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Synthesis and fungitoxicity evaluation of schiff bases of 4-amino-3-mercapto-5-phenyl-1,2,4-triazole

Arnab Roy Chowdhury and RL Gupta

Abstract
Schiff base is a functional group or a chemical compound containing, carbon-nitrogen double bond. It is also called imine or azomethine. Schiff bases of various heterocyclic moieties find their applications as drugs and have also been classified under pesticides. Schiff bases of 4-amino-1,2,4-triazoles have already been reported for their antifungal, antibacterial and PGR activities. Some derivatives of 4-amino -1,2,4-triazoles have recently been reported to exhibit potential fungicidal activity.

In an attempt to discover potential fungicides, a series of twenty Schiff bases (SB1 to SB20), 4-arylidenamino-3-mercapto-5-phenyl-4H-1,2,4-triazoles having different substitution in the aryl ring attached to imino group were synthesized following a five step synthesis scheme starting with benzoic acid. Three of the five steps of this synthesis were accomplished by using microwaves. The microwave synthesis has been found much faster and efficient than conventional method. The yields of the synthesized Schiff bases were obtained in range of 52-92%. The structures of the Schiff bases were characterized by elemental analysis, FT-IR and NMR spectroscopy.

The Schiff bases were evaluated for fungitoxicity against three phytopathogenic fungi viz. *Rhizoctonia solani*, *Fusarium oxysporum* and *Bipolaris sorokiniana*. Among all the compounds in this series, SB-9 having methyl group in *meta* position of aryl ring (ED_{50} = 17.34 ppm), SB-4 having chlorine in the *para* position of aryl ring (ED_{50}=95.55 ppm) and SB-3 having chlorine in the *meta* position of aryl ring (ED_{50}=181.3 ppm) exhibited the higher activity against *R. solani*, *F. oxysporum* and *B. sorokiniana* respectively. The most active compound in this series was SB-9 exhibited highest activity than the parent triazole against *R. solani*. Thus, the Schiff bases of traizoles may find its application as potential fungicides in the near future.

Keywords: Schiff base, triazole, microwave synthesis, antifungal evaluation

Introduction
The pesticides suffer from high rate of obsolescence due to resistance, change in pest problems, various environmental considerations and also competition from new introductions. Therefore, newer pesticides with greater potency and increased safety are required to be developed to replace the older ones.

Schiff bases have been reported to possess antifungal [1-8], herbicidal activity [9], antibacterial [10-14], anticancer [15], anti HIV [12], antitumor activity [16], and antiviral activity [17]. Some Schiff bases are also reported to act as plant growth regulators [18-20]. The synthesis and assaying of biological potential of compounds containing carbon-nitrogen double bond have received considerable attention in recent years. Schiff bases of triazoles and other heterocycles have a great potential for discovering new potent pesticides. In search for new fungicides and in continuation to earlier investigation on 5-aryl-4-amino-3-mercapto-1,2,4-triazoles [21] which led to some potential fungicidal molecules, a series of Schiff bases of 4-amino-3-mercapto-

5-phenyl-1,2,4-triazole having different substitution in the benzylidene ring attached to imine group, were designed for the present investigation.

