

Synthesis and PGR Assessment of Some Novel Chalcones and Pyrazoles

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Abstract: Now a day's the plant growth regulators-PGRs have developed as an essential part of horticultural and agricultural industries. Consequently, there is great demand for novel and cost-effective products. However, the market is restricted due to inadequate innovation. In such situation chemical genomics should focus his attention on this arena. An integral part of agricultural and horticultural field had developed by Plant growth regulators (PGRs). Subsequently, there is an increased demand for novel and cost efficient products but the market is limited due to unsatisfactory development. Hence the chemical moiety has secured attention on specific route i.e. PGR. In line of this, a valuable discussion and synthesis of some novel Chalcones : 3,4/5-bis((E)-4-chlorobenzylidene)-1-(N-methylpyridin-2-yl)pyrrolidine/ piperidine -2,5/6-dione, and Pyrazoles : 3,4/5-bis(4-chlorophenyl)-7/8-(N-methylpyridin-2-yl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo[2,3-c:5,4-c']dipyrazole/2,3,3a,4,4a,5,6,8-octahydrodipyrazolo[3,4-b:4',3'-e]pyridine were carried out. Most of the synthesized compounds have shown synergetic plant growth activities for maize and moong seeds.

I. Introduction

Agriculture-Industry has a number of challenges to rack up the growing requirement of feasible food production and to ensure better quality nutrition for a speedily growing population. To ensure sufficient food production, it is very important to increase the yield per area of fertile land (Altman and Hasegawa, 2012). A process for achieving this target has been accomplished by plant growth regulators (PGR). Plant growth regulators (PGR) are texture in specific formulations. When it is delivered to plants or seeds it promotes, inhibit and modify anatomical traits. It helps in development as well as stress response (Research, 2014). PGRs are useful to increase productivity and quality. Perhaps it improves consistency in production by overcoming genetic and abiotic limitations in plant productivity. Generally PGRs involves hormones such as cytokinins, auxins (Basra, 2000), mepiquat chloride (Greene, 2012) and paclobutrazol (Wu et al., 2013). The application of PGRs in the field of agriculture has steadily increased in a period of the last twenty years. It happen because of benedictions has become better understood by farmers. Fatally, the expansion of the PGR market may be obstructed by a lack of innovation. To create a demand for new products there is need of steady innovation and discovery of novel, cost-efficient (Metzger, 2001), specific, effective and cheap PGRs (Walsh, 2013). This is main cause for increasing attention of bio-active (Lamberth et al., 2013) molecules (<500 Da).

Chalcone and its bis-pyrazole derivatives oblige a key role in an evolution of heterocyclic chemistry as well as organic synthesis. The present task is negotiating with the eco-friendly synthesis of some novel Chalcones : 3,4/5-bis((E)-4-chlorobenzylidene)-1-(N-methylpyridin-2-yl)pyrrolidine/ piperidine -2,5/6-dione, and Pyrazoles : 3,4/5-bis(4-chlorophenyl)-7/8-(N-methylpyridin-2-yl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo[2,3-c:5,4-c']dipyrazole/2,3,3a,4,4a,5,6,8-octahydrodipyrazolo[3,4-b:4',3'-e]pyridine from N-phenyl succinimide and N-phenyl glutarimides.

Chalcones are the resourceful pioneer of heterocycle dynasty and could be prepared by the condensation (Voskiene et al., 2007) of the substituted aldehyde, ketones and cyclic imide groups (Dhivare et al., 2018; Dhivare and Rajput, 2015; Rajput, 2012; Chaudhari and Rajput, 2016; Patil et al., 2009; Ghosh and Das, 2014). The chalcones are synthesized with the help of various synthetic routes like Knoevenagel condensation (Khalaf et al., 2012), solid phase Claisen- Schmidt, acid catalyst, cross aldol condensation, coupling reaction (Suwito et al., 2014) and microwave assisted synthesis (Chaudhari and Rajput, 2018; Dhivare and Rajput, 2015; Chaudhari and Rajput, 2016).

The another important pioneer of heterocycle dynasty; chalcone based five membered pyrazoles: which can be prepared by hydrazine hydrate or aromatic hydrazines in presence of acetic acid (Tala et al., 2013; Ehsan et al., 2014; Ibrahim et al., 2012), catalysts (Kalirajan et al., 2011; Swarnkar et al., 2014; Awad et al., 2012; Thakrar and Shah, 2012), facile grinding (Poovan et al., 2014), chromine ring opening (Khodairy, 2007), solvent free (Thirunarayanan and Guna Sekar, 2013), one pot tandem (Mohammadi and Adib, 2014) and regio- selective (Lokhande et al., 2005) methods.

Some novel bioactive pyrazoles (Yusuf and Jain, 2014; Kendre and Baseer, 2013) are synthesized by modernistic eco-friendly techniques like solvent free, solid support, microwave (Dabholkar and Gavande, 2003; Bhagat, 2008; Chandak, 2012; Dhivare and Rajput, 2015) and ultrasound synthetic methods which are more constructive than old traditional reflux methods (Arora and Jain, 2013).

II. MATERIAL AND METHODS:

Melting points were recorded in open glass capillaries and uncorrected. The chemical structures of the obtained compounds were confirmed by spectral analyses. IR spectra in (KBr pellets) were recorded on Simadzu and ATR Bruker alpha FT-IR spectrophotometer. ¹H NMR spectra were recorded on 500 MHz by Bruker spectrophotometer. The chemical shifts were reported as parts per million (ppm) with (CH₃)₄Si (TMS) as an internal standard. Signal multiplicities are represented by: s (singlet), d (doublet), t (triplet), m (multiplet). The purity of compound was checked by thin layer chromatography which was performed by using pre-coated silica gel aluminium plates with mixture of diethyl ether and ethyl acetate 7:3 proportion.

2.1 Reagents used for Synthesis:

2.1.1 Conventional Method:

All the compounds (IVa-f and Va-f) were synthesized from the corresponding Succinic/Glutaric Anhydride derivatives; commercially purchased aromatic aldehyde, hydrazine hydrate, glacial acetic acid and ethanol.

2.1.2 Green Method:

All the compounds (IVa-f and Va-f) were synthesized from the corresponding Succinic/Glutaric Anhydride derivatives; commercially purchased aromatic aldehyde, hydrazine hydrate, and neutral Al_2O_3 .

2.1.3 Material used for PGR:

In the material method, the 85 mm Dia. X 15 mm Ht., Petri Dish, Sterile, Disposable: procured from Laxbro Manufacturing Company, W-53, MIDC, Bhosari, Pune-411026. Seeds: maize (Rajeshwar), moong (PKVM-8802) were made available from MAHABEEJ: Maharashtra State Seed Corporation Limited, "Mahabeej Bhavan", Gultekdi, Market Yard, Pune -411008 [India].

