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# Synthesis of Some New Annulated Pyranopyrazole Derivatives, a New Series of Herbicidal Substances and Some Related Compounds

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**Abstract:** In this study we aimed to synthesis the substituted pyranopyrazole and oxinobispyrazole derivatives having biological activity as herbicidal activity. The bifunctional pyrano-pyrazole derivatives were prepared by the reaction of some active methylene compounds, namely malononitrile, cyanoacetic acid, ethylacetoacetate, diethylmalonate, pyrazolone and cyanoacetamide with 3-formylchromone in the presence of ammonium acetate or piperidine, respectively. The structures of the new compounds were substantiated and characterized by means of their IR, <sup>1</sup>H-NMR and mass spectra. The herbicidal activity against grass weeds and some of broad leaf weeds.

**Keywords:** Echinochola crus-galli, 3-formylchromone, Herbicidal activity, pyrazolinone.

## I. INTRODUCTION

The compounds that include a chromone moiety have great importance for their biological actions and for their reactivity against nucleophiles [1]. The condensation reaction of effective methylene group with aldehyde function of 3-formylchromone was studied by many researchers [2]. The present investigations have provided that, the new chromone derivatives possessing important cytotoxic prospect [3].

The 3-formylchromone derivatives were estimated by use of various *in vivo* and *in vitro* examination patterns for anti-inflammatory activity and their effects were compared with known standard drug like aspirin and indomethacin, showed promising anti-inflammatory activities [4]. The one-pot reaction of pyrazolone [5]-[11], 3-formylchromone, malononitrile in the presence of piperidine or ammonium acetate produced the bifunctional compounds [12]-[18]. A novel series were synthesized by means of one-pot reaction by the condensation of 2-aminomethylbenzothiazole with alcohols and aldehydes. The bioassay results elucidated that some prepared compounds had good herbicidal activity towards both dicotyledon and monocotyledon weeds [19].

It is known that the herbicides illustrate a class of xenobiotics (foreign chemicals) that are commonly used to control the growth and reproduction of unwanted vegetation. A structurally different group of organic molecules, herbicides contain reactive moieties, like hydroxyl, alkyl, amino, nitro, amide, carboxyl, and halogen groups that can be modified by a wide variety of enzymatic reactions, commonly occurring reactions include oxidative, reductive, hydrolytic or conjugative alterations of the herbicide molecule [20], Figure I shows the chemical structure of standard herbicidal (bispyribac).

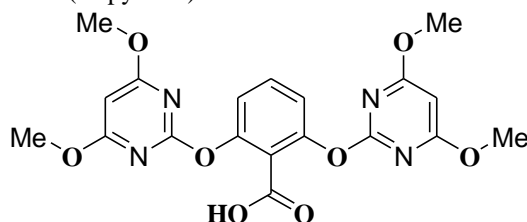


Fig I. Chemical structure of standard herbicidal (bispyribac)

In the light of these facts and based on the previous survey towards the herbicides, this study aimed to synthesis some novel compounds having herbicidal efficiency.



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## II. MATERIALS AND METHODS

### Chemistry

The chemicals and organic solvents used in this part were obtained from Sigma-Aldrich (USA) chemical company. Melting points were determined in opened glass capillary tubes with an "Electro Thermal" Digital melting point apparatus, (model: IA9100) and are uncorrected. The IR spectra were recorded in a Pyc-Unicam SP 1200 spectrophotometer using the KBr water technique. The  $^1\text{H-NMR}$  spectra were recorded on a Varian GEMINI 200 MHz NMR spectrophotometer using  $\text{DMSO-}d_6$  as solvent. The abbreviation exch. is used to indicate exchangeable protons. Mass spectra were recorded on a GCMS OP 1000 EX (70EV spectrometer). Elemental analyses were carried out at the Micro analytical Center, Cairo University.

### General procedure for the synthesis compounds (2-4).

To a mixture of 4-oxo-4H-benzopyran-3-carbaldehyde (0.01 mol), 3-methyl-pyrazolone, 3-methyl-1-phenylpyrazolone (0.01 mol), ammonium acetate (0.03 mol) or a few drops of piperidine were added. The mixture was heated at  $190^\circ\text{C}$  for  $\frac{1}{2}$ h in methanol. After cooling, the obtained solid was washed with water, dried and crystallized from ethanol.