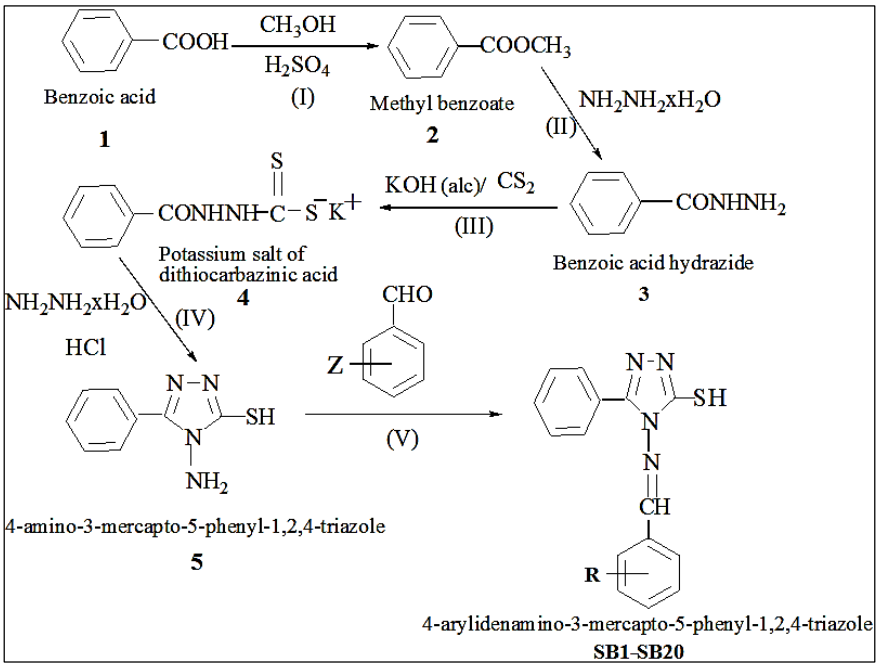
Results and Discussion

Chemistry

The synthesis of the Schiff bases, 4-arylidenamino-3-mercapto-5-phenyl-4H-1,2,4-triazoles were accomplished according to the five step reactions shown in Scheme-I. Among the five steps reactions, the first four steps were carried out according to the method described by earlier reports [21]. First, methyl esters of benzoic acids (2) were prepared by acid mediated esterification of benzoic acid (1). The methyl benzoate reacted with the hydrazine hydrate to prepare benzoic acid hydrazide (3), which were converted to potassium salt of dithiocarbamate acids (4). The 4-amino-5-aryl-3-mercapto-(4*H*)-1,2,4-triazole (5) were obtained in the by refluxing with hydrazine hydrate and finally the Schiff bases, 4-arylidenamino-3-mercapto-5-phenyl-1,2,4-triazoles (6-25) were prepared following a general procedure that involved refluxing of 4-amino-3-mercapto-5-phenyl-1,2,4 triazole in ethanol with respective aldehydes for 2-4 hrs. Three of the five steps of this synthesis i.e. Methyl benzoate to Benzoic acid hydrazide; dithiocarbamic acid salt to triazole and triazole to Schiff base were accomplished by using microwaves. The microwave methods have been found much faster and efficient than conventional method (Table 1).

Table 1: Comparison of conventional and microwave assisted reaction

Reaction step	Reactions		Conventional		Microwave	
			Time	Yield	Time	Yield
2	Methyl benzoate	Benzoic acid Hydrazide	4-5hr	87.4%	4 min	92%
4	Potassium salt of dithiocarbamic acid	4-Amino-3-mercapto-5-phenyl-1,2,4- triazole	4hr	88.5%	36 sec	95.6%
5	4-Amino-3-mercapto-5-phenyl-1,2,4-triazole	Schiff bases of triazole	2-3 hr	75%	5 min	80%



Scheme 1

Compound No.	Substituent (R)
SB1	H
SB2	2-Cl
SB3	3-Cl
SB4	4-Cl
SB5	2-NO_2
SB6	3-NO_2
SB7	4-NO_2
SB8	2-CH_3
SB9	3-CH_3
SB10	4-CH_3
SB11	2-OCH_3
SB12	3-OCH_3
SB13	4-OCH_3
SB14	2-OH
SB15	3-OH
SB16	4-OH
SB17	4-F
SB18	4-Br
SB19	4-CN
SB20	4-$N(CH_3)_2$

Fungicidal activity

The Schiff bases, 4-arylidenamino-3-mercapto-5-phenyl-1,2,4-triazoles were evaluated for fungitoxicity against *Rhizoctonia solani*, *Fusarium oxysporum* and *Bipolaris sorokiniana* by the poisoned food technique using potato-dextrose–agar (PDA) media. The ED_{50} (ppm) values for each compound were determined from the data on inhibition of fungal growth and presented in Table 2. Among all the compounds in this series, SB9 (ED_{50} = 17.34 ppm); SB4 (ED_{50}=95.55 ppm) and SB3 (ED_{50}=181.3 ppm) exhibited highest activity against *R. solani*, *F. oxysporum* and *B. sorokiniana* respectively.

The compounds in general showed least activity against *B. sorokiniana*, whereas some compounds showed higher activity against *R. solani* than *F. oxysporum* and vice versa. The fungitoxicity data against the three fungi showed that the nature of the substituent present in the benzylidene ring in different compounds is differently influencing the fungicidal activity against the three fungi viz. *R. solani*, *F. oxysporum* and *B. sorokiniana*. The most active compound in this series i.e. 4-(3-Methylbenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB9 exhibited higher activity (ED_{50} = 17.34 ppm) than the parent triazole, 4-amino-5-phenyl-3-mercapto-1,2,4-triazole, 5 (ED_{50}=76 ppm).