- i. Whatman Filter Paper No. 1 (Quantitative Circles 125 mm ϕ).
- ii. Standard – I: VIM – 95 (Humic Acid 95%, Fulvic Acid, K_2O).
- iii. Standard – II: BIOZYME Crop+ (Seaweed-Ascophyllum Nodosum Extract, Proteins, Carbohydrates, Inorganic Salts, Other inherent nutrients contained in product of vegetable and animal origin: 22% w/w; Associated manufacturing derivatives, preservatives, stabilizers, aqueous diluent: 78% w/w)
- iv. Standard – III: DMSO.

2.2 Concentration of compounds:

- i. Stock solution 100 ppm [0.1 gram per liter] of each compound was prepared in DMSO and water.
- ii. Standard – I solution 100 ppm [0.1 gram per liter] of VIM – 95 was prepared in DMSO and water.
- iii. Standard – II solution 100 ppm [0.1 gram per liter] of BIOZYME Crop+ was prepared in DMSO and water.
- iv. Standard – III solution 100 ppm [0.1 gram per liter] was prepared in DMSO and water.

2.3 PGR Protocol:

- i. Healthy seeds of maize (Rajeshwar), moong (PKVM-8802) are of equal size were selected.
- ii. Petri Dish (Sterile, Disposable of size 85 mm Dia. X 15 mm Ht.) were labeled by using appropriate tag.
- iii. Whatman Filter Paper No. 1 (Quantitative Circles 125 mm ϕ) was kept inside Petri Dish.
- iv. Healthy seeds (each maize and moong) of equal size were in sowed in the Petri Dishes which contain Whatman Filter Paper No. 1.
- v. 3ml of Stock solution of compounds as well as Standard Solution I,II,II were taken in Petri Dishes.
- vi. The petri dishes were kept under the incubator at temperature $30^{\circ}C$ and observations made after 6 hours in a day.
- vii. Root length and shoot length were measured after 3, 6 and 9 days later. Weight of root and shoot before and after heating were measured after 9 days later. For heating, roots and shoots were kept in Oven at $50^{\circ}C$ for an hour.

2.4 General Procedure of Synthesis:

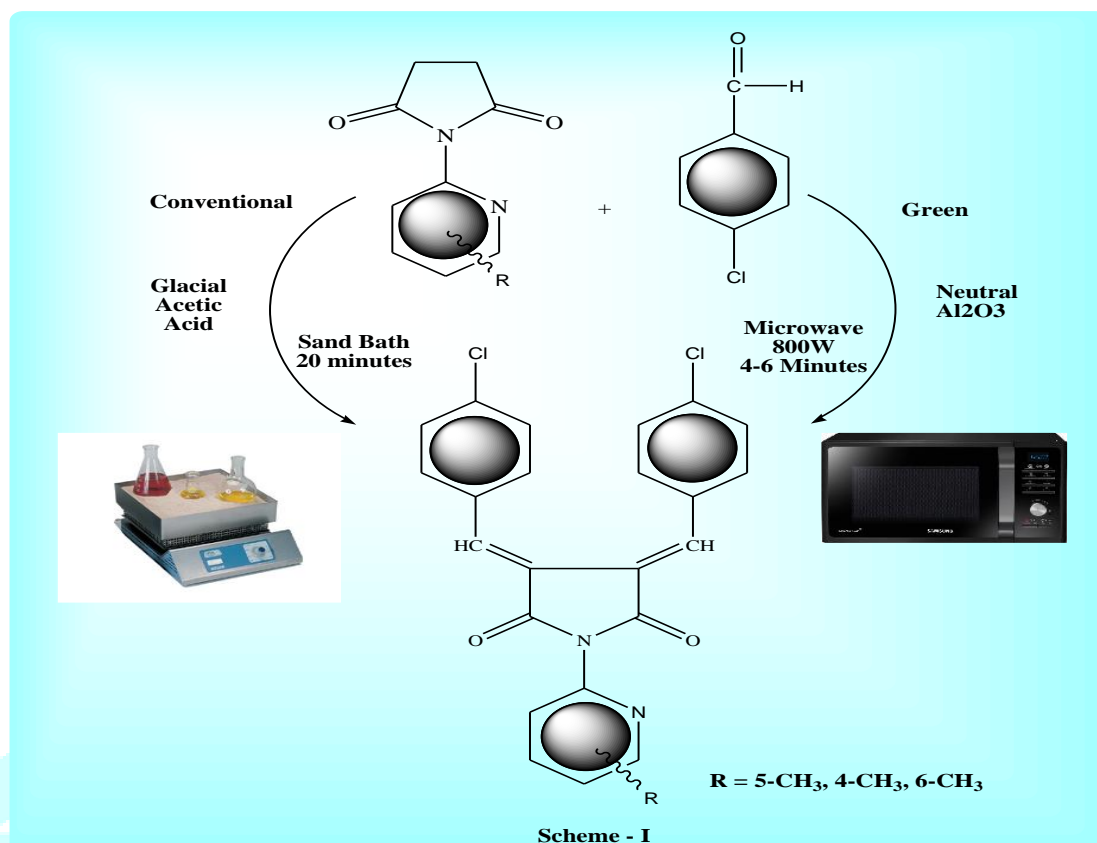
2.4.1 Preparation of bis chalcones (IVa-f) from N-phenyl Succinimide, N-phenyl Glutaramide derivatives:

2.4.1.1 Conventional Method:

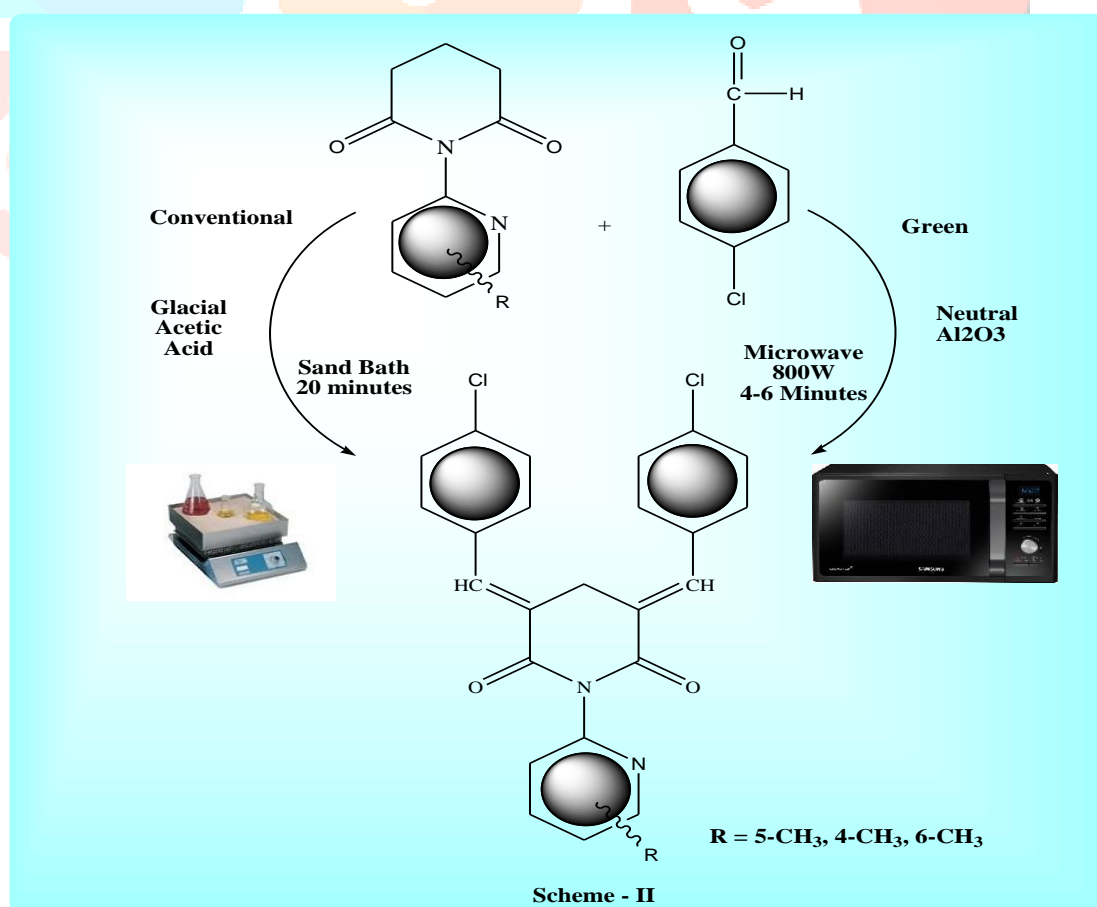
A mixture of N-phenyl Succinimide/N-phenyl Glutaramide derivatives (0.01mole) and substituted aromatic aldehyde (0.02mole) in glacial acetic acid (15ml) was taken into a beaker. The reaction mixture was heated on sand bath for 15 minutes and left overnight at room temperature. The bis chalcones were separated as colored crystals. The crude product is filtered, dried and recrystallized from ethanol (As shown in Scheme – I and II).

