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Studies in the Synthesis of Some Substituted Pyrimidines and their Effects on Phytotic Growth of Some Grain and Vegetable Crops

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Abstract: In the present work the substituted β-diketones (4a-d) react with urea and thiourea respectively in DMF solvent and refluxed it at 75^{0}C to obtained a novel series of substituted 2-Hydroxy Pyrimidines (5a-d) and 2-Mercapto Pyrimidines (6a-d) respectively. The newly synthesized compounds were elucidated on the basis of molecular weight, elemental analysis and their spectral data analysis. The titled compounds were evaluated for their growth promoting activity on some grain and vegetable crops viz. Gram/*Cicer arietinum*, Green gram/*Vigna radiata*, Tomato/*Lycopersicum* and Lady's Finger/*Abelmoschus esculentus.*

Keywords: Propan-1,3-diones, Urea, Thiourea, 2-Hydroxy Pyrimidines, 2-Mercapto Pyrimidines, Growth promoting activities.

I. INTRODUCTION:

Heterocyclic compounds are abundant in nature such as alkaloids, vitamins, amino acids, antibiotics, hormones, hemoglobin etc.They containing heterocyclic atoms which are very important for the synthesis of organic compounds. Among these compounds pyrimidines containing Nitrogen heterocyclic ring which play an important role in Medicinal chemistry, Biochemistry and pharmacological studies. Pyrimidine is a six-member heterocyclic compound which contains two nitrogen atoms at positions 1 and 3. Pyrimidine derivatives are known to be biologically active compounds. Pyrimidine and its derivatives exhibited several applications such as antimicrobial [1-2], anti-inflammatory [3-4], antioxidant [5-6], anticancer [7], anti-diabetic [8]. The synthesis of substituted 2-mercapto pyrimidines [9-10] and 2-hydroxy pyrimidines [11-12] and their phytotic growth effects of some crop plants [13-20] are attracting research work because it involves both S, N and O atoms in their ring. In previse research work substituted 2-mercapto pyrimidines [21] and 2-hydroxy pyrimidines [22] was synthesized from 4-bromo phenol as a precursor containing β-diketones as intermediate. Now in present work studies the synthesis of some substituted pyrimidines and their effects on phytotic growth of Gram/*Cicer arietinum*, green gram/*Vigna radiata*, Tomato/*Lycopersicum* and Lady's Finger/*Abelmoschus esculentus* grain and vegetable crops.

II. MATERIALS AND METHODS:

All the solvents and chemicals were of research grade and highest purity. The IR spectrum was recorded by using Shimadzu IR affinity-1FTIR instrument, H^{1}NMR spectra were recorded on Bruker advance II-400 MHz spectrometer, Mass spectra were recorded on ESI and Melting point were determined by open capillary tube method which are uncorrected. All the synthesized compounds were purified by recrystallization method and purity of the compound was checked by TLC and elemental analysis.

2.1 General procedure for the Synthesis of 2-Hydroxy-4,6-disubstituted phenyl Pyrimidines (5a-d)

The compounds of substituted propan-1,3-diones (4a-d) (0.02 M) was mixed with Urea (0.02 M) in DMF solvent. It was refluxed on water bath at 75^{0}C for 1hr. then reaction mixture was cooled and pour in ice cold water. The product was recrystallized by aq. alcohol to obtained a series of 2-Hydroxy-4,6-disubstituted phenyl Pyrimidine derivatives (5a-d).

2.2 General procedure for the Synthesis of 2-Mercapto-4,6-disubstituted phenyl Pyrimidines (6a-d)

The compounds of substituted propan-1,3-diones (4a-d) (0.02 M) was mixed with Thiourea (0.02 M) in DMF solvent. It was refluxed on water bath at 75^{0}C for 1hr. then reaction mixture was cooled and pour in ice cold water. The product was recrystallized by aq. alcohol to obtained a series of 2-Mercapto-4,6-disubstituted phenyl Pyrimidine derivatives (6a-d).
The general reaction scheme for the Synthesis of 2-Hydroxy-4,6-disubstituted phenyl Pyrimidines (5a-d) and 2-Mercapto-4,6-disubstituted phenyl Pyrimidines (6a-d) as shown in Figure-1 and their physical data in Table-1.

