



SYNTHESIS, CHARACTERIZATION AND FUNGICIDAL ACTIVITY OF KETOAZOMETHINES, 2-KETO-3-(SUBSTITUTED ARYL)-1-THIAZOLIDIN-4-ONES AND METAL COMPLEXES

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(Received : 08.10.2011, Revised : 24.10.2011, Accepted : 25.10.2011)

ABSTRACT

Four ketoazomethines, five 2-keto-1-thiazolidin-4-ones and six metal complexes of 2-keto-1-thiazolidin-4-ones have been synthesized and characterized. These compounds are tested for antifungal activity against four hazardous agriculture fungi, *fusarium oxyspoum*, *pythium*, *sclerotium*, *alternaria brassicola*.

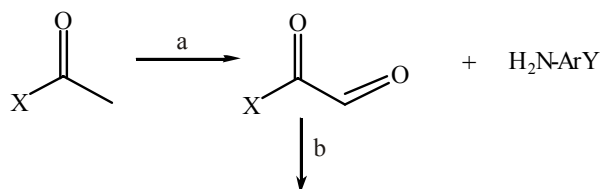
All the new products exhibited considerable activity only against *Fusarium* but benzoylmethyl ketoazomethine and Fe (III) complex of phenylamidomethylketo-2-(2-hydroxy phenyl)-1-thiazolidin-4-one showed highest fungicidal activity (65-70%) as compared to others. Fifteen compounds are reported in this communication.

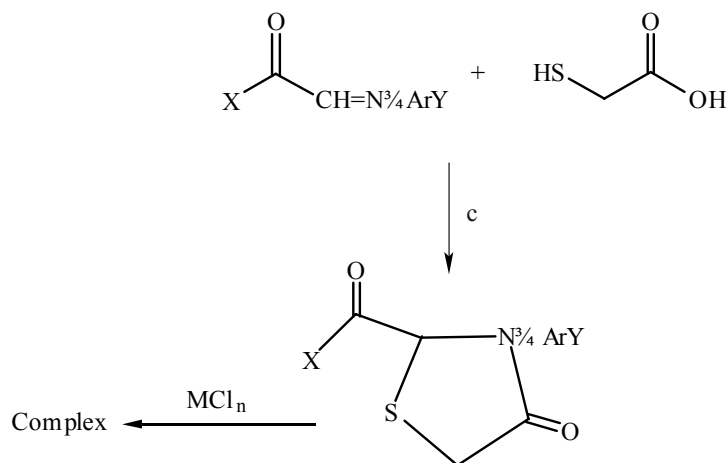
Key words: Plant fungi, Fusarium, Thiazolidinones, ketoazomethines, Metal chelates.

INTRODUCTION

Herbal fungicides used against agriculture fungi generally have not shown significant results¹⁻⁴, whereas synthetic products including Ketoazomethines⁵⁻⁶, 3-thiazolidin-4-ones⁷⁻¹⁰, metal chelates showed remarkable effects. This tempted us to synthesize a few ketoazomethines by condensation of glyoxals with primary amines, 2-keto-1-thiazolidin-4-ones by cyclo-addition of ketoazomethines with thioglycolic acid and metal complexes of ketothiazolidinones and to test them against four hazardous agriculture fungi, *fusarium oxyspoum*, *pythium*, *sclerotium*, *alternaria brassicola*.

Reactions leading to formation of glyoxals, ketoazomethines (Ketoazomethines), thiazolidinones and metal chelates of thiazolidinones are as below.





Scheme 1: Reagent and conditions : (a) SeO₂, Methanol, rh, 2 h; (b), Respective primary amines, MeOH/benzene, rh, 6-8 h; (c) Thioglycolic acid, dry alcohol/benzene rh, 15-20 h

EXPERIMENTAL

Synthesis of glyoxal

For the synthesis of phenylamidomethyl glyoxal, acetoacetanilide (35.4 g, 0.2 mole) and SeO₂ (22.2 g, 0.2 mole) and for the synthesis of benzoylmethyl glyoxal, benzoyl acetone (32.4 g, 0.2 mole) and SeO₂ (22.2 g, 0.2 mole) were mixed in alcohol and refluxed for ~2 h. Concentrated reaction mixtures were poured into 2 litre hot water and refluxed for 1 h. Products were extracted with ether and collected as viscous liquid after evaporation of solvent on water-bath. The yield of R₁CHO is 35.1 g (91.8%) and the yield of R₂CHO is 34.0 g (96.5%).