### 3-(3,5-Dimethyl-1,7-diphenyl-4,7-dihydro-1H-pyrano[2,3-c;6,5-c']dipyrazol-4-yl)-chromen-4-one (2):

Yield: 75%; pale-orange crystals; m.p.  $228^\circ\text{C}$ . IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3433 (=N), 3067 (CH, Ar-H), 2916 (CH-aliphatic) and 1643 (CO, Chromone).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  (ppm): 2.4 (s, 3H, pyrazolinyl- $\text{CH}_3$ ), 7.2-8.2 (m, 9H, arom. and olefinic), 10.8 (s, 1H,  $\text{C}_2$ -H of Chromone moiety), 6.50-7.57 (m, 4H, Ar-H), 3.76 (s, 1H, 4H-pyran). Analysis of  $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_3$  (%): calcd: C, (74.06); H, (4.56); N, (11.52); O, (9.87); found: C, (74.01); H, (4.32); N, (11.25). MS  $m/z$ =486 (36.93%), 77(100%), 91(36.79%), 121(15.93%), 273(11.81%), 302(15.93%) and 330(10.89%).

### 3-(3, 5-Dimethyl-4, 7-dihydro-1H-pyrano [2, 3-c; 6, 5-c'] dipyrazol-4-yl) chromen-4-one (3):

Yield: 69%; pale-yellow crystals; m.p.  $235^\circ\text{C}$ . IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3246 (NH), 3069 (CH-aromatic), 2924 (CH-aliphatic), 1631 (CO- chromone).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  (ppm): 2.5 (s, 3H, pyrazolinyl- $\text{CH}_3$ ), 10.89 (s, 1H,  $\text{C}_2$ -H of chromone moiety), 6.84-7.93 (m, 4H, Ar-H), 7.45 (s, 2H, 2NH), 3.32 (s, 1H, CH). Analysis of  $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_3$  (%): Calcd: C, (64.66); H, (4.22); N, (16.76); O, (14.36); Found: C, (64.41); H, (4.11); N, (16.31). MS  $m/z$ =334 (48.54%), 77(67.65%), 92(89.54%), 121(100%), 146(38.56%), 206(50%) and 254(34.64%).

### 3-(3,5-Dimethyl-1-phenyl-4,7-dihydro-1H-pyrano[2,3-c;6,5-c']dipyrazol-4-yl)-chromen-4-one (4):

Yield: 78%; yellow crystals; m.p.  $222^\circ\text{C}$ . IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3070 (CH-aromatic), 2923 (CH-aliphatic), 1632 (CO-chromone).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  (ppm): 2.4 (s, 3H, pyrazolinyl- $\text{CH}_3$ ), 7.5-7.9 (m, 8H, arom. and olefinic), 10.7 (s, 1H,  $\text{C}_2$ -H of chromone), 6.27-6.65 (m, 4H, Ar-H), 3.86 (s, 1H, CH-pyran), 7.30 (s, 1H, NH). Analysis of  $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_3$  (%): Calcd.: C, (70.23); H, (4.42); N, (13.65); O, (11.13). Found: C, (70.11); H, (4.21); N, (13.42). MS  $m/z$ = 410 (65.18%), 77(100%), 91(23.17%), 121(22.05%), 240(11.92%) and 302(9.79%).

### General procedure for synthesis compounds (5-10).

To a mixture of 4-Oxo-4H-benzopyran-3-carbaldehyde (0.01 mol), pyrazolone (0.01 mol), malononitrile (0.01 mol) or cyanoacetic acid, ethylacetoacetate, diethyl-malonate, cyanoacetamide (0.01 mol), ammonium acetate (0.03 mol) or a few drops of piperidine were added. The mixture was heated at  $120^\circ\text{C}$  for  $\frac{1}{2}$ h in methanol. After cooling, the obtained solid was washed with water, derided and crystallized from ethanol.

