Synthesis and Herbicidal Activity of Heterocyclic Azlactone and Imidazolinone Derivatives

Yonis M. Badawy[1]; Ali F. El-Sayed[1], Foaud Sh. Soliman[2], and Mohamed S. Mohy-Aldin[3]

ABSTRACT

4-Heteroarylidene-2-phenyl-1,3-oxazol-5(4H)-ones were prepared by reactions of hippuric with 3-formylchromone. Structure elucidation of synthesized compounds has been made on the basis of their elemental analysis and spectral data of IR, ^{1}HNMR and MS. The herbicidal activity of the synthesized compounds has been evaluated against Echinochloa crus-galli.

Key words: Imidazolinone, herbicidal activity, Echinochloa crus-galli.

INTRODUCTION

The study incorporates the topic "AZLACTONE" because it provides a basic skeleton structure and which is also a part of a great importance for its drug characteristics. The basic nucleus imidazole emerges from the drug intermediate azlactone. The azlactones possess oxazolone moiety. The azlactones are known to exhibit antifungal, antibacterial (Rakesh and Desai, 2005) (Evans, 1965) and anti-inflammatory activities. They are also of great importance to produce penicillin type of drug intermediates (Clinic and Rochester, 2015) and they are also useful to produce synthetic hormonal compounds (Cornforth *et al.*, 1949).

Imidazole is a planer five-membered heterocyclic ring system with three carbon and two nitrogen atoms in 1 and 3 positions. Imidazolones are keto dihydro imidazoles. Imidazolone that is known as oxoimidazoline is a five-membered heterocyclic ring system having nitrogen atoms in 1 and 3 positions and carbonyl group in 5 position. Oxoimidazoline, which is also known as imidazolinone is reported to exhibit a wide variety of therapeutic activities such as sedative, hypnotic, CNS depressant etc. Imidazolinone derivatives have also been reported to possess antihistaminic antihypertensive and antiparkinsonian activities. (Savjani, Gajjar. 2011; Yutilov, 2005; Grimmett, 1996).

The 4-arylidene-2-phenyl oxazol-5(4H)-ones thus prepared are converted into new imidazolinone derivatives by reaction with aryl amines by following literature method.All these observation and the essential role of heterocyclic azlactone derivatives and imidazolinone derivatives, in certain biological reactions prompted us to synthesis all these heterocyclic derivatives.

The search for a new chemical structure of a biocide is to decrease or prevent the environmental pollution. To raise the success rate of the search, more and more design and optimization procedures such as structure-activity relationship are adopted, (El-Nawawy and El-Kheshin 1960, El-nawawy *et al,*1973, Kadous *et al*,1979, Morsy *et al.*,1981, Abdalah *et al.*, 1981 and 1985, Ahmed and Mokhtar 1985).

The imidazolinone herbicides were discovered in the 1970_s by scientists at American Cyanamid Company. The discovery of the imidazolinone herbicide has led to the development of four worlds – class herbicides. Because of their versatility, low toxicity and environmental safety, these herbicides are used in many different crops and play a vital role in the production of food and fiber throughout the world. The imidazolinones represent one of the new classes of herbicides that will lead us into the 21st Century. Due to the importance of the imidazlinone in weed control in agriculture, a great deal of research has been conducted on the efficiency and potential use of these compounds to weed control.

The derivatives of imidazlinone sulfonamide general structure had attracted the attentions of many scientists to find out biologically and specifically active derivatives. Different biological effects of these compounds were studied as herbicides during the 1980s. Four new herbicidal classes emerged that were potent, selective, brood-spectrum inhibitors of plant growth at field rates measured in grams rather than kilograms per hectare the herbicide groups are sulphonyl ureas, imidazolinones, triazolopyrimidines and pyrimidinyl thiobenzoate, yet all share the same site of action, namely acetoacetate synthase (ALS), a key enzyme in the biosynthesis of the branched-chain amino acids, leucine, isoleucine and valine. They are able to control a very wide spectrum of trouble some annual grass and broadleaf weeds with very low doses.

[1]Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.
[2] Pesticide Chemistry Dept. Faculty of Agriculture (El- Shatby), Alexandria University.
[3]New Material, City of Scientific Research and Application Technologyies Alexandria.
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Furthermore, Formulations have proved to be both foliar and soil active with very low mammalian toxicity. Chlorsulfuron, tribenuron-methyl and imazamethabenzen give selective weed control in crops (Gulidov and Norezhnaga 1994, Montazeri, 1995, Koscelny and peeper,1996, Koscelny et al, 1996, Kumer, et al, 1996, Sabra, et al, 1999, Punia, et al, 2008 and Pawan et al, 2012). Sulfonamide is a new active herbicidal group against grassy and broad leaf weeds with low doses. The synthesis of new imidazolinone sulfonamide derivatives may give herbicidal activity against grassy and broad leaf weeds in different field crops.

All these observations and the essential role of heterocyclic azlactone derivatives and imidazolinone derivatives, in certain biological reactions prompted us to synthesis all these heterocyclic dervivatives (3 – 16).

MATERIALS AND METHODS

1. General

Melting points are not corrected. The IR spectra were recorded on a Pyc-Unicam SP 1200 spectrophotometer using the KBr water technique. The ^{1}H-NMR spectra were recorded on a Varian GEMINI 200 MHz NMR spectrophotometer using 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.

2. Synthesis of target compounds:

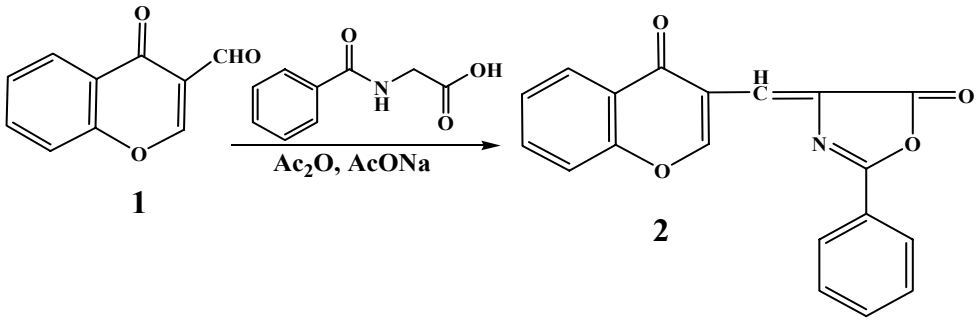
A mixture of N-benzoylglycine (Hippuric acid) (0.01 mol) and 3-formylchromone 1 (0.01mol) in acetic anhydride (15 ml) and in the presence of freshly fused sodium acetate (0.5gm) were heated under reflux on the water-bath for 1 hour. After cooling, the resulting oxazolone was washed first with 50% aqueous alcohol then with ether and recystallised from alcohol-acetone as bright yellow needles, to give 2, yield (88%), m.p. 195-197˚C,IR(KBr) ν_{max} cm^{-1}: 1801.4 cm^{-1} (CO lactone), 1647.2 cm^{-1}(CO of chromone), 1615.6 cm^{-1}(C=C & C=N), The spectra also show an intensive absorption bands at 3066.4 and 3035.5 cm^{-1}. (aromatic CH), ^{1}HNMR (DMSO-d6) δ (ppm): 7.35 - 8.18 (m, l0H, Ar-H + CHpyran.) ; 9.69 (s, IH, CH = C).