Synthesis of ketoazomethines and 2-keto(phenylamidomethyl/benzoylmethyl)-3-(substituted aryl)-1-thiazolidin-4-ones

Ketoazomethines of p-chloro, p-bromo and p-nitro were precipitated on mixing the solution of corresponding amine and glyoxal containing equimolar quantities (amine in slight excess) of reactants in ether. Precipitates were filtered, washed with ether and dried in hot air oven.

o-Hydroxy ketoazomethines were prepared by mixing equimolar (0.03 mol) solutions of amine and each glyoxal (slight excess), refluxing the reaction mixtures for 4-10 h. and evaporating the solvent. Solid residues was washed with ether to remove unreacted glyoxal, if any, then dried in air.

All the 2-keto(phenylamidomethyl/benzoylmethyl)-3-(substituted aryl)-1-thiazolidin-4-ones were prepared by mixing equimolar solutions of thioglycolic acid and each ketoazomethine in 3:1 ratio in dry methanol/benzene/DMF followed by 15-25 h refluxing. Reaction mixtures after concentration on water bath were neutralized with aqueous NaHCO₃ solution and solids obtained were washed with water repeatedly and dried in oven at ~60°C. All the new products were purified by column chromatography using resolving solvents identified by TLC (Table 1).

Preparation of complexes

All the simple complexes of Cu (II), Fe (III) and Co (II) metal ions were prepared by refluxing reaction mixture of metal chloride and ligand in 3 : 1 molecular ratio in acetone for 2-8 h. until colour change appears. Residue obtained after evaporation of solvent on waterbath was washed with water repeatedly to remove unreacted metal salts and dried in hot air oven at ~70°C.

Table 1: Compounds, their colour, percentage yield, resolving solvents and elemental analysis

S. No.	Compound	Temp. [°C]	Colour	Yield [%]	Resolving solvent	Elemental analysis		
						C%	H%	N%
1	R ₁ CH=N-Ar-a	135	Brown	67.00	MeOH	71.96	4.82	5.26
2	R ₁ CH=N-Ar-c	137	Canary yellow	87.72	(Et) ₂ O	64.82	4.07	9.56
3	R ₁ CH=N-Ar-e	110	Yellow	96.55	(Et) ₂ O	58.14	3.67	4.25
4	R ₂ CH=N-Ar-a	144	Light brown	65.76	MeOH	68.11	4.92	9.89
5	R ₁ COC ₃ H ₃ SON-Ar-a	>320	Brown	51.14	MeOH	63.31	4.52	4.08
6	R ₁ COC ₃ H ₃ SON-Ar-c	> 300	Yellow	75.00	CH ₂ Cl ₂	58.37	3.69	7.52
7	R ₁ COC ₃ H ₃ SON-Ar-d	194	Light yellow	61.00	(Et) ₂ O	60.18	3.81	3.87
8	R ₁ COC ₃ H ₃ SON-Ar-e	> 300	Brown	57.22	C ₆ H ₆	53.42	3.41	3.49
9	R ₂ COC ₃ H ₃ SON-Ar-a	238	Brown	45.05	EtOH	60.32	4.56	7.84
10	[Cu(R ₁ COC ₃ H ₃ SON-Ar-b) ₂]	> 300	Light brown	68.70	C ₆ H ₆	58.76	3.71	3.47
11	[Fe(Cu(R ₁ COC ₃ H ₃ SON-Ar-b) ₂) ₃ Cl ₃ .2H ₂ O]	>320	Brown	48.70	MeOH	53.98	3.26	3.50
12	[Cu(R ₂ COC ₃ H ₃ SON-Ar-a)(H ₂ O)]	>340	Brown	63.53	EtOH	48.97	3.52	6.37
13	[Fe ₂ (R ₂ COC ₃ H ₃ SON-Ar-a)(H ₂ O) ₂ Cl ₄]	>340	Light yellow	56.61	EtOH	33.68	2.47	4.43
14	[Co ₂ (R ₂ COC ₃ H ₃ SON-Ar-a)(H ₂ O) ₄ Cl ₂]	>320	Brown	72.58	CH ₂ Cl ₂	37.96	3.92	4.48
15	[FeCu(R ₂ COC ₃ H ₃ SON-Ar-a)(H ₂ O) ₂ Cl ₃].2H ₂ O]	>320	Light yellow	49.55	MeOH	33.67	3.72	4.57