### 3-Methyl-6-oxo-4-(4-Oxo-4H-chromen-3-yl)-1,6-dihydro-pyrano[2,3-c]pyrazole-5-carbonitrile (5):

Yield: 80%; orange red crystals; m.p.  $238$ - $240^\circ\text{C}$ ; IR(KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3203(NH), 3077(CH-aromatic), 2925 (CH-aliphatic), 2210 ( $\text{C}\equiv\text{N}$ ), 1631 (CO-Chromone).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  (ppm): 2.5 (s, 3H, pyrazolinyl- $\text{CH}_3$ ), 7.1-8.2 (m, 9H, aromatic and olefinic protons), 10.8 (s, 1H,  $\text{C}_2$ -H of chromone moiety), 6.67-7.52 (m, 4H, Ar-H), 7.42 (s, 1H, NH), 3.65 (s, 1H, CH). Analysis of  $\text{C}_{17}\text{H}_9\text{N}_3\text{O}_4$  (%): Calcd: C, (63.95); H, (2.84); N, (13.16); O, (20.04). Found: C, (63.11); H, (2.31); N, (13.12). MS  $m/z$  = 319(68.32%), 77 (100%), 91(36.79%), 121(15.93%), 273(11.81%), 302(15.93%) and 303(10.89%).

### 5-Acetyl-3-methyl-4-(4-Oxo-4H-chromen-3-yl)pyrano[2,3-c]pyrazol-6(1H)-one (6):

Yield: 85%; orange red crystals; m.p.  $232$ - $234^\circ\text{C}$ ; IR(KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3187 (NH), 2979 (CH-aliphatic), 1709 (CO).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  (ppm): 2.4 (s, 3H, pyrazolinyl -  $\text{CH}_3$ ), 2.3 (s, 3H,  $\text{R}_2=\text{CH}_3$ ), 7.2-7.9 (m, 8H, arom. and olefinic), 10.9 (s, 1H,  $\text{C}_2$ -H of chromonemioety), 6.77-7.43 (m, 4H, Ar-H), 7.35 (s, 1H, NH), 3.46 (s, 1H, CH). Analysis of  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_5$  (%): Calcd.: C, (64.29); H, (3.60); N, (8.33); O, (23.79); found: C, (64.11); H, (3.2); N, (8.11). MS  $m/z$ =336 (71.13%), 77 (100%), 91(36.79%), 121(15.93%), 273(11.81%), 302(15.93%) and 303(10.89%).



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**Ethyl-3-methyl-6-oxo-4-(4-Oxo-4H-chromen-3-yl)-1,6-dihydropyran[2,3-c]pyrazole-5-carboxylate**

**(7):** Yield: 90%; red crystals; m.p. 253-254°C; IR (KBr):  $\nu_{\max}/\text{cm}^{-1}$  3263 (NH); 2926 (CH-aliphatic); 1688, 1631 (CO).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$  (ppm): 2.5 (s, 3H, pyrazolinyl-CH<sub>3</sub>), 1.28 (m, 4H, 2CH<sub>2</sub>), 1.62 (m, 2H, CH<sub>2</sub>), 3.46 (s, 1H, NH), 6.68-7.56 (m, 4H, Ar-H), 10.7 (s, 1H, C<sub>2</sub>-H of chromone moiety), 7.2-7.9 (m, 8H, arom. and olefinic). Analysis of C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>5</sub> (%). Calcd.: C, (65.14); H, (4.03); N, (8.00); O, (22.84); found: C, (65.11); H, (4.01); N, (8.00). MS  $m/z$ =366 (65%), 77 (100%), 121(78.36%), 188 (73.13%), 277 (70.15%), 303 (58.21) and 363 (67.16%).

**6-Amino-3-methyl-4-(4-Oxo-4H-chromen-3-yl)-1-phenyl-1, 4-dihydropyran [2, 3-c] pyrazole-5-**

**carbonitrile (8):** Yield; 86%; orange red crystals; m.p. 266-268°C; IR (KBr):  $\nu_{\max}/\text{cm}^{-1}$  3336, 3188 (NH<sub>2</sub>), 2924 (CH-aliphatic), 2190 (C≡N), 1649 (CO).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$  (ppm): 2.5 (s, 3H, pyrazolinyl-CH<sub>3</sub>), 3.76 (s, 1H, 4H-pyran), 6.11 (s, 2H, NH<sub>2</sub>), 6.50-7.57 (m, 4H, Ar-H), 10.6 (s, 1H, C<sub>2</sub>-H of chromone moiety), 7.5-7.9 (m, 8H, arom. and olefinic). Analysis of C<sub>23</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub> (%). Calcd.: C, (69.69); H, (4.07); N, (14.13); O, (12.11); found: C, (69.22); H, (4.02); N, (14.11). MS  $m/z$ =396 (72.2%), 77(100%), 95(82.42%), 152(94.74%), 272(88.42%), 328(83.16%), 342(68.42%) and 364(93.88%).

