (40.03), 219 (81.35), 196 (53.85), 190 (36.89), 165 (26.17), 152 (23.87), 145 (26.87), 122 (56.54), 116 (62.60), 104 (57.77), 92 (30.14), 85 (50.06), 77 (100), 63 (69.44), 54 (28.73) and 51 (40.40).

II- Fungitoxic Effects Measurements:

The pathogenic fungi were grown on Czapeck-Dox medium for seven days, before using in the tests. Measurements were carried out using radial growth test according to the conventional method reviewed by Torgeson (1967). A definite volume of the well-known Czapek-Dox medium (12 ml) containing agar (4.5 gm/100 ml water) was sterilized in conical flasks. Citrate-Phosphate buffer solution (3 ml) was separately autoclaved; both solutions were mixed in the conical flask. The tested compounds in dimethylsulfoxide (DMSO) were added at 10, 100, 200, 500 and 1000 ppm. The contents of each flask (36 ml) were distributed in three sterilized petri-

dishes and considered as one treatment. The additions were done under sterile conditions. After solidification, the inoculum disc (7 mm in diameter) of each tested fungus was located in the center of the petri-dish. Control in the presence of the calculated volume of dimethylsulfoxide only to be 1 % as its final concentration was concurrently conducted. The results were recorded by measuring the diameter of the hyphal growth in each petri-dish at fixed intervals to see the effect of exposure time on the activity, and when the growth of the untreated fungi completely covered the surface of petri-dish, the treatments were measured. The inhibition percent of the hyphal growth were calculated according to Topps and Wain formula (1957). IC_{50} values as ppm (the effective concentration caused 50% inhibition in the hyphal growth) were determined for each compound and using probit analysis method (Finney, 1971).

III- Phytocidal Effects of The Tested Compounds:

The phytocidal effects of the prepared compounds were tested against wheat seedlings (*Triticum aestivum*) and squash seedlings (*Cucurbita pepo*) by using the plain agar (1%) technique according to Zemanek, (1963). The tested concentrations were 10, 20, 50, 100, 200, 500, 1000 and 2000 ppm. Pre-germinated seeds were sown in the solidified treated agar in three replicates for each treatment. Control was conducted at the same conditions. The test tubes were watered with a constant volume and kept until the roots reach the bottom of a tube. The length of both the root and shoot systems were measured and inhibition percentages were calculated. IC_{50} values were recorded on a semi-log paper sheet and compared with that caused by the used standard herbicide.

IV- Insecticidal Effect on *Spodoptra littoralis*:

A laboratory cotton leaf worm strain *Spodoptra littoralis* (Boisid), Lepidoptera was reared on castor bean leaves according to Eldefrawi *et al.* (1964). Sixty larvae (in the 4^{th} instar) were treated in three replicates for each treatment at 50, 100, 500, 1000, 2000 and 4000 ppm using the leaf dipping technique (Kubo and Nakanishi, 1977). The castor bean leaves were cut into equivalent circles and immersed in the tested solutions for 30 seconds and dried before introducing to insects in plastic pots. The experiment was carried out at 25 ± 2 °C and 70% relative humidity. Control was done under the same conditions. After 24 hours, both mortality percent and palatability of each compound were calculated by comparing the

average consumed food of each larva in control and treatment based on Abivandl and Benz (1984):

$$\% P = 100 \times (T / C)$$

where:

P: palatability C: consumed food/control larva T: consumed food/treated larva

RESULTS AND DISCUSSION

I- Fungitoxic Effects of The Tested Compounds:

The toxic effect of the tested compounds on fungi as IC_{50} values was recorded in Table (1). It illustrated that comparing with the used standard fungicide, metalaxyl (Radomil) it was found that *Rhizoctonia solani* was less affected with the tested compounds than the other fungi. 3,5-Dimethylpyrazole (**1**) proved to be moderately toxic with IC_{50} values = 470, 380 and 330 ppm against *Pythium debarianum*, *Fusarium calmorum* and *Macrofomina phaseoli*, respectively after 6 days exposure, whereas 1-benzoyl-3,5-dimethylpyrazole (**2**) reduced the activity against all the tested fungi and 3-methyl-1-phenylpyrazol-5-one (**3**) enhanced the activity against *R. solani* with IC_{50} value = 155 ppm after 4 days exposure, *P. debarianum* and *M. phaseoli* with IC_{50} values = 68 and 170 ppm after 6 days exposure, respectively whereas it was inactive on *F. calmorum* as its IC_{50} was >500 ppm. On the other hand, 3-methyl-1-(2,4-dinitrophenyl)pyrazol-5-one (**4**) caused the toxic effect against *R. solani*, *F. calmorum* and *M. phaseoli* with 100, 440 and 140 ppm IC_{50} values, respectively after the same exposure time. From the previous results, it was found that some of the prepared compounds exceeded the standard fungicide in their effects against the tested fungi under the used experimental conditions.