R₁ = ArCOCH₂CO and R₂ = ArNHCOCH₂CO

a = o-OH, b = m-OH, c = p-NO₂, d = p-Cl, e = p-Br

In the synthesis of heterobinuclear complexes, simple Cu (II) complexes of 2-keto(benzoylmethyl)-3-(3-hydroxyphenyl)-1-thiazolidin-4-ones and 2-keto(phenylamido methyl)-3-(2-hydroxyphenyl)-1-thiazolidin-4-ones metallomers were used as ligands for complexation with FeCl₃. Equimolar solutions of FeCl₃ (0.3 mol) and each copper (II) metallomer of 2-keto(benzoylmethyl)-3-(3-hydroxyphenyl)-1-thiazolidin-4-ones and 2-keto(phenylamido methyl)-3-(2-hydroxyphenyl)-1-thiazolidin-4-ones (0.2 mol) in acetone were mixed and refluxed for 35-42 h. In both cases, reaction mixtures were evaporated to dryness under reduced pressure. Residues thus obtained were washed with water repeatedly to remove excess FeCl₃ and dried in hot air oven at 70°C. All the complexes were purified by crystallization from alcohol.

Analytical studies

Melting points were recorded in open capillaries and are not corrected. IR spectra (KBr disks) were recorded using Thermo Nicolet Nexus FT-IR spectrometer. ¹H NMR spectra were recorded in DMSO

medium using Me₄Si as an internal reference. Chemical shifts are in ppm. C, H, N analyses (Table 1) were carried out with Euro EA elemental analyzer.

Fungicidal studies

Fungicidal studies were done by paper disc method.

Standard solutions (1000 ppm) of compounds were prepared by dissolving calculated quantities of compounds in known volumes of dimethylsulphoxide (DMSO).

RESULTS AND DISCUSSION

Azomethine $\nu(\text{C}=\text{N})$ and chain ketonic $\nu(\text{C}=\text{O})$ characteristic groups of ketoazomethines display bands in infrared spectra at ca. 1589 cm⁻¹ and at ca 1645 cm⁻¹, respectively whereas 2-keto(substituted aryl)-3-(substituted aryl)-1-thiazolidin-4-ones exhibit their characteristic bands corresponding to $\nu(\text{C}-\text{S}-\text{C})$, $\nu(\text{C}-\text{N})$, $\nu(\text{C}=\text{O}$ chain) and $\nu(\text{C}=\text{O}$ ring) at ca. 733 cm⁻¹, ca. 1279 cm⁻¹, ca. 1605 cm⁻¹ and 1655 cm⁻¹, respectively.

NMR spectra of o-hydroxyphenyl ketoazomethine of phenylamidomethyl glyoxal and its cyclocondensation product were examined as typical examples of present series of compounds. Both products display three common singlets common peaks at ca. 5.05 δ , ca. 2.55 δ and ca. 7.40 δ corresponding to Ar-NH-R, CH₂(chain) and substituted benzene protons, respectively whereas an additional singlet at 6.95 δ of -CH=N- in ketoazomethine and two additional peaks at 2.6 δ and 4.75 δ due to thiazolidinone ring CH₂ and CH-N protons respectively observed are in conformity of infrared inferences.

In spectra of C₆H₅COCH₂COC₃H₃SON-C₆H₅OH(m) and their complexes 10 and 11 almost same values of $\nu\text{C}=\text{O}$ ring, $\nu\text{C}=\text{O}$ chain and $\nu\text{C}-\text{S}-\text{C}$ bands indicate that these groups retained out of the coordination zone of metals whereas considerable lowering in $\nu\text{C}-\text{N}$ ring frequency of ligand from 1273 cm⁻¹ to 1244 cm⁻¹, 1257 cm⁻¹, respectively on complexation clearly shows involvement of this group in coordination. Lowering or disappearance of phenolic $\nu\text{C}-\text{O}$ band(s) of ligand in complexes shows participation of phenolic group in both the complexes. New bands corresponding to $\nu\text{Cu}-\text{O}$ and $\nu\text{Cu}-\text{N}$ at 492 cm⁻¹ and 550 cm⁻¹ respectively in No. 10 evidently support the coordination of phenolic OH and $\nu\text{C}-\text{N}$ ring groups. In heteropolynuclear complex No. 11 which is product of Cu (II) metallomer and FeCl₃, $\nu\text{Cu}-\text{N}$ and $\nu\text{Cu}-\text{O}$ bands of metallomer observed at lower frequencies and an additional band at 456 cm⁻¹ attributed to $\nu\text{Fe}-\text{O}$ indicate subsequent coordination of pre-coordinated phenolic oxygen(s) of metallomer No. 10. These results are consistent with 1 : 3 electrolytic nature and analysis data of complex No. 11.