Table 2: Effective dose required for 50% inhibition of fungal growth, ED_{50} (ppm) of synthesized Schiff bases against test fungi

Compound No	Substituent (R)	ED_{50} (ppm)		
		R. solani	***F. oxysporum***	***B. sorokiniana***
SB1	H	78.08	197.29	209.10
SB2	2-Cl	220.05	138.18	230.51
SB3	3-Cl	240.29	156.68	180.31
SB4	4-Cl	173.32	95.55	227.31
SB5	2-NO_2	165.98	152.5	197.30
SB6	3-NO_2	205.15	192.09	216.66
SB7	4-NO_2	224.52	154.74	201.46
SB8	2-CH_3	168.35	224.93	367.42
SB9	3-CH_3	17.34	221.02	336.60
SB10	4-CH_3	235.82	218.73	390.89
SB11	2-OCH_3	261.65	229.79	303.41
SB12	3-OCH_3	92.42	223.98	336.78
SB13	4-OCH_3	164.29	223.98	414.70
SB14	2-OH	83.96	160.70	362.44
SB15	3-OH	65.30	203.63	336.21
SB16	4-OH	84.26	224.82	327.93
SB17	4-F	130.99	127.73	306.44
SB18	4-Br	131.92	136.35	364.95
SB19	4-CN	67.73	252.33	242.25
SB20	4-$N(CH_3)_2$	263.34	226.59	398.23
Triazole, 5		76	57	29

Experimental Section

All the required solvents and reagents were procured as AR grade from Merck, India. TLC was performed using 250 µm thick silica gel G (containing 30% gypsum as binder) plates, coated with oxalic acid (by developing the plates in 1% oxalic acid solution) and activated at 110 °C for 1hr. Iodine vapour was used as visualizing agent. Melting point (°C) of the solid compounds were determined by using sulphuric acid bath and are uncorrected. The infrared spectra were recorded on a Shimadzu Fourier Transform Infra-red spectrometer (Model IR Prestige 21), the samples were dissolved in UV grade chloroform and analyzed in NaCl cell. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer (Model Advance 400) in DMSO-d_6 using tetramethylsilane (TMS) as an internal standard. The chemical shift (δ) were expressed in ppm and coupling constant (J) in Hz. The elemental analysis of the compounds for C, H, N and S was done on EURO-EA elemental analyzer using sulphanilamide as reference standard.

Methyl benzoate, 2

The Benzoic acid (0.25 mol) was reacted with methanol in presence of concentrated sulphuric acid under reflux condition for 5-6hrs and process accordingly method described by Bijul, 2009. The methyl benzoate was obtained as a colourless liquid. (B.p. 198-199 °C; Yield 78.64%).

Benzoic acid hydrazide, 3

Conventional

Methyl benzoate (0.1mol) reacted with hydrazine hydrate (0.2mol) in the methanol as solvent under reflux condition for 4hrs and processed using method Bijul, 2009. The benzoic acid hydrazide was further purified by recrystallization using CCl_4 and obtained as white crystalline solid and purity was checked by melting point and T.L.C. using acetone as developing solvent and iodine vapor as visualizing agent. (M.p. 115 °C; R_f 0.4; Yield 87.48%).

Microwave

Mixture of methyl benzoate (0.1mol) and hydrazine hydrate (0.2mol) was irradiated in microwave at 900 Watt for 4 minutes until the solution become yellowish in colour and processed accordingly. (M.p. 115 °C; Yield 92%).

Potassium salt of benzoyl dithiocarbamic acid, 4

The benzoic acid hydrazide (0.1 mol) was reacted with saturated solution of chilled methanolic potassium hydroxide and Carbon disulphide (0.12 mol) under cold condition (0-5 °C) for 15-20 min. The solids were filtered and washed with cold distilled acetone and obtained dried cream coloured solid. (Yield 20 g, 80%).

4-amino-3-mercapto-5-phenyl-1,2,4 triazole, 5

Conventional

A suspension of potassium salt of benzoyl dithiocarbamic acid (0.1 mol), hydrazine hydrate (0.2 mol) and water was refluxed with stirring for 4hr until the evolution of hydrogen sulfide ceased. After that the reaction mixture was acidified with Conc. HCl. Triazole was precipitated as white solid and recrystallized with methanol water. The purity was checked by melting point and T.L.C. using methanol as developing solvent and iodine vapor as visualizing agent (M.p. 203-205 °C; R_f 0.94; Yield 88.5%).

