Synthesis of Some New Halogenated N-Thiazolyl Substituted Hydroxy Acid Amides and Their Use as Possible Fungicides†

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A large number of new N-thiazolyl, chloro-thiazolyl, bromo-thiazolyl and iodothiazolyl amides of salicylic, hydroxy naphthoic acids, both halogenated and non-halogenated ones have been synthesised by condensing simple as well as halogenated thiazoles with different aromatic hydroxy acids, viz. salicylic, chloro- and bromo-salicylic, hydroxy naphthoic and bromo hydroxyl naphthoic acids. All these compounds are assayed for their fungicidal activity using *Piricularia oryzae* (Cav.), *Helminthosporium oryzae* and *Carvularia lunata* as the test fungi. An attempt has been made to establish a relationship between chemical structure and fungicidal activity.

The use of salicylic acid, salicylanilides and their halogen derivatives are quite well known for their fungicidal properties. Some of the halogen derivatives of salicylanilides are used in the treatment of epidermphytosis.¹⁾ Multifungin, a trade name for 5-bromo salicyl-4-chloro anilide is a commercial fungicide used in the treatment of human fungus-diseases. Bromo salicylic acid shows marked fungicidal activity²⁾ against fungus-diseases in plant.

Hydroxy naphthoic acids and their anilides have also shown marked antifungal activity.³⁾ The use of thiazole derivatives including halogenated ones as fungicides has gained importance during the recent years.⁴⁾

In view of the above observations, it was considered worthwhile to synthesize a few anilides by condensing salicylic acid, halogenated salicylic acids, hydroxy naphthoic acids and bromo hydroxy naphthoic acids in one hand and thiazolyl amines and their chloro-, bromo-, and iododerivatives on the other hand, with the hope that the resulted anilides which contain all the potential fungicidal groupings, i.e. thiazole moiety, halogens and aromatic hydroxy acids in a single molecule would certainly show powerful fungicidal activity. Further, to compare the effectiveness of these

hydroxy amido thiazoles some aromatic amines have also been condensed with the hydroxy acids with the view to have a comparative evaluation of the fungicidal activity of the thiazole moiety and to arrive at a conclusion regarding the relation between chemical structure and fungicidal activity of such compounds.

EXPERIMENTAL PROCEDURE

1. *3: 5-Dichloro-salicylic acid.* Salicylic acid (5.0g) was dissolved in minimum volume of glacial acetic acid and to this solution dry chlorine gas was bubbled for 2 hr with occasional shaking when a white crystalline solid separated. The residue was collected by filtration, washed with excess of water and finally crystallized from ethanol; yield 80%; mp 219°C (Found: Cl, 34.58; $C_7H_4O_3Cl_2$ requires Cl, 34.30%).

2. *5-Bromo-salicylic acid.* Salicylic acid (7.0 g) was dissolved in minimum volume of glacial acetic acid and was taken in a dry conical flask kept in ice-bath and was stirred mechanically. Bromine (8.0 g) in glacial acetic acid (15 ml) was then added dropwise from a separating funnel. Stirring was continued for a further period of 30 min at room temperature and then the resulting solution was poured into large volume of water. A white precipitate was obtained which was collected by filtration, washed with water and finally crystallised from ethanol; yield 65%; mp 157°C (Found: Br, 36.21; $C_7H_5O_3Br$ requires Br, 36.86%).

3. *4-Bromo-1-hydroxy-2-naphthoic acid.* 1-Hydroxy-2-naphthoic acid (9.5 g) was brominated with

† Search for New Fungicides. Part I.

bromine (8.0 g) in glacial acetic acid medium by the method outlined in 2. Yield 85%; mp 238°C (Found: Br, 29.80; $C_{11}H_7O_3$ Br requires Br, 30.00%).

4. *4-Bromo-3-hydroxy-2-naphthoic acid*. 3-Hydroxy-2-naphthoic acid (9.5 g) was brominated with bromine as above. Yield 80%; mp 233~34°C, (Found: Br, 29.71; $C_{11}H_7O_3$ Br requires Br, 30.00%).