2.4.1.2 Green Method:

A mixture of N-phenyl Succinimide/N-phenyl Glutaramide derivatives (0.01mole) and substituted aromatic aldehyde (0.02mole) in 1 gm of neutral Al_2O_3 were condensed with the help of microwave irradiations. This mixture is maintained in microwave at 800W power for 4-6 minutes in solvent free condition. The novel developed compounds were recrystallized from ethanol (As shown in Scheme – I and II).



Scheme-I: Preparation of bis chalcones (IVa-c) from N-phenyl Succinimide by using Conventional and Green Method



Scheme – II: Preparation of bis chalcones (IVd-f) from N-phenyl Glutarimide by using Conventional and Green Method

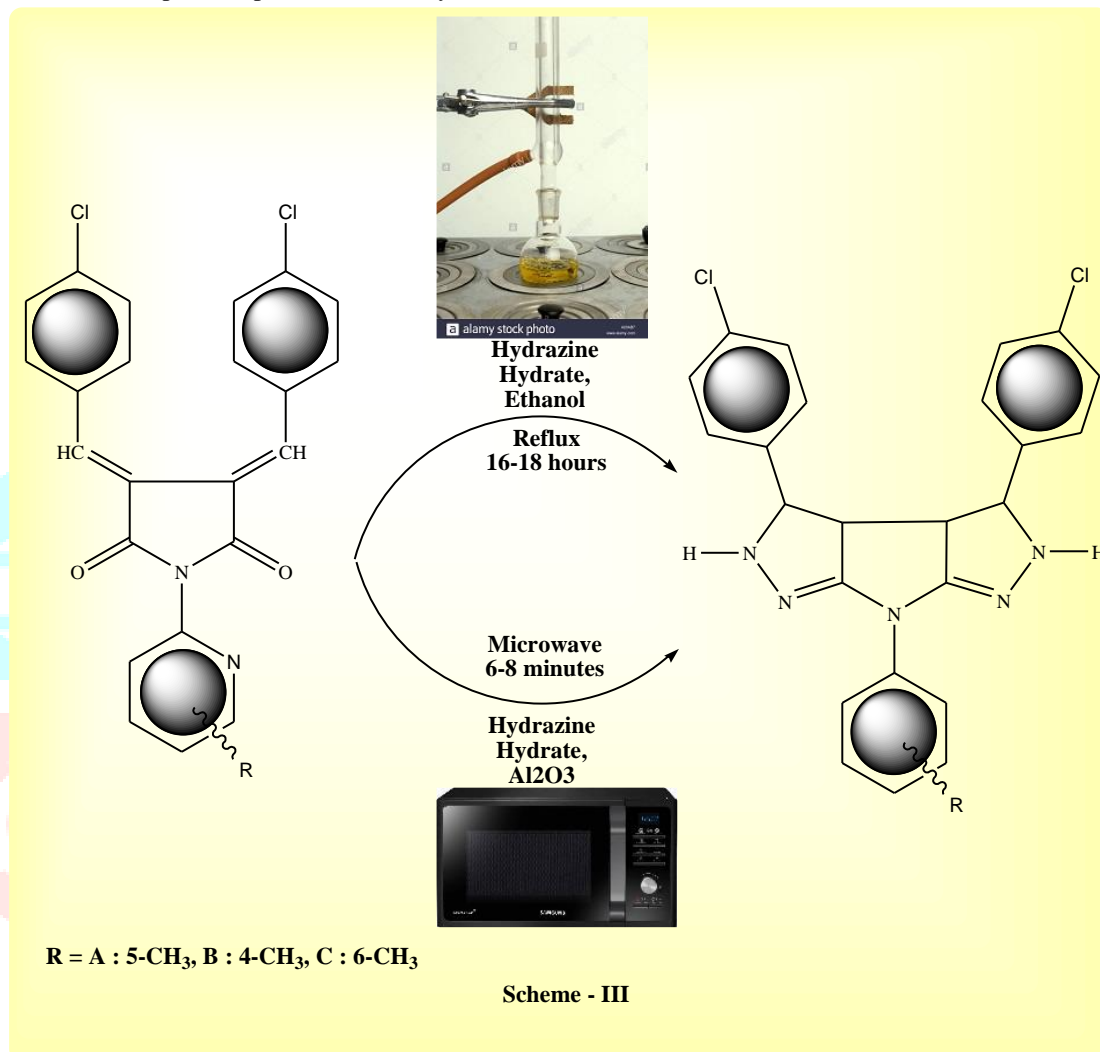
2.4.2 Preparation of pyrazoles (Va-f) from bis chalcones (IVa-f)