**3-Methyl-6-oxo-4-(4-Oxo-4H-chromen-3-yl)-1-phenyl-1,6-dihydro-pyran[2,3-c]pyrazole-5-carbonitrile**

**(9):** Yield; 82%; red crystals; m.p. 236-238°C: IR (KBr):  $\nu_{\max}/\text{cm}^{-1}$  3071 (CH-aromatic), 2920 (CH-aliphatic), 2202 (C≡N), 1643 (CO).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$  (ppm): 2.19 (s, 3H, pyrazolinyl-CH<sub>3</sub>), 7.2-7.9 (m, 8H, arom. and olefinic), 10.6 (s, 1H, C<sub>2</sub>-H of chromone moiety), 6.87-7.78(m, 4H, Ar-H), 8.34-8.40 (s, 1H, OH), 3.76 (s, 1H, 4H-pyran). Analysis of C<sub>23</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub> (%). Calcd.: C, (69.87); H, (3.31); N, (10.63); O, (16.19); found: C, (69.62); H, (3.11); N, (10.32). MS  $m/z$  = 395 (69.54%) with base peak at 77(100%) and we could observe the other significant peaks at 91 (38.21%), 121 (41.04%), 161 (59.43%), 229 (38.21%) and 352 (40.57%).

**6-Amino-3-methyl-4-(4-Oxo-4H-chromen-3-yl)-1-phenyl-1,4-dihydro-pyran[2,3-c]pyrazole-5-**

**carboxamide (10):** Yield; 80%; red crystals; m.p. 266-268°C: IR(KBr):  $\nu_{\max}/\text{cm}^{-1}$  3441, 3361 (NH<sub>2</sub>), 1694, 1633 (CO).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$  (ppm): 2.4 (s, 1H, CH-pyran), 5.87 (s, 2H, NH<sub>2</sub>), 6.27-6.65 (m, 4H, Ar-H), 6.91 (s, 2H, CONH<sub>2</sub>), 10.7 (s, 1H, C-H of chromone moiety). Analysis of C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>(%). Calcd.: C, (66.66); H, (4.38); N, (13.52); O, (15.44); found: C, (66.21); H, (4.12); N, (13.21). MS  $m/z$ =414(61%), 77(100%), 93(81.42%), 140(81.42%), 216(67.12%), 314(76.99%) and 344 (79.65%).

