Chemical and biological studies on Some Novel Benzimidazole Derivatives for Management of Certain Pathogenic Citrus Fungi

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Abstract: New twelve benzimidazole derivatives that are recently published were evaluated for their fungicidal activity. Such compounds having numerous functional groups attached to C-2 of benzimidazole ring. The mentioned substitutes are thiocarbamate, thiophosphate, phenylamine and other different phenoxy groups. The evaluation process was carried out on *Penicillium digitatium* and *Penicillium italicium* fungi that affect badly on the storage process of citrus. Data obtained revealed that, the sensitivity of fungi to the tested compounds depends on the functional groups belt in the benzimidazole ring system and the type of fungi. Generally, some thiophosphate, flouro and nitrochlorophenoxy derivatives were found to be highly active towards the tested fungi.
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1. Introduction

Fungicides represent the main class of pesticides in Egypt and all over the world. They constitute an important tool for managing many fungal diseases attacking plants for more than two decades. Unlike insecticides and herbicides that kill established insects or weeds, fungicides are also commonly applied to protect healthy plants from infection by pathogens, so in Egypt the major type of pesticides registered and used is the fungicides (Agricultural Pesticides Committee, 2012). As a result, looking for new bioactive heterocyclic compounds is considered as an important field of research. Literature survey revealed that many imidazole and benzimidazole derivatives were proved to be highly active as fungicides (Giri *and Gupta,*1979; Mishra *et al.,*1993; Gulgun *et al.,* 1996 and Tuncbilek *et al.,* 1997),insecticides (Miesel, 1977; Kisida *et al.,* 1986 and Hansheng *et al.,* 1990), acaricides (Kisida *et al.,* 1986 and Maki *et al.,*1989). Many herbicidal active benzimidazoles were also reported by Plath *et al.* (1985), Ogretir *and* Demirayak (1986), Yamamoto *et al.* (1986) and Heywang *et al.* (1988). In addition, nematocides and other plant protective agents were reported by Heywang *et al.* (1988), Lunkenteimer *et al.* (1994) and Borum and Sinclair (1968). Prompted by the previous facts and in continuation with our recently published works (Madkour *et al.,*2006), we aimed to study the biological activity of some selected and new published benzimidazole derivatives against two fungi *Penicillium digitatium* and *Penicillium italicium* attacking citrus that constitutes a main export for Egypt.

2. Materials and Methods

1- The Standard fungicide.

Thiabendazole (Tecto, 50 % SC) that belongs to the benzimidazole group and recommended to fight these fungi was used as a standard fungicide.

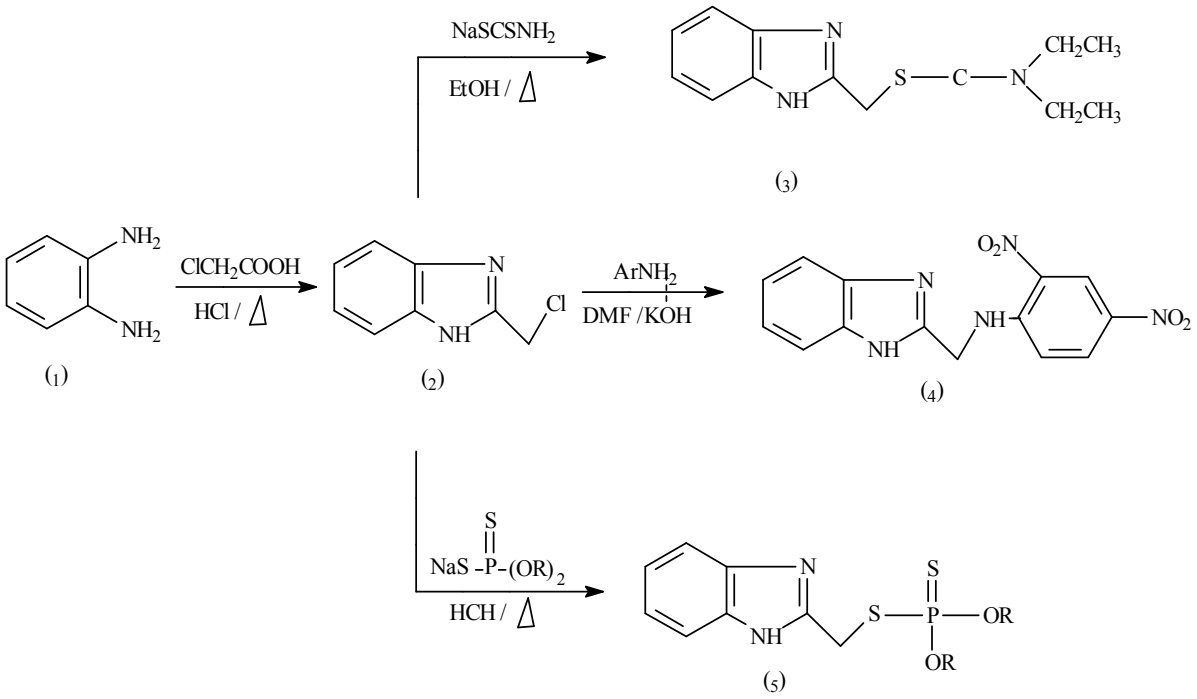
2- Preparation of the new benzimidazole derivatives.