II- Phytocidal Effects of The Tested Compounds:

The toxic effects of the tested compounds on root and shoot systems of wheat and squash seedlings were increased with increasing the concentration Table (2). The activity of 3,5-dimethylpyrazole (1) was decreased on wheat shoot system by substitution with 1-benzoyl moiety as its IC_{50} values changed from 190 to 380 ppm, whereas it reduced the inhibitory effect on the root system by IC_{50} values from 230 to 120 ppm. Although 3-methyl-1-phenyl pyrazol-5-one (3) was less effective with IC_{50} values 480 and 135 ppm on shoot and root systems, its toxicity was raised by introducing with 2,4-dinitro moiety in 3-methyl-1-(2,4-dinitro-phenyl)pyrazol-5-one (4) with IC_{50} values 45 and 58 ppm, exceeding the

used standard herbicide, metribuzin (sencor) that gave 52 and 86 ppm in case of wheat and squash seedlings. The standard herbicide was found to be less effective than the tested compounds on the squash shoot system. The tested compounds were nearly equal in their effects to the standard herbicide on squash root system.

III- Insecticidal Effects of The Tested Compounds:

The insecticidal effects of the tested compounds was recorded Table (3). Pyrazole derivative was inactive, its activity slightly increased to 10% mortality by substitution of the 1-benzoyl- moiety. The effect became 23% mortality with reduction of palatability to 8.5-50 % of control in case of phenylpyrazol-5-one in non-systematic arrangement. Substitution of phenyl with 2,4-dinitrophenyl- moiety decreased the activity to 14 % mortality and 50-67 % palatability.

From the mentioned results, although these compounds exhibited weak lethal activity, they inhibited the tested insect palatability. They exhibited moderate to high fungitoxic and phytotoxic effects according to the chemical structure, treated fungus and the tested plant seedlings. Pyrazolone derivatives; 3-Methyl-1-phenylpyrazol-5-one **(3)** and 3-methyl-1-(2,4-dinitro-phenyl)pyrazol-5-one **(4)** appeared more effective than the other tested derivatives exceeding the used standard fungicide on *R. solani*, *P. debarianum* and *M. phaseoli.* The standard herbicide, metribuzin (sencor) **(5)** was overcame by 3-methyl-1-(2,4-dinitro-phenyl)-pyrazol-5-one **(4)** in its phytocidal effect on both the two plants seedlings, while the other tested compounds were less effective or nearly equal the standard herbicide against wheat and squash seedlings.

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Table (1): Effect of The Tested Compounds on *R. solani*, *P. debarianum*, *F. calmorum* and *M. phaseoli*; Shown as IC_{50} (ppm) Values at Different Times (Days).

Compounds	*R. solani*		*P. debarianum*		*F. calmorum*		*M. phaseoli*	
	2	4	4	6	4	6	4	6
3,5-Dimethyl pyrazole (1)	>500	>500	450	470	370	380	170	330
1-Benzoyl-3,5-dimethyl pyrazole (2)	>500	>500	>500	>500	>500	>500	>500	>500
3-Methyl-1-phenyl pyrazol-5-one (3)	165	155	88	68	>500	>500	180	170
3-Methyl-1-(2,4-dinitro-phenyl) pyrazol-5-one (4)	40	100	160	140	270	440	88	140
Metalaxyl (Radomil) (6)	130	>500	340	355	49	140	175	220

Table (2): Phytocidal Effects of The Tested Compounds on Root and Shoot Systems of Wheat (*Triticum aestivum*) and Squash (*Cucurbita pepo*) Seedlings, Shown as IC_{50} Values.