Analysis of $C_{19}H_{11}NO_4$ (%):Calad.: C, 71.92; H, 3.49; N, 4.41; O, 20.17; Found: C, (71.41); H, (3.13); N, (4.21). Mass spectrum showed molecular ion peak at m/z=317 (85.16%) with base peak at mlz: 105. Other significant peaks were observed at m/z= 77 (98.32%), 206 (6.57%), 266 (5.85%) and 302 (7.83%).

General procedure for synthesis compounds (3-16).

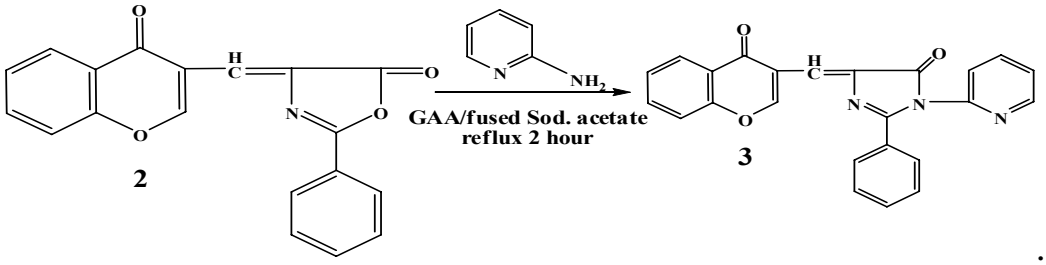
A mixture of (0.01 mol) of compound 2, (0.8gm) of freshly fused sodium acetate and aryl amines or amino acid esters and substituted hydrazine (0.01 mol) in (10 ml) of glacial acetic acid was refluxed for 2 hr. After cooling the mixture a solid precipitate occurs, to give compounds (3 – 16), yield (76-83%)

4-((4 -Oxo- *4H*-chromen-3-yl) methylene) -2-phenyloxazol -*5(4H)* –one (2)



1 2

4- (4-Oxo-*4H*-chromen-3-yl) methylene)-2-phenyl-1-(pyridin-2-yl)-*1H*-imidazol-*5(4H)*-one (3



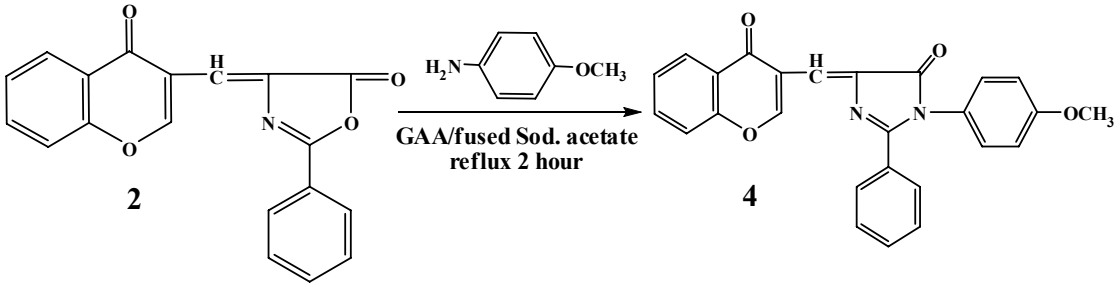
2 3

Yield: 78%; orange red crystals; mp 216-218°C; IR(KBr) ν_{max} cm^{-1} 1715 cm^{-1} CO of imidazolin-5-one, 1646 cm^{-1} CO of chromone, 1617 cm^{-1} C ≡ N , 3046 cm^{-1} CH-aromatic. Analysis of $C_{24}H_{15}N_3O_3$ (%): Calcd: C, 73.27; H, 3.84; N, 10.68; O, 12.20. Found: C, (73.11); H, (3.32); N, (10.36). Mass spectrum showed molecular ion peak at m/z = 393(78.19%) with base peak at m/z: 105 and we could observe the other significant peaks at 77 (69.53%), 121 (16.42%), 172 (13.31%), 226 (13.91%) and 359 (12.72%).

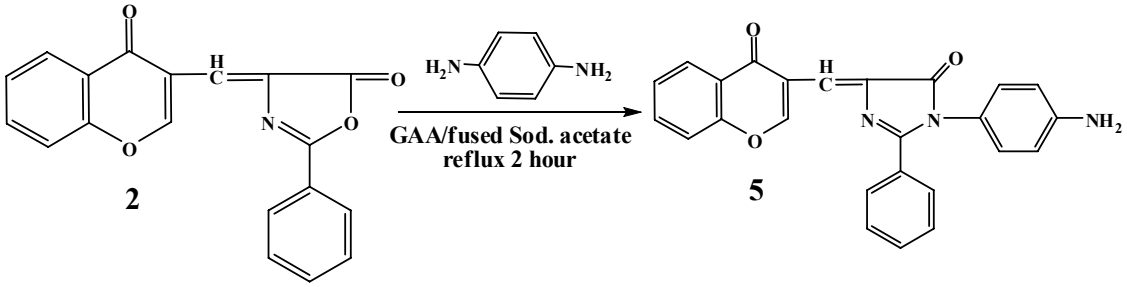
Yield: 76%; orange red crystals; mp 204-208°C; IR (KBr) ν_{max} cm^{-1} CO of imidazolin-5-one at 1718 cm^{-1}, CO of chromone at 1644 cm^{-1} CH-aliph at 2951 cm^{-1}, CH-aromatic 3061 cm^{-1}. Analysis of $C_{26}H_{18}N_2O_4$ (%): Calcd: C, 73.92; H, 4.29; N, 6.63; O, 15.15. Found: C, (73.51); H, (4.12); N, (6.31). Mass spectrum showed molecular ion peak at m/z = 422 (74.12%) with base peak at m/z: 105 (100%) and other significant peaks at 77 (80.43%), 210 (29.71%), 305 (9.07%) and 406 (9.31%).

Yield: 78%; orange red crystals; mp 190-192°C; IR (KBr) ν_{max} cm^{-1}: ν CO of imidazolin-5-one at 1716 cm^{-1}, CO of Chromone at 1650 cm^{-1}, 3424, 3316 cm^{-1} of NH_2, and CH-aromatic at 3058 cm^{-1}. Analysis of $C_{25}H_{17}N_3O_3$ (%): Calcd: C, 73.70; H, 4.21; N, 10.31; O, 11.78. Found: C, (73.52); H, (4.12); N, (10.11). Mass spectrum showed molecular ion peak at m/z = 407 with base peak at m/z: 105 and peaks at 77 (70.52%), 121 (31.21%), 171(26.59%), 222 (24.28) and 401 (21.39%).