Twelve benzimidazole derivatives **(2)** – **(6)** that are recently published starting from the precursor 1,2-phenlinediamine **(1)** were prepared. The method of synthesis was adopted by Ibrahim (2008) and Madkour *et al.* (2006). Melting points of the prepared compounds were measured as grade technical substances and found to be compatible with the reported ones. The synthetic path ways we followed up are shown in the following schemes.

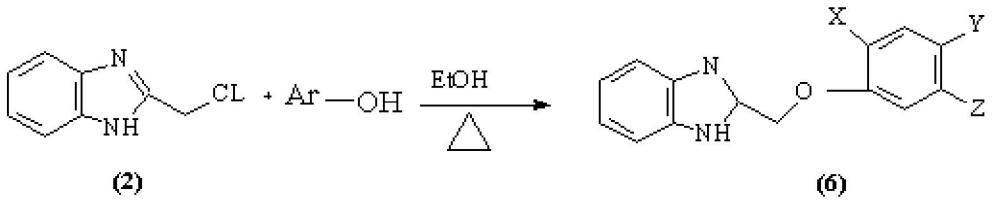
2-Chloromethyl-1H-benzimidazole (2).

A mixture of 1,2-phenlinediamine **(1)** (10.8 gm, 0.1 mole) and chloroacetic acid (11.3 gm,0.12 mole) in 100 ml 15% hydrochloric acid solution was heated under reflux for 7.5 hrs. The reaction mixture was cooled in refrigerator for about 1hr, crushed ice was added to the mixture and stirred. Drops of ammonia solution were then added to the cooled reaction mixture with continuous stirring keeping the temperature of reaction does not exceed to 20 °C. After addition of about 20 ml of ammonia solution, solid product of 2-chloromethylbenzimidazole was precipitated. The reaction mixture was kept in refrigerator for about 1hr

and then filtered off, dried and recrystallized from benzene to give the title compound. Reaction yield is 92%, m.p =145 ^{0}C and the reported m.p = 146-148 °C.



Compd No.	R
5a	CH_3
5b	CH_2CH_3
5c	$CH_2CH_2CH_3$



Compd No.	X	Y	Z
6a	Cl	Cl	H
6b	Cl	NO_2	H
6c	NO_2	Cl	H
6d	F	F	H
6e	NO_2	Br	H
6f	H	H	$CH(CH_3)_2$
6g	H	NO_2	CH_3

S-(1H-Benzimidazol-2-yl)methyl-N,N-diethyldithiocarbamate (3).