5. *2-Amino-4-phenyl-5-chloro-thiazole*. 2-Amino-4-phenyl thiazole (2.0 g) was treated with HCl (Conc. 3.0 ml) and the hydrochloride salt was dissolved in glacial acetic acid (25 ml), and the mixture was stirred well. Dry chlorine gas was bubbled at a slow and steady rate through the above hydrochloride solution of the thiazole, with occasional shaking until a solid separated. The residue was separated by filtration and was treated with liquor NH_4OH to liberate the free base. This was collected by filtration and finally crystallised from ethanol. Yield 68%; mp 160°C (Found: S, 15.18; Cl, 16.52; $C_9H_7N_2S$ Cl requires S, 15.20; Cl, 16.86%).

6. *2-Amino-4-phenyl-5-bromo-thiazole*. 2-Amino-4-phenyl thiazole was brominated by the method of Mahapatra.⁵

7. *2-Amino-4-phenyl-5-iodo-thiazole*. 2-Amino-4-phenyl thiazole was iodinated by the method of Garreau⁶ with certain modifications. 2-Amino-4-phenyl thiazole (2.0 g) was treated with pure and redistilled HI (6.5 ml) and the hydriodide salt was dissolved in glacial acetic acid (25 ml) and the mixture was kept stirring mechanically on an ice-bath. Pure and resublimed iodine (3 g) in glacial acetic acid (30 ml) was added dropwise. The stirring was continued for one more hour and the resulting solution was allowed to stand at room temperature for 15 min and then a pinch of red oxide of mercury was added and refluxed on a water-bath for 30 min. The excess of the solvent was distilled off and the oily mass was poured into large excess of water. The gummy residue separated was treated with liquor NH_4OH to liberate the free base. The product was separated by filtration and finally crystallised from ethanol. Yield 65%; mp 103°C (Found: I, 40.28; $C_9H_7N_2$ SI requires I, 42.06%).

8. *2-(α -Hydroxyl- β -naphthoylamido)-4-phenyl-thiazole*. 1-Hydroxy-2-naphthoic acid (1.0 g) was taken in a clean and dry conical flask. To it was added thionyl chloride (2 ml) and the resulting mixture was refluxed on a water-bath for about an hour so as to convert the acid completely into the acid chloride. Excess of thionyl chloride was driven off, the residue was cooled and to it was added a solution of 2-amino-4-phenyl thiazole (1.0 g) in dry acetone. It was then

refluxed on a water-bath for 10 min and then water (50 ml) was added. The solid was collected by filtration, washed thoroughly and finally crystallised from ethanol. Yield 65%; mp 200°C (Found: S, 9.62; $C_{20}H_{14}N_2O_2S$ requires S, 9.25%).

The condensation of halogenated hydroxy acids with non-halogenated and halogenated 2-amino thiazoles was carried out as above. The mp, yield and analytical data of such hydroxy acid amido compounds are given in table I.

Fungicidal test

For the fungicidal assay of these compounds, the method of Montgomery and Moore,⁷ with slight modification was used. *Piricularia oryzae* (Cav.), *Helminthosporium oryzae*, the causative organisms of rice blast and *Carvularia lunata*, the fungus causing brown spots in rice plants have been used as the test fungi. Some of the compounds (numbered 8, 9, 17, 18, 26, 27, 35, 36, 52, 53, 61, 62, 70, 71, 79 and 80 in Table I) which show maximum fungicidal activity against *Piricularia oryzae* (Cav.) are also tested against *Helminthosporium oryzae*. The results as evident from Table I show that these are also very active against *Helminthosporium oryzae*. The chemicals in different concentrations were kept in contact with the spores for 24 hr. The percentage of germination of spores at 10 ppm and 1 ppm of the fungicides is given in Table I.