2.4.2.1 Conventional Method:

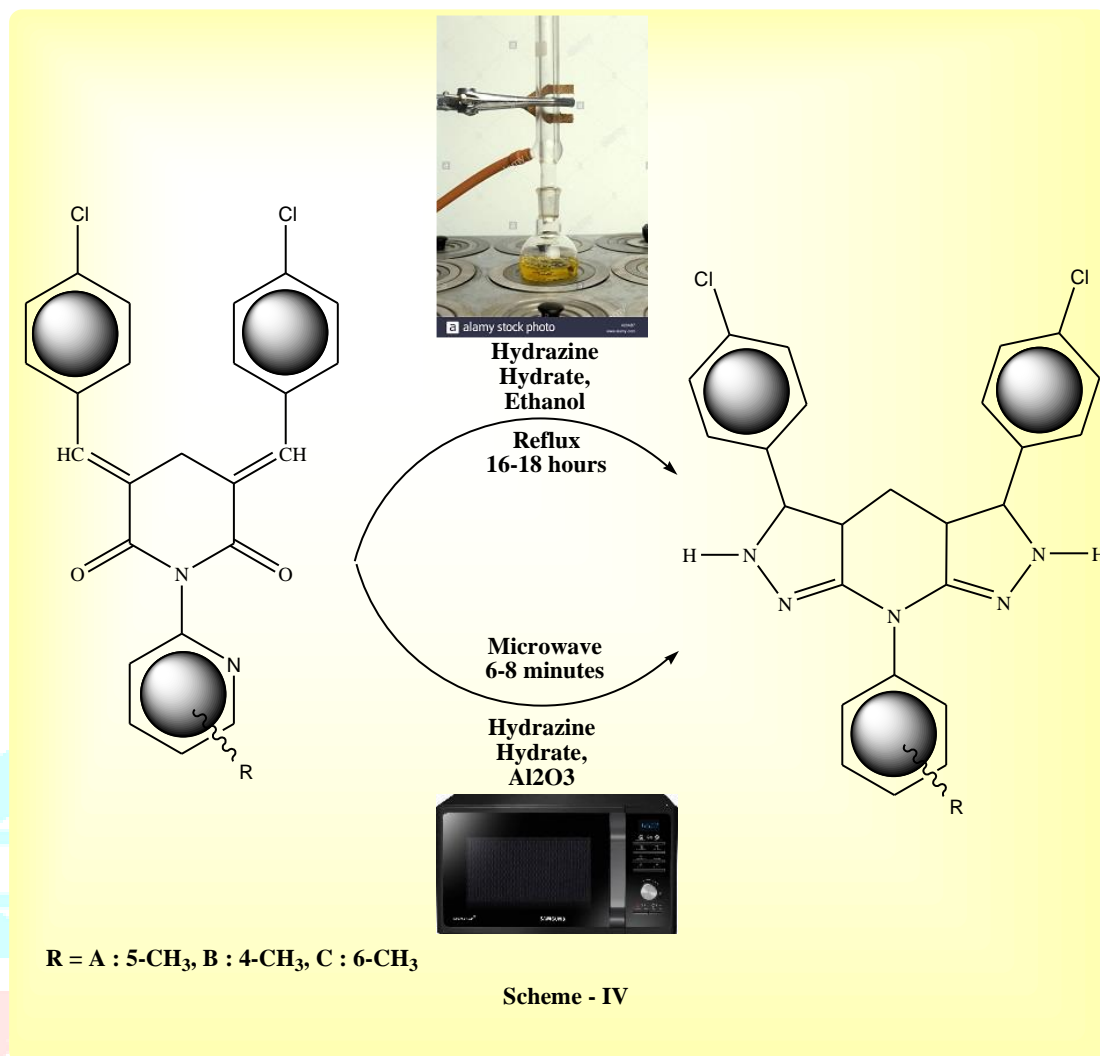
A mixture of bis-chalcone – IVa-f (0.01mole) and hydrazine hydrate (0.02mole) in ethanol (50ml) was refluxed on water bath for 16-18 hrs. It was cooled and poured into ice water. The product thus separated was filtered, washed with water, dried and recrystallized from ethanol (As shown in Scheme – III and IV).

2.4.2.2 Green Method:

A mixture of bis-chalcone – IVa-f (0.01mole) and hydrazine hydrate (0.02mole) in 1 gm of neutral Al_2O_3 were condensed with the help of microwave irradiations. This mixture is maintained in microwave at 800W power for 6-8 minutes in solvent free condition. The novel developed compounds were recrystallized from ethanol (As shown in Scheme – III and IV).



Scheme-III: Preparation of pyrazoles (Va-c) from bis chalcones (IVa-c) by using Conventional and Green Method



Scheme-IV: Preparation of pyrazoles (Vd-f) from bis chalcones (IVd-f) by using Conventional and Green Method

III. RESULTS AND DISCUSSION:

3.1 RESULTS

The series of bis-chalcones(IVa-f) were prepared by the reaction of N-phenyl Succinimide/N-phenyl Glutaramide derivatives and substituted aromatic aldehyde by using conventional and green path. It has been seen that in greener route reasonable yield is obtained than conventional. The formations of bis-chalcones were confirmed by FTIR, ^1H NMR and elemental analysis.

The series of pyrazoles(Va-f) were prepared by the reaction of corresponding bis-chalcones and substituted hydrazine hydrate by using conventional and green path. It has been seen that reasonable yield is obtained for both type of synthesis. But more or less better yield is obtained in case of greener route. The formations of pyrazoles were confirmed by FTIR, ^1H NMR and elemental analysis.

3.1.1 Characterization of Compound IVa-f and Va-f:

3.1.1.1 Physicochemical data of Compound IVa-f and Va-f:

Table No. 01: Physicochemical data of Compound IVa-f and Va-f

Comp No.	Nature/ Color	% of Yield		M.P.	M.F.	M.W.	Composition
		Conventional	Green				
IVa	Traffic Yellow solid	63.37	85.13	258-60 °C	$\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}_2$	435.30	C (66.95%) H (3.21%) N (6.99%)
IVb	Dahlia Yellow Solid	73.55	86.15	278-80 °C	$\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}_2$	435.30	C (66.73%) H (3.03%) N (6.08%)
IVc	Broom Yellow Solid	61.64	84.79	290-92 °C	$\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}_2$	435.30	C (65.98%) H (3.03%) N (6.08%)
IVd	Ivory Solid	64.73	84.74	264-66 °C	$\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}_2$	449.32	C (66.57%) H (4.21%) N (6.93%)

IVe	Olive Brown Solid	70.48	82.59	308-10 °C	C ₂₅ H ₁₈ O ₂ N ₂ Cl ₂	449.32	C (66.17%) H (4.34%) N (6.87%)
IVf	Broom Yellow Solid	60.46	82.26	292-94 °C	C ₂₅ H ₁₈ O ₂ N ₂ Cl ₂	449.32	C (66.19%) H (4.39%) N (6.81%)
Va	Traffic Yellow Solid	52.45	81.22	296-98 °C	C ₂₄ H ₂₀ N ₆ Cl ₂	463.36	C (63.04%) H (3.97%) N (18.74%)
Vb	Melon Yellow Solid	59.74	70.38	208-10 °C	C ₂₄ H ₂₀ N ₆ Cl ₂	463.36	C (62.78%) H (4.46%) N (18.82%)
Vc	Sulfur Yellow Solid	50.16	83.68	304-06 °C	C ₂₄ H ₂₀ N ₆ Cl ₂	463.36	C (62.85%) H (4.68%) N (18.92%)
Vd	Cream Solid	57.47	71.59	240-42 °C	C ₂₅ H ₂₂ N ₆ Cl ₂	477.38	C (63.01%) H (4.97%) N (17.01%)
Ve	Pastel Orange Solid	57.47	71.59	238-40 °C	C ₂₅ H ₂₂ N ₆ Cl ₂	477.38	C (62.11%) H (4.07%) N (17.09%)
Vf	Zinc Yellow Solid	49.61	72.59	318-20 °C	C ₂₅ H ₂₂ N ₆ Cl ₂	477.38	C (62.19%) H (4.08%) N (17.22%)