In complexes Nos. 12, 13, 14 and 15 and their ligand C₆H₅NHCOCH₂COCO-C₃H₃SON-C₆H₅OH(o), almost same values of $\nu\text{C}=\text{O}$ ring, $\nu\text{C}-\text{S}-\text{C}$ bands indicate that these groups retained out of the coordination zone of metals whereas considerable shifting of $\nu\text{C}-\text{N}$ ring frequency of ligand on lower side from 1303 cm⁻¹ to 1239 cm⁻¹, 1244 cm⁻¹, 1247 cm⁻¹, 1243 cm⁻¹, respectively in complexes Nos. 12, 13, 14 and 15 clearly shows involvement of this group in coordination in lowering in frequencies of $\nu\text{C}-\text{O}$ (phenolic) of ligand in all these four complexes also indicates coordination of phenolic group of ligand. One of the two bands corresponding to $\nu\text{M}-\text{O}$ band occurring in 496 cm⁻¹, 445 cm⁻¹, 487 cm⁻¹ – 426 cm⁻¹ regions legitimately indicate coordination on phenolic group of ligand whereas second one could be due to deprotonated chain enolic group. Two new bands in complex spectra appearing in 1516 cm⁻¹ – 1528 cm⁻¹ and 533 cm⁻¹ – 514 cm⁻¹ region attributed to two $\nu\text{M}-\text{N}$ vibrations could only be accounted for in terms of coordination of $\nu\text{N}-\text{H}$ (except complex No. 12) and C-N ring nitrogens.

Table 2: IR frequencies shown by different Schiff's bases, thiazolidinones and complexes

Comp. No.	ν C=O ring	ν (C=N)/ ν C-N ring	ν C-S-C	ν C = O chain	ν M-O	ν M-N
1.	-	1588	-	1588	-	-
2.	-	1592	-	1704	-	-
3.	-	1591	-	1637	-	-
4.	-	1585	-	1652	-	-
5.	1593	1282	696, 754	1593	-	-
6.	1647	1258	748	1597	-	-
7.	1646	1241, 1327	752	1610	-	-
8.	1727	1326	758	1612, 1619	-	-
9.	1661	1242	693	1596	-	-
10.	1607	1244	701	1607	492	550
11.	1622	1257	704	1622	485, 456	545
12.	1652	1239	694	1603 d	495, 487	558
13.	1661	1244	697	1599	492, 485	561, 533
14.	1665	1247	696	1600	496, 429	528, 514
15.	1705	1243	700	1609	442, 426	520, 560

Table 2: continued-

Comp. S. No.	ν M-Cl	ν M-Cl-M	ν M-H ₂ O	ν OH, Intramolecular H-bonding	ν C-O phenolic + δ OH
1.	-	-	-	-	-
2.	-	-	-	-	-
3.	-	-	-	-	-
4.	-	-	-	-	-
5.	-	-	-	-	-
6.	-	-	-	-	-
7.	-	-	-	-	-
8.	-	-	-	-	-
9.	-	-	-	-	-
10.	-	-	-	2921	1300, 1170
11.	-	-	3401	2926	-
12.	-	-	-	-	1373, 1174, 1116
13.	339	301	-	3061	1383
14.	339	293	-	2962	1381
15.	339	302, 282,	3441, 1609	-	1376

In complex No. 15 besides change of all the ligand frequencies as in complex No. 12 metallomer lowering in $\nu\text{Cu-O}$ bands of metallomer and appearance of a new additional $\nu\text{Fe-N}$ band ascertains coordination of Cu (II) metallomer with Fe (III) through some bridging atom probably chlorine as supported by $\nu\text{Cu-Cl-Fe}$ bands at 302 cm^{-1} , 282 cm^{-1} and 256 cm^{-1} . New $\nu\text{M-Cl}$ and $\nu\text{M-Cl-M}$ bands in No. 13, 14 and 15 show coordinated chlorine with metal ions in bridging as well as in terminal position. I.R. spectra inferences are consistent with non-electrolytic nature of these complexes.