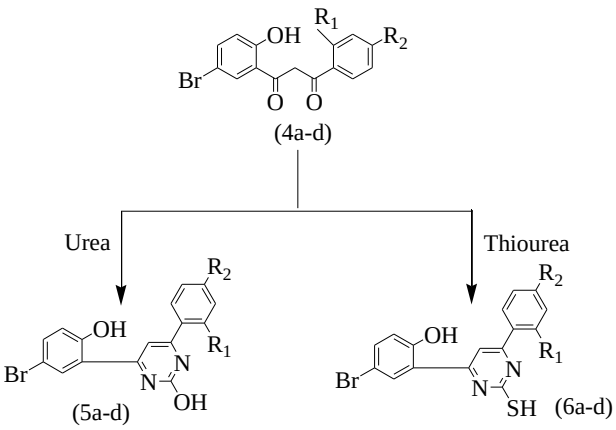


Figure 1: Reaction scheme for the synthesis of 2-Hydroxy-4,6-disubstituted phenyl pyrimidines (5a-d) and 2-Mercapto-4,6-disubstituted phenyl Pyrimidines (6a-d)

Table 1: Physical data of 2-hydroxy Pyrimidines (5a-d) and 2-Mercapto Pyrimidines (6a-d)

Compound Code	Compound Name	Mol. Formula / Mol. Wt. (g/mol)	-R1	-R2	*Rf* value	M.P. (^{0}C)	Yield (%)
5a	2-hydroxy-4-(4-methyl phenyl)-6-(2-hydroxy-5 bromo phenyl) pyrimidine	$C_{17}H_{13}BrN_2O_2$/ (357.20)	-H	$-CH_3$	0.72	80-86	58
5b	2-hydroxy-4-(4-nitro phenyl)-6-(2-hydroxy-5 bromo phenyl) pyrimidine	$C_{16}H_{10}BrN_3O_4$/ (388.17)	-H	$-NO_2$	0.68	116-122	71
5c	2-hydroxy-4-(2-chloro phenyl)-6-(2-hydroxy-5 bromo phenyl) pyrimidine	$C_{16}H_{10}BrClN_2O$/ (377.96)	-Cl	-H	0.66	74 -78	61
5d	2-hydroxy-4-(4-chloro phenyl)-6-(2-hydroxy-5 bromo phenyl) pyrimidine	$C_{16}H_{10}BrClN_2O$/ (377.96)	-H	-Cl	0.70	112-116	65
6a	2-mercapto-4-(4-methyl phenyl)-6-(5-bromo, 2-hydroxy phenyl) Pyrimidine	$C_{17}H_{13}BrN_2OS$/ (373.27)	-H	$-CH_3$	0.71	154-156	74
6b	2-mercapto-4-(4-nitro phenyl)-6-(5-bromo,2-hydroxy phenyl) Pyrimidine	$C_{16}H_{10}BrN_3O_3S$/ (404.24)	-H	$-NO_2$	0.65	276-278	81
6c	2-mercapto-4-(2-chloro phenyl)-6-(5-bromo,2-hydroxy phenyl) Pyrimidine	$C_{16}H_{10}BrClN_2OS$ / (393.69)	-Cl	-H	0.62	214-217	66
6d	2-mercapto-4-(4-chloro phenyl)-6-(5-bromo,2-hydroxy phenyl) Pyrimidine	$C_{16}H_{10}BrClN_2OS$/ (393.69)	-H	-Cl	0.68	254-256	70