Microwave

Potassium salt of benzoyl dithiocarbamic acid (4 mmol) and hydrazine hydrate (8 mmol) was taken in a R.B. flask. The R.B. flask was then connected with a specially designed apparatus containing lead acetate powder. The lead acetate works as a trap for hydrogen sulphide, which is emitted during the microwave reaction. The microwave was used at 900 Watt and the microwave irradiation was done for 36 seconds till a white solid appeared at the bottom or the hydrogen disulphide emission cease and processed accordingly. (M.p. 203-205 °C; R_f 0.94; Yield 95.6%).

4-Arylidenamino-3-mercapto-5-phenyl-1,2,4-triazoles SB1-SB20

Conventional

4-amino-3-mercapto-5-phenyl-1,2,4 triazole (0.01 mole) was was dissolved in ethanol and then required amount of aldehyde (0.01 mol) was added to this solution. The mixture was refluxed for 2-4 hrs. The resulting solution was poured into the crushed ice. The precipitate which got separated was dried and recrystallized from benzene- hexane mixture. The purity of the product was checked by melting point and t.l.c. using benzene: acetone (9:1) as developing solvent and iodine vapor as visualizing agent. (M.p. 210ºC; R_f 0.73; Yield 75.02%).

Compounds SB1 to SB20 were synthesized by similar method using respective benzaldehydes having substituents at aryl ring.

Microwave

4-amino-3-mercapto-5-phenyl-1,2,4 triazole (0.01 mol) was dissolved in minimum amount of ethanol and then required amount of benzaldehyde (0.01 mol) was added to this solution. The reaction mixture was irradiated using microwave at 900 Watt 5 minutes until the solution become yellowish in colour and processed accordingly. This method was standardized only for SB1. (M.p. 210 ºC; R_f 0.73; Yield 2.24 g, 80%).

4-Benzylidenamino-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB1

M.p. 210 ºC; R_f 0.73; Yield 75.02%.

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 7.34-8.06 (m, 10H, Ar-H), 9.69 (s, 1H, N=CH), 14.65 (s, 1H, SH).

^{13}C NMR δ $^{DMSO\text{-}d6}$ (ppm): 122.7, 126.4, 128.7, 129.2, 129.9, 132.7 (aromatic carbons), 161 (N=CH), 177.8 (triazole carbons).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{15}H_{12}N_4S$ (280): C, 64.28; H, 4.28; N, 20; S, 11.42; Found (%): C, 62.69; H, 3.91; N, 18.89; S, 10.72.

4-(2-Chlorobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB2

M.p. 212 ºC; R_f 0.66; Yield 92.04%).

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 7.28-7.80 (m, 9H, Ar-H), 10.2 (s, 1H, N=CH), 14.27 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1600 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{15}H_{11}N_4SCl$ (314.5): C, 57.23; H, 3.49; N, 17.80; S, 10.17; Found (%): C, 58.43; H, 3.44; N, 17.43; S, 10.47.

4-(3-Chlorobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB3

M.p. 203-205 ºC; R_f 0.63; Yield 91.72%.

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 7.28-7.80 (m, 9H, Ar-H), 9.54 (s, 1H, N=CH), 14.27 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1600 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{15}H_{11}N_4SCl$ (314.5): C, 57.23; H, 3.49; N, 17.80; S, 10.17; Found (%): C, 56.62; H, 3.91; N, 17.21; S, 10.95.

4-(4-Chlorobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB4

M.p. 190 ºC; R_f 0.64; Yield 79.49%.

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 7.34-7.90 (m, 9H, Ar-H), 9.72 (s, 1H, N=CH), 14.27 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1600 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{15}H_{11}N_4SCl$ (314.5): C, 57.23; H, 3.49; N, 17.80; S, 10.17; Found (%): C, 58.12; H, 3.45; N, 18.92; S, 10.65.

4-(2-Nitrobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB5

M.p. 207-209 ºC; R_f 0.64; Yield 66.46%.

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 7.34-8.19 (m, 9H, Ar-H), 10.49 (s, 1H, N=CH), 14.30 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic) 3051(C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{15}H_{11}O_2N_5S$ (325): C, 55.38; H, 3.38; N, 21.53; S, 9.84; Found (%): C, 55.96; H, 2.85; N, 21.86; S, 10.73.

4-(3-Nitrobenzyidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB6

M.p. 205-206 ºC; R_f 0.64; Yield 73.23%

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 7.34-8.64 (m, 9H, Ar-H), 10.04 (s, 1H, N=CH), 14.33 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{15}H_{11}O_2N_5S$ (325): C, 55.38; H, 3.38; N, 21.53; S, 9.84; Found (%): C, 57.92; H, 2.93; N, 20.67; S, 11.92.

