

Synthesis and Growth Promoting Effects of Chlorosubstituted Pyrazolines on Vegetable Crop Plants

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Abstract

The present study was aimed at investigation of synthesized chloro-substituted heterocyclic like pyrazolines for seed treatment and to test their growth promoting hormonal effect on common vegetable crops like *Capsicum annum* L. (Chilly), *Solanum melongena* (Brinjal), *Raphanus sativus* L. (Radish) and *Ipomoea batatas* (L.) Lamk. (Ratali) with predetermined periodicity.

Keywords: Pyrazolines, *capsicum annum* L., *Solanum melongena*, *Raphanus sativus* L., *Ipomoea batates* (L.) Lamk.

Introduction

Recent developments in the field of agricultural sciences indicated that scientists across the globe are emphasizing on an interdisciplinary approach to control the plant diseases, enhance vegetative growth and to increase the yield. Chillies are widely used throughout the tropics and are major ingredients of curry powder in the culinary preparations.

The green chillies are rich in rutin, which is of immense pharmaceutical need¹. Green chillies are rich in Vitamin A and C and the seed contain traces of starch². Brinjal is an annual crop, largely grown in almost all parts of India as one of the principle vegetable; it is quite high in nutritive value. Radish is cultivated for its edible root and top is cooked as leafy vegetable and is rich in minerals and Vitamin A and C. Sweet potato is chiefly used for human consumption and for manufacture of starch and alcohol. It is a subsidiary food crop and efficient caloric supplier³. The

choice of these crops were selected by their enormously vast utilities and also the indispensability for the survival of the human race, all across the globe.

Muller et al.⁴ reported 4-aminomethyl diphenyl-2, 4-diphenylhydro-3H-pyrazoline-3-ones as herbicides. Salman and Roger⁵ prepared 2-(4-pentafluorosulphonylphenyl) pyrazoles as insecticides and acaricides. Process for the preparation of substituted pyrazoline has been reported by Gallen Kamp et al.⁶, the compounds are proved to be insecticide intermediate.

T. Subai, Shinichi et al.⁷ synthesized (phenyl aminocarbonyl) pyrazoline, which showed insecticidal activity. Its mortality in 7 days against larvaespodspetra litera found in sweet potato plants at 40 ppm concentration. Modi et al.⁸, reported the synthesis of 1-phenyl-3-(2-hydroxy-4-methoxy-5-nitrophenyl)-5-substituted-phenyl-2-pyrazolines from the corresponding chalcone derivative on treatment with phenylhydrazine. These compounds showed activity against pathogenic bacteria. Recently Maurya⁹ reported the growth promoting effects of pyrazolines and isoxazolines on agricultural crop plants.

The present work deals with the synthesis and growth promoting effects of some chlorosubstituted pyrazolines on cultivated crop plants namely- *Capsicum annuum* L. (Chilly), *Solanum melogena* (Brinjal), *Raphanus sativus* L. (Radish) and *Ipomea batates* Lam (Sweet potato).

Experimental

Synthesis of chlorosubstituted 3, 5 – diaryl – 1 – substituted pyrazolines.

1, 3-Diaryl-prop-2-ene-1-ones (0.01 mol) (1a-b) was refluxed with thiosemicarbazide/isonicotinic acid-hydrazide/semicarbazide hydrochloride (0.02 mol) for 6 to 7 hours in ethanol/DMF solvent. Water containing a little HCl was added to decompose DMF. The product obtained was filtered, washed with sufficient water and crystallized from ethanol to obtain pyrazolines (2a-b).