Analysis of the results of fungicidal activity shows a definite pattern from which the following conclusions can be derived:

- i) The thiazole nucleus attached to the amide nitrogen atom definitely improved the fungicidal activity in comparison to the aromatic nucleus attached to the same nitrogen.
- ii) Salicylamides are more active than the naphthoic acid amides.
- iii) Introduction of halogen to the acid part improved the fungicidal activity over the non-halogenated acid amides. Chloro derivatives are found to have greater fungicidal property than the bromo derivatives.
- iv) When halogen is introduced into the thiazolyl part the fungicidal activity is augmented.
- v) The most active compounds are those in which chlorine is on both the acid and thiazolyl parts, except in a few cases.
- vi) The position of the hydroxyl group in the naphthoic acid either in α or β position does not change the fungicidal activity in a conclusive way.
- vii) These compounds are most active towards *Piricularia oryzae* (Cav.), less towards *Helminthosporium oryzae* and least towards *Carvularia lunata*. All these are disease-causing fungi of rice plant.

TABLE I. ANALYTICAL DATA AND FUNGICIDAL RESULTS OF N-THIAZOLYL SUBSTITUTED HYDROXY ACID AMIDES

Sl. No.	Nature of R.	mp °C	Yield %	Halogen (%)		Sulphur (%)		Fungicidal results		
				Found	Calc.	Found	Calc.	Ger. at 10 ppm %	Ger. at 1 ppm %	Test fungus
1	2	3	4	5	6	7	8	9	10	11

(Fungicidal assay in control—93~95% germination)

1.	β -Naphthyl	124	72	5.13 (Nitrogen)	5.24	—	—	0	25	<i>Carvularia lunata</i>
2.	(o)Chlorophenyl	148	80	14.6	14.4	—	—	18	90	"
3.	4-Phenyl-2-thiazolyl	155	65	—	—	10.65	10.81	6	45	<i>Piricularia oryzae</i> (Cav.)
4.	4-(β -Naphthyl)-2-thiazolyl	120	68	—	—	8.92	9.25	4	50	"
5.	4-(α -Naphthyl)-2-thiazolyl	95	62	—	—	8.88	9.25	4	50	"
6.	4-(p-Hydroxyphenyl)-2-thiazolyl	180	65	—	—	10.02	10.25	7	52	"
7.	4-(p-Methoxyphenyl)-2-thiazolyl	175	62	—	—	9.48	9.81	4	50	"
8.	4-(p-Chlorophenyl)-2-thiazolyl	162	60	—	—	9.42	9.68	2/5*	25/45*	"
9.	4-(p-Bromophenyl)-2-thiazolyl	115	64	—	—	8.22	8.53	3/6*	30/55*	"
10.	4-(β -Phenylethyl)-2-thiazolyl	187	72	—	—	9.44	9.88	4	45	"
11.	4- β -(p-Methoxyphenyl)-ethyl-2-thiazolyl	212	68	—	—	8.78	9.04	4	45	"
12.	4-Phenyl-5-chloro-2-thiazolyl	110	62	10.12	10.74	—	—	3	30	"
13.	4-(α -Naphthyl)-5-chloro-2-thiazolyl	103	65	9.84	9.33	—	—	3	28	"
14.	4-(β -Naphthyl)-5-chloro-2-thiazolyl	186	65	9.76	9.33	—	—	3	32	"
15.	4-(p-Hydroxyphenyl)-5-chloro-2-thiazolyl	181	61	10.52	10.24	—	—	5	40	"
16.	4-(p-Methoxyphenyl)-5-chloro-2-thiazolyl	173	65	10.12	9.85	—	—	5	40	"
17.	4-(p-Chlorophenyl)-5-chloro-2-thiazolyl	169	62	19.64	19.45	—	—	3/6*	30/55*	"
18.	4-(p-Bromophenyl)-5-chloro-2-thiazolyl	148	64	29.43	28.20	—	—	3/6*	30/58*	"
19.	4-(β -Phenylethyl)-5-chloro-2-thiazolyl	152	65	10.22	9.90	—	—	5	40	"
20.	4- β -(p-Methoxyphenyl)-ethyl-5-chloro-2-thiazolyl	130	65	9.82	9.14	—	—	4	35	"
21.	4-Phenyl-5-bromo-2-thiazolyl	130	70	20.83	21.33	—	—	5	38	"
22.	4-(α -Naphthyl)-5-bromo-2-thiazolyl	144	68	18.01	18.82	—	—	5	40	"
23.	4-(β -Naphthyl)-5-bromo-2-thiazolyl	158	65	17.98	18.82	—	—	4	75	"
24.	4-(p-Hydroxyphenyl)-5-bromo-2-thiazolyl	207	58	19.63	20.46	—	—	5	40	"