2-Chloromethylbenzimidazole **(2)** (1.67 gm, 10 mmole) was added to a solution of sodium N,N-diethyldithiocarbamate (2.25 gm, 10m mole) in 50ml of methanol and the reaction mixture was refluxed for 3hrs. The reaction mixture was cooled at room temperature and poured portionwise with good stirring to crushed ice containing drops of ammonia solution and left over night in refrigerator. The obtained solid

product was filtered off, dried and recrystallized from benzene to give the thiocarbamate derivative **3**. Reaction yield is 80%, m.p is 151-153 °C and the reported m.p is 153-155 ^{0}C.

N-(1H-Benzimidazol-2-yl)methyl-2,4-dinitroaniline (4).

A mixture of 2,4- dinitroaniline (10 mmole) and potassium hydroxide KOH (10 mmole in 5ml of water) in 50 ml of dimethylformamide was stirred for 1hr. Benzimidazole derivative **(2)** (10 mmole) and potassium iodide (10 mmole) were added and the reaction mixture was heated at 100 °C for 6 hrs. The reaction mixture was left aside at room temperature and poured onto crushed ice-water mixture. The solid product that precipitated was filtered off and recrytallized from acetonitrile to give the title product **4**. Reaction yield is 72%, m.p.is 175-177 °C and the reported m.p.is 178-180 °C.

N-(1H-Benzimidazol-2-yl)methyl-O,O-dialkyl phosphorodithioates (5a-c).

A mixture of dialkyldithiophosphate sodium salt (12 mmole) and benzimidazole **(2)** (10 mmole) was stirred at 65 °C in 50 ml ethanol for 5hrs. The precipitated NaCl salt was filtered off and the reaction mixture was poured into crushed ice with good stirring and kept in refrigerator overnight. After filtration a sticky substance was formed, in each case, which was treated several times with worm benzene to give the title compound with yields ranged from 50% to 60%.

2-Aryloxymethyl-1H-benzimidazoles (6a-g).

Substituted phenol (10 mmole) was dissolved in 40 ml DMF containing 1.5 gm K_2CO_3 (in 5 ml water) and the mixture was stirred for 1hr. Compound **(2)** (10 mmole) and few crystals of KI were added and the reaction mixture was refluxed for 6hrs. After cooling at room temperature, the mixture was poured into crushed ice. The formed solid products were filtered off, air dried and recrystallized from the proper solvents as follows.

Compd No.	Yield%	m.p.	Reported m.p.	Crystalization
6a	81%	169-172 ^{0}C	174 ^{0}C	dil.EtOH
6b	64%	115-118 ^{0}C	118-120 ^{0}C	EtOH
6c	71%	195-197 ^{0}C	195-200 ^{0}C	EtOH
6d	85%	110-114 ^{0}C	113-115 ^{0}C	dil.EtOH
6e	70%	187-190 ^{0}C	185-187 ^{0}C	EtOH
6f	80%	semisolid	semisolid	dil.EtOH
6g	77%	90-92 ^{0}C	93-95 ^{0}C	dil.EtOH

3- Biological study.

I- Fungicidal activity of the synthesized compounds *in vitro.*

Potato-dextrose agar (PDA) was used to evaluate the effect of the examined compounds on the mycelial linear growth of both fungi *Penicillium digitatium* and *Penicillium italicium*. Fifty milliliters of the aforementioned medium were poured into 150 ml conical flasks and autoclaved at 121^{o}C for 20 min. Three drops of 25% lactic acid were added to prevent bacterial contamination. Solutions of each compound were prepared (v/v) by dissolving appropriate amounts of the compound in 10 ml of Dimethyl Sulfoxide (DMSO). Equal volumes of DMSO containing diluted compounds were added to sterile molten (40^{o}C) PDA to get a series of concentrations of 50, 75, 100, 150, 250, 500 and 750 ppm for each compound in PDA (Tremblay *et al.,* 2003).