Magnetic moments, 1.86 BM and 1.79 BM, of complex No. 10 and 12, respectively, less than 20.00 BM, indicate their square planar geometry whereas magnetic moments of 5.96 BM and 6.13 BM of heterobinuclear complex No. 11 and isobinuclear complex No. 13, respectively reveals their high-spin (5/2) octahedral geometry involving sp^3d^2 hybridization. Hetero binuclear complex No. 15 displaying 3.17 BM magnetic moment, between spin-only values for $S = 1/2$ and $S = 5/2$ states, indicates low-spin to high-spin crossover in octahedral geometry. 2.95 BM magnetic moment of binuclear cobalt (II) complex (No. 14), neither close to spin-only value (1.73 BM) of spin-paired d^7 octahedral complexes nor to spin-free octahedral stereochemistry (3.87 BM), could be accounted for considering metal-metal interactions and/or high-spin to low-spin crossover in it. Band splitting patterns in the electronic spectra of all these complexes are consistent with the inferences derived from their magnetic studies.

Table 3: Electronic spectral bands with their assignments and ligand field parameters of complex compounds

Compound S. No.	Molarity of complex solution	O.D.	Extension coefficient (ϵ)	Band frequency (cm^{-1})	Assignment
10.	1/1859.68	0.890	1654	13889	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
		0.677	1259	15873	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$
		1.605	2984	25641	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$
11.	1/36165.76	0.368	13309	13699	Ligand field band of Fe(III)
		0.570	20616	15873	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$
		0.882	31899	25641	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$
12.	1/1088.68	0.989	1077	13699	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
		0.733	798	15873	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$
		1.529	1665	25641	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$
13.	1/1609	0.727	1170	15873	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ (G)
		0.635	1022	21742	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ (G)
		1.392	2241	25640	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ (G)
14.	1/8744.94	0.595	5203	13698	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$
		0.680	5947	15625	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}$
		1.235	10800	25000	L-M charge transfer
15.	1/16303.19	0.075	1222	15873	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$
		0.188	3065	23810	Ligand field band of Fe (III)
		0.547	8917	25641	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$

Table 3: continued-

Compd. S. No.	Racah parameters B & C (cm ⁻¹)	10 Dq (cm ⁻¹)	β	LFSE (cm ⁻¹)	Effective susceptibility $\chi'_M \times 10^6$ (C.G.S.)	Effective magnetic moment μ_{eff} (B.M.)	Hybridization
10	-	-	-	-	1406.41	1.86	dsp ²
11	-	-	-	-	15053.86	5.96	sp ³ d ²
12	-	-	-	-	1361.94	1.79	dsp ²
13	B = 661 C = 2962	7275	0.51	0	15911.06	6.13	sp ³ d ²
14	B = 862 C = 3362	8236	0.77	4942	3687.50	-	d ² sp ³
15	-	-	-	-	4253.16	3.17	d ² sp ³ \rightleftharpoons sp ³ d ²

Perusal of data (Table 4) of inhibition of a few selected ketoazomethines, their 1-thiazolidin-4-ones and metal complexes against four fungi reveals that compound No. 5 and compound No. 13 showed highest inhibition against *Fusarium oxysporum* fungus to the extent of 65% and 69.6%, respectively whereas compound No. 1 inhibits 45.48% fungus growth. Other compounds did not show appreciable inhibition as compared to reference fungicidal, diethane (M-45).

Table 4: Percentage inhibition shown by Schiff's bases, thiazolidinones and their complexes against different hazardous fungi.