TABLE I. (Continued)

Sl. No.	Nature of R.	mp °C	Yield %	Halogen (%)		Sulphur (%)		Fungicidal results		
				Found	Calc.	Found	Calc.	Ger. at 10 ppm %	Ger. at 1 ppm %	Test fungus
1	2	3	4	5	6	7	8	9	10	11
25.	4-(<i>p</i> -Methoxyphenyl)-5-bromo-2-thiazolyl	115	60	18.65	19.75	—	—	4	36	<i>Piricularia oryzae</i> (Cav.)
26.	4-(<i>p</i> -Chlorophenyl)-5-bromo-2-thiazolyl	168	64	26.45	27.23	—	—	3/5*	31/45*	"
27.	4-(<i>p</i> -Bromophenyl)-5-bromo-2-thiazolyl	166	68	34.66	35.24	—	—	3/8*	30/70*	"
28.	4-(β -Phenylethyl)-5-bromo-2-thiazolyl	141	65	18.86	19.86	—	—	4	36	"
29.	4- β -(<i>p</i> -Methoxyphenyl)-ethyl-5-bromo-2-thiazolyl	155	62	17.62	18.48	—	—	3	30	"
30.	4-Phenyl-5-iodo-2-thiazolyl	108	52	29.12	30.09	—	—	3	35	"
31.	4-(α -Naphthyl)-5-iodo-2-thiazolyl	149	55	25.65	26.91	—	—	5	40	"
32.	4-(β -Naphthyl)-5-iodo-2-thiazolyl	123	55	25.51	26.91	—	—	4	34	"
33.	4-(<i>p</i> -Hydroxylphenyl)-5-iodo-2-thiazolyl	105	50	27.56	28.99	—	—	6	45	"
34.	4-(<i>p</i> -Methoxyphenyl)-5-iodo-2-thiazolyl	100	52	27.11	28.09	—	—	6	47	"
35.	4-(<i>p</i> -Chlorophenyl)-5-iodo-2-thiazolyl	118	54	34.72	35.58	—	—	3/8*	29/75*	"
36.	4-(<i>p</i> -Bromophenyl)-5-iodo-2-thiazolyl	130	60	40.01	41.32	—	—	2/8*	25/78*	"
37.	4-(β -Phenylethyl)-5-iodo-2-thiazolyl	101	51	27.03	28.18	—	—	3	28	"
38.	4- β -(<i>p</i> -Methoxyphenyl)-ethyl-5-iodo-2-thiazolyl	128	55	25.51	26.46	—	—	4	33	"

(Fungicidal assay in control—95% germination)

39.	Phenyl	112	64	24.64	25.18	—	—	10	70	"
40.	(<i>p</i>)Tolyl	161	65	23.48	23.99	—	—	11	70	"
41.	(<i>p</i>)Chlorophenyl	175	70	33.14	33.65	—	—	10	70	"
42.	(<i>p</i>)Bromophenyl	182	70	41.62	41.83	—	—	11	75	"
43.	(<i>p</i>)Iodophenyl	127	68	47.82	48.53	—	—	12	78	"
44.	(<i>p</i>)Nitrophenyl	142	65	21.43	21.72	—	—	12	75	"
45.	(α)Naphthyl	158	70	20.78	21.39	—	—	7	52	"
46.	(β)Naphthyl	168	72	20.81	21.39	—	—	10	68	"
47.	4-Phenyl-2-thiazolyl	210	64	19.05	19.45	—	—	4	34	"
48.	4-(α -Naphthyl)-2-thiazolyl	145	65	16.85	17.11	—	—	4	35	"
49.	4-(β -Naphthyl)-2-thiazolyl	198	70	18.21	17.11	—	—	4	35	"
50.	4-(<i>p</i> -Hydroxylphenyl)-2-thiazolyl	222	68	19.02	18.66	—	—	3	29	"
51.	4-(<i>p</i> -Methoxyphenyl)-2-thiazolyl	152	65	18.26	17.98	—	—	3	31	"