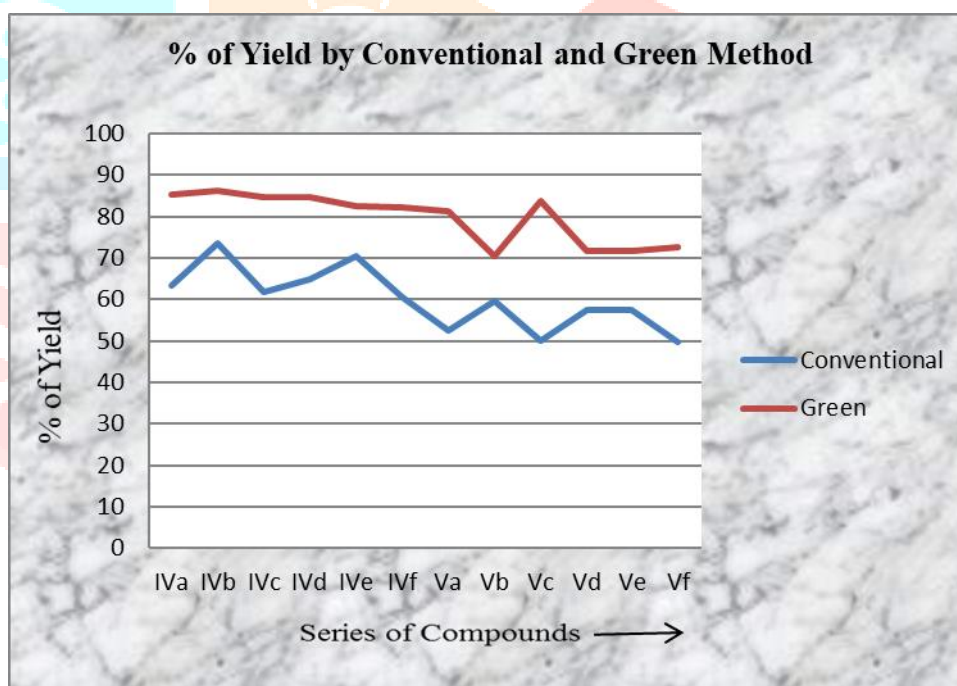


Chart 01: % of Yield by Conventional and Green Method

3.1.1.2 Spectral Analysis Data of Compound IVa-f and Va-f:

3,4-bis((E)-4-chlorobenzylidene)-1-(5-methylpyridin-2-yl)pyrrolidine-2,5-dione (IVa)

FTIR (KBr): -C-Cl:698.90; >C=C<: 1691.36; >C=O: 1741.89; aromatic ring (3-Peaks): 3006.02, 888.08, 833.37; -CH₃: 2856.79; C-N (Aliphatic): 1154.25; C-N (Aromatic): 1289.42; -C-C- Stretch in a ring(2-Peaks): 1579.03, 1532.43; -CH₃ bend: 1478.00, 1380.15 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 7.73 (m, 2H, ethylene), 7.40-7.94 (m, 11H, aromatic), 2.28 (s, 3H, CH₃-pyridine).

3,4-bis((E)-4-chlorobenzylidene)-1-(4-methylpyridin-2-yl)pyrrolidine-2,5-dione (IVb)

FTIR (KBr): -C-Cl:708.51; >C=C<: 1690.83; >C=O: 1742.35; aromatic ring (3-Peaks): 3006.08, 861.08, 837.54; -CH₃: 2875.09; C-N (Aliphatic): 1165.32; C-N (Aromatic): 1279.31; -C-C- Stretch in a ring(2-Peaks): 1587.33, 1543.56; -CH₃ bend: 1465.31, 1374.27 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 7.70 (m, 2H, ethylene), 7.20-7.66 (m, 11H, aromatic), 2.34 (s, 3H, CH₃-pyridine).

3,4-bis((E)-4-chlorobenzylidene)-1-(6-methylpyridin-2-yl)pyrrolidine-2,5-dione (IVc)

FTIR (KBr): -C-Cl:824.68; >C=C<: 1593.26; >C=O: 1740.61; aromatic ring (3-Peaks): 3022.30, 997.50, 792.13; -CH₃: 2969.28; C-N (Aliphatic): 1090.20; C-N (Aromatic): 1300.04; -C-C- Stretch in a ring(2-Peaks): 1593.26, 1535.09; -CH₃ bend: 1454.81, 1372.23 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 7.71 (m, 2H, ethylene), 6.93-7.94 (m, 11H, aromatic), 2.40 (s, 3H, CH₃

-pyridine).

3,5-bis((E)-4-chlorobenzylidene)-1-(5-methylpyridin-2-yl)piperidine-2,6-dione (IVd)

FTIR (KBr): -C-Cl:661.47; >C=C<: 1655.55; >C=O: 1732.12; aromatic ring (3-Peaks): 3024.31, 871.66, 814.72; -CH₃: 2960.63; -CH₂: 2926.28; C-N (Aliphatic): 1088.85; C-N (Aromatic): 1310.27; -C-C- Stretch in a ring(2-Peaks): 1570.83, 1530.27; -CH₃ bend: 1413.19, 1372.17; -CH₂ bend: 1462.84 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 7.27 (m, 2H, ethylene), 2.64 (d, 2H, methylene), 7.40-8.12 (m, 11H, aromatic), 2.24 (s, 3H, CH₃ -pyridine).

3,5-bis((E)-4-chlorobenzylidene)-1-(4-methylpyridin-2-yl)piperidine-2,6-dione (IVe)

FTIR (KBr): -C-Cl:664.20; >C=C<: 1679.69; >C=O: 1736.21; aromatic ring (3-Peaks): 3026.78, 879.56, 815.57; -CH₃: 2927.37; -CH₂: 2920.71; C-N (Aliphatic): 1088.95; C-N (Aromatic): 1297.14; -C-C- Stretch in a ring(2-Peaks): 1572.36, 1533.20; -CH₃ bend: 1408.33, 1371.88; -CH₂ bend: 1461.58 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 7.26 (m, 2H, ethylene), 2.64 (d, 2H, methylene), 7.32-7.94 (m, 11H, aromatic), 2.30 (s, 3H, CH₃ -pyridine).

3,5-bis((E)-4-chlorobenzylidene)-1-(6-methylpyridin-2-yl)piperidine-2,6-dione (IVf)

FTIR (KBr): 667,1704,1740,3006,861,817,2967,2925,1088,1300,1571,1395,1371,1458 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 7.62 (t,4H, Ar-H,J=7.5), 7.68 (t,4H,Ar-H,J=7.5), 7.21 (d, 2H, ethylene), 2.63 (t, 2H, methylene), 6.88 (t, 1H, pyridine,J=7.5), 7.63 (t, 1H, pyridine,J=7.5), 7.35 (t, 1H, pyridine,J=7.5), 2.46 (s, 3H, CH₃-pyridine).