A zero (o) concentration treatment was prepared for each fungus, which contains equivalent volume of solvent only, and used as control. Compounds-amended PDA were dispensed aseptically into 9 cm diameter petridishes. Plugs of mycelium (4 mm diameter) were cut from the margins of actively growing cultures of the *P. digitatium* and *P.italicium* fungi and placed in the center of compound-amended and unamended PDA plates. All treatments were replicated four times and incubated at 25 ± 1^{o}C. Colony diameter (in millimeters) was measured after complete growth of control plugs for each fungus. The percentage of growth inhibition was calculated for each compound. The estimated effective concentration [the minimum inhibition concentration (MIC) that reduces the fungal radial growth], toxicity index (T.I) and slopes of toxicity lines for each compound under investigation were determined and tabulated in Tables (1-4).

II- Post-harvest evaluation of both local and standard compounds.

A series of concentrations from 10 ppm to 200 ppm were prepared from the local formulation in water. Fresh oranges were selected without any injuries and had been commercially harvested no more than 3 days prior to use were randomized and inoculated with both two fungi for 24 (±2) hrs before treatment. Inoculation process was carried out by immersing a stainless steel rod with a probe tip 1 mm wide and 2 mm in length into the spore suspension and wounding each fruit once. The temperature of the fruit at the time of inoculation and subsequent storage until treatment was 20°C (±1°C).This inoculation method simulates infections and has been recommended for determining

the effectiveness of fungicides (Eckert and Brown, 1986). Twenty four hours after inoculation and storage in paper sacs under room conditions,one replicate consists of twenty five oranges were dipped individually for 60 seconds in both new formulation and the recommended fungicide. After 14 days, infection percentages were determined and tabulated in Tables (5) and (6).

Table (1) Fungicidal activity of the new prepared benzimidazole derivatives on *Penicillium digitatium and Penicillium italicum* fungi.

Compd. No.	Conc. (ppm)	*Penicillium digitatium*				*Penicillium italicum*			
		% Inhibition	MIC (ppm)	Slope	T.I	% Inhibition	MIC (ppm)	Slope	T.I
3	50 75 100 150 250 500 750	00.0 16.0 30.0 44.5 83.8 100.0 100.0	**510.7**	3.97 ± 0.3	52.2	00.0 00.0 21.2 39.8 70.6 80.4 100.0	**965.9**	3.29 ± 0.2	26.4
4	50 75 100 150 250 500 750	00.0 35.6 40.1 57.8 100.0 100.0 100.0	**349.4**	4.62 ± 0.4	76.3	23.0 47.0 64.0 88.0 100.0 100.0 100.0	**274.5**	4.23 ± 0.4	92.9
5a	50 75 100 150 250 500 750	61.9 69.8 72.1 83.3 100.0 100.0 100.0	**460.3**	2.07 ± 0.2	57.9	68.3 74.8 80.3 89.9 100.0 100.0 100.0	**357.1**	2.28 ± 0.3	71.4
5b	50 75 100 150 250 500 750	55.5 72.9 73.3 73.8 74.0 76.1 100.0	**1370.9**	0.86 ± 0.1	19.0	66.2 74.0 83.8 86.7 90.3 94.4 100.0	**1216.2**	1.38 ± 0.2	21.0
5c	50 75 100 150 250 500 750	43.3 56.1 65.3 74.6 76.6 80.7 89.9	**7336.5**	1.07 ± 0.1	3.6	51.1 70.2 71.0 76.3 81.1 83.6 90.0	**10871.1**	0.89 ± 0.1	2.3
6a	50 75 100 150 250 500 750	00.0 00.0 26.4 38.9 55.0 56.1 86.1	**3008.2**	2.05 ± 0.2	8.9	00.0 00.0 6.8 10.0 15.9 23.0 56.5	**10889.9**	1.95 ± 0.2	2.3

Contin: Table (1)