4-(4-Nitrobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB7

M.p. 209-210 ºC; R_f 0.66; Yield 86.15%.

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 7.36-8.08 (m, 9H, Ar-H), 10.49 (s, 1H, N=CH), 14.75 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{15}H_{11}O_2N_5S$ (325): C, 55.38; H, 3.38; N, 21.53; S, 9.84; Found (%): C, 54.82; H, 3.67; N, 22.45; S, 10.35.

4-(2-Methylbenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB8

M.p. 160 ºC; R_f 0.69; Yield 54.42%.

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 2.4 (s, 3H, Ar-CH_3), 7.48-8.01 (m, 9H, Ar-H), 9.72 (s, 1H, N=CH), 14.27 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).

Calcd (%) for $C_{16}H_{14}N_4S$ (294): C, 65.30; H, 4.76; N, 19.04; S, 10.88; Found (%): C, 61.24; H, 4.11; N, 17.89; S, 12.43.

4-(3-Methylbenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB9

M.p. 155 ºC; R_f 0.70; Yield 79.59%.

^{1}H NMR δ $^{DMSO\text{-}d6}$ (ppm): 2.4 (s, 3H, Ar-CH_3), 7.11-8.00 (m, 9H, Ar-H), 9.66 (s, 1H, N=CH), 14.25 (s, 1H, SH).

IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd. (%) for $C_{16}H_{14}N_4S$ (294): C, 65.30; H, 4.76; N, 19.04; S, 10.88; Found (%): C, 52.17; H, 2.67; N, 19.83; S, 16.24.

4-(4-Methylbenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB10
M.p. 158-160 ºC; R_f 0.71; Yield 59.18%).
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 2.4 (s, 3H, Ar-CH_3), 7.48-8.01 (m, 9H, Ar-H), 9.72 (s, 1H, N=CH), 14.27(s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd. (%) for $C_{16}H_{14}N_4S$ (294): C, 65.30; H, 4.76; N, 19.04; S, 10.88; Found (%): C, 64.82; H, 4.13; N, 18.93; S, 11.63.

4-(2-Methoxybenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB11
M.p. 172-174 ºC; R_f 0.54; Yield 53.54%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 3.35 (s, 3H, Ar-OCH_3), 7.34-8.01 (m, 9H, Ar-H), 9.34 (s, 1H, N=CH), 14.75 (s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051(C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{16}H_{14}ON_4S$ (310): C, 61.93; H, 4.51; N, 18.06; S, 10.32; Found (%): C, 57.78; H, 4.62; N, 17.75; S, 11.96.

4-(3-Methoxybenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB12
M.p. 173-175 ºC; R_f 0.54; Yield 70.96%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 3.35 (s, 3H, Ar-OCH_3), 6.99-7.88 (m, 9H, Ar-H), 9.56 (s, 1H, N=CH), 14.75 (s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{16}H_{14}ON_4S$ (310): C, 61.93; H, 4.51; N, 18.06; S, 10.32; Found (%): C, 63.41; H, 4.92; N, 18.55; S, 11.43.

4-(4-Methoxybenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB13
M.p. 210-211 ºC; R_f 0.55; Yield 56.77%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 3.35(s, 3H, Ar-OCH_3), 7.34-8.01 (m, 9H, Ar-H), 9.34 (s, 1H, N=CH), 14.75 (s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051(C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd. (%) for $C_{16}H_{14}ON_4S$ (310): C, 61.93; H, 4.51; N, 18.06; S, 10.32; Found (%): C, 59.73; H, 5.12; N, 19.44; S, 10.72.

4-(2-Hydroxybenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB14
M.p. 189-190 ºC; R_f 0.71; Yield 67.90%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 3.9 (s, 1H, Ar-OH), 7.4-8.1 (m, 9H, Ar-H), 10.2 (s, 1H, N=CH), 14.27(s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{15}H_{12}ON_4S$ (296): C, 60.81; H, 4.05; N, 18.92; S, 10.81; Found (%): C, 58.32; H, 4.71; N, 18.64; S, 13.92.

4-(3-Hydroxybenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB15
M.p. 198-200 ºC; R_f 0.74; Yield 64.19%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 3.9 (s, 1H, Ar-OH), 7.1-8.1 (m, 9H, Ar-H), 10.35 (s, 1H, N=CH), 14.25 (s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051(C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{15}H_{12}ON_4S$ (296): C, 60.18; H, 4.05; N, 18.92; S, 10.81; Found (%): C, 59.47; H, 4.81; N, 17.98; S, 11.81.