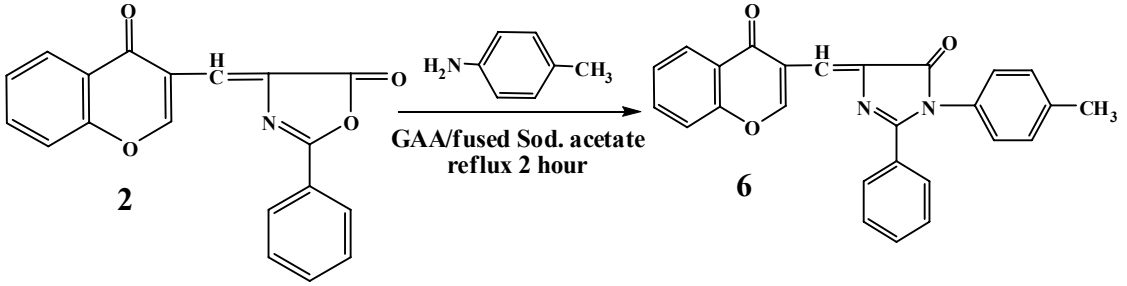
1- (4-Methoxyphenyl) -4- ((4- Oxo - 4H- chromen- 3-yl) methylene) -2-phenyl-1H-imidazol-5(4H)-one (4)



1-(4-Aminophenyl) -4- ((4-Oxo-4H-chromen-3-yl) methylene)-2- phenyl-1H-imidazol-5(4H)-one (5)



4-((4-Oxo-*4H*-chromen-3-yl) methylene) -2- phenyl -1- p-tolyl-*1H*-imidazol-*5(4H)*-one (6)



Yield: 79%; red crystals; mp 200°C; IR (KBr) ν_{max} cm^{-1}: 3058 cm^{-1} (CH-aromatic), 1719 cm^{-1} of imidazolin-5-one and 1645 cm^{-1} CO of Chromone. Analysis of $C_{26}H_{18}N_2O_3$ (%): Calcd: C, 76.83; H, 4.46; N, 6.89; O, 11.81. Found: C, (76.52); H, (4.21); N, (6.23). Mass spectrum showed molecular ion peak at m/z = 406 (59.32) with base peak at m/z: 105 (100%) and the other significant peaks were observed at m/z=77 (63.13%), 194 (21.40%), 257 (14.21%) and 373 (16.01%).

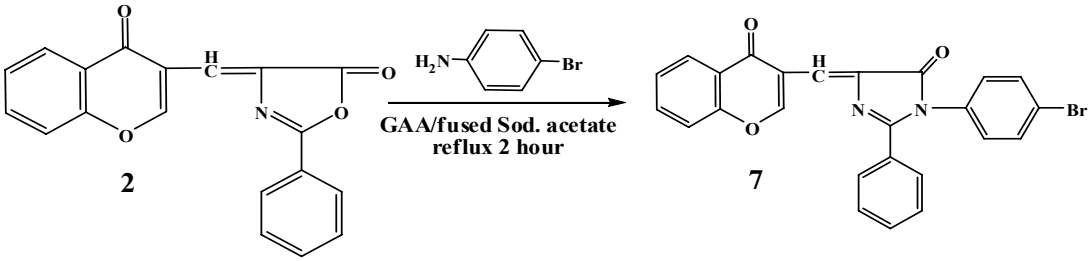
Yield: 80%; red crystals; mp 205°C; IR (KBr) ν_{max} cm^{-1}: ν CO of imidazolin-5-one at 1722 cm^{-1}, CO of chromone at 1647 cm^{-1}, and 3059 cm^{-1} CH-aromatic. Analysis of $C_{25}H_{15}BrN_2O_3$ (%): Calcd: C, 63.71; H, 3.21; Br, 16.95; N, 5.94; O, 10. 18. Found: C, (63.32); H, (3.0); Br, (16.21); N, (5.31). Mass spectrum showed molecular ion peak at m/z: 470 (72.13%) with base peak at 105 (100%). and the other significant peaks were observed at 91 (63.49%), 120 (12.15%), 157 (12.87%) and 258 (13.53%).

Yield: 81%; red crystals; mp 210°C; IR (KBr) ν_{max} cm^{-1}: CO of chromone coupled with CO of imidazolin-5-one 1615cm^{-1}; ν OH at 3393 cm^{-1}, CH-aliphatic at 2922 cm^{-1} and CH-aromatic at 3067 cm^{-1}, Analysis of $C_{25}H_{16}N_2O_4$ (%): Calcd: C, 73.52; H, 3.95; N, 6.86; O, 15.67. Found: C, (73.22); H, (3.34); N, (6.62). Mass spectrum showed molecular ion peak at m/z: 408 (68.15%) with base peak at m/z: 105 (100%) and the other significant peaks were observed at m/z=77 (67.48%), 121 (24.72%), 174 (22.27%), 221 (17.37%) and 304 (15.81%).

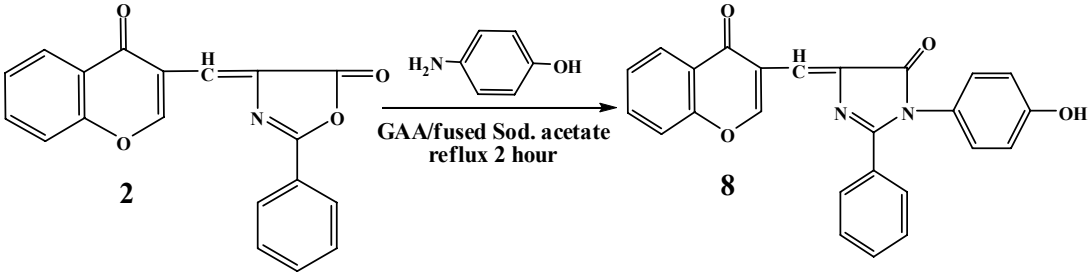
Yield: 82%; red crystals; mp 215°C; IR (KBr) ν_{max} cm^{-1}: 1716 cm^{-1} (CO of imidazolin-5-one), 1646cm^{-1} (CO of chromone) and 3430 cm^{-1}, 3295 (NH), ^{1}H NMR (DMSO-d_6) δ (ppm): 2.50 (s, 3H, CH_3); 6.73-825 (m, 17H, ArH + pyran-H);10.42 (s, 1H, CH=C); 11.56 (s, 1H, $NHSO_2$); 6.33 (s,1H, CH isoxazole). Analysis of $C_{29}H_{20}N_4O_6S$ (%): Calcd: C, 63.04; H, 3.65; N, 10.14; O, 17.37; S, 5.80. Found: C, (63.00); H, (3.24); N, (10.0); S, (5.55). Mass spectrum showed molecular ion peak at m/z: 552 (74.18) with base peak at m/z: 105 and peaks at 77 (62.24%), 152 (40.25%), 209 (39.00%), 370 (39.42) and 469 (44.81%).