3,4-bis(4-chlorophenyl)-7-(5-methylpyridin-2-yl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo[2,3-c:5,4-c']dipyrazole (Va)

FTIR (KBr): -C-Cl:620.11; -N-H: 3115.40; >C=N: 1652.10; aromatic ring (2-Peaks): 2997.48, 707.15; -CH₃: 2939.90; C-N (Aliphatic): 1211.72; C-N (Aromatic): 1287.74; -C-C- Stretch in a ring(2-Peaks): 1591.61, 1393.89; -CH₃ bend: 1483.08, 1371.87 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 2.18 (t, 2H, Methine), 3.07 (d, 2H, Methine), 9.98 (s, 2H,-N-H), 6.54-7.90 (m, 11H, aromatic), 2.37 (s, 3H, CH₃-pyridine).

3,4-bis(4-chlorophenyl)-7-(4-methylpyridin-2-yl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo[2,3-c:5,4-c']dipyrazole (Vb)

FTIR (KBr): -C-Cl:627.55; -N-H: 3154.93; >C=N: 1646.39; aromatic ring (2-Peaks): 3026.84, 818.55; -CH₃: 2939.56; C-N (Aliphatic): 1210.89; C-N (Aromatic): 1289.86; -C-C- Stretch in a ring(2-Peaks): 1595.31, 1486.04; -CH₃ bend: 1437.12, 1372.70 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 2.20 (t, 2H, Methine), 3.27 (d, 2H, Methine), 9.89 (s, 2H,-N-H), 6.65-7.81 (m, 11H, aromatic), 2.28 (s, 3H, CH₃-pyridine).

3,4-bis(4-chlorophenyl)-7-(6-methylpyridin-2-yl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo[2,3-c:5,4-c']dipyrazole (Vc)

FTIR (KBr): -C-Cl:819.27; -N-H: 3201.96; >C=N: 1623.04; aromatic ring (2-Peaks): 3049.70, 819.27; -CH₃: 2940.94; C-N (Aliphatic): 1211.40; C-N (Aromatic): 1312.08; -C-C- Stretch in a ring(2-Peaks): 1623.07, 1592.09; -CH₃ bend: 1485.25, 1401.16 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 2.21 (t, 2H, Methine), 3.37 (d, 2H, Methine), 9.95 (s, 2H,-N-H), 6.57-7.95 (m, 11H, aromatic), 2.45 (s, 3H, CH₃-pyridine).

3,5-bis(4-chlorophenyl)-8-(5-methylpyridin-2-yl)-2,3,3a,4,4a,5,6,8-octahydrodipyrazolo[3,4-b:4',3'-e]pyridine (Vd)

FTIR (KBr): -C-Cl:617.28; -N-H: 3107.51; >C=N: 1645.88; aromatic ring (2-Peaks): 2999.81, 817.23; -CH₃: 2938.67; -CH₂: 2930.17; C-N (Aliphatic): 1207.85; C-N (Aromatic): 1287.37; -C-C- Stretch in a ring(2-Peaks): 1594.26, 1485.31; -CH₃ bend: 1445.73, 1373.12; -CH₂ bend: 1483.17 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 2.23 (m, 2H, methine), 3.62 (m, 2H, methine), 1.75 (m, 2H, methylene), 9.96 (s, 2H,-N-H), 7.19-7.90 (m, 11H, aromatic), 2.07 (s, 3H, CH₃-pyridine).

3,5-bis(4-chlorophenyl)-8-(4-methylpyridin-2-yl)-2,3,3a,4,4a,5,6,8-octahydrodipyrazolo[3,4-b:4',3'-e]pyridine (Ve)

FTIR (KBr): -C-Cl:619.00; -N-H: 3197.33; >C=N: 1651.00; aromatic ring (2-Peaks): 3044.50, 817.33; -CH₃: 2933.31; -CH₂: 2929.54; C-N (Aliphatic): 1209.55; C-N (Aromatic): 1286.58; -C-C- Stretch in a ring(2-Peaks): 1594.13, 1559.83; -CH₃ bend: 1444.53, 1398.11; -CH₂ bend: 1484.15 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 2.33 (m, 2H, methine), 3.83 (m, 2H, methine), 1.88 (m, 2H, methylene), 9.86 (s, 2H,-N-H), 6.76-7.90 (m, 11H, aromatic), 2.22 (s, 3H, CH₃-pyridine).

3,5-bis(4-chlorophenyl)-8-(6-methylpyridin-2-yl)-2,3,3a,4,4a,5,6,8-octahydrodipyrazolo[3,4-b:4',3'-e]pyridine (Vf)

FTIR (KBr): -C-Cl:621.16; -N-H: 3189.14; >C=N: 1659.67; aromatic ring (2-Peaks): 2996.61, 818.41; -CH₃: 2941.86; -CH₂: 2930.22; C-N (Aliphatic): 1211.03; C-N (Aromatic): 1288.86; -C-C- Stretch in a ring(2-Peaks): 1620.80, 1589.06; -CH₃ bend: 1459.24, 1371.19; -CH₂ bend: 1484.26 cm⁻¹. ¹H NMR (500.13 MHz, DMSO-d₆, δ ppm): 2.37 (m, 2H, methine), 3.77 (m, 2H, methine), 1.88 (m, 2H, methylene), 9.86 (s, 2H,-N-H), 6.32-7.61 (m, 11H, aromatic), 2.21 (s, 3H, CH₃-pyridine).

3.1.2 Plant Growth Regulator Activities of IVa-f and Va-f:

All the novel synthesized bis-chalcones (9a-f), pyrazoles (12a-f) and standard I, II, III were screened for their plant growth activity against maize (Rajeshwar) and moong (PKVM-8802) seeds using DMSO solvent. All these compounds were screened for root length shoot length and weight of root before and after heating (at 50^o C). The seeds were made available from MAHABEEJ: Maharashtra State Seed Corporation Limited, "Mahabeej Bhavan", Gultekdi, Market Yard, Pune Pune 411008 [India]. Some of the compound showed moderate to good activities as shown in the Table – 2 to 6 and Chart – 2 to 6;

Table No. 02: Root/Shoot Length (in mm) after 3 days for IVa-f and Va-f

Sample	Root Length (in mm)		Shoot Length (in mm)	
	Maize	Moong	Maize	Moong
Iva	8	3	12	9
IVb	9	2	10	7
IVc	7	3	23	12
IVd	8	0	6	2
IVe	7	0	16	3
IVf	10	2	18	5

Va	3	3	14	8
Vb	9	5	13	13
Vc	10	0	15	15
Vd	8	4	11	8
Ve	5	2	17	11
Vf	4	2	9	6
Standard-I	10	3	14	11
Standard-II	11	2	15	16
Standard-III	9	4	12	10