4-(4-Hydroxybenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB16
M.p. 205 ºC; R_f 0.72; Yield 70.94%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 3.9 (s, 1H, Ar-OH), 7.4-7.8 (m, 9H, Ar-H), 10.2 (s, 1H, N=CH), 14.27(s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{15}H_{12}ON_4S$ (296): C, 60.81; H, 4.05; N, 18.92; S, 10.81; Found (%): C, 62.81; H, 5.16; N, 19.11; S, 11.21.

4-(4-Fluorobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB17
M.p. 205-206 ºC; R_f 0.52; Yield 1.98 g, 66.44%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 6.9-7.87 (m, 9H, Ar-H), 9.88 (s, 1H, N=CH), 14.76 (s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051(C-H, aromatic) 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{15}H_{11}N_4SF$ (298): C, 60.40; H, 3.69; N, 18.79; S, 10.74; Found (%): C, 62.64; H, 3.69; N, 19.54; S, 10.52.

4-(4-Bromobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB18
M.p. 203-204 ºC; R_f 0.57; Yield 84.96%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 7.3-8.05 (m, 9H, Ar-H), 9.72 (s, 1H, N=CH), 14.27(s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517(C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd. (%) for $C_{15}H_{11}N_4SBr$ (359): C, 50.14; H, 3.34; N, 15.59; S, 8.91; Found (%): C, 55.68; H, 5.82; N, 16.72; S, 9.51.

4-(4-Cyanobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB19
M.p. 181-182 ºC; R_f 0.46; Yield 1.60 g, 52.45%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 7.34-7.91 (m, 9H, Ar-H), 9.16 (s, 1H, N=CH), 14.09 (s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{16}H_{11}N_5S$ (305): C, 62.95; H, 3.61; N, 22.95; S, 10.49; Found (%): C, 63.22; H, 2.69; N, 21.03; S, 6.02.

4-(4-Dimethylaminobenzylidenamino)-3-mercapto-5-phenyl-4H-1,2,4-triazole, SB20
M.p. 184-185 ºC; R_f 0.58; Yield 72.13%.
^{1}H NMR δ $^{DMSO-d6}$ (ppm): 3.34(s, 6H, Ar-N $(CH_3)_2$), 7.34-8.11 (m, 9H, Ar-H), 9.95 (s, 1H, N=CH), 14.32 (s, 1H, SH).
IR spectrum υ ^{CHCl_3} (cm^{-1}): 2434 (SH), 1517 (C=N), 2896 (C-H, aliphatic), 3051 (C-H, aromatic), 1476, 1251, 1046, 931 (N-C=S).
Calcd (%) for $C_{16}H_{17}N_5S$ (323): C, 63.16; H, 5.26; N, 21.67; S, 9.90; Found (%): C, 56.04; H, 3.59; N,17.60; S, 13.25.

Fungicidal activity

The fungitoxicity testing of 4-arylidenamino-3-mercapto-5-phenyl-1,2,4-triazoles was carried out by Poisoned food technique. Poisoned food technique using potato-dextrose agar (PDA) medium against *Rhizoctonia solani* Kühn. *Fusarium oxysporum* (Padwik) Snyd. & Hans. and *Bipolaris sorokiniana*. Cultures of *Rhizoctonia solani*, *Fusarium oxysporum*, *Bipolaris sorokiniana* were obtained from the Division of Plant Pathology, IARI, New Delhi. The cultures were maintained on PDA slants at 25ºC and were subcultured in petridishes prior to testing. The required amount of test compounds were dissolved in DMSO and added in the media for 1000, 500, 250 and 125 ppm conc of the test compounds. DMSO and parent triazole was taken as positive and negative control respectively. A 5 mm thick disc of fungus (spores and mycelium) cut from earlier subcultured fungus in a petridish was inoculated aseptically to the centre of the petridishes. Both treatment and control petridishes were kept in B.O.D incubator at 25 ± 1 ºC till the fungal growth in the control petridishes was almost complete. Fungus mycelial growth in both treated (T) as well as in control (C) was measured diametrically and % inhibition of growth (%I) was calculated from the following formula:

% Inhibition of growth (%I) = [(C-T)/ C] x 100

Effective dose required for 50% inhibition of fungus growth, ED_{50} values were determined by using BASIC LD_{50} programme version 1.1 [22] using % Inhibition of growth data.

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