Spectral Interpretation

2a) IR (ν_{\max}) (cm^{-1}):

3427 (–OH stretch), 2960 (N–H stretch), 1605 (C=N stretch)
1243 (C–N stretch), 717 (C–Cl stretch)

NMR (CDCl_3 + DMSO) (δ ppm)

3.7 (s, 3H, –OCH₃), 3.1–3.4 (dd, 1H_a, –CH), 3.8–4 (dd, 1H_b, –CH), 5.9–6 (dd, 1H_c, –CH), 6.8 (s, 2H, –NH₂), 6.9–7.4 (m, 7H, Ar–H), 9.6 (s, 1H, –OH)

Synthesis of 4-bromo pyrazolines

Chlorosubstituted 3, 5-diaryl-1-substituted pyrazolines (0.005 mol) and NBS (0.005 mol) in CCl₄ (25 ml) refluxed on water bath for about one hour. The contents of the flask were filtered while hot and CCl₄ was distilled off. The residue thus obtained was washed with hot water and crystallized from ethanol to obtain 4-bromo pyrazolines. The identity of the products was confirmed by their IR and ¹H NMR spectroscopic data studies.

Spectral Interpretation3a) IR (ν_{\max}) (cm^{-1}):3427 (–OH stretch), 2960 (N–H stretch), 717 (C–Cl stretch),
1606 (C=N stretch), 1247 (C–N stretch), 2836 (C–H stretch).**NMR (CDCl₃ + DMSO) δ ppm**3.3 (s, H, –OH), 3.8 (s, 3H, –OCH₃), 6 (dd, H_a, –CH), 4 (dd, H_b, –CH), 6.8 (s, 2H, –NH₂), 6.9–7.4 (m, 7H, Ar–H)**Methodology**

The beds of black cotton soil 2.5 x 2.5 meter size were prepared on an open field. The seeds of all four species under examination were sowed in these beds separately by conventional method. The plant beds were irrigated as and when required with tap water. The plants from each bed were divided into two groups (A) and (B). The group (A) plants were kept unsprayed and termed as control group whereas the plants from group (B) designated as treated group (B) plants were sprayed with the compounds being tested. The seeds of group (B) were also treated with test compounds before sowing to screen growth-promoting effects. The spraying solution of newly synthesized chlorosubstituted heterocyclic compound like pyrazolines was prepared in dioxane (0.01 dilution) separately and sprayed thrice at fortnightly intervals (15, 30, 45 days).

All the field experiments were conducted to compare the treated plants of group (B) with the plants from control group (A). The samples were taken at 15, 30, 45, 60, 75 and 90 days after sowing, corresponding to early vegetative, late vegetative, pod filling and pod maturation stages. The plants were carefully examined and number of leaves and heights of shoots were recorded (Table No. 1–4). The data obtained was subjected to analysis of growth parameters.

Effect of Newly Synthesized Compound on the Growth of Cultivated Crops**Table No. 1**

Name of the test compound	Periodicity of the observation (days)	Cultivated Crops															
		Chilly				Brinjal				Radish				Sweet Potato			
		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	T		
1-thiocarboxamido-3-(2-hydroxy-5-chlorophenyl-5-(4-methoxyphenyl)pyrazoline (L ₁) ₂ a	15	1.5	2	2	3	1.5	1.5	3	3	--	--	4	4	2	2.5	7	7
	30	3	4	6	10	3.5	4	7	8	--	--	7	9	5.5	4.5	10	13
	45	4.5	6	11	21	5	6.5	11	15	--	--	9	12	9	8.5	16	20
	60	5	7.5	17	32	7	8.5	14	23	7	9	11	17	14	13	22	31
	75	6	8.5	19	40	8.5	10	16	29	11.5	13.5	14	22	15.5	16	27	42
	90	6	8.5	24	47	8.5	12	16	22	16	21	10	16	18	17	32	38