Yield: 80%; red crystals; mp 220°C; IR (KBr) ν_{max} cm^{-1}: CO of imidazolin-5-one 1718 cm^{-1}, CO of chromone 1652 cm^{-1} CH-aliphatic at 2924 cm^{-1}, CH-aromatic at 3065 cm^{-1} and NH at 3394 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.30 (s, 3H, CH_3); 11, 76 (S, 1H, NH SO_2); 6.33 - 8.25 (m, 17H,Ar-H+ Pyran-H); 10.52 (s,1H, CH=C); 8.74 (s, 1H, CH-olefenic). Analysis of $C_{31}H_{23}N_5O_5S$ (%): Calcd: C, 64.46; H, 4.01; N, 12.12; O, 13.85; S, 5.55. Found: C, (64.21); H, (4.0); N, (12. 1); S, (5.11). Mass spectrum showed molecular ion peak at m/z: 577 (78.20) with base peak at m/z: 105 (100%) and other peaks at 77 (67.42%), 117 (22.85%), 198 (13.80%), 418 (95.00) and 515 (8.26%).

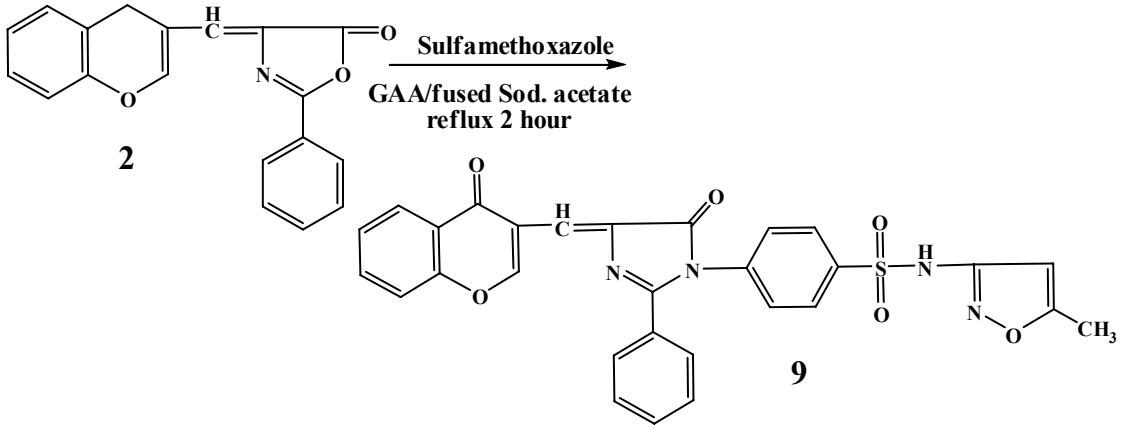
Synthesis of 1-(4-Bromophenyl) -4- ((4-Oxo-4H-chromen-3-yl) methylene)-2-phenyl-1H-imidazol-5(4H)-one (7)



Synthesis of 1-(4-Hydroxyphenyl)-4-((4-Oxo-4H-chromen-3-yl)methylene)-2-phenyl-1H-imidazol-5(4H)-one(8)

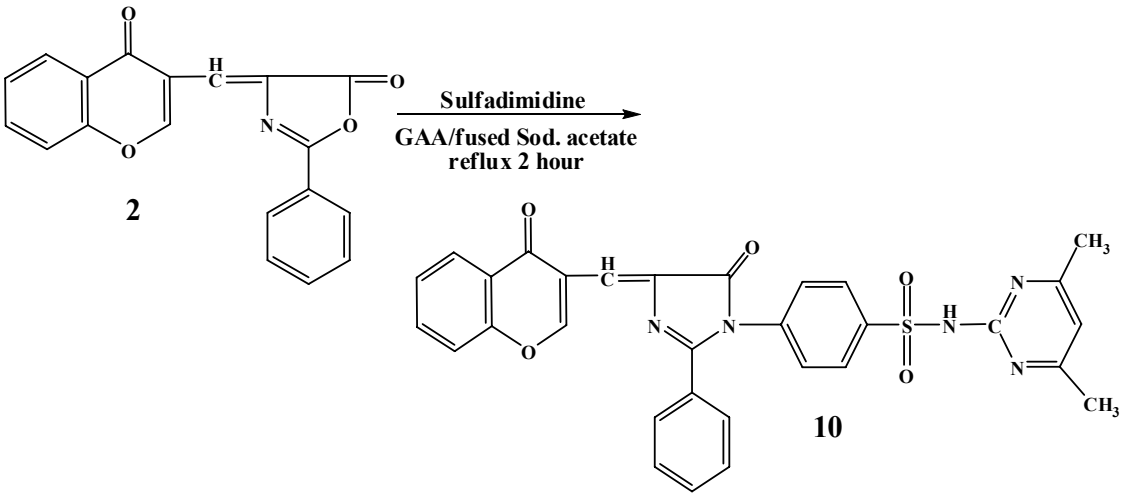


N- (5-Methylisoxazol-3-yl) -4- (5-Oxo-4- ((4 – Oxo-4H-chromen-3-yl) methylene) -2-phenyl -4, 5- dihydro-1H-imidazol-1-yl) benzenesulfonamide (9)



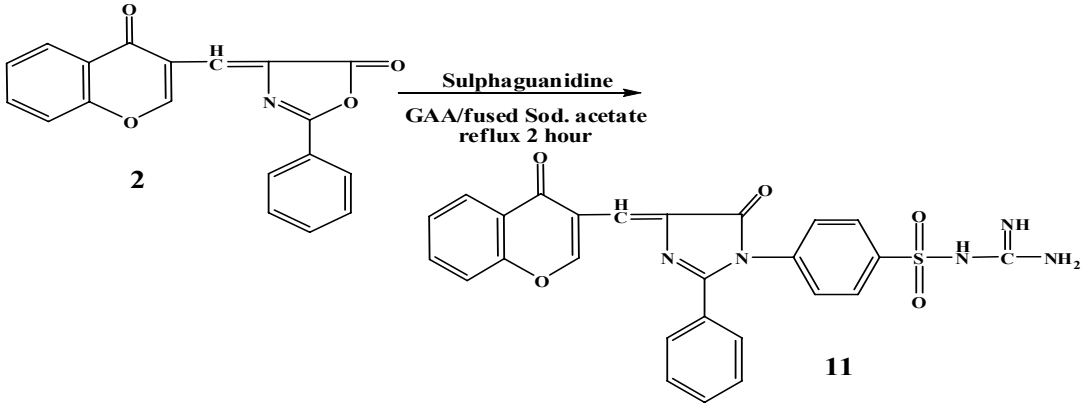
2 **9**

N- (4, 6-Dimethylpyrimidin-2-yl) -4- (5-Oxo-4- ((4-Oxo-4H-chromen-3-yl) methylene)-2-phenyl-4, 5-dihydro-1H-imidazol-1-yl) benzenesulfonamide (10)