TABLE I. (Continued)

Sl. No.	Nature of R.	mp °C	Yield %	Halogen (%)		Sulphur (%)		Fungicidal results		
				Found	Calc.	Found	Calc.	Ger. at 10 ppm %	Ger. at 1 ppm %	Test fungus
1	2	3	4	5	6	7	8	9	10	11
52.	4-(<i>p</i> -Chlorophenyl)-2-thiazolyl	134	66	27.21	26.66	—	—	5/7*	41/70*	<i>Piricularia oryzae</i> (Cav.)
53.	4-(<i>p</i> -Bromophenyl)-2-thiazolyl	147	55	32.88	34.01	—	—	5/7*	45/75*	"
54.	4-(β -Phenylethyl)-2-thiazolyl	184	64	18.35	18.07	—	—	4	35	"
55.	4- β -(<i>p</i> -Methoxyphenyl)-ethyl-2-thiazolyl	138	60	17.12	16.79	—	—	4	30	"
56.	4-Phenyl-5-chloro-2-thiazolyl	235	54	25.13	26.67	—	—	1	10	"
57.	4-(α -Naphthyl)-5-chloro-2-thiazolyl	138	60	22.62	23.70	—	—	1	10	"
58.	4-(β -Naphthyl)-5-chloro-2-thiazolyl	195	60	23.11	23.70	—	—	1	15	"
59.	4-(<i>p</i> -Hydroxyphenyl)-5-chloro-2-thiazolyl	175	61	24.86	25.64	—	—	1	18	"
60.	4-(<i>p</i> -Methoxyphenyl)-2-chloro-2-thiazolyl	200	64	23.86	24.79	—	—	2	22	"
61.	4-(<i>p</i> -Chlorophenyl)-5-chloro-2-thiazolyl	230(d)	62	31.83	32.72	—	—	0/0*	15/15*	"
62.	4-(<i>p</i> -Bromophenyl)-5-chloro-2-thiazolyl	108	60	38.08	38.97	—	—	0/0*	15/18*	"
63.	4-(β -Phenylethyl)-5-chloro-2-thiazolyl	238	58	24.15	25.03	—	—	2	25	"
64.	4- β -(<i>p</i> -Methoxyphenyl)-ethyl-5-chloro-2-thiazolyl	156	60	22.82	23.28	—	—	3	30	"
65.	4-(<i>p</i> -Phenyl)-5-bromo-2-thiazolyl	225	62	33.18	34.01	—	—	2	24	"
66.	4-(α -Naphthyl)-5-bromo-2-thiazolyl	176	62	29.42	30.57	—	—	2	25	"
67.	4-(β -Naphthyl)-5-bromo-2-thiazolyl	162	68	29.51	30.57	—	—	3	30	"
68.	4-(<i>p</i> -Hydroxyphenyl)-5-bromo-2-thiazolyl	153	60	31.53	32.83	—	—	3	32	"
69.	4-(<i>p</i> -Methoxyphenyl)-5-bromo-2-thiazolyl	112	58	30.62	31.85	—	—	3	32	"
70.	4-(<i>p</i> -Chlorophenyl)-5-bromo-2-thiazolyl	181	60	37.63	38.97	—	—	3/5*	30/50*	"
71.	4-(<i>p</i> -Bromophenyl)-5-bromo-2-thiazolyl	198	60	43.03	44.17	—	—	3/5*	30/45*	"
72.	4-(β -Phenylethyl)-5-bromo-2-thiazolyl	160	62	31.21	32.00	—	—	3	32	"
73.	4- β -(<i>p</i> -Methoxyphenyl)-ethyl-5-bromo-2-thiazolyl	112	60	29.31	30.08	—	—	4	36	"
74.	4-Phenyl-5-iodo-2-thiazolyl	222	56	38.68	40.33	—	—	4	35	"
75.	4-(α -Naphthyl)-5-iodo-2-thiazolyl	141	55	34.82	36.60	—	—	4	37	"
76.	4-(β -Naphthyl)-5-iodo-2-thiazolyl	217	56	35.01	36.60	—	—	4	37	"
77.	4-(<i>p</i> -Hydroxyphenyl)-5-iodo-2-thiazolyl	146	55	37.82	39.05	—	—	3	35	"
78.	4-(<i>p</i> -Methoxyphenyl)-5-iodo-2-thiazolyl	196	56	36.55	38.01	—	—	3	32	"