C – Control, T - Treated

Table No. 2

Name of the test compound	Periodicity of the observation (days)	Cultivated Crops															
		Chilly				Brinjal				Radish				Sweet Potato			
		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
		C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	T
1-thiocarboxamido-3-(2-hydroxy-5-chlorophenyl-4-bromo-5-(4-methoxyphenyl) pyrazoline (L ₂)3a	15	1.5	1	2	2	1.5	2	3	4	--	--	4	4	2	3	7	10
	30	3	3	6	8	3.5	4	7	6	--	--	7	9	5.5	5	10	14
	45	4.5	5.5	11	16	5	6.5	11	12	--	--	9	13	9	8.5	16	24
	60	5	9	17	23	7	8.5	14	21	7	6	11	17	14	14	22	36
	75	6	10.5	19	32	8.5	10.5	16	28	11.5	12.5	14	20	15.5	16.5	27	44
	90	6	10.5	24	38	8.5	11	14	26	16	18	10	16	18	17	32	40

C – Control, T - Treated

Table No. 3

Name of the test compound	Periodicity of the observation (days)	Cultivated Crops															
		Chilly				Brinjal				Radish				Sweet Potato			
		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
		C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	T
1-thiocarboxamido-3-(2-hydroxy-5-chlorophenyl-5-phenyl) pyrazoline (L ₃)2b	15	1.5	1	2	2	1.5	2	3	3	--	--	4	5	2	2	7	5
	30	3	2.5	6	5	3.5	3.5	7	6	--	--	7	7	5.5	6	10	14
	45	4.5	4	11	11	5	6	11	9	--	--	9	13	9	12	16	22
	60	5	6.5	17	21	7	8.5	14	15	7	8	11	17	14	18	22	30
	75	6	7	19	29	8.5	10.5	16	19	11.5	11	14	22	15.5	21	27	38
	90	6	7	24	22	8.5	10.5	16	14	16	19	10	16	18	23	32	36

C – Control, T - Treated

Table No. 4

Name of the test compound	Periodicity of the observation (days)	Cultivated Crops															
		Chilly				Brinjal				Radish				Sweet Potato			
		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
		C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	T
1-thiocarboxamido-3-(2-hydroxy-5-chlorophenyl-4-bromo-5-phenyl) pyrazoline (L ₄)3b	15	1.5	1	2	2	1	1.5	2	3	--	--	4	5	2	2	7	6
	30	3	2.5	6	5	3.5	3.5	8	7	--	--	7	8	5.5	4.5	10	14
	45	4.5	4.5	11	12	5.5	5	13	11	--	--	9	10	9	9	16	19
	60	5	5.5	17	20	8	7	15	16	7	6	11	14	14	16	22	34
	75	6.5	7	19	24	9.5	8.5	20	18	11.5	10	14	18	15.5	19	27	38
	90	6.5	7	24	26	9.5	8.5	18	16	16	15.5	10	13	19	21	30	26