2 **10**

N-Carbamimidoyl -4- (5-Oxo-4- ((4-Oxo-4H-chromen-3-yl) methylene) -2- phenyl -4,5-dihydro- 1H-imidazol-1-yl) benzenesulfonamide (11)

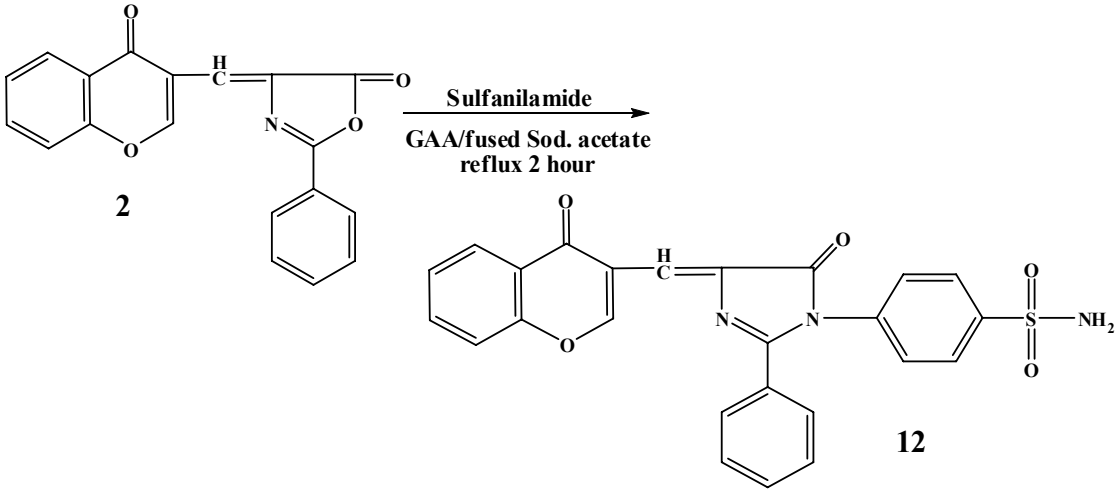


2 **11**

Yield: 81%; red crystals; mp 225°C; IR (KBr) ν_{max} cm^{-1}: CO of imidazolin-5-one at 1719 cm^{-1}, CO of chromone at 1647 cm^{-1}, SO_2 at 1350,1157 cm^{-1}, CH-aromatic at 3067 cm^{-1} and NH at 3398 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ (ppm): 6.65 - 8.25 (m, 17H, Ar-H + Pyran-H); 10.46 (s, 1H, CH=C); 11.67 (s, 1H, NH SO_2). Analysis of $C_{26}H_{19}N_5O_5S$ (%): Calcd: C, 60.81; H, 3.73; N, 13.64; O, 15. 58; S, 6.24. Found: C, (6.62); H, (3.41); N, (13.21); S, (6.11). Mass spectrum showed molecular ion peak at m/z = 513 (63.18) with base peak at m/z = 105 (100%) and other peaks at m/z = 77 (62.39%), 213 (12.54%), 303 (8.87%), 414 (7.91) and 495 (9.84%).

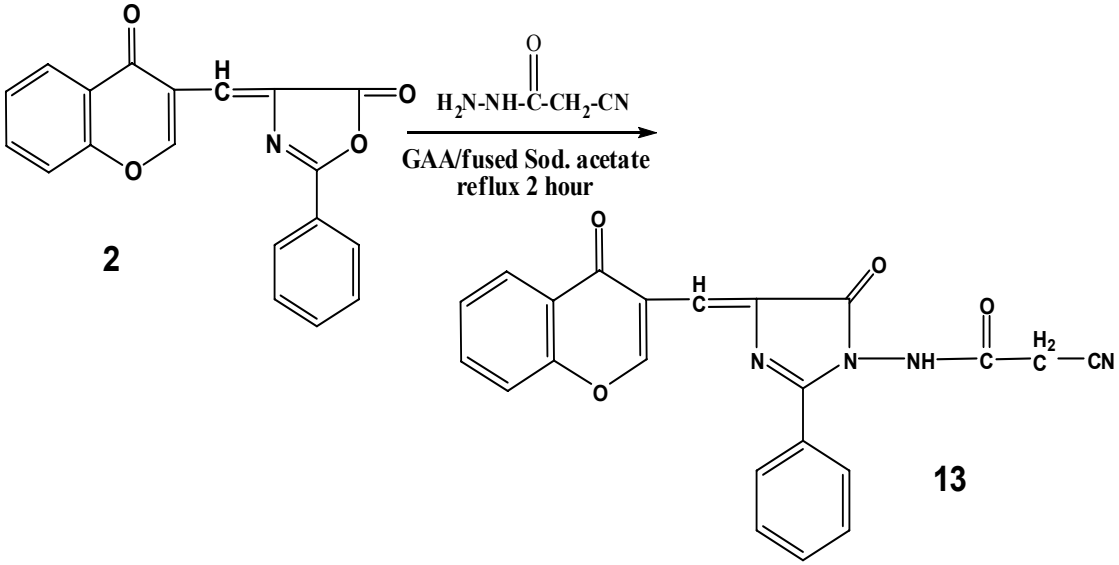
Yield: 80%; red crystals; mp 230°C; IR (KBr) ν_{max} cm^{-1}: CO of imidazolin-5-one at 1715.4cm^{-1}, CO of chromone at 1616.6cm^{-1} , SO_2 1342.21, 1160.7cm^{-1}, aromatic CH at 3063.5 cm^{-1}, NH, of SO_2NH_2 at 3337.9 (antisymm.) and 3249.0 (symm.) cm^{-1}. Analysis of $C_{25}H_{17}N_3O_5S$ (%): Calcd: C, 63.69; H, 3.63; N, 8.91; O, 16.97; S, 6.80. Found: C, (63.21); H, (3.23); N, (8.56); S, (6.51). Mass spectrum showed molecular the ion peak at mlz: 471 (79.50%) with base peak at mlz: 105 (100%). and other peaks at m/z = 77 (57.87%), 316 (4.01%), 355 (5.54%) and 401 (7.51%).