2.3 Phytotic growth promoting effect of the titled compounds on some grain and vegetable crops.

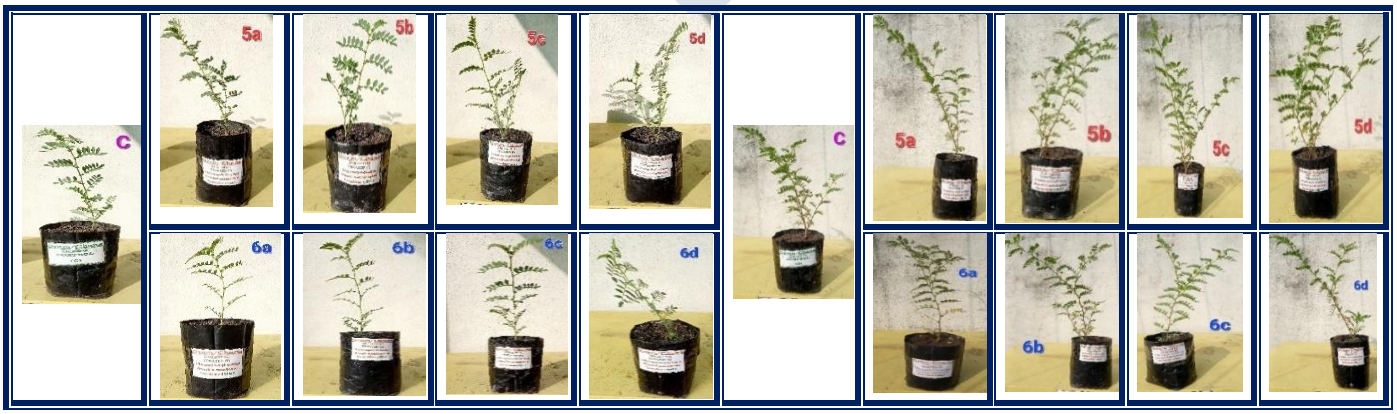
Seed Treatment: Collected all pregerminated seeds of some grains i.e. Gram (*Cicer arietinum*), Green gram (*Vigna radiata*) and vegetable crops i.e. Tomato (*Solanum lycopersicum*), Lady's Finger (*Abelmoschus esculentus*) from agricultural source. With a view to safeguard dormant seed's potential from harmful external agencies, the seeds of the test grain and vegetable crops were treated by test compounds i.e. 2-Hydroxy Pyrimidines (5a-d) and 2-Mercapto Pyrimidines (6a-d). Before sowing the seeds, the solution of the test compounds was prepared by using DMSO solvent having concentrations (0.01 mg/ml) then immersed the dry seeds in test solution for 24 hrs. at room temperature for socking.

Field experiment: The pots of black cotton soil were prepared for sowing the seeds. Take 8 x 12-inch size high density polythene (HDPE) bags containing black soil and labelled on it. These pots ware divided in to two groups i.e. Group A was not sprayed by test compound solution called as 'Control' and Group B was with sprayed by test compound solution called as 'Treated'. The seeds of all four species of crops under examination were sowed in black soil containing bags separately by conventional methods and irrigated it by water. The spraying solution of newly synthesized 2-Hydroxy Pyrimidines (5a-d) and 2-Mercapto Pyrimidines (6a-d) compounds have been prepared in dioxane (0.01 dilution) separately and sprayed at fortnightly intervals 15,30 and 45 days on both crop plants. For analysis of growth promoting impact on the test plants after germination of seeds the plants were carefully examined the number of leaves and shoot heights were recorded after 7, 14, 21, 28, 35, 42,49 and 56 days. The data obtained subjected to analysis of growth parameter as shown in Table no.02,03,04 and 05.