C – Control, T – Treated

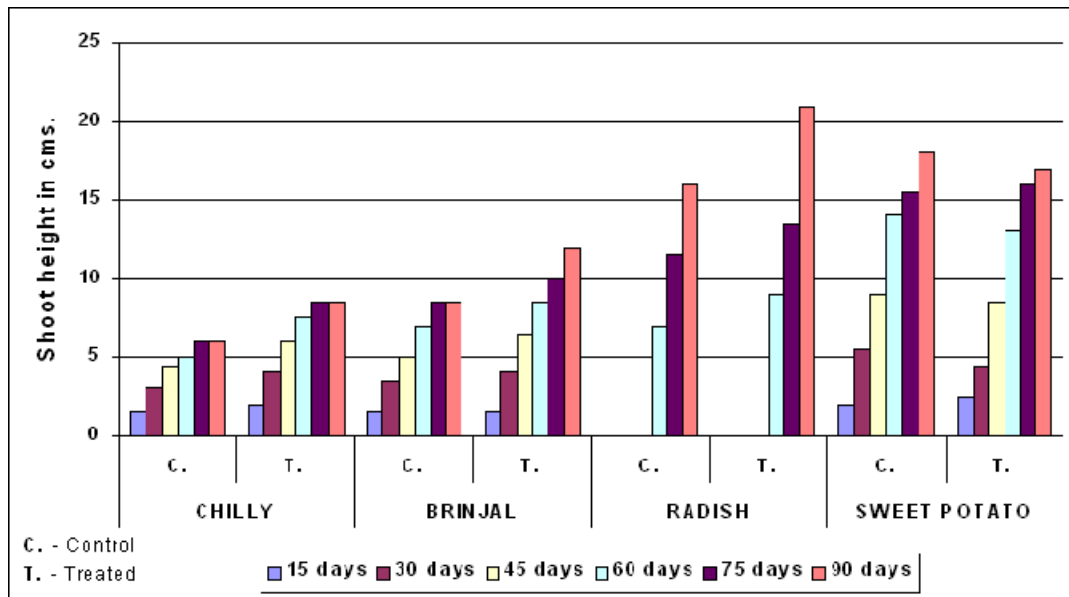


Figure 1 Graph showing relation between shoot height in cms. And no. Of days for control and treated plants (ligand 1).

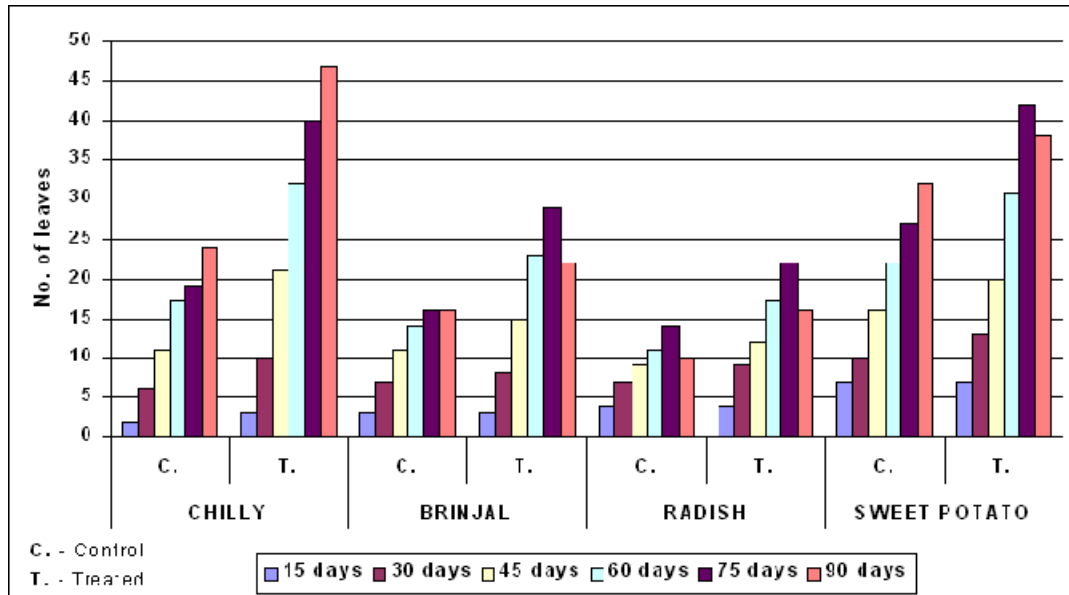


Figure 2: Graph showing relation between no. Of leaves and no. Of days for control and treated plants (ligand 1).