Compound	IC_{50} values (ppm)			
	Triticum aestivum		*Cucurbita pepo*	
	shoot	root	shoot	root
3,5-Dimethyl pyrazole (1)	190	230	38	95
1-Benzoyl-3,5-dimethyl pyrazole (2)	380	120	90	109
3-Methyl-1-phenyl pyrazol-5-one (3)	480	135	60	95
3-Methyl-1-(2,4-dinitro-phenyl) pyrazol-5-one (4)	250	45	78	58
Sencor (5)	81	52	115	86

Table (3): Insecticidal Activity of The Tested Compounds Against *Spodoptera littoralis*; Shown as mortality% (A) and palatability% (B)

Compound	Effect %	Concentration (ppm)							LC_{50}
		0	50	100	500	1000	2000	4000	
3,5-Dimethyl pyrazole (1)	A	0	0	0	0	0	0	0	> 4000
	B	100	142	138	133	125	120	117	
1-Benzoyl-3,5-dimethyl pyrazole (2)	A	0	0	0	3	7	7	10	> 4000
	B	100	-	66	83	100	103	108	
3-Methyl-1-phenyl pyrazol-5-one (3)	A	0	0	0	3	7	14	23	> 4000
	B	100	50	8.3	20	25	30	48	
3-Methyl-1-(2,4-dinitro-phenyl) pyrazol-5-one (4)	A	0	0	0	0	7	10	14	> 4000
	B	100	67	67	50	58	58	67	

الملخص العربى

النشاط الابادى لبعض مشتقات البيرازول

أحمد صبرى عبد العاطى

قسم كيمياء المبيدات – كلية الزراعة – جامعة الإسكندرية – الشاطبى – الاسكندرية- مصر

تم تحضيرأربعة من مشتقات البيرازول وهى: ٥،٣-ثنائى ميثايل بيرازول (١) و ١-بنزويل-٥،٣-ثنائى ميثايل بيرازول (٢) و ٣-ميثايل-١-فينيل بيرازول-٥-ون (٣) و٣-ميثايل-١-(٤،٢- ثنائى نيتروفينيل) بيرازول-٥-ون (٤) .

تم التعرف على هذه المركبات بتقدير نقطة الانصهار لها وكذلك بالتحليل الطيفى باستخدام الرنين النووى المغناطيسى NMR و مطياف الكتلة Mass spectroscopy .

تم تقدير النشاط الابادى لهذه المركبات على مجموعة من الفطريات الهامه جدا اقتصاديا و هى الـ فيوزاريوم كالمورام ، بيثيوم ديباريانم ، رايزوكتونيا سولانى و كذلك فطر الـ ماكروفومينا فاصيولاى *Fusarium calmorum, Pythium debarianum, Rhizoctonia solani* and *Macrofomina phaseoli* مقارنة بمركب الـ Metalaxyl (Radomil) كمبيد فطرى قياسى. كماتم تقدير النشاط الابادى لهذه المركبات على العمر الرابع للطور اليرقى لدودة ورق القطن. درست أيضا تاثيراتها الاباديه على مرحلة تشكل البادرة فى كل من القمح (كمثال لرفيعة الأوراق) والكوسة (كمثال لعريضة الأوراق) مقارنة بمبيد الحشائش metribuzin (sencor) كمركب قياسى.

أثبتت هذه المركبات سمية فطرية معتدلة إلى عالية كما وجدت مشتقات الـ بيرازول-٥-ون (٣-ميثايل-١-فينيل بيرازول-٥-ون (٣) و٣-ميثايل-١-(٤،٢- ثنائى نيتروفينيل) بيرازول-٥-ون (٤)) أعلى سمية من باقى المشتقات المختبرة متعدية بذلك مبيد الفطرىالقياسى المستخدم على فطريات الـ بيثيوم ديباريانم ، رايزوكتونيا سولانى و كذلك فطر الـ ماكروفومينا فاصيولاى.

أظهرت هذه المركبات المختبرة سمية حشرية إيادية ضعيفة خافضة قابلية العشيرة المعاملة للطعم المستخدم.

أوضحت النتائج أيضا أن مركب الـ٣-ميثايل-١-(٤،٢- ثنائى نيتروفينيل) بيرازول-٥-ون (٤) قد فاق مبيد الحشائش القياسىالمستخدم على النباتين محل الدراسة، بينما قل أونسبيا تساوى تأثير المشتقات الأخرى معه.