4-(5-Oxo-4- ((4-Oxo-*4H*-chromen-3-yl) methylene) -2-phenyl-4, 5-dihydro-*1H*-imidzol-1-yl) benzenesulfonamide (12)



2 12

2-Cyano-N-(5-Oxo-4-((4-Oxo-*4H*-chromen-3-yl) methylene)-2-phenyl-4, 5-dihydro-*1H*-imidazol-1-yl) acetamide (13)



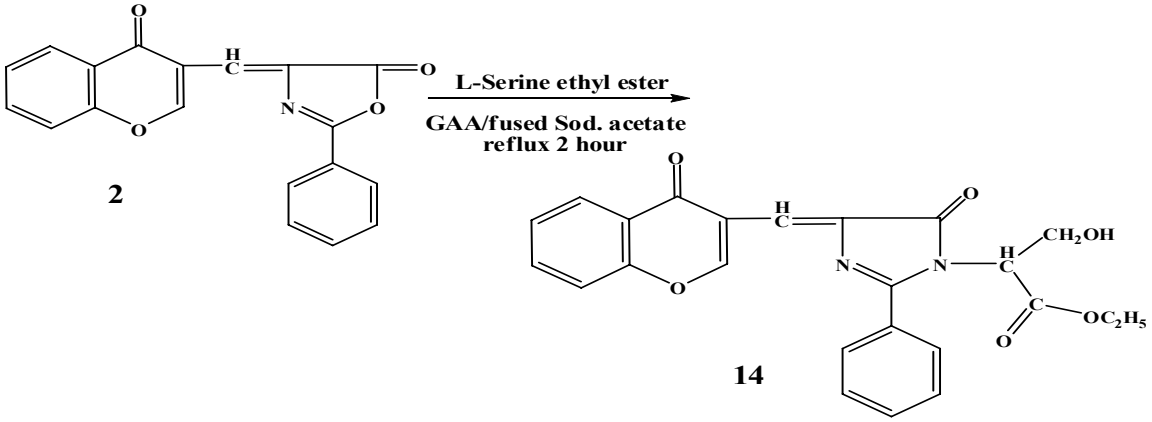
2 13

Yield: 81%; red crystals; mp 220°C; IR (KBr) ν_{max} cm^{-1}: CO of N-NHCOCH$_2$ at 1652 cm^{-1}, CN at 2259cm^{-1}, CH-aliphatic at 2923 cm^{-1} CH-aromatic at 3046 cm^{-1}, and NH at 3177 cm^{-1}. Analysis of $C_{22}H_{14}N_4O_4$ (%): Calcd: C, 66.33; H, 3.54; N, 14.06; O, 16.06. Found: C, (66.12); H, (3.32); N, (14.01). Mass spectrum showed molecular ion peak at m/z: 398 with base peak at m/z: 77, and other peaks at m/z = 105 (91.12%), 219 (57.99%), 302 (41.42%) and 471 (47.93).

Yield: 75%; red crystals; mp 218°C; IR (KBr) ν_{max} cm^{-1}: CO ester at 1742.2 cm^{-1}, CO of chromone at 1652.5 cm^{-1}, OH at 3269.5 cm^{-1}, CH-aromatic at 3062.4 cm^{-1}, and CH-aliph., at 2955.8 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.25 (t, 2H, CH$_3$-ester); 1.62 (t, 2H, CH$_2$); 1.84 (m, 1H, CH); 4.23 (q, 1H, CH$_2$-ester); 7.55 (q, 1H, N-CH); 6.96-8.16 (m, 9H, Ar-H); 8.67 (s, 1H, CH-pyran); 8.76 (s, 1H, CH=C). Analysis of $C_{24}H_{20}N_2O_6$ (%): Calcd: C, 66.66; H, 4.66; N, 6.48; O, 22.20. Found: C, (66.25); H, (4.43); N, (6.21). Mass spectrum of compound **14** showed molecular ion peak at m/z: 432(71.32) with base peak at m/z: 105 (100%) and the other at 77 (50.43%), 180 (17.82%), 303 (11.82%) and 408 (12.36%).

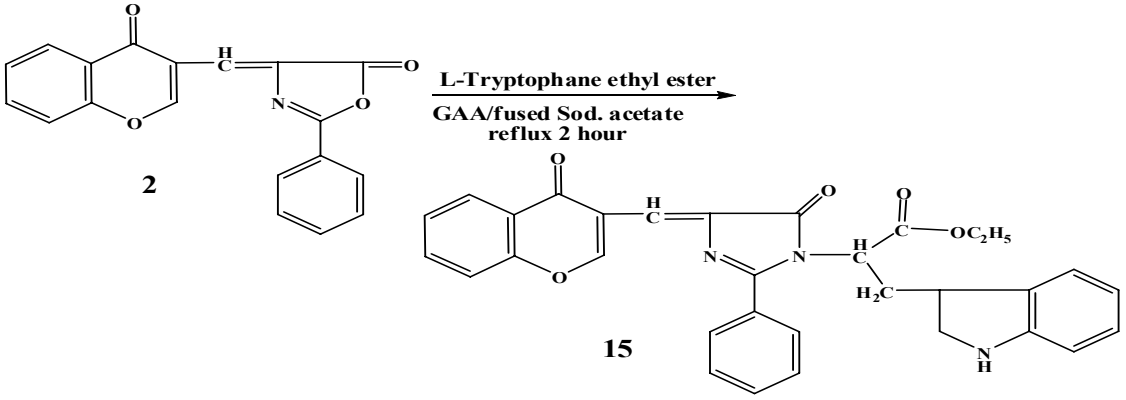
Yield: 75%; red crystals; mp 218°C; IR (KBr) ν_{max} cm^{-1}: CO ester at 1731.9 cm^{-1},CO of chromone at 1655.8 cm^{-1}, NH at 3336.4 cm^{-1}, CH-aromatic at 3059.6 cm^{-1}, and CH-aliph., at 2981.5 and 2931.4 cm^{-1}, ^{1}H NMR (DMSO-d$_6$) δ (ppm):1.29 (t, 2H, CH$_3$-ester); 1.70 (t, 2H, CH$_2$); 1.91 (m, 1H, CH); 4.19 (q, 1H, CH$_2$-ester); 7.65 (q, 1H, N-CH); 6.94-8.16 (m, 9h, Ar-H); 8.80 (s, 1H, CH-pyran); 8.75 (s, 1H, CH=C). Analysis of $C_{32}H_{27}N_3O_5$ (%): Calcd: C, 72.03; H, 5.10; N, 7.88; O, 14.99. Found: C, (72.0); H, (5.0); N, (7.21). Mass spectrum of compound **15** showed molecular ion peak at m/z: 532 (79.83%) with base peak at m/z: 105 (.100%) and the other peaks at 77 (59.29%), 130 (38.57%), 221 (18.10%), 310 (15.48%) and 510 (18.57%).