Table 2-Effects of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Gram/*Cicer arietinum* Crop

Test Compound	Gram/*Cicer arietinum* crop									
	Periodicity of Observations →		07 Days	14 Days	21 Days	28 Days	35 Days	42 Days	49 Days	56 Days
5a	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	5	14	19	24	33	38	46	59
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	12	60	170	195	334	510	545	598
5b	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	4	12	16	23	32	33.2	40	49
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	13	51	105	146	382	759	788	806
5c	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	3.5	13	20	26	35	40	45	62
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	14	84	202	228	417	856	872	896
5d	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	6	14.5	19	24	32	36.6	44	56
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	12	99	174	210	351	720	756	798
6a	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	2.5	13	18.5	25	35	42.1	47.5	59
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	9	67	97	147	210	376	395	413
6b	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	5.5	15	21.5	28.5	37.5	41	45	55.5
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	17	79	168	201	334	635	681	701
6c	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	7	15	22	27	30	41	56	67
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	20	50	129	159	298	443	564	585
6d	Shoot height (cm)	C	5	13	19	23	31	35	42	51
		T	4	11	18	24.8	33	39	47	55
	No. of leaves	C	16	80	144	196	377	534	571	612
		T	7	66	88	138	271	550	568	588

(C= Control, T= Treated)



After 21 days Grams After 42 days Grams

Figure 2: Impact of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Gram/Cicer arietinum

Table 3-Effects of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Green gram/ *Vigna radiata* Crop

Test Compound	Green gram/*Vigna radiata* crop									
	Periodicity of Observations →		07 Days	14 Days	21 Days	28 Days	35 Days	42 Days	49 Days	56 Days
5a	Shoot height (cm)	C	5	7	8	8.5	9	9.5	10	11
		T	3	5	7	7.6	8	8.5	9	10
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	5	5	8	10	10	11	13
5b	Shoot height(cm)	C	5	7	8	8.5	9	9.5	10	11
		T	3	6	9	10	12	16	17	17.5
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	5	8	8	8	11	14	14
5c	Shoot height(cm)	C	5	7	8	8.5	9	9.5	10	11
		T	4.3	7	8.5	9	9.5	10	10.5	12
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	2	5	5	8	8	11	14
5d	Shoot height(cm)	C	5	7	8	8.5	9	9.5	10	11
		T	4.8	6	8.1	8.6	9	9.5	10.2	11.6
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	5	5	8	11	13	13	16
6a	Shoot height(cm)	C	5	7	8	8.5	9	9.5	10	11
		T	2	6	8	10	12	15.2	16	17
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	5	8	8	11	11	14	15
6b	Shoot height(cm)	C	5	7	8	8.5	9	9.5	10	11
		T	3.5	6	8	9.7	12	16	17	18
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	5	5	8	11	14	16	16
6c	Shoot height(cm)	C	5	7	8	8.5	9	9.5	10	11
		T	4	5	8.5	8.6	14	17	17.6	18.5
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	5	8	11	14	16	17	19
6d	Shoot height(cm)	C	5	7	8	8.5	9	9.5	10	11
		T	4.5	6.5	7.5	8.2	9	9.2	10.2	10.7
	No. of leaves	C	2	5	5	8	8	9	9	10
		T	2	5	5	8	8	8	9	10

(C= Control, T= Treated)

After 21 days Green Grams After 42 days Green Grams

Figure 3: Impact of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Green gram/*Vigna radiata* crop

Table 4-Effects of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Tomato/ *Solanum Lycopersicum* Crop

Test Compound	Tomato/*Solanum Lycopersicum*									
	Periodicity of Observations →		07 Days	14 Days	21 Days	28 Days	35 Days	42 Days	49 Days	56 Days
5a	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	2.3	5	6.2	10	21	36	38	40
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	17	30	36	47	56	64
5b	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	3	4	8	9	20	35	36	37
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	16	26	39	54	62	68
5c	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	3	5	8	11	21	37	39	41
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	15	24	31	49	57	63
5d	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	2.5	4	6	8	26	40	41	42
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	12	20	53	65	68	71
6a	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	2.6	6	9.6	15	23	38	39	41
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	16	38	43	53	60	65
6b	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	4	6.5	11	19	40	40	55	57
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	19	40	61	76	81	85
6c	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	2.9	5.5	7.5	14	29	43	44	45
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	18	38	56	62	67	72
6d	Shoot height(cm)	C	3	5	9	14	16	22	23	25
		T	3	4.5	7.5	10	22	41	42	43
	No. of leaves	C	2	8	18	36	41	46	52	60
		T	2	8	18	28	45	60	65	68