**Seedling growth bioassay**

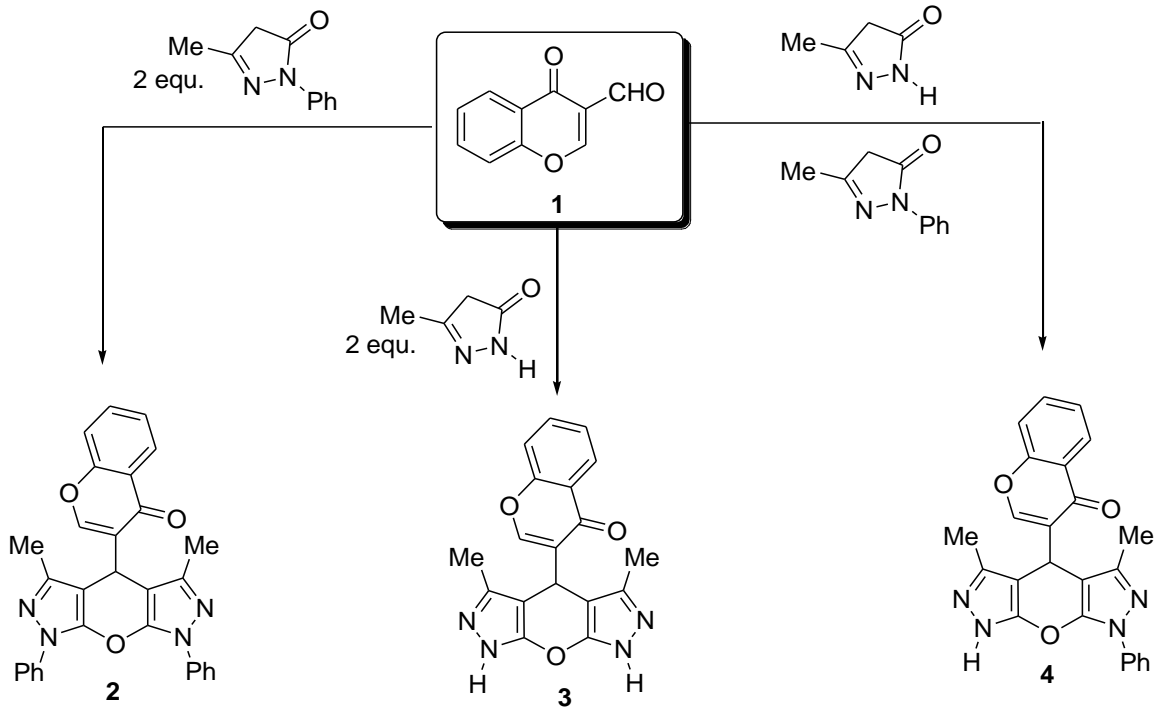
The herbicidal activities of the substituted pyranopyrazole and oxinobispyrazole derivatives (**2-10**) and bispyribac herbicide as standard were studied against *Echinochloa crus-galli* (barnyard grass weed) and *portulacaoleraceae* broadleaf weed. All derivatives were dissolved in DMSO (dimethyl sulfoxide). The tested concentrations from each compound and standard herbicide were 0.01, 0.05, 0.1, and 0.5 ppm. On the other hand, the effect of DMSO (control) and distilled water (control) against two weeds were also carried. Three replicates, each of 0.2 gm of purslane and barnyard grass were prepared for each treatment using glass Petri-dish (9 cm) lined with Whatman no.2 filter paper. 6 mL of each test solution were added to each Petri-dish. Then, Petri-dish was located in the undermost of 0.1 mm polyethylene bags (15 x 30 cm) that were widened to full of air and after that, sealed at the top with rubber bands to control and prevent the loss of humidity. The Petri-dish was kept on a germination cabinet at  $20 \pm 1$  °C. After 10 days of sowing root and shoot lengths measured. The growth inhibition percentages of root and shoot lengths [21].

### III. RESULTS AND DISCUSSION

**Chemistry**

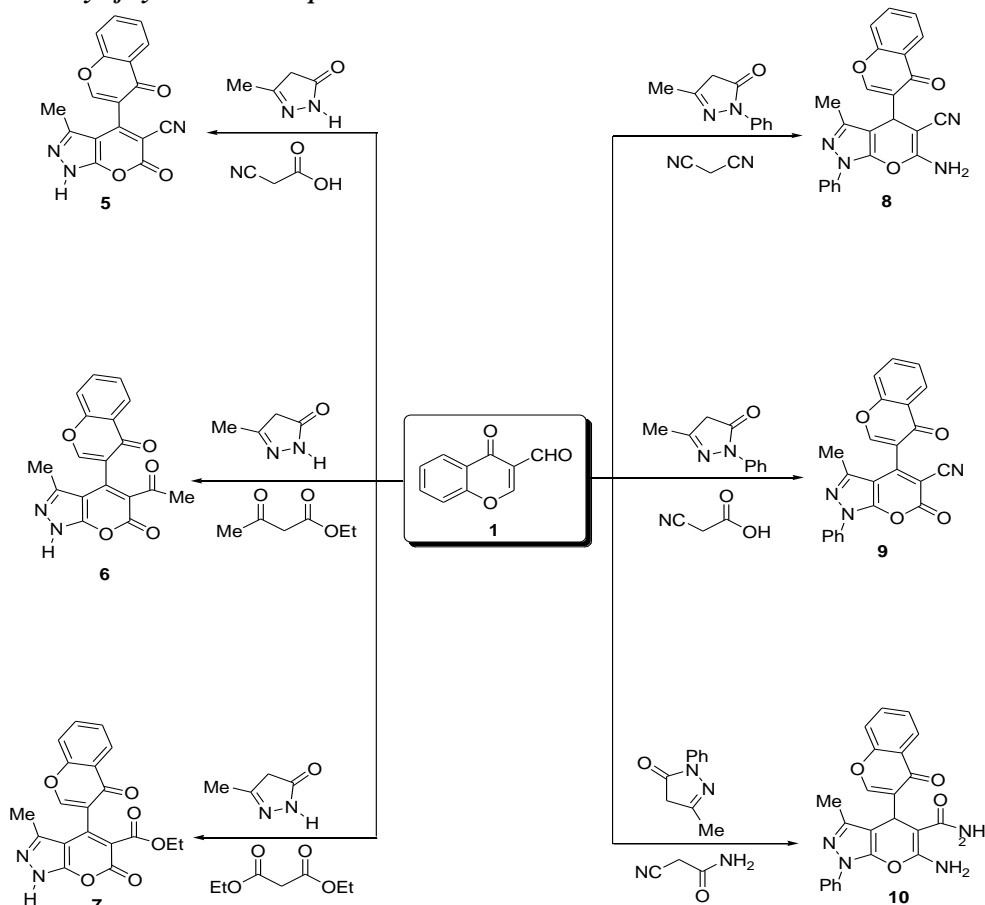
In the present work, we wish to introduce a newer route for the condensation of 4-oxo-4H-benzopyran-3-carbaldehyde with active methylene compound, 3-methyl-1-phenyl-1H-pyrazol-5(4H)- and 3-methyl-3-pyrazolin-5-one.