TABLE I. (Continued)

Sl. No.	Nature of R.	mp °C	Yield %	Halogen (%)		Sulphur (%)		Fungicidal results		
				Found	Calc.	Found	Calc.	Ger. at 10 ppm %	Ger. at 1 ppm %	Test fungus
1	2	3	4	5	6	7	8	9	10	11
79.	4-(<i>p</i> -Chlorophenyl)-5-iodo-2-thiazolyl	112	55	43.52	44.43	—	—	4/7*	50/60*	<i>Piricularia oryzae</i> (Cav.)
80.	4-(<i>p</i> -Bromophenyl)-5-iodo-2-thiazolyl	200	54	47.13	48.76	—	—	5/7*	52/65*	"
81.	4-(β -Phenylethyl)-5-iodo-2-thiazolyl	216	52	37.21	38.15	—	—	4	45	"
82.	4-(β -(<i>p</i> -Methoxyphenyl)-ethyl-5-iodo-2-thiazolyl	186	54	35.12	36.07	—	—	4	42	"
<div style="text-align: center;"> <p>(Fungicidal assay in control—94% germination)</p> </div>										
83.	(<i>o</i>)Bromophenyl	152	63	43.35	43.12	—	—	0	20	<i>Carvularia lunata</i>
84.	(<i>p</i>)Bromophenyl	176	72	42.60	43.12	—	—	0	20	"
85.	(<i>o</i>)Chlorophenyl	171	82	35.03	35.37	—	—	10	75	"
86.	(<i>p</i>)Chlorophenyl	210~212	60	35.20	35.37	—	—	4	50	"
87.	(β)Naphthyl	176	68	23.83	23.40	—	—	6	50	"
88.	4-(β -Phenylethyl)-2-thiazolyl	84	55	20.06	20.00	—	—	23	90	"
89.	4-Phenyl-5-bromo-2-thiazolyl	130	60	33.53	35.26	—	—	27	90	"
90.	4-(β -Phenylethyl)-5-bromo-2-thiazolyl	104	60	33.53	33.33	—	—	1	20	"
91.	4-(<i>p</i> -Tolyl)-5-bromo-2-thiazolyl	98	58	34.08	34.18	—	—	32	90	"
<div style="text-align: center;"> <p>(Fungicidal assay in control—97% germination)</p> </div>										
92.	Phenyl	155~56	80	4.87	5.32	—	—	17	90	<i>Piricularia oryzae</i> (Cav.)
93.	(<i>o</i>)Chlorophenyl	140	72	12.21	11.94	—	—	18	95	"
94.	(<i>m</i>)Chlorophenyl	198	65	11.62	11.94	—	—	15	85	"
95.	(<i>p</i>)Chlorophenyl	175	70	11.64	11.94	—	—	12	90	"
96.	(<i>p</i>)Bromophenyl	188	68	22.92	23.24	—	—	13	90	"
97.	4-Phenyl-2-thiazolyl	199~200	65	—	—	9.62	9.25	16	90	"
98.	4-(<i>p</i> -Bromophenyl)-2-thiazolyl	150~151	70	—	—	7.32	7.53	16	90	"
99.	4-(β -Phenylethyl)-2-thiazolyl	183	68	—	—	8.94	8.82	15	90	"
100.	4-(Isobutyl)-2-thiazolyl	215	68	—	—	9.63	9.41	13	90	"
101.	4-(<i>p</i> -Methoxyphenyl)-2-thiazolyl	186	65	—	—	8.12	8.54	10	89	"
102.	4-(<i>p</i> -Chlorophenyl)-2-thiazolyl	182	64	—	—	8.93	8.43	12	90	"
103.	4-Methyl-5-carbethoxy-2-thiazolyl	178	64	—	—	9.37	9.76	10	90	"