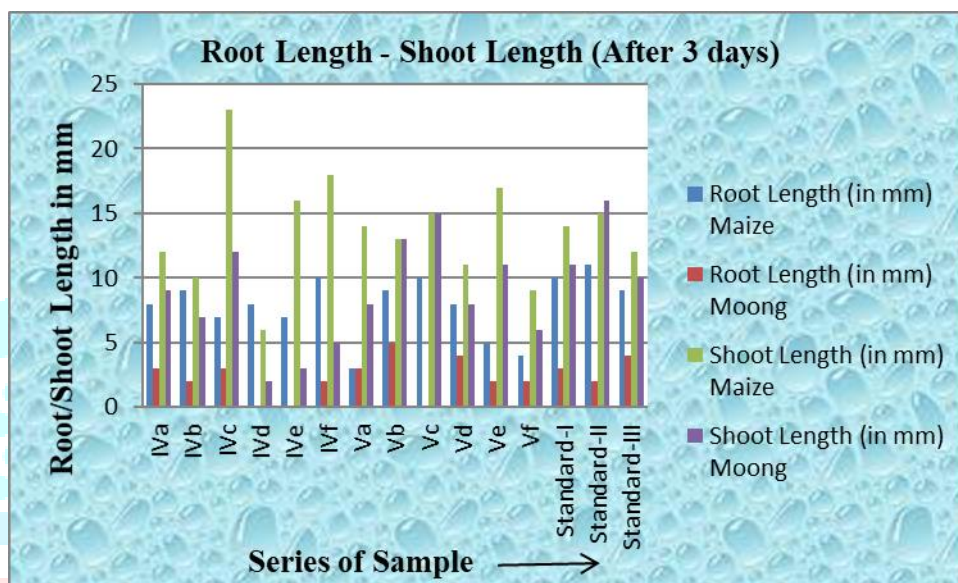


Chart 02: Root/Shoot Length (in mm) after 3 days for IVa-f and Va-f
 Table No. 03: Root/Shoot Length (in mm) after 6 days for IVa-f and Va-f

Sample	Root Length (in mm)		Shoot Length (in mm)	
	Maize	Moong	Maize	Moong
Iva	16	7	27	19
IVb	17	4	28	18
IVc	18	7	38	32
IVd	14	2	19	6
IVe	18	2	31	8
IVf	22	5	33	11
Va	8	6	26	22
Vb	11	10	29	33
Vc	22	3	25	27
Vd	15	6	21	15
Ve	10	4	30	19
Vf	9	3	24	14
Standard-I	12	6	34	20
Standard-II	15	8	39	29
Standard-III	11	12	30	22

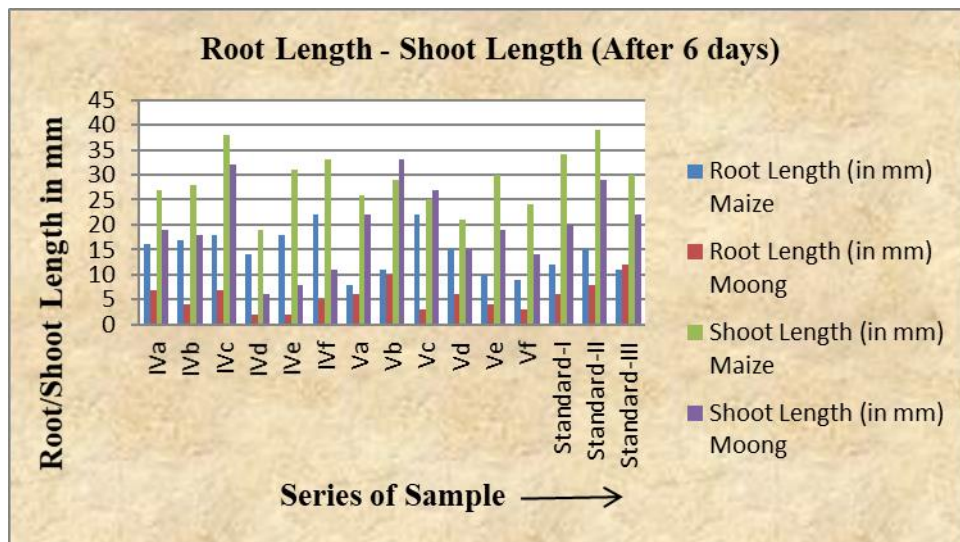


Chart 03: Root/Shoot Length (in mm) after 6 days for IVa-f and Va-f
 Table No. 04: Root/Shoot Length (in mm) after 9 days for IVa-f and Va-f

Sample	Root Length (in mm)		Shoot Length (in mm)	
	Maize	Moong	Maize	Moong
Iva	25	12	35	27
IVb	34	8	36	24
IVc	33	11	60	57
IVd	22	5	26	10
IVe	31	6	48	18
IVf	43	8	54	22
Va	16	9	36	34
Vb	37	18	41	53
Vc	44	7	47	43
Vd	32	10	40	27
Ve	23	8	58	29
Vf	18	7	44	24
Standard-I	34	10	58	31
Standard-II	36	11	57	45
Standard-III	30	19	46	40

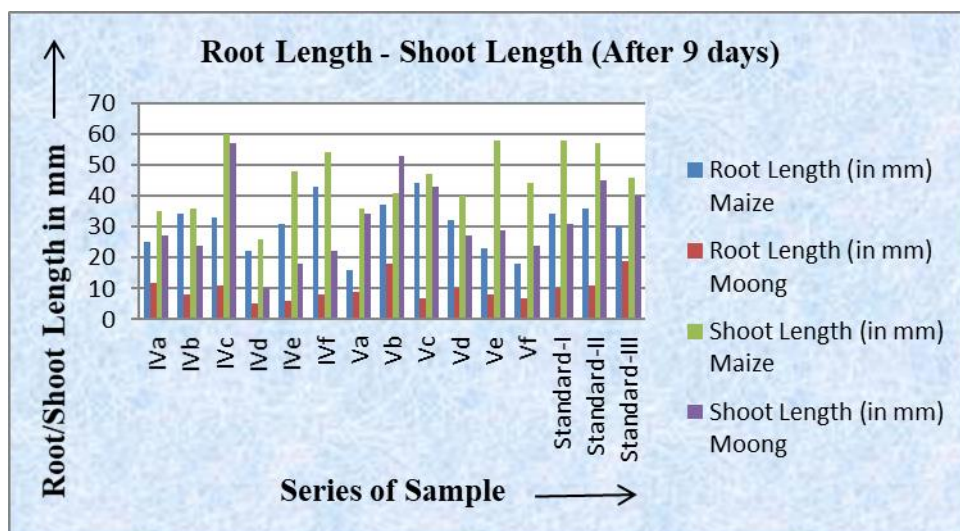
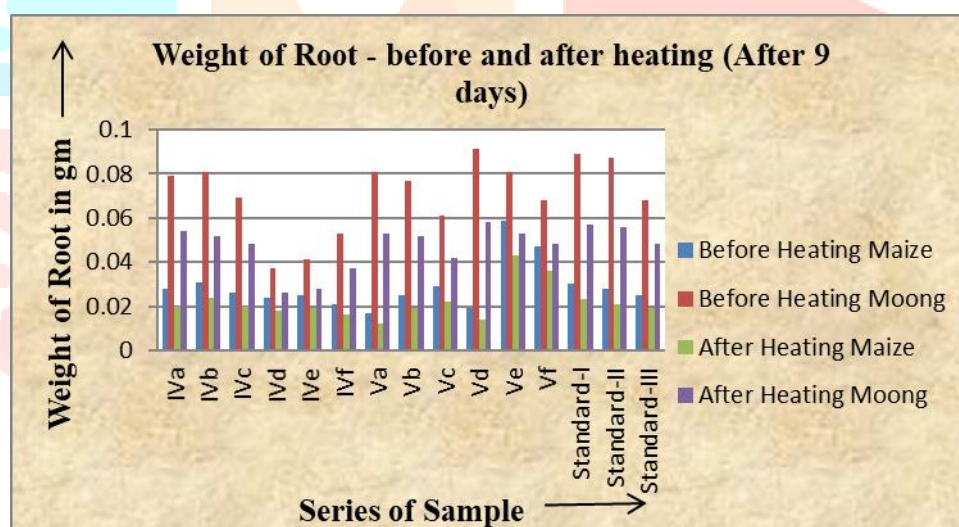