Scheme I shows the formation of the oxinobispyrazole derivatives (**2-4**) from the one-pot reaction of equimolar amounts of pyrazole and 3-formylchromone that were refluxed in absolute methanol in the presence of piperidine as a basic catalyst. After 1/2h an insoluble fraction was isolated as pale-orange, pale-yellow and yellow crystals in the percentage 75%, 69% and 78% respectively, and identified as the oxino-bispyrazole. Otherwise, compounds (**5-10**) that illustrated in Scheme II were obtained from the one-pot reaction of pyrazolone with 3-formylchromone and other active methylene, in the presence of piperidine according to the reported methods [22]-[24].



Scheme I. Synthetic routes for the oxinobispyrazole derivatives (2-4)

*Herbicidal activity of synthesized compounds*



Scheme II. Synthetic routes for the pyranopyrazole derivatives (5-10)



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The biological activities of the tested pyranopyrazole derivatives, and oxinobispyrazoleis are summarized in (Tables I, II and III). The preliminary herbicidal test results showed that the target compound **6** has inhibitory activities against the roots and stalks of plants like *Echinochloa crus-galli* and *portulacaoleraceae* in higher concentration. Otherwise, compound **7** has some inhibitory activity against the roots and stalks of plants (Table I).

Under these conditions, the yields were significantly improved and the reaction time was reduced dramatically. These processes are very simple and environmentally benign.

**Table I: Herbicidal activity of pyranopyrazole and oxinobispyrazole derivatives against Echinochloa crus-galli and portulacaoleraceae.**

Compound no.	Echinochloa crus-galli		Portulacaoleraceae	
	Shoot	Root	Shoot	Root
<b>1</b>	×	×	√	√
<b>2</b>	×	×	√	√
<b>3</b>	×	×	√	√
<b>4</b>	×	×	√	√
<b>5</b>	×	×	√	√
<b>6</b>	√	√	√	√
<b>7</b>	√	√	√	√
<b>8</b>	×	×	√	√
<b>9</b>	×	×	√	√
<b>10</b>	×	×	√	√
Water control	×	×	×	×
DMSO control	×	×	×	×
Bbp	√	√	√	√

×= not active, √= active

The herbicidal activities of the compound no. **6**, **7** and bispyribac against root and shoot barnyard grass are summarized in (Tables II and III), respectively. Compounds no. **6** and **7** gave good percentages inhibition to root of barnyard grass weed at 0.5ppm concentration and the percent of inhibition reach up to 70%. It is imperative's in view of GI<sub>50</sub> which were 0.09ppm to compound **6** and 0.16ppm to compound **7** compared to > 0.5ppm to bispyribac standard herbicide (Table II).