6b	50 75 100 150 250 500 750	4.0 14.3 43.2 51.9 75.6 100.0 100.0	**600.3**	3.61 ± 0.2	44.4	13.6 24.1 46.1 54.5 87.9 100.0 100.0	**567.8**	3.37 ± 0.2	44.9
6c	50 75 100 150 250 500 750	18.2 40.6 66.2 87.7 100.0 100.0 100.0	**266.5**	4.59 ± 0.3	**100.0**	00.0 34.9 55.1 77.4 100.0 100.0 100.0	**254.9**	5.59 ± 0.4	**100.0**
6d	50 75 100 150 250 500 750	00.0 20.0 51.4 61.6 79.0 100.0 100.0	**511.9**	3.78 ± 0.3	52.1	00.0 10.0 35.1 50.8 60.8 100.0 100.0	**683.1**	3.66 ± 0.2	37.3
6e	50 75 100 150 250 500 750	00.0 10.0 36.6 44.6 91.2 100.0 100.0	**423.5**	4.76 ± 0.3	62.9	00.0 12.0 44.4 81.8 100.0 100.0 100.0	**256.3**	7.27 ± 0.6	99.5
6f	50 75 100 150 250 500 750	41.2 49.2 52.3 56.7 61.1 65.6 76.4	**2.15**[5]	0.69 ± 0.1	0.12	80.9 81.2 88.8 90.3 94.6 100.0 100.0	**569.0**	1.48 ± 0.2	44.8
6f	50 75 100 150 250 500 750	00.0 10.0 21.2 49.8 84.2 100.0 100.0	**459.9**	4.57 ± 0.3	57.9	00.0 12.0 19.0 50.9 80.4 98.6 100.0	**522.6**	4.31 ± 0.3	48.8

MIC: Minimum Inhibitory Concentration T.I : Toxicity Index

Table (2):-Fungicidal activity of the local formulation on *Penicillium digitatium* fungus as compared with the standard fungicide.

Conc. (ppm)	**Local formulation**			**Standard formulation (Tecto)**		
	Inhibition %	MIC (ppm)	Slope	Inhibition %	MIC (ppm)	Slope
10	0.0	328.4	4.55 ± 0.26	0.0	319.3	5.36 ± 0.29
20	0.0			0.0		
30	2.3			0.0		
40	4.6			0.0		
50	5.7			8.3		
75	10.1			19.2		
100	22.2			31.3		
125	43.7			39.5		
150	50.6			56.7		
175	72.4			88.8		
200	93.1			96.8		
250	100.0			100.0		

Table (3):-Fungicidal activity of the local formulation on *Penicillium italicum* fungus as compared with the standard fungicide.

Conc. (ppm)	Local formulation			Standard formulation (Tecto)		
	Inhibition %	MIC (ppm)	Slope	Inhibition %	MIC (ppm)	Slope
10	0.0	316.3	4.83 ± 0.27	0.0	303.4	5.01 ± 0.29
20	0.0			0.0		
30	0.0			0.0		
40	0.0			2.3		
50	12.3			9.3		
75	15.2			17.7		
100	19.1			21.2		
125	46.3			45.6		
150	51.7			53.4		
175	71.6			81.3		
200	93.5			100.0		
250	100.0			100.0		

Table (4):- Post-harvest evaluation of both local and standard fungicides on *Penicillium digitatum* fungus during orange storage.

Conc. (ppm)	Local formulation			Standard fungicide (Tecto)		
	% of infection	Corrected % of inhibition	MIC (ppm)	% of infection	Correct % of inhibition	MIC (ppm)
Control (0 ppm)	100.0	00.0	219.4	100.0	00.0	237. 7
10	95.8	4.2		100.0	00.0	
30	91.8	8.2		95.8	4.2	
50	62.5	37.5		83.3	16.7	
75	41.7	58.3		79.2	20.8	
100	20.8	79.2		50.0	50.0	
125	8.3	91.7		16.7	83.3	
150	00.0	100.0		4.2	95.8	
200	00.0	100.0		00.0	100.0	
250	00.0	100.0		00.0	100.0	

Table (5):- Post-harvest evaluation of both local and standard fungicides on *Penicillium italicum* fungus during orange storage.