C= Control, T= Treated

After 21 days Tomato After 42 days Tomato

Figure 4: Impact of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Tomato/*Solanum Lycopersicum*

Table 5-Effects of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Lady's Finger / *Abelmoschus esculentus* Crop

Test Compound	Lady's Finger / *Abelmoschus esculentus*									
	Periodicity of Observations →		07 Days	14 Days	21 Days	28 Days	35 Days	42 Day	49 Days	56 Days
5a	Shoot height (cm)	C	2	4.5	6.5	7	10	13	15	17
		T	1.2	7	10	12	18	21	23	26
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	4	5	5	6	7
5b	Shoot height(cm)	C	2	4.5	6.5	7	10	13	15	17
		T	2.1	5.5	6	7	10	15	17	19
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	5	5	6	6	7
5c	Shoot height(cm)	C	2	4.5	6.5	7	10	13	15	17
		T	2	6	7	10	15	17	18	23
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	5	5	6	6	7
5d	Shoot height(cm)	C	2	4.5	6.5	7	10	13	15	17
		T	3.2	6	7	10	12	17	18	24
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	4	5	5	6	7
6a	Shoot height(cm)	C	2	4.5	6.5	7	10	13	15	17
		T	2	6	7	8	13	18	20	24
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	5	5	6	7	7
6b	Shoot height(cm)	C	2	4.5	6.5	7	10	13	15	17
		T	2	7	8	10	20	25	27	29
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	4	5	5	6	7
6c	Shoot height(cm)	C	2	4.5	6.5	7	10	13	15	17
		T	2.3	5.4	7	10	16	20	23.5	25
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	4	5	6	6	7
6d	Shoot height(cm)	C	2	4.5	6.5	7	10	13	15	17
		T	2.5	5.5	7	10	15	19	22.5	25.5
	No. of leaves	C	2	3	4	4	4	5	5	6
		T	2	3	4	5	5	6	7	8

C= Control,
T= Treated

After 21 days Lady's Finger After 42 days Lady's Finger

Figure 5: Impact of 2-hydroxy Pyrimidines (5a-d) and 2-mercapto Pyrimidines (6a-d) on the growth of Lady's Finger / *Abelmoschus esculentus*

III. RESULTS AND DISCUSSION

The study of comparison of morphological character i.e. number of leaves and shoot height of grain and vegetable crops was made between treated and controlled crops, it was interesting to note that all the treated (T) crops exhibited remarkable result of

shoot growth and considerable increase in the number of leaves as compared with the control (C) crops. When all the treated crops were compared among themselves with control crops, it was distinctly observed that the compound 5c and 6c shows more no. of leaves and shoot height of in Gram /*Cicer arietinum* grain plant, the compound 6c and 6b shows dominant result in green gram/ *Vigna radiata* grain plant as well as in Tomato/ *Solanum Lycopersicum* vegetable plant respectively. In lady's Finger /*Abelmoschus esculentus* crop plant shows more growth rate on their shoot height and no. of leaves by 6b and 6d compounds respectively. In the first interval of 14 to 28 days the growth of treated crops gradually increases but after 28 days it was rapidly increases and shows good result. Because nitrogen holds a pivotal regulatory function in multiple biological processes such as carbon and amino acid metabolism, nucleic acid procedures, and protein synthesis.

IV. CONCLUSION

The nitrogen containing 2-hydroxy pyrimidines (5a-d) and Sulphur containing 2-mercapto pyrimidines (6a-d) compounds shows remarkable phytotic growth effects on grain and vegetable crops as compared with 'control' crops and it will protect the crop from microbial infections.

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