**Table II: Effect of compound no. 6, 7 and Bbp herbicide in barnyard grass root growth after 10 days of sowing.**

Conc. mg/L	Compound no. 6		Compound no. 7		Bbp herbicide	
	Root length (cm) ±SD	I (%)	Root length (cm) ±SD	I (%)	Root length (cm) ±SD	I (%)
0	3.40±0.23 <sup>a</sup>	0.0	3.40±0.23 <sup>a</sup>	0.0	3.40±0.23 <sup>b</sup>	0.0
0.01	3.23±0.23 <sup>a</sup>	5.0	3.67±0.31 <sup>a</sup>	-7.9	3.97±0.12 <sup>a</sup>	-16.8
0.05	2.03±0.06 <sup>b</sup>	40.3	2.67±0.31 <sup>b</sup>	21.5	3.27±0.23 <sup>b</sup>	3.8
0.1	1.57±0.0 <sup>c</sup>	53.8	1.80±0.10 <sup>c</sup>	47.1	2.77±0.021 <sup>c</sup>	18.5
0.5	1.0±0.20 <sup>d</sup>	70.6	1.0±0.0 <sup>d</sup>	70.6	2.0±0.0 <sup>d</sup>	41.2
GI <sub>50</sub>	0.09		0.16		>0.5	

This result showed that better herbicidal activity than the standard herbicide against E. crus-galli and promising to be developed in further study. Also, the results of compounds no. **6** and **7** gave very good inhibition to shoot of E. crus-galli, the inhibition percentages are 83.4 and 80.1 respectively for the highest concentration (0.5ppm). However, from the dose response curve, GI<sub>50</sub> values represent 0.03ppm to two compounds. Otherwise, bispyribac standard herbicide gave GI<sub>50</sub> 0.12ppm (Table III).





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Table III: Effect of compound no. 6, 7 and Bbp herbicide in barnyard grass shoot growth after 10 days of sowing.

Conc. mg/L	Compound no. (6)			Compound no. (7)			Bbp herbicide	
	Shoot (cm) ±SD	length	I (%)	Shoot ±SD	length (cm)	I (%)	Shoot length (cm) ±SD	I (%)
0	10.07±0.68 <sup>a</sup>		0.0	10.07±0.68 <sup>a</sup>		0.0	10.07±0.68	0.0
0.01	6.33±0.58 <sup>b</sup>		37.1	6.57±0.40 <sup>b</sup>		34.8	7.77±0.25 <sup>b</sup>	22.8
0.05	4.33±0.58 <sup>c</sup>		57.0	3.80±0.20 <sup>c</sup>		62.3	6.30±0.26 <sup>c</sup>	37.4
0.1	2.67±0.58 <sup>d</sup>		73.5	2.83±0.29 <sup>d</sup>		71.9	4.90±0.36 <sup>d</sup>	51.3
0.5	1.67±0.58 <sup>e</sup>		83.4	2.0±0.0 <sup>c</sup>		80.1	3.57±0.40 <sup>e</sup>	64.5
GI <sub>50</sub>	0.03(0.01-0.04)			0.03(0.01-0.04)			0.12 (0.08-0.21)	

From GI<sub>50</sub> values of inhibition of root and shoot system of barnyard grass weed of compound no. 6, 7 and bispyribac herbicide, the study concludes that they obtained results are proving that the new synthesized pyranopyrazole derivatives are much better and promising as herbicides and current studies are going on which will be declared in near future. Generally, we found that, the novel substituted pyranopyrazole and oxinobispyrazole derivatives especially compound no. 6 and 7, have promising herbicidal efficiency and demonstrated significant activities against *Echinochloa crus-galli* and *Portulacaoleraceae*. Our results are fully in accordance to the modern survey and agree with the previous studies [6]-[8], [13].

#### IV. CONCLUSIONS

Our target in this work aimed to describe the synthesis and structure-activity relationship of novel pyranopyrazole and oxinobispyrazole derivatives. The substituted pyranopyrazole and oxinobispyrazole derivatives (2-10) revealed promising herbicidal activity. Among them, compound no. 6 and 7 possessed the highest herbicidal activity. Both compounds showed excellent herbicidal activity against grass weeds and some of broad leaf weeds. These findings suggest that *E. crus-galli* weed in paddy fields control using these compounds might be feasible and further work on this is recommended.

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#### CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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