Compd. No.	No. of days growth	% Inhibition shown by following fungi			
		<i>Fusarium</i>	<i>Pythium</i>	<i>Sclerotium</i>	<i>Alternaria</i>
1.	6	45.48	-3.07	-9.87	25.83
2.	6	17.81	20.32	-1.71	-8.26
3.	6	17.81	0.00	-1.60	-37.83
4.	6	38.00	7.69	20.80	21.39
5.	6	64.93	-8.85	1.33	10.83
6.	6	25.21	10.64	9.33	-14.78
7.	6	17.81	0.00	-1.60	-37.83
8.	6	0.27	-11.54	2.67	-8.26
9.	6	37.53	-1.15	37.60	7.39
10.	6	32.60	-7.69	-12.20	-14.78
11.	4	29.29	4.19	-11.70	-15.22
12.	6	35.07	32.26	-12.68	-11.74
13.	6	69.59	15.16	-9.27	-18.26
14.	6	33.70	25.81	-9.27	-16.52
15.	6	14.80	-5.48	-11.95	-3.48
Diethane (M-45)	6	33.15	0.96	1.71	-16.96

If inhibition data of compounds against each of the other three fungi is compared with that of reference compound which is common in all the cases than complexes of compound No. 12 and compound No. 14 and compound No. 2 could be said selective antifungal against *Pythium* fungus, compound No. 4 and compound No. 9. its thiazolidinone are selective against *Sclerotium* fungus. Compound No. 1 and compound No. 4 are selective against *Alternaria Brassicola*.

REFERENCES

1. M. Isabel, G. Roncero, Hera Concepción, Ruiz-Rubio Manuel, I. Maceira Fe, P. García and Madrid Marta, Caracuel Zaira, Calero Fernando, Delgado-Jarana Jesús, Roldán-Rodríguez Raquel and Martínez-Rocha Ana Lilia, Fusarium as a Model for Studying Virulence in Soilborne Plant Pathogens, *J. Physiol. Molecular Plant Pathol.*, **62**, 87-98 (2003).
2. A. Portillo, R. Vila, B. Freixa, T. Adzet and S. Cañigüeral, Antifungal Activity of Paraguayan Plants Used in Traditional, *J. Ethnopharmacol.*, **76**, 93-98 (2001).
3. J. Grayer Renée and B. Harborne Jeffrey, A Survey of Antifungal Compounds from Higher Plants, *Phytochem.*, **37**, 19-42 (1994).
4. F. R. G. Terras, S. Torrekens, F. V. Leuven, R. W. Osborn, J. Vanderleyden, B. P. A. Cammue and W. F. Broekaert, A New Family of Basic Cysteine-Rich Plant Antifungal Proteins from Brassicaceae, *Species*, *FEBS Letters*, **316**, 233-240 (1993).
5. M. A. Baseer, V. D. Jadhav, R. M. Phule, Archana and Y. B. Vibhute, Synthesis and Antimicrobial Activity of Some New Schiff Bases, *Orient. J. Chem.*, **16**, 553-556 (2000).
6. S. N. Pandeya, D. Sriram, G. Nath and E. De Clercq, Synthesis and Antimicrobial Activity of Schiff and Mannich bases of Isatin and its Derivatives with Pyrimidine, *IL Farmaco*, **54**, 624-628 (1999).
7. W. M. Singh and B. C. Dash, Synthesis of Some New Schiff Bases Containing Thiazole and Oxazole Nuclei and their Fungicidal Activity, *Pesticides*, **22**, 33-37 (1988).
8. R. R. Shah, Y. M. Mehta and S. P. Patel, Synthesis and Antifungal Activity of Some Diphenylmethane Containing Bis-(2-arylimino-3-yl-thiazolidinones) and Bis-(1-aryl-3-yl-2-thiohydantoins) Derived from 2, 7-Dihydroxynaphthalene, *Res. J. Chem. Environ.*, **7**, 3 (2003).
9. H. Singh, L. D. S. Yadav, S. N. Shukla and R. Dwivedi, Synthesis of Substituted 5-hydrothiazolo [4,3-b]-1,3,4-oxa (thia) Diazoles and 5-hydrothiazolo [3,4-b]-1,2,4-Triazoles as Potential Antifungal Agent, *J. Agri. Food Chem.*, **40**, 1409-1412 (1992).
10. R. Lakhan, R. L. Singh, The Synthesis and Evaluation of 2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones and their 5-Aryldene Derivatives as Potential Agricultural Fungicidal, *Indian Acad. Sci.*, **17**, 33-41 (1991).