Conc. (ppm)	Local formulation			Standard fungicide (Tecto)		
	% of infection	Corrected % of inhibition	MIC (ppm)	% of infection	Corrected % of inhibition	MIC (ppm)
Control (0 ppm)	100.0	00.0	307.3	100.0	00.0	262.2
10	88.0	12.0		100.0	00.0	
30	86.0	14.0		88.0	12.0	
50	64.0	36.0		86.0	14.0	
75	48.0	52.0		52.0	48.0	
100	24.0	76.0		40.0	60.0	
125	8.0	92.0		12.0	88.0	
150	00.0	100.0		00.0	100.0	
200	00.0	100.0		00.0	100.0	
250	00.0	100.0		00.0	100.0	

3. Results and Discussion

Data in Table (1) clearly show that, the percentages of inhibition for all fungal growth increase as the concentrations of the tested compounds increase. It is also clear that, fungicidal activity of the tested compounds mainly depends on the functional groups attached to the position 2 of benzimidazole ring system as well as the type of fungi. The obtained data showed that, *Penicillium digitatium* fungus is highly sensitive to compound **6c** followed by compound **4** and **6e** where their MIC values are 266.5, 349.4 and 423.5 ppm, respectively. Data also indicated that, *Penicillium italicum* fungus is found to be highly sensitive to compounds **6c** followed by **6e, 4** and **5a** where their MIC's are 254.9, 256.3, 274.5 and 357.1 ppm respectively. On the other hand, *Penicillium digitatium* fungus was found to be highly resistant to compound **6f** while *Penicillium italicum* fungus exhibited high resistance to compound **6a.** From the obtained data we can conclude that compound **6c** is the most effective one on both two fungi where it has 100.0 toxicity index so it was formulated in the form of emulcifable concentrate (10% EC). Physico-chemical characteristics of this local formulation were found to be acceptable according to the standard methods of testing (WHO 1979). The components of the new formulation are shown as follows:-

Compound **6c** (a.i)	10.00 % (w/w)
Antifoam (silicon)	0.20 % (w/v)
Wetting agent (T_{80})	1.30 % (w/v)
Surface active agent (Toximol 500)	2.47 % (w/v)
Solvent 1 (propunol)	15.20 % (w/v)
Solvent 2 (DMF)	70.83 % (w/v)
Total	100.00

To discover the effect of the previous additives on the activity of compound **6c** we reassayed its activity on the same fungi and compared this activity with the standard fungicide thiabendazole (Tecto 50 % SC) as shown in tables (2) and (3).

Data in Table (2) represent the activity of both local formulation and the standard fungicide on *Penicillium digitatium* fungus under laboratory conditions. It is clear that MIC values for both formulations are close and recorded 328.4 and 319.3 ppm, respectively. The same trend was shown in case of *Penicillium italicum* fungus where the MIC values are 316.3 and 303.4 ppm for both local and standard formulations, respectively (Table,3).

The obtained data revealed that our local formulation exhibited an excellent fungicidal activity against the target fungi, so it can be used as an alternative fungicide to encourage the national pesticides industry parallel with reducing the exported ones. To ensure this hypothesis an *in vivo* experiment was carried out under storage or field conditions.

Data in Table (4) represents the fungicidal activity of our local formulation as compared with the standard fungicide under field conditions. Data show that, *Penicillium digitatium* fungus posses more sensitivity to our local formulation than the standard fungicide as its MIC values for both are 219.4 and 237.7 ppm, respectively. This means that, under storage conditions the local formulation showed higher fungicidal activity than the standard fungicide. On the other hand, *Penicillium italicum* fungus showed to some extent more sensitivity to the standard fungicide than the local formulation where their MIC values are 262.2 and 307.3 ppm, respectively, (Table,5).

Conclusion

1- The fungicidal activity of the new synthesized benzimidazole derivatives varies according to the type of substitution in position 2 of benzimidazole nucleus.

2- Chloro and nitro phenoxy derivatives (compound **6c**) showed the highest potency while propylthiophosphate derivatives (compound **5c**) showed the lowest potency.

3- Formulation of the most potent compound increases its fungicidal activity against the tested fungi.

4- Evaluation of local formulation under laboratory conditions showed no significant difference as compared with the standard fungicide tecto 50 % SC.

5- Field experiment revealed the advantage of our local formulation when compared with the standard fungicide especially in case of *Penicillium digitatium* fungus.

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