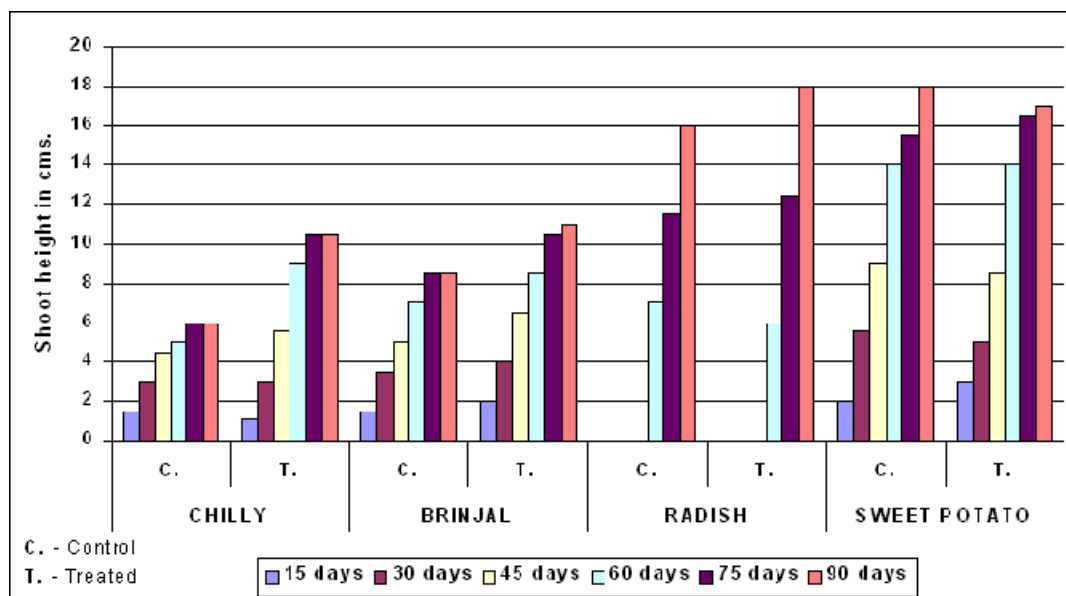


Figure 3: Graph showing relation between shoot height in cms. And no. Of days for control and treated plants (ligand 2).

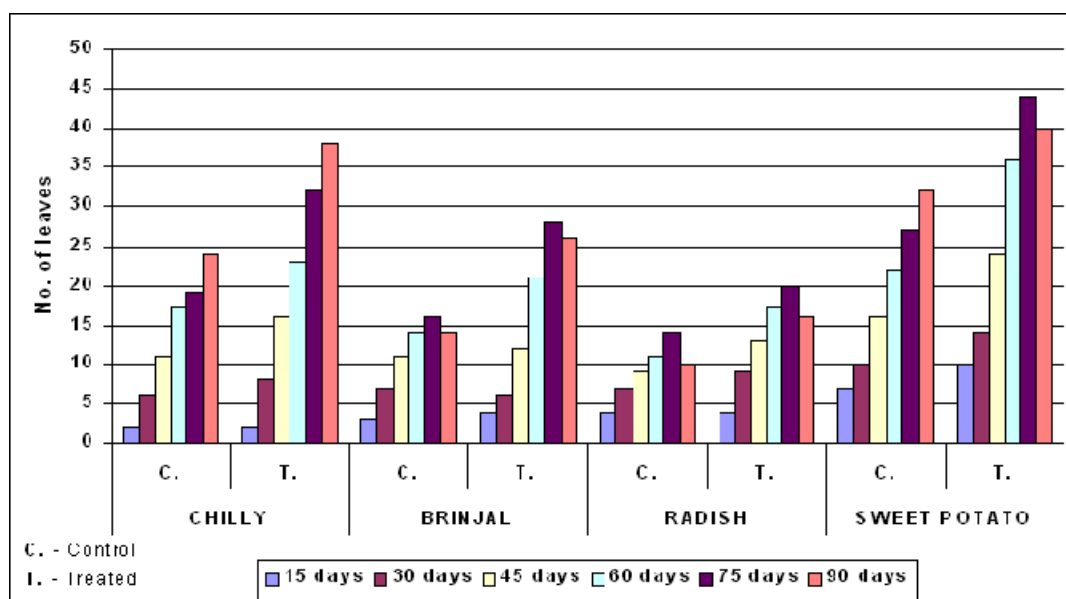


Figure 4: Graph showing relation between no. Of leaves and no. Of days for control and treated plants (ligand 2).