Chart 04: Root/Shoot Length (in mm) after 9 days for IVa-f and Va-f

Table No. 05: Weight of Root (in gm) before and after heating (after 9 days) for IVa-f and Va-f

Sample	Before Heating		After Heating	
	Maize	Moong	Maize	Moong
Iva	0.028	0.079	0.020	0.054
IVb	0.031	0.081	0.024	0.052
IVc	0.026	0.069	0.020	0.048
IVd	0.024	0.037	0.018	0.026
IVe	0.025	0.041	0.019	0.028
IVf	0.021	0.053	0.016	0.037
Va	0.017	0.081	0.012	0.053
Vb	0.025	0.077	0.019	0.052
Vc	0.029	0.061	0.022	0.042
Vd	0.019	0.091	0.014	0.058
Ve	0.059	0.081	0.043	0.053
Vf	0.047	0.068	0.036	0.048
Standard-I	0.03	0.089	0.023	0.057
Standard-II	0.028	0.087	0.021	0.056
Standard-III	0.025	0.068	0.019	0.048

#Observations are made after 6 hrs during 24 hrs for 9 days

**Chart 05:** Weight of Root (in gm) before and after heating (after 9 days) for IVa-f and Va-f**Table No. 06:** Weight of Shoot (in gm) before and after heating (after 9 days) for IVa-f and Va-f

Sample	Before Heating		After Heating	
	Maize	Moong	Maize	Moong
Iva	0.324	0.183	0.249	0.074
IVb	0.525	0.295	0.368	0.102
IVc	0.572	0.257	0.395	0.094
IVd	0.453	0.189	0.331	0.077
IVe	0.387	0.197	0.298	0.079
IVf	0.543	0.231	0.380	0.088
Va	0.357	0.356	0.275	0.108
Vb	0.544	0.343	0.381	0.105

Vc	0.553	0.28	0.382	0.097
Vd	0.374	0.459	0.288	0.11
Ve	0.382	0.253	0.294	0.093
Vf	0.49	0.32	0.343	0.103
Standard-I	0.49	0.281	0.358	0.097
Standard-II	0.552	0.269	0.381	0.095
Standard-III	0.44	0.215	0.326	0.084
#Observations are made after 6 hrs during 24 hrs for 9 days				

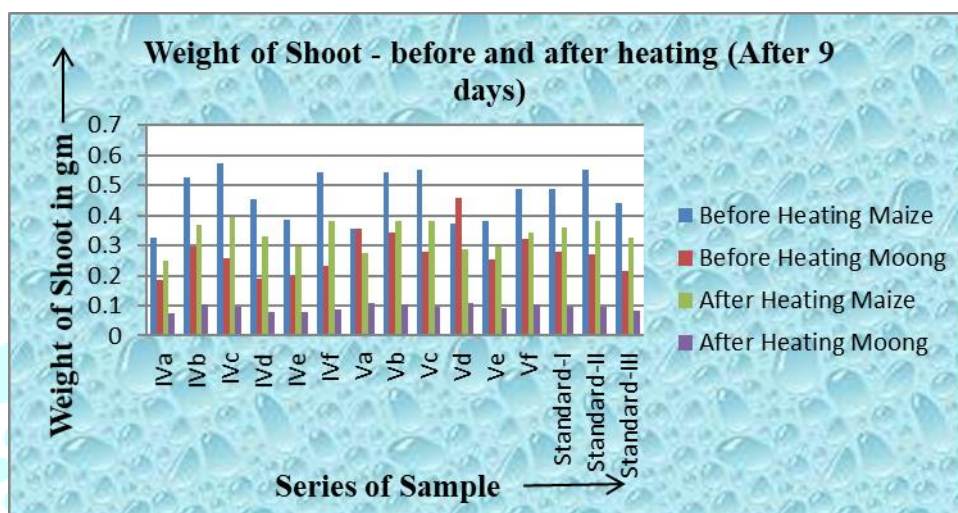


Chart 06: Weight of Shoot (in gm) before and after heating (after 9 days) for IVa-f and Va-f

3.2 DISCUSSION:

The series of bis-chalcones (IVa-f) were prepared by the reaction of N-phenyl Succinimide/N-phenyl Glutaramide derivatives and substituted aromatic aldehyde by using conventional and green path. It has been seen that in greener route reasonable yield is obtained than conventional. Also, the series of pyrazoles (Va-f) were prepared by the reaction of corresponding bis-chalcones and substituted hydrazine hydrate by using conventional and green path. It has been seen that reasonable yield is obtained for both synthesis. But more or less better yield is obtained in case of greener route. The formation of bis-chalcones and pyrazoles were confirmed by FTIR, ¹H NMR and elemental analysis. All the novel synthesized bis-chalcones (9a-f), pyrazoles (12a-f) and standard I, II, III were screened for their plant growth activity against maize (Rajeshwar) and moong (PKVM-8802) seeds using DMSO solvent. Some of the compound showed moderate to good activities.

Now a day's the plant growth regulators-PGRs have developed as an essential part of horticultural and agricultural industries. Consequently, there is great demand for novel and cost-effective products. However, the market is restricted due to inadequate innovation. In such situation chemical genomics has suppose to focus his attention on this arena.

IV. CONCLUSION:

To come to the point, we have synthesized the series of a novel class of chalcones (IVa-f); by regimen of N-phenyl succinimides/glutarimides with p-chloro benzaldehyde. Also, a novel class of pyrazoles (Va-f); was comprehended by regimen of chalcones with hydrazine hydrate by conventional as well as greener approach. Conspicuous difference is found in the yield of greener methodology than conventional. In case of bis-chalcone (IVb) and pyrazole (Vc), highest yield is obtained by using green pathway. All innovative class of synthesized compounds have shown enhanced activities as plant growth regulator for maize (Rajeshwar) and moong (PKVM-8802) seeds. Vb and Vc entitles excellent progress regulator for root of maize as compared to Std- I, II and III. Also, the compound Vb is found remarkable agents for growth of shoot relevant to moong.

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Conflict of interest disclosure:

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