Ethyl 3-Hydroxy -2- (5-Oxo-4 ((4-Oxo-*4H*-chromen-3-yl) methylene)-2-phenyl-4, 5-dihydro-*1H*-imidazol-1-yl) propanoate (14)



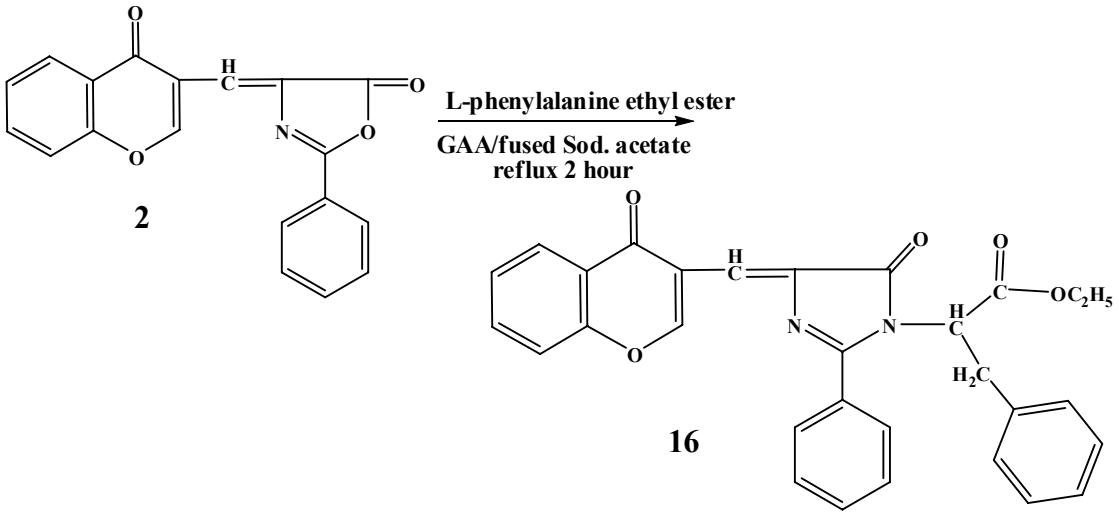
2 14

Ehyl 3-(Indolin-3-yl)-2-(5-Oxo-4-((4-Oxo-*4H*-chromen-3-yl) methylene)-2-phenyl-4, 5-dihydro-*1H*-imidazol-1-yl) propanoate (15)



2 15

Ethyl 2- (5- Oxo-4-((4-Oxo-4H-chromen-3-yl) methylene)-2-phenyl-4, 5-dihydro-1H-imidazol-1-yl) -3-phenylpropanoate (16)



2

16

Yield: 77%; red crystals; mp 220°C; IR (KBr) ν_{max} cm^{-1}: CO of ester at 1716 cm^{-1}, CO of imidazolin-5-one at 1667 cm^{-1}, CO of off chromone at 1644 cm^{-1}, CH-aromatic at 3062.41 $cm^{-1}$and CH-aliphatic 2926.45 cm^{-1}, ^{1}H NMR (DMSO-d_6) δ (ppm): 6.94-8.16 (m, 9H, Ar-H); 8.55 (s, 1H, CH=C); 8.75 (s, 1H, CH-pyran); 4.39 (q, 1H, CH_2-ester); 1.4 (t, 3H, CH_3-ester); 1.70 (t, 2H, CH_2); 1.91 (m, 1H, CH). Analysis of $C_{30}H_{24}N_2O_5$ (%): Calcd: C, 73.16; H, 4.91; N, 5.69; O, 16.24. Found: C, (73.11); H, (4.25); N, (5.11). Mass spectrum of compound **16** showed molecular ion peak at m/z: 492 (76.80) with base peak at m/z: 105 (100%). and other peaks at m/z = 77 (73.96%), 261 (5.50%), 404 (4.43%) and 421 (5.10%).

3. Seedling growth bioassay

The herbicidal activity of 12 compounds from imidazolinone sulfonamide derivatives and bispyribac herbicide as standard was evaluated against *Echinochloa crus-galli* (barnyard grass weed) and *portulaca oleraceae*. 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 0.5ppm. On the other hand, the effect of DMSO and distl. water against two weeds were also carried out the phytotoxicity test carried out according to the method described by Thomas and Cline, 1985. The tested compounds and a reference herbicide, bispyribac, were dissolved in dimethyl sulfoxide (DMSO) followed by dilution with distilled water to obtain a stock solution of 2.7 ppm. Then a series of concentrations (0.01, 0.05, 0.1 and 0.5ppm) was prepared by dilution with distilled water. An aqueous solution of DMSO was used as control treatment. Three replicates, each of 0.2 gm of purslane and barnyard grass were prepared for each treatment using glass Petri-dish (9cm) lined with whatman No.2 filter paper. Six milliliters of each test solution were added to each Petri-dish. Afterward, Petri-dish were placed in the bottom of 0.1mm thick polyethylene bags (15 x 30 cm) that were expanded to contain air and then closed at the top with rubber bands to prevent the loss of moisture. The Petri-dishs were kept on a germination cabinet at 20 ± 1°C. After 10 days of sowing root and shoot lengths were determined. The growth inhibition percentages of root and shoot lengths were calculated from the following equation %I = (1-T/C) × 100; T is the length of treatment (cm) and C is the length of control (cm). The concentrations causing 50% inhibition (GI_{50}) of root and shoot growth were calculated from a probit analysis (Finney, 1971). Root lengths and shoot length were subjected to one –way analysis of Variance followed by student-Newman-Keuls test (Cohort software Inc. 1985) to determine significant differences among mean values at the probability level of 0.05

RESULTS AND DISCUSSION

1. Synthesis of azlactone and imidazolinone derivatives

Reaction of 3-formylchromone with hippuric acid led to the product containing a 1,3-oxazol-5(4H)-one ring as starting materials for synthesis is well known.

This aimed to incorporate these heterocyclic biologically active moieties into new heterocyclic systems. This research is continuation of our earlier works in which we described theoretical, spectral and biological properties of the new synthesized chromone

and chromanone derivatives. The aim of this study was the preparation of some new five-membered-nitrogen heterocyclic derivatives of chromone. These analogs could be valuable for using as intermediates and as well as available by condensation reaction. 3- Formylchromones were chosen as synthetically versatile molecules with reactive carbonyl group. They have a considerable significance not only for their biological activities (Collins and Alan. 2014) but also for their reactivity towards nucleophiles that enables the synthesis of a wide variety of heterocyclic. The starting 3-formylchromones used in this work are accessible via vilsmeier-double formylation of appropriate o-hydroxyacetophenones (Borrell, et al. 2004) the reactions processes are outlined in schemes.

2. Herbicidal activity of synthetized compounds

The preliminary herbicidal test results showed that the target compound **9** had inhibitory activities against root and shoot (*Echinochloa crus-galli* and *Portulaca oleraceae*) at higher concentration. Compound 15 had some inhibitory activity against the roots and shoots (*crus-galli* and *Portulaca oleraceae*) (1, 2 and 3).