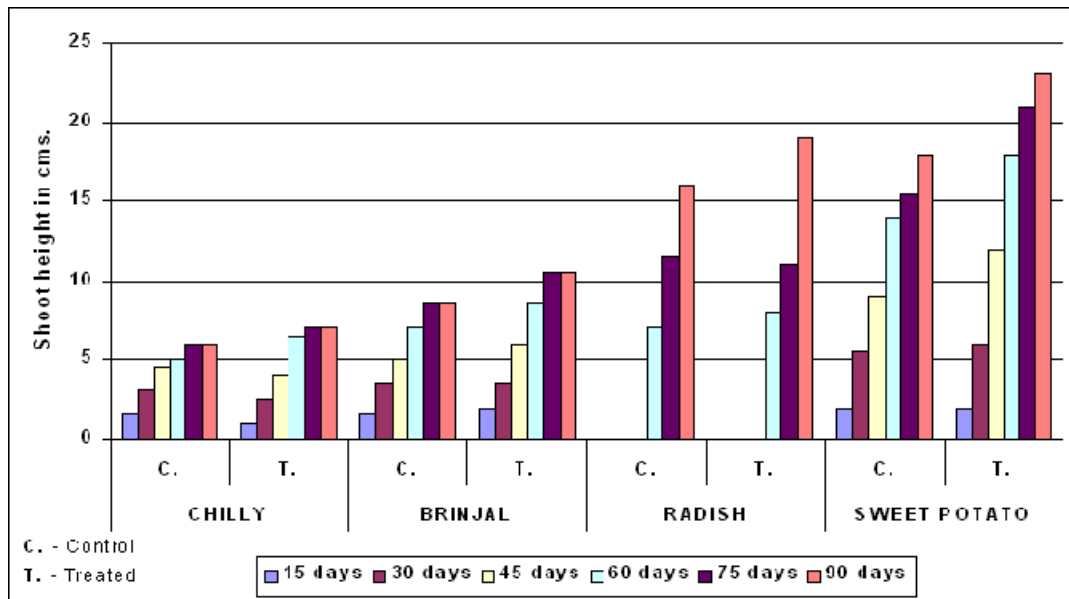


Figure 5: Graph showing relation between shoot height in cms. And no. Of days for control and treated plants (ligand 3).