TABLE I. (Continued)

Sl. No.	Nature of R.	mp °C	Yield %	Halogen (%)		Sulphur (%)		Fungicidal results		
				Found	Calc.	Found	Calc.	Ger. at 10 ppm %	Ger. at 1 ppm %	Test fungus
1	2	3	4	5	6	7	8	9	10	11
04.	4-Phenyl-5-bromo-2-thiazolyl	169	66	—	—	6.98	7.53	11	80	<i>Piricularia oryzae</i> (Cav.)
05.	4-(<i>p</i> -Bromophenyl)-5-bromo-2-thiazolyl	180	70	—	—	6.10	6.35	3	30	"
06.	4-(<i>p</i> -Methoxyphenyl)-5-bromo-2-thiazolyl	168	71	—	—	6.84	7.03	6	52	"
07.	4-(<i>p</i> -Chlorophenyl)-5-bromo-2-thiazolyl	250	72	—	—	6.63	6.96	3	31	"

(Fungicidal assay in control—95% germination)

108.	Phenyl	192	68	23.20	23.40	—	—	9	70	"
109.	(<i>o</i>)Chlorophenyl	180	72	30.45	30.67	—	—	10	80	"
110.	(<i>m</i>)Chlorophenyl	218	68	30.61	30.67	—	—	9	70	"
111.	(<i>p</i>)Chlorophenyl	195	66	30.20	30.67	—	—	9	75	"
112.	(<i>p</i>)Bromophenyl	215	60	37.73	37.99	—	—	12	85	"
113.	4-Phenyl-2-thiazolyl	195	70	18.57	18.82	—	—	5	40	"
114.	4-(<i>p</i> -Bromophenyl)-2-thiazolyl	195	71	31.54	31.74	—	—	13	85	"
115.	4-(<i>β</i> -Phenylethyl)-2-thiazolyl	182	72	17.45	17.66	—	—	14	19	"
116.	4-(Isobutyl)-2-thiazolyl	> 250	70	19.48	19.75	—	—	12	81	"
117.	4-(<i>p</i> -Methoxyphenyl)-2-thiazolyl	185	60	17.32	17.58	—	—	6	55	"
118.	4-(<i>p</i> -Chlorophenyl)-2-thiazolyl	190	68	24.91	25.14	—	—	12	85	"
119.	4-Methyl-5-carbethoxy-2-thiazolyl	150	66	18.10	18.35	—	—	12	84	"
120.	4-Phenyl-5-bromo-2-thiazolyl	212	68	31.48	31.74	—	—	3	8	"
121.	4-(<i>p</i> -Bromophenyl)-5-bromo-2-thiazolyl	> 250	68	40.75	41.09	—	—	7	55	"
122.	4-(<i>p</i> -Methoxyphenyl)-5-bromo-2-thiazolyl	231	70	29.64	29.90	—	—	10	80	"
123.	4-(<i>p</i> -Chlorophenyl)-5-bromo-2-thiazolyl	192	70	35.98	36.24	—	—	5	40	"

(Fungicidal assay in control—95% germination)

124.	Phenyl	243	70	4.94 (Nitrogen)	5.32	—	—	17	95	"
125.	(<i>p</i>)Tolyl	221	71	4.58 (Nitrogen)	5.04	—	—	15	90	"
126.	(<i>α</i>)Naphthyl	222	65	4.12 (Nitrogen)	4.47	—	—	12	85	"