The biological activities of the tested 1, 2, 4-trisubstituted 2- imidazolin -5- ones derivatives showed in tables 1, 2 and 3. The results in Table (1) showed that, the all synthetized chemical compounds exhibited a complete inhibition of root and shoot growth of purslane weed at all of the tested concentrations compared to untreated chek. On the other hand, all the tested compounds did not give any herbicidal activity against shoot and root growth of barmyard grass weed at tested concentrations except for compounds 9 and 15 and standard herbicide (bispyribac) which have been shown inhibition of root and shoot growth. These results are consistent with those reported elsewhere for other imidazolinone herbicidal groups (Graph and kleifeld, 1988; and Singh *et al*, 2009). The herbicidal activity of the compounds 9, 15 and bispyribac against root and shoot of barnyard grass is shown in Tables 2 and 3. Compounds 9 and 15 gave a good percentages inhibition to root of barnyard grass weed at 0.5 ppm concentration and the percent of inhibition reached up to 70%. It is imperative in view of GI_{50} which were 0.09 or compound 9 and 0.16 ppm for compound 15 compared to > 0.5 ppm to bispyribac.

Table 1. Herbicidal activity of 1, 2, 4-trisubstituted 2-imidazolin-5-ones, derivatives against Echinochloa crus-galli and portulaca oleraceae

compounds	*Echinochloa crus-galli*		*Portulaca oleraceae*	
	Shoot	**Root**	**Shoot**	**Root**
1	×	×	√	√
2	×	×	√	√
3	×	×	√	√
4	×	×	√	√
5	×	×	√	√
6	×	×	√	√
7	×	×	√	√
8	×	×	√	√
9	√	√	√	√
10	×	×	√	√
11	×	×	√	√
12	×	×	√	√
13	×	×	√	√
14	×	×	√	√
15	√	√	√	√
16	×	×	√	√
Water control	×	×	×	×
DMSO control	×	×	×	×
Bbp	√	√	√	√

×= not active, √= active

Table 2. Effect of compounds 9 and 15, and bispyribac in *barnyard grass* root growth after 10 days of sowing

Conc. mg/L	Compound (9)		Compound (15)		bispyribac	
	Root length (cm) ±SD	I(%)	Root length (cm) ±SD	I(%)	Root length (cm) ±SD	I(%)
0	3.40±0.23[a]	0.0	3.40±0.23[a]	0.0	3.40±0.23[b]	0.0
0.01	3.23±0.23[a]	5.0	3.67±0.31[a]	-7.9	3.97±0.12[a]	-16.8
0.05	2.03±0.06[b]	40.3	2.67±0.31[b]	21.5	3.27±0.23[b]	3.8
0.1	1.57±0.0[c]	53.8	1.80±0.10[c]	47.1	2.77±0.021[c]	18.5
0.5	1.0±0.20[d]	70.6	1.0±0.0[d]	70.6	2.0±0.0[d]	41.2
GI_{50}	0.09		0.16		>0.5	

Table 3. Effect of compounds 9 and 15, and bispyribac in *barnyard grass* shoot growth after 10 days of sowing

Conc. mg/L	Compound (9)		Compound (15)		bispyribac	
	Shoot length (cm) ±SD	I (%)	Shoot length (cm) ±SD	I (%)	Shoot length (cm) ±SD	I (%)
0	10.07±0.68a	0.0	10.07±0.68a	0.0	10.07±0.68	0.0
0.01	6.33±0.58b	37.1	6.57±0.40b	34.8	7.77±0.25b	22.8
0.05	4.33±0.58c	57.0	3.80±0.20c	62.3	6.30±0.26c	37.4
0.1	2.67±0.58d	73.5	2.83±0.29d	71.9	4.90±0.36d	51.3
0.5	1.67±0.58e	83.4	2.0±0.0c	80.1	3.57±0.40e	64.5
GI_{50}	0.03(0.01-0.04)		0.03(0.01-0.04)		0.12 (0.08-0.21)	

It is known that the herbicides represent a class of xenobiotics (foreign chemicals) that are commonly used to control the growth and reproduction of unwanted vegetation. A structurally diverse group of organic molecules, herbicides contain reactive moieties, such as hydroxyl, alkyl, amino, nitro, amide, carboxyl, nitrile 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.

In the light of these facts and based on the previous survey towards the herbicides, this study aimed to synthesize some novel compounds having herbicidal efficiency. The results showed that better herbicidal activity of synthesized compounds than the standard herbicide against *E. crus-galli* and promising to be developed in further study of some synthesized compounds. Also, the results of compounds 9 and 15 gave very good inhibition to shoot of E. *Crus-galli*, the inhibition percentages are 83.4 and 80.1 respectively for the highest concentration (0.5pp). However, from the dose response curve, GI_{50} values represents 0.03 ppm to two compounds. On the other hand, bispyribac standard herbicide gave GI_{50} 0.12 ppm.

In general, from GI_{50} values of inhibition of root and shoot system of barnyard grass weed by compounds 9 and 15, and bispyribac herbicide, the study concludes that, the obtained results are proving that the new synthesized imidazolinone derivatives may be used as herbicides.

Both compounds (9, 15) showed excellent herbicidal activity against grass weeds and some of broad leaf weeds.Our lead compound 9 is associated with the chromone (4-Oxo-4H-1-benzopyran) family and structurally unrelated to any other class of herbicides known to us up until now.

The first member 9 of this class displayed promising activity *in vitro*; inhibit growth of several weeds, new herbicidal activity profile, compound 9 was investigated as a clue to develop potential herbicidal activity.

CONCLUSIONS

As a part of our program aimed at developing new pesticides, we have interested in synthesizing nitrogen heterocyclic compounds such as 9 and 15 because nitrogen helerocycles play an important role among a wide variety of hetercycles that have been used for developing useful herbicides. Both compounds showed excellent herbicidal activity against grass weeds; especially against *Echinochloa oryzicola* (E.O., barnyardgrass), one of the most harmful weeds in paddy fields. Their structures were confirmed by IR, ^{1}HNMR and MS spectral and elemental analysis.

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الملخص العربي

تخليق والنشاط الإبادي للحشائش لمشتقات الأزالاكتون والإيميدازيلينون

يونس محمود بدوي، على سيف السيد، فؤاد شعبان سليمان، محمد سمير محى الدين

تم تحضير مركبات 4-Heteroarylidene-2-phenyl-1, 3-oxazol-5(4H)-ones بتفاعل حمض الهيبوريك hippuric acid مع 3-formylchrmone . التركيب الكيميائى للمركبات المحضرة تم التعرف عليه بواسطة التحليل الطيفى بأجهزة لأشعة تحت الحمراء والرنين النووى المغناطيسى ومطياف الكتلة. النشاط الإبادى للمركبات المحضرة تم تقييمه على حشيشة الدنيبة.