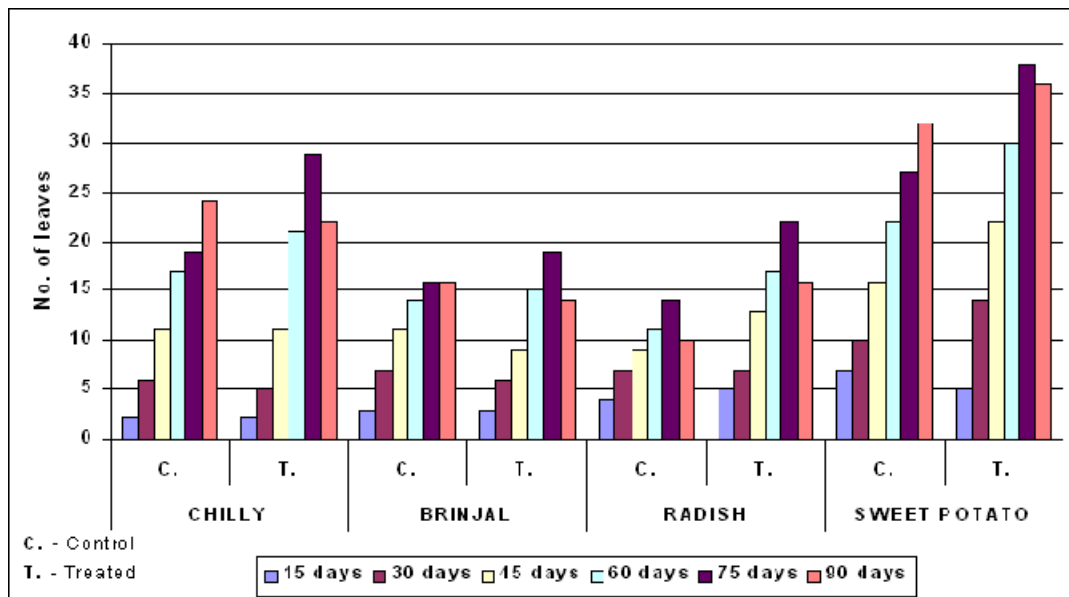


Figure 6: Graph showing relation between no. Of leaves and no. Of days for control and treated plants (ligand 3).

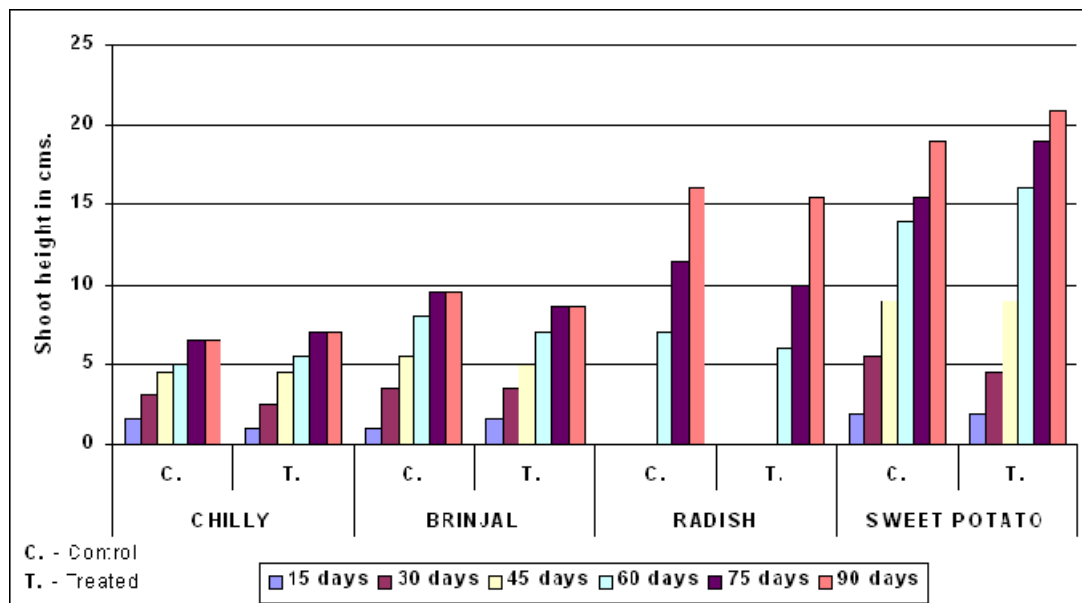


Figure 7: Graph showing relation between shoot height in cms. And no. Of days for control and treated plants (ligand 4).

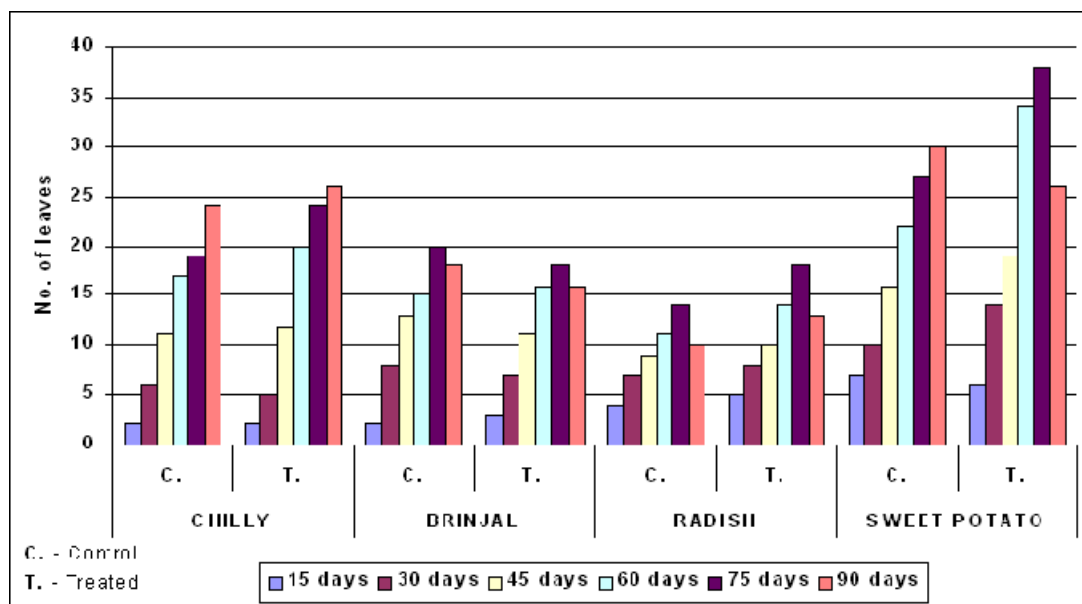


Figure 8: Graph showing relation between no. Of leaves and no. Of days for control and treated plants (ligand 4).

Results and Discussion

The efforts have been made to investigate and analyze the convergence and divergence of the effects of test compounds on the morphology of plants under investigation.

From figures 1-8, it is observed that when the first observation of morphological characters was made between those of treated and control group plants, it was interesting to note that, all the treated plants exhibited remarkable shoot growth and considerable increase in the number of leaves as compared to those untreated ones¹⁰⁻¹³. The biomass of the treated plant increases by the heterocyclic compounds containing thio group ($-CSNH_2$) and nitrogen. This observation may be attributed to the presence of nitrogen containing heterocyclic rings in the test compounds, which might have encouraged the formation of nitrogen fixing nodular growth in the plant roots.

References

- [1] Bose T. K. and Som M.G., "*Vegetable crops in India*", (1986), 253.
- [2] Sayed S. and Bagavandas M., *South Indian Hort.*, 28(1980), 42-47.
- [3] Das P. C., *Vegetable crops of India*, Kalyani Publishers (1993).
- [4] Muller Peter, Wold Hikmar, Santel Hans, Schmidt, *Chem. Abstr.*, 119 (1993), 95516 k.
- [5] Salman, Roger, *Chem. Abstr.*, 119(1993), 39218w.
- [6] Gallen Kamp, Bernd, Duchs, Rainer, *Chem. Abstr.* 119(1993), 203408n.
- [7] Subai, T., Shinichi, *Eur. Pat. Appl.*, EP 537, 581 (CI. CO7D401/048), 21 Apr. 1993, *J. Appl.* 91/297, 7793, 18 Oct. 1991; 21 PP. *Chem. Abstr.*, 109(1993), 139219.
- [8] Modi S. R., Patel M. R., *Chem. Dep. South Gujarat Uni. Surat, India J. Inst. Chem. (India)*, 66(1)1994, 17-18 (Eng.) *Chem. Abstr.*, 122, 105753P (1995).
- [9] Maurya M. R., Parate V. V., Tidke J. A. and Rajput P. R., *Asian J. Chem.*, 15(3)(4)(2003), 1759-1763.
- [10] Raychaudhari S. P., *Ren. Appl. Mycol.*, 46, 577(1963).
- [11] Raychaudhari S. P., *History of Plant Pathology in India*, *Annu. Rev. Phytopathol.*, 10-21.
- [12] Singha R. S., *Plant Diseases*, 5th Edn., Oxford and IBH Publishing Co., New Delhi (1983).
- [13] Mehta P. R., *Plant Pathology in India: Past, Present and Prospects*, *Indian Phytopath.*, 16, 1(1963).

Schemes