TABLE I. (Continued)

Sl. No.	Nature of R.	mp °C	Yield %	Halogen (%)		Sulphur (%)		Fungicidal results		
				Found	Calc.	Found	Calc.	Ger. at 10 ppm %	Ger. at 1 ppm %	Test fungus
1	2	3	4	5	6	7	8	9	10	11
127.	(β)Naphthyl	243	66	3.98 (Nitrogen)	4.47	—	—	10	80	<i>Piricularia oryzae</i> (Cav.)
128.	(<i>o</i>)Chlorophenyl	225	66	11.78	11.94	—	—	16	90	"
129.	(<i>m</i>)Chlorophenyl	241	68	11.69	11.94	—	—	15	85	"
130.	(<i>p</i>)Chlorophenyl	238	70	11.81	11.94	—	—	12	80	"
131.	(<i>p</i>)Bromophenyl	248~49	70	22.92	23.24	—	—	13	85	"
132.	4-Phenyl-2-thiazolyl	>250	65	—	—	8.87	9.25	14	85	"
133.	4-(<i>p</i> -Bromophenyl)-2-thiazolyl	233	64	—	—	7.38	7.53	4	45	"
134.	4-(<i>p</i> -Chlorophenyl)-2-thiazolyl	250	70	—	—	8.12	8.43	6	55	"
135.	4-(<i>p</i> -Methoxyphenyl)-2-thiazolyl	195	72	—	—	8.32	8.54	8	60	"
136.	4-Phenyl-5-bromo-2-thiazolyl	130	68	—	—	7.21	7.53	5	50	"
137.	4-(<i>p</i> -Bromophenyl)-5-bromo-2-thiazolyl	>250	68	—	—	5.98	6.35	7	50	"
138.	4-(<i>p</i> -Chlorophenyl)-5-bromo-2-thiazolyl	175	66	—	—	6.61	6.96	5	45	"
139.	4-(<i>p</i> -Methoxyphenyl)-5-bromo-2-thiazolyl	200	66	—	—	6.82	7.03	7	50	"

(Fungicidal assay in control—96% germination)

140.	Phenyl	161	70	23.24	23.40	—	—	9	70	"
141.	(<i>p</i>)Tolyl	105	71	22.10	22.44	—	—	9	75	"
142.	(α)Naphthyl	152	70	20.21	20.40	—	—	9	72	"
143.	(β)Naphthyl	135	66	20.74	20.40	—	—	9	70	"
144.	(<i>o</i>)Chlorophenyl	203	64	30.68	30.67	—	—	10	75	"
145.	(<i>m</i>)Chlorophenyl	160	65	31.21	30.67	—	—	9	70	"
146.	(<i>p</i>)Chlorophenyl	215	70	30.68	30.67	—	—	9	75	"
147.	(<i>p</i>)Bromophenyl	190	68	38.31	38.00	—	—	12	80	"
148.	4-Phenyl-2-thiazolyl	>250	68	18.57	18.82	—	—	12	80	"
149.	4-(<i>p</i> -Bromophenyl)-2-thiazolyl	210	70	31.54	31.74	—	—	4	28	"
150.	4-(<i>p</i> -Chlorophenyl)-2-thiazolyl	200	71	24.91	25.14	—	—	5	31	"
151.	4-(<i>p</i> -Methoxyphenyl)-2-thiazolyl	225	70	17.32	17.58	—	—	7	50	"
152.	4-Phenyl-5-bromo-2-thiazolyl	220	68	31.48	31.74	—	—	4	30	"
153.	4-(<i>p</i> -Bromophenyl)-5-bromo-2-thiazolyl	238	71	40.75	41.09	—	—	6	45	"
154.	4-(<i>p</i> -Chlorophenyl)-5-bromo-2-thiazolyl	220	70	35.98	36.24	—	—	3	30	"
155.	4-(<i>p</i> -Methoxyphenyl)-5-bromo-2-thiazolyl	232	70	29.64	29.90	—	—	5	40	"

* Shows % of germination of *Helminthosporium